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Organic and Inorganic Low-Dimensional Crystalline Materials

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FINAL REPORT
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GRANT
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"Ultrathin Film Characterization of the Organic Rectifier Project"
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Partial support (50%) was received to purchase major instruments to assist in scientific measurements for the Organic Rectifier Project. The grant was awarded on 15 April 1986 to Prof. Robert M. Metzger when he was still at the University of Mississippi, but was transferred, with the consent of the Scientific Officer, Dr. Kenneth J. Wynne, Code 1113, USONR Arlington, to the University of Alabama, where Dr. Metzger moved in August 1986. The original grant was for the acquisition of three instruments: (1) Fourier Transform Infrared Spectrometer, (2) Automatic Ellipsometer, (3) Solid State Probe for planned acquisition of a Nuclear Magnetic Resonance (NMR) Spectrometer. Since at the University of Alabama (Tuscaloosa) there already was a Nicolet 200 MHz NMR with solid-state capabilities, item (3) was replaced, with permission of Dr. Wynne, by item (3') A MicroVAX-II laboratory superminicomputer. The grant was supplemented by \$ 96,800 as matching costs from the University of Alabama, for a total budget of \$ 193,600.

The following instruments were purchased:

- (1) Bruker IFS-88 Fourier Transform Infra-Red Spectrometer, with additional wavelength capabilities ranging from the ultraviolet (UV), through the visible, to the near and mid-Infrared range (frequency range $40,000\text{ cm}^{-1}$ to 400 cm^{-1} , or wavelength range 250 nm to $25\text{ }\mu\text{m}$, resolution 0.25 cm^{-1}), and with a mid-IR microscope ($4000 - 400\text{ cm}^{-1}$, or $2.5 - 25\text{ }\mu\text{m}$). Approximate cost \$ 135,000 (with discount)
- (2) Rudolph Auto-EL-III Automatic Ellipsometer, 632.8 nm source, 70° fixed incidence and refraction. Approximate cost \$ 25,400.
- (3) Digital Equipment Corporation (DEC) MicroVAX-II, with 9 MB memory, Emulex 380 MB disk storage, 800-1600 bpi Kennedy 9000 magnetic tape recorder, LN03 laser printer, TK-50 cartridge tape system, 16-terminal multiplexor, modem. Approximate cost \$ 33,000.

The equipment has been used since 1987, and the following publications have benefited directly: FTIR [1-4], Ellipsometer [3], MicroVAX [5].

The use of the FTIR for detection of domains within LB films has not yet reached full maturity: our use so far has been more conventional, in the spectral characterization of LB films [1-4]. (The recent purchase of a scanning tunneling microscopy, to probe electrical conductivity through the film without worrying about domain realignment, represents a shift in our research approach). Nevertheless, the FTIR has represented a growing research tool in our laboratory, and we are now turning to studies of conducting LB films and of second-harmonic generating crystals (MAP-MNA).

The ellipsometer has been used to characterize film thicknesses [3], and will be used to obtain the index of refraction of a new second-harmonic generation crystal (MAP-MNA).

The MicroVAX-II has been used to compute fits between observed and calculated X-ray powder diffraction data (program TAUPIN) [5], and for band structure calculations [6], which were ancillary to investigations about the metal-to-insulator boundary in transition metal oxides [7]. These band structure calculations will be published soon.

REFERENCES.

- [1] R. M. Metzger and C. A. Panetta, "Langmuir-Blodgett Films of Donor-Sigma-Acceptor Molecules and Prospects for Organic Rectifiers", *NATO ASI Series*, **B168**, 271-285 (1987).

91 5 15 012

- [2] R. M. Metzger and C. A. Panetta, "Langmuir-Blodgett Films of Potential Donor-Sigma-Acceptor Organic Rectifiers" *J. Mol. Electronics* **5**, 1-17 (1989).
- [3] R. M. Metzger, D. C. Wiser, R. K. Laidlaw, M. A. Takassi, D. L. Mattern, and C. A. Panetta, "Monolayers and Z-Type Multilayers of Donor- σ -Acceptor Molecules with One, Two, and Three Dodecoxy Tails", *Langmuir* **6**, 350-357 (1990).
- [4] R. M. Metzger and C. A. Panetta, "The Quest for Unimolecular Devices", *New J. Chem.* **15**, 209-221 (1991).
- [5] D. A. Robinson, C. Asavaroengchai, A. Morrobel-Sosa, C. Alexander, Jr., R. M. Metzger, J. S. Thrasher, M. Abbot Maginnis, and D. A. Stanley, "Zero Resistance at 100 K in the Superconductor $GdBa_2Cu_3O_{7-x}$ ", *J. Phys. C: Solid State Phys.* **21**, 4091-4096 (1988).
- [6] C. Asavaroengchai, Ph. D. dissertation, Univ. of Alabama, 1990.
- [7] J. B. Torrance, P. Lacorre, C. Asavaroengchai, and R. M. Metzger, *J. Solid State Chem.* **90**, 168-172 (1990).



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LETTERS TO THE EDITOR

Simple and Perovskite Oxides of Transition-Metals: Why Some Are Metallic, While Most Are Insulating

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Communicated by J. M. Honig, October 1, 1990

Some 76 simple and perovskite transition-metal oxides are classified as "metals," "insulators," and those exhibiting metal-insulator transitions. Using the framework of Zaanen, Sawatzky, and Allen and a simple ionic model to estimate the two relevant energies (Δ_0 and U_0), we can find boundaries which separate the insulating oxides from two types of metals: low Δ_0 metals and low U_0 metals. In addition, compounds with metal-insulator transitions are found to be on (or near) these boundaries. It is concluded that the large differences in conductivity behavior of oxides are largely due to differences in the ionization potentials of the transition metal cations. © 1991 Academic Press, Inc.

The discovery (1-3) of superconductivity at high temperatures has generated considerable effort at understanding the physical properties of bismuth and copper oxides. It is important to recognize that these oxides are members of the broad class of perovskite and simple transition metal oxides that usually do not exhibit metallic conductivity and even less often exhibit superconductivity. As part of an overall understanding of high temperature superconductivity, it is important to understand the fundamental elec-

tronic energies that determine why some oxides are metallic, whereas the majority have low conductivity. It is these fundamental energies for the undoped oxide systems that provide the basis for understanding the hole-doped systems and lie behind the assumptions of the various theories for high-temperature superconductivity.

The conductivity of a large number of simple and perovskite oxide compounds has been compiled in several review articles (4-9). In Table I we list (10) 76 such systems involving transition metals (including rare earths) in formally divalent (II), trivalent (III), and tetravalent (IV) oxidation states. Here the conductivity behavior of these ox-

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TABLE I

BINARY OXIDES MO AND PEROVSKITE (OR PEROVSKITE-LIKE) OXIDES $A MO_3$ (ORDERED BY ATOMIC NUMBER, THEN BY FORMAL VALENCY) CONDUCTIVITY (M = METALLIC, I = INSULATING) OXYGEN-METAL ATOM MAPPING SITE POTENTIAL DIFFERENCES ΔV_M (VOLTS), AND PARAMETERS E_M (eV) AND ΔE_M (eV)

Compound	Conductivity	ΔV_M (V)	E_M (eV)	ΔE_M (eV)
TiO	M	48.2	9.0	20.0
TiO ₂	M I	58.3	10.8	15.9
LaTiO ₃	M I	58.2	12.2	15.8
TiO ₂	I	70.6 ^a	51.1	12.3
SrTiO ₃	I	69.4	52.3	11.1
Sr ₂ TiO ₇	I	70.4	52.2	12.0
VO	M	49.6	9.7	19.8
V ₂ O ₅	M I	57.7	12.5	13.6
LaVO ₃	I	58.6	13.7	14.4
LaSrVO ₄	I	59.4	13.7	14.9
VO ₂	M I	71.8 ^a	13.5	9.9
SrVO ₃	M	70.7	14.8	8.7
Sr ₂ VO ₇	I	70.7	14.8	8.7
Cr ₂ O ₃	I	60.3	13.0	14.3
LaCrO ₃	I	59.3	14.4	13.3
LaSrCrO ₄	I	60.5 ^a	14.4	14.3
CrO ₂	M	72.6	15.3	8.2
SrCrO ₃	M	71.0 ^a	16.4	6.7
MnO	I	45.4	13.4	15.6
β -Mn ₂ O ₇	I	60.2	12.9	11.6
LaMnO ₃	I	59.9	13.8	11.2
(La,Sr)MnO ₃	I	59.3 ^a	13.8	10.5
β -MnO	M	73.3	16.2	6.8
SrMnO ₃	I	68.1 ^a	17.6	2.0
Sr ₂ MnO ₇	I	71.6	17.4	5.1
FeO	I	46.7	9.7	16.1
α -Fe ₂ O ₃	I	59.6	19.3	13.9
LaFeO ₃	I	58.4 ^a	20.5	12.9 ^a
LaSrFeO ₄	I	59.2 ^a	20.4	13.4
SrFeO ₃	M	70.1	16.5	0.1
CoO	I	47.2	11.7	15.7
La ₂ CoO ₄	I	50.4	12.7	18.2
LaCoO ₃	I	60.9	14.1	12.2
LaSrCoO ₄	I	60.5	14.0	11.7
SrCoO ₃	M	70.2	24.5	3.7
NiO	I	48.3	12.1	15.3
La ₂ NiO ₄	I	49.6	13.3	16.2
LaNiO ₃	M I	61.0	16.0	10.7
LaSrNiO ₄	M	60.0	16.0	9.6
CuO	I	48.0	11.6	12.6
La ₂ CuO ₄	I	49.2	12.8	13.7
LaCuO ₃	M	60.5	14.6	8.6
LaSrCuO ₄	M	60.4	14.6	8.2
NbO	M	41.1	5.9	12.3
NbO ₂	I	67.8 ^a	7.1	14.7
β -MoO ₃	M	69.2 ^a	10.1	7.8
SrMoO ₄	M	68.2	11.2	6.9
Sr ₂ MoO ₇	M	69.2 ^a	11.1	7.8

TABLE I-Continued

Compound	Conductivity	ΔV_M (V)	E_M (eV)	ΔE_M (eV)
LaRuO ₃	M	58.1 ^a	12.7	14.8
RuO ₂	M	70.4	12.4	5.4
SrRuO ₃	M	69.1 ^a	13.3	4.2
Sr ₂ RuO ₇	M	70.1 ^a	13.3	5.1
Rh ₂ O ₃	I	58.7 ^a	12.5	12.8
LaRhO ₃	I	58.4 ^a	13.8	12.5
RhO ₂	M	70.8	12.6	2.0
SnO	I	39.0	12.0	10.1
SnO ₂	I	67.9	27.0	12.4
SrSnO ₃	I	67.2 ^a	28.0	11.6
Sr ₂ SnO ₇	I	68.4	28.0	12.8
La ₂ O ₃	M	39.1	4.2	14.8
La ₂ O ₂	I	49.0	27.0	16.0
CeO	M	39.6	5.4	15.3
Ce ₂ O ₃	I	49.5 ^a	12.8	15.5
CeO ₂	I	61.9	24.3	11.3
SrCeO ₃	I	63.2 ^a	24.8	12.0
PrO	M	40.0	7.0	16.1
Pr ₂ O ₃	I	50.0 ^a	13.6	14.5
PrO ₂	I	62.5	14.7	9.6
SrPrO ₃	I	63.4 ^a	15.1	10.0
NdO	M	40.3	7.3	16.1
Nd ₂ O ₃	I	50.6 ^a	14.5	14.6
EuO	I	39.1	9.7	14.6
Eu ₂ O ₃	I	51.0	13.3	12.1
YbO	I	41.3	8.7	15.5
Yb ₂ O ₃	I	52.8	14.6	13.7
LaYbO ₃	I	54.3	15.4	14.9

^a Averaged between crystallographically inequivalent sites.

^b Ref. (12).

In-plane M and O only.

^c Estimated (from known calculations) or for approximate crystal structure.

ides has been crudely and arbitrarily divided into "metals" and "insulators" on the basis of the magnitude of their conductivity, $\sigma(300\text{ K})$, at room temperature: "metals" are defined as having $\sigma(300\text{ K}) > 1\text{ S/cm}$, while "insulators" have $\sigma(300\text{ K}) < 1\text{ S/cm}$. A few oxides have metal-insulator transitions and are so labeled in Table I.

A simple, and yet powerful, framework which includes correlation effects has been introduced and developed by Zaanen, Sawatzky, and Allen (ZSA) (11). According to this picture, oxides (as well as halides, sulfides, etc.) can be described in terms of

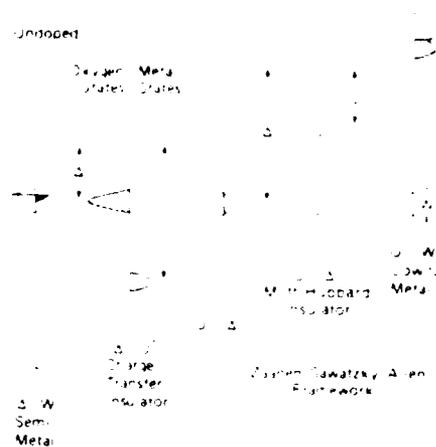


FIG. 1. A schematic diagram of the energy levels of the ZSA framework, specifying the definitions of Δ , U' , and W .

the relative energies of three electronic energy levels near the Fermi level, shown in Fig. 1. The fully occupied oxygen $2p$ states are shown as the shaded band on the left side of the vertical energy axis. On the right side of the vertical energy axis and shown unshaded is the lowest unoccupied metal orbital (corresponding to the metal conduction band) which lies at an energy Δ above the former. Δ is seen to increase in going toward the right in Fig. 1. This unoccupied metal orbital lies at an energy U' above the highest occupied (shaded) $3d$ - or $4d$ -metal states, as shown in Fig. 1. (The prime on U' signifies that this energy (defined in Fig. 1) is not always the Hubbard U .) For simplicity, we assume that the width, W , of these three bands is the same.

For the case of $W < \Delta$, U' , the compounds are insulating, and ZSA (11) distinguish two different types of insulators:

(1) Charge transfer insulators when $W < \Delta < U'$ (left of Fig. 1). In this case, the gap $\sim(\Delta - W)$ is dominated by the value of Δ ; and

(2) Mott-Hubbard insulators, when $W < U' < \Delta$ (right of Fig. 1). Here the gap $\sim(U' - W)$ is dominated by U' .

A metal results when either of these two gaps approaches zero. Hence, there exist two types of correlated electron metals:

(1) "Low- Δ metals", when $\Delta < W$ (far left of Fig. 1), in which the lowest-lying metal conduction band overlaps the occupied oxygen $2p$ -valence states; and

(2) "Low- U' metals", when $U' < W$ (far right of Fig. 1), in which case the two metal orbitals merge to form a partially filled band.

The goal of this paper is to obtain values of U' and Δ for each of the 76 compounds in Table I and examine these within the ZSA framework. While experimental values for a few of these compounds are available, a comparison among all oxide systems is more appropriately carried out with a self-consistent set of approximate values, obtained in the same manner for each. Such a set may be obtained, if we approximate these oxides as ionic solids containing transition metal cations M^{v+} and oxygen anions O^{2-} , with a negligible wave function overlap. The values of U' and Δ obtained in this approximation are called U'_0 and Δ_0 , where the zero subscript serves as a reminder that they are theoretically calculated values for the simple ionic model. The energy U'_0 corresponds to the excitation of an electron from one transition metal cation to its neighbor (at a distance d_{M-M}), and is specified in terms of the ionization potential I_{v+1} of M^{v+} and its electron affinity $A = -I_v$:

$$U'_0 = I_{v+1}(M) - I_v(M) - e^2/d_{M-M}. \quad (1)$$

Correspondingly, the energy Δ to excite an electron from O^{2-} to a neighboring transition metal (at a distance d_{M-O}) involves the ionization potential $I(O^{2-})$ of O^{2-} (the negative of the electron affinity ($A(O^-)$)) and the electron affinity $A = -I_v$ of M^{v+} . In addition, there exists a term ΔV_M , the difference in electrostatic Madelung site potentials, that the electron experiences when it changes sites:

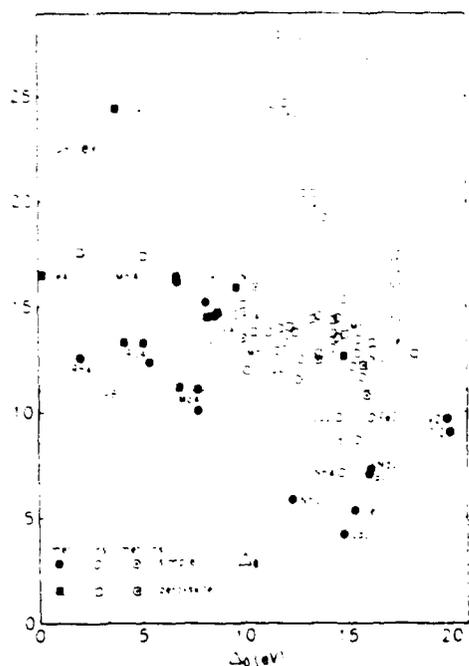


FIG. 2. A plot of the calculated values of U'_0 and Δ_0 for the 76 oxides in Table I. The lines attempt to separate the "insulators" (open symbols) from the "metals" (solid symbols) according to the ZSA framework.

$$\Delta_0 = \Delta V_M - I_c(M) - A(O^-) - e^2/d_{M-O}. \quad (2)$$

In this very simple ionic model, the values for U'_0 and Δ_0 depend only on the electrostatic interactions between ions and the gas-phase ionization potentials. In Table I, we show values of ΔV_M , calculated earlier (12) or here (13), together with the values of U'_0 and Δ_0 calculated from Eqs. (1) and (2), using the experimental (14) gas-phase values for I_c , while a value (15) of 7.70 eV was used for $A(O^-)$. In Fig. 2, we plot U'_0 versus Δ_0 for each of the simple and perovskite oxides. In this letter, we present the major features of these data and discuss the details elsewhere (10). It is clearly seen in Fig. 2 that the "metallic" oxides tend to have low values of either Δ_0 or U'_0 . In fact, one can separate most of the "insulators" from the "metals" by drawing a vertical boundary line and a

horizontal one, such that the metals have either $\Delta_0 \leq \Delta_B = 10$ eV or $U'_0 \leq U'_B = 11$ eV. Thus, there are eight metals in Fig. 2 which we can classify as low- U' metals and 16 metals which are classified as low- Δ metals. Within this framework, oxides with metal-insulator transitions should fall on (or near) the boundaries in Fig. 2. Such is the case for each of the five examples in Table I (shown in Fig. 2 as symbols with a dot in the center).

We should recall the approximations made in the ionic model calculations of Δ_0 and U'_0 . We have neglected the effects of the electronic overlap between ions (covalency, crystal field splittings, screening, electronic polarizability) and the motion of the ions (lattice relaxation, ionic polarizability). Our basic assumption is *not* that these effects are small, rather, that they are similar for all the oxides in Table I, so that the differences in Δ and U' are caused by the large differences in I_V and ΔV_M via Eqs. (1) and (2). The main consequence of these neglected effects is to reduce (or screen) the actual values of Δ and U' well below the ionic values of Δ_0 and U'_0 in Table I. For example, for an electron or a hole in La_2CuO_4 , the decrease in energy due to screening is calculated (16) to be ~ 5 –6 eV. For an excitation of a neighboring electron and hole (as for U'_0 and Δ_0), the decrease should be considerably less than twice this value. This screening will decrease the metal-insulator boundaries at $\Delta_B \sim 10$ eV and $U'_B \sim 11$ eV to values comparable with estimates (17) of the electronic bandwidth $W \sim 6$ eV. Thus, the magnitudes of Δ_B and U'_B in Fig. 2 are not unreasonable.

There are a few insulating oxides that lie deep in the metallic regions of Fig. 2, such as SrMnO_3 , Sr_2MnO_4 , and NbO_2 (which has a strong pairing of metal cations). There are several more minor exceptions nearer the boundary, many of which can (10) be related to the assumption that the bandwidths W and hence the boundaries U'_B and Δ_B are the

same for all three types of orbitals in Fig. 1 and for all oxides. Among the oxides in Table I there are significant differences in W between the rare earth and the first series transition metal oxides, for example, as well as differences due to distortions and to different dimensionalities. Taking these factors into consideration (10), there still remains an uncertainty of ~ 1 – 2 eV in the location of the boundaries in Fig. 2, which is an estimate of the relative errors in the agreement between the data and our ionic model of the ZSA framework. Considering the simplicity of the ionic model and the number of factors neglected, the combination of an ionic model and the ZSA framework forms a remarkably good starting point for an understanding of the electronic structure of both simple and perovskite oxides of transition metals. In this way, a simple picture is able to account for the differences in conductivity for a wide range of oxides and to attribute these differences primarily to differences in the ionization potentials of the transition-metal cations. It is hoped that such a broad perspective of oxides will complement the common approach of examining each particular compound in detail.

References

1. A. W. SLEIGHT, J. L. GILLSON, AND P. E. BIERSTEDT, *Solid State Commun.* **17**, 27 (1975).
2. J. G. BEDNORZ AND K. A. MÜLLER, *Z. Phys. B* **64**, 189 (1986).
3. R. J. CAVA, B. BATLOGG, J. J. KRAJEWSKI, R. FARROW, AND L. W. RUPP, *Nature (London)* **332**, 814 (1988).
4. J. B. GOODENOUGH AND J. M. LONGO, Landolt-Börnstein Tabellen, Vol. III 4a, Springer-Verlag, Berlin (1970); S. NOMURA, Landolt-Börnstein Tabellen, Vol. III 12a, Springer-Verlag, Berlin (1978); J. B. GOODENOUGH, *Prog. Solid State Chem.* **5**, 149 (1971).
5. D. ADLER, *Radiat. Eff.* **4**, 123 (1970).
6. C. N. R. RAO AND G. V. SUBBARAO, *Phys. Status Solidi A* **1**, 597 (1970); C. N. R. RAO, *Annu. Rev. Phys. Chem.* **40**, 291 (1989).
7. M. POUCHARD *et al.*, *Mater. Rev. Symp. Proc.* **156**, 13 (1989).
8. G. V. SAMSONOV (Ed.), *The Oxide Handbook*,IFI Plenum, New York (1982).
9. A. W. SLEIGHT, "Proceedings of the Welch Conference on Valency," p. 123 (1989).
10. For a more complete account of this work, see J. B. TORRANCE, P. LACORRE, C. ASVAROENGCHAI, and R. M. METZGER, submitted for publication.
11. J. ZAAANEN, G. A. SAWATZKY, AND J. W. ALLEN, *Phys. Rev. Lett.* **55**, 418 (1985).
12. J. Q. BROUGHTON AND P. S. BAGUS, *J. Electron Spectrosc. Relat. Phenom.* **20**, 261 (1980).
13. R. M. METZGER, *J. Chem. Phys.* **57**, 1870 (1972); *J. Chem. Phys.* **64**, 2069 (1976); J. B. TORRANCE AND R. M. METZGER, *Phys. Rev. Lett.* **63**, 1515 (1989).
14. "CRC Handbook of Physics and Chemistry," CRC Press, Boca Raton, FL (1981); W. C. MARTIN, L. HAGAN, J. READER, and J. SUGAR, *J. Phys. Chem. Ref. Data* **3**, 771 (1974).
15. M. O'KEEFE, *J. Solid State Chem.* **85**, 108 (1990).
16. M. S. ISLAM, M. LESLIE, S. M. TOMLINSON, AND C. R. A. CATLOW, *J. Phys. C Solid State Phys.* **21**, L109 (1988).
17. See, for example, W. E. PICKETT, *Rev. Mod. Phys.* **61**, 433 (1989).

Zero resistance at 100 K in the superconductor $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$

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Abstract. Superconductivity in $\text{GdBa}_2\text{Cu}_3\text{O}_7$ has been detected by ω_0 and ω_1 electrical resistance measurements. For both cases the onset temperature for the superconducting transition is 108 K, with a zero-resistance estimate of $T_c = 100$ K for the ω_0 measurement and 99 K for the ω_1 measurement. X-ray diffraction analysis indicates that the sample is mostly single phase.

1. Introduction

Since the reports by Bednorz and Müller (1986) on superconductivity in the quaternary mixed-valence system $\text{La}_2\text{Ba}_2\text{CuO}_7$, with onset temperatures in excess of 30 K, and by Wu *et al* (1987) on superconductivity in single-phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, with an onset at 93 K and T_c ('zero' resistance) = 80 K, many laboratories around the world, including our own, embarked on a desperate search for higher critical temperatures throughout the entire lanthanide series. Within a few months there were several reports of such compounds with values of T_c in the 90–100 K range (Cava *et al* 1987, Stacy *et al* 1987, Takagi *et al* 1987), i.e. well above the boiling temperature of liquid nitrogen.

As a result of these efforts, superconductivity has been observed in materials with the general formula $\text{R}_x\text{A}_2\text{CuO}_7$, in which a certain amount (x) of the trivalent rare-earth ion (R), or its analogue, coexists with a divalent alkaline-earth ion (A, usually Ba or Sr). A possible mixed-valence Cu(II)–Cu(III) state, in which the copper (a Jahn–Teller ion) can be either square-planar-coordinated or square-pyramidally coordinated in a one- or two-dimensional array, results from the vacancy of a certain fraction of the oxide sites ($6.7 \leq w \leq 6.9$). The almost planar ('dimpled') arrays of Cu and O atoms, of stoichiometry CuO_2 , surmounted by apical O atoms, yield a square-pyramidal (i.e. distorted octahedral) coordination about Cu. These '2D planes' may be responsible for T_c around 40 K. There is also a '2D ribbon' motif of square-planar Cu and O atoms, of

stoichiometry CuO_3 , which may be responsible for T_c around 90 K in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure.

To aid in our studies on the lanthanide effect on superconductivity we considered the published onset and zero-resistance values of T_c versus the ionic radii of the lanthanide ions. Clearly, evaluations of this nature should consider the various experimental differences amongst the many reports, but it is nevertheless useful for obtaining qualitative information from the resulting trends. Other than for Y, there exists an optimisation window between Ho, Gd and Eu for consistently achieving the highest values of T_c in compounds with the $\text{RBa}_2\text{Cu}_3\text{O}_7$ composition. Our observations also indicate this trend, even for two-phase materials with overall composition $\text{R}_2\text{Ba}_2\text{Cu}_4\text{O}_7$ (Robinson *et al* 1987), in agreement with others (Brown *et al* 1987, Fisk *et al* 1987).

We have recently reported our results on superconductivity in single-phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Morrobel-Sosa *et al* 1987). Here we present our studies on the synthesis, powder x-ray diffraction and conductivity of $\text{GdBa}_2\text{Cu}_3\text{O}_7$, for which we find $T_c = 100$ K (onset at 108 K). We also present a comparison of these findings with our previous work on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, prepared under similar conditions and studied using the same experimental configuration and equipment. A preliminary and partial account of this effort is given elsewhere (Asavaroenchai *et al* 1987).

2. Experimental methods

The $\text{GdBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples used for this work were prepared by conventional ceramic powder methods. Appropriate molar mixtures of fine powders of Gd_2O_3 (Aesar), Y_2O_3 (Molycorp), BaCO_3 (Mallinckrodt), and CuO (Aldrich), all with purity $>95\%$, were mixed and ground in ceramic media. Samples of the Y-Ba-Cu-O mixture were pre-fired in air at 950°C for 24 h and cooled in a muffle furnace to room temperature. Cylindrical pellets (typical dimensions, 1.25 cm in diameter and 0.1 to 0.2 cm thick) of the material were pressed at 1.2 kbar and placed in a ceramic (alumina) boat, inside a Lindberg tube furnace, for sintering at 950°C for 8 h. The samples were then annealed at 500°C for 6 h and slow-cooled. The Gd-Ba-Cu-O samples were pressed at 1.2 kbar and sintered at 950°C for 12 h, slow-cooled, reground and pressed, followed by further sintering for 16 h. These pellets were then annealed at 500°C for 5 h and oven-cooled to room temperature. The entire heating/annealing schedules were performed under flowing oxygen. If preliminary electrical resistance (DC) measurements did not indicate the presence of a superconducting transition, the samples were submitted to further heating after being reground and pressed. Some of the Y-Ba-Cu-O samples required further heating at 900°C for 12 h and at 500°C for 5 h, while some Gd-Ba-Cu-O samples required an additional 18 h at 980°C , in flowing oxygen. The resulting pellets were black throughout. The experiments we report here were performed on those samples.

Four-probe measurements of electrical resistance versus temperature were performed on pellet samples that were attached, from the bottom, to the cold finger of a closed-cycle refrigerator unit (CTI-Cryogenics model 22C) with electrical insulating varnish (General Electric 7031). The temperature was measured with a calibrated chromel versus Au-0.07% Fe thermocouple attached to the top surface of the sample with the same varnish. Four parallel leads were painted onto the top surface of the pellet with conductive silver paint (DuPont 7713). The small amount of solvent present in the

paint was evaporated by heating the pellets to 540 °C in a flow of oxygen for approximately 10 min. Copper wire contacts were soldered directly onto the leads.

The DC measurements were made by reading the voltage drop across the inner leads of the sample using a nanovoltage amplifier (Keithley Model 140). A constant sample current of less than 1.5 mA was maintained throughout the experiment to diminish the possible suppression of the superconducting transition. The AC measurements were performed using the reference output voltage of 0.747 V (at a frequency of 2 kHz) of a lock-in amplifier (Princeton Applied Research Model 120), as the constant current source, through a 1 k Ω resistor in series with the sample. The sample voltage was pre-amplified and detected by the signal channel of the lock-in. Data acquisition and analysis for both measurements were performed with a personal computer (Hewlett-Packard Model 9816) and a data-acquisition control unit (Hewlett-Packard Model 3497A). The temperature data were digitised with a Scientific Instruments temperature indicator, which was also interfaced to the acquisition control unit. All measurements were performed in both decreasing and increasing temperatures for both samples. No measurable hysteresis was detected for either of the two materials. Small specimens of each sample, obtained from crushed pellets, were studied by x-ray diffraction (Phillips Model 3100 generator) with Cu K α radiation, where $\lambda(\text{Cu K}\alpha_1) = 1.540598 \text{ \AA}$, $\lambda(\text{Cu K}\alpha_2) = 1.541877 \text{ \AA}$. The data range was 2.000 to 70.000 $^\circ$, with a step size of 0.020 $^\circ$ and count times of 0.50 s.

3. Results and discussion

The x-ray powder diffraction patterns for $YBa_2Cu_3O_{7-x}$ and for $GdBa_2Cu_3O_{7-x}$ are given in tables 1 and 2, respectively. Only 5 very weak lines out of 35 could not be indexed for

Table 1. The x-ray powder diffractogram for $YBa_2Cu_3O_{7-x}$.

hkl	$d_{\text{obs}}(\text{Å})$	$d_{\text{calc}}(a, b, c)(\text{Å})$	II	hkl	$d_{\text{obs}}(\text{Å})$	$d_{\text{calc}}(a, b, c)(\text{Å})$	II
001	31.570	0.120	3	005	2.336	0.002	73
002	5.818	0.027	11	113	2.232	0.002	6
003	3.890	0.007	43	114	1.990	0.004	1
010	—	0.001	—	006	1.948	0.000	10
100	3.812	0.012	7	200	1.911	0.000	6
012	3.236	0.003	—	115	1.774	0.001	2
102	3.195	0.004	2	023	1.738	0.002	1
a	3.147	0.013	1	007	1.670	0.000	13
b	3.064	—	1	116	1.586	0.001	13
b	2.990	—	1	213	1.570	0.000	6
004	2.915	0.008	5	017	1.533	0.002	1
c	2.827	0.008	1	025	1.496	0.001	1
013	2.750	0.003	22	205	1.480	0.000	1
103	2.729	0.000	30	008	1.460	0.001	1
111	2.651	0.005	1	117	1.425	0.001	1
d	2.519	0.003	1	026	1.377	0.000	3
112	2.469	0.002	1	220	1.365	0.000	8

* Attributed to the 101 reflection of CuO ($a = 4.684 \text{ \AA}$, $b = 3.425 \text{ \AA}$, $c = 5.120 \text{ \AA}$, $B = 99.47^\circ$, $d_{\text{calc}} = 3.160 \text{ \AA}$).

^b Unassigned.

† Attributed to the 011 reflection of CuO ($d_{\text{calc}} = 2.835 \text{ \AA}$).

‡ Attributed to the 11-1 reflection of CuO ($d_{\text{calc}} = 2.522 \text{ \AA}$).

Table 2. The x-ray powder diffractogram for GdBa₂Cu₃O₇.

<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{obs} - <i>d</i> _{calc} (Å)	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	<i>d</i> _{calc} (Å)	<i>d</i> _{obs} - <i>d</i> _{calc} (Å)	<i>I</i> / <i>I</i> ₀
001	11.508	0.160	3	201	1.913	0.012	5
100	3.862	0.007	28	120	1.733	0.003	2
a	3.544	—	1	a	1.665	—	14
b	3.136	0.015	1	008	1.664	0.009	9
a	2.907	—	1	007	1.631	0.010	3
c	2.833	-0.002	4	123	1.582	0.009	11
110	2.737	0.005	12	1	1.571	-0.009	3
103	2.716	0.016	20	a	1.529	—	1
a	2.616	—	2	214	1.480	0.006	3
d	2.550	0.028	1	a	1.456	—	1
112	2.489	0.028	7	008	1.423	0.005	2
e	2.329	0.007	21	215	1.382	0.009	2
113	2.228	0.014	4	221	1.365	0.009	5
200	1.939	0.011	100				

¹ Unassigned

² Attributed to the 222 reflection of Gd₂O₃ (*a* = 10.813 Å, *d*_{calc} = 3.121 Å), or to the 111 reflection of BaO (*a* = 5.523 Å, *d*_{calc} = 3.188 Å)

³ Attributed to the 0-1-1 reflection of CuO (*a* = 4.684 Å, *b* = 3.425 Å, *c* = 5.120 Å, β = 99.47°, *d*_{calc} = 2.835 Å)

⁴ Attributed to the 11-1 reflection of CuO (*d*_{calc} = 2.522 Å)

⁵ Attributed to the 111 reflection of CuO (*d*_{calc} = 2.322 Å)

⁶ Attributed to the 202 reflection of CuO (*d*_{calc} = 1.580 Å)

the known structure of Y-Ba-Cu-O, with some of the intensities matching closely though not exactly. The calculated lattice parameters yield: *a* = 3.824(1) Å, *b* = 3.891(1) Å and *c* = 11.690(3) Å, in very good agreement with the values *a* = 3.8218(7) Å, *b* = 3.8913(7) Å and *c* = 11.677(2) Å (Cava *et al* 1987). The x-ray diffraction pattern for GdBa₂Cu₃O₇ consists of 27 peaks, of which 16 belong to a unit cell of dimensions very similar to those of YBa₂Cu₃O_{7-x}. Four of the remaining reflections can be attributed to CuO, and one to either Gd₂O₃ or to BaO, while the rest are weak. The calculated lattice parameters obtained from this pattern are: *a* = 3.855(5) Å, *b* = 3.872(4) Å and *c* = 11.348(1) Å, in good agreement with the reported values *a* = 3.89 Å, *b* = 3.89 Å and *c* = 11.73 Å attributed to GdBa₂CuO₇ by Hor *et al* (1987).

The normalised plots of DC resistance versus temperature for YBa₂Cu₃O_{7-x} and GdBa₂Cu₃O_{7-x} are shown in figure 1. The data were normalised with respect to *R*(*T* = 265 K) = 20.99 mΩ for YBa₂Cu₃O_{7-x} and *R*(*T* = 265 K) = 6.38 mΩ for GdBa₂Cu₃O_{7-x}, to compare the qualitative features of these materials. The higher-temperature data show the metallic behaviour of both samples. The onset temperature for superconductivity in the YBa₂Cu₃O_{7-x} pellet was 102 K and the zero-resistance temperature was 96 K. The result is consistent, within a few degrees kelvin, with values of *T*_c reported by other groups. In comparison, the onset temperature for GdBa₂CuO_{7-x} was 108 K, with zero resistance reached at 100 K. The measurement of AC resistance versus temperature for GdBa₂Cu₃O_{7-x} is shown in figure 2. For this case the onset temperature is also 108 K, but zero resistance was achieved at 99 K.

These values are a few degrees higher than those reported by others (Hor *et al* 1987, Mei *et al* 1987) which, when coupled with the presence of some CuO reflections in the x-ray pattern, may be indicative of slight deviations from stoichiometry; for example,

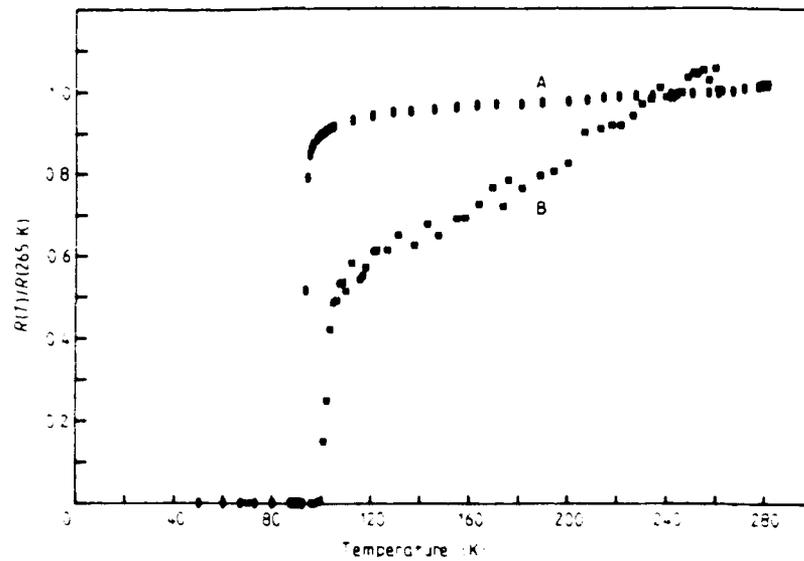


Figure 1. The normalised (DC) resistance, $R(T)/R(265\text{ K})$, as a function of temperature for pellets of (A) $YBa_2Cu_3O_{7-x}$, and (B) $GdBa_2Cu_3O_{7-x}$.

the oxygen composition for the $YBa_2Cu_3O_{7-x}$ material was determined to be 6.8 to 6.9 from thermogravimetric analysis (Morrobel-Sosa *et al* 1987). Nevertheless, the measurements are reproducible for both the AC and DC methods and show no detectable hysteresis effects upon the cycling of temperature, and the x-ray data do indicate the presence of a mostly pure phase in these samples.

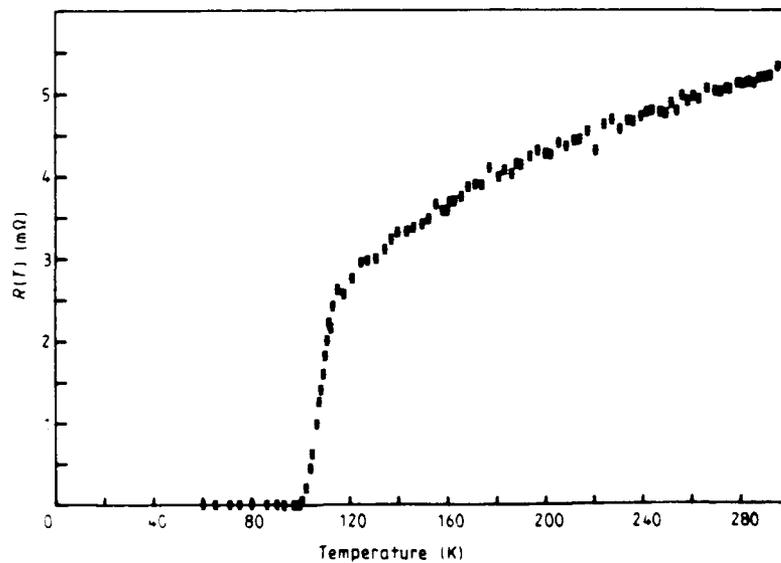


Figure 2. The resistance (AC) of a pellet of $GdBa_2Cu_3O_{7-x}$, as a function of temperature.

4. Conclusions

We have examined the temperature dependence of the electrical resistance, by both AC and DC methods, for mostly single-phase $\text{GdBa}_2\text{Cu}_3\text{O}_x$ prepared (sintered and annealed) in the presence of a flowing oxygen atmosphere, by comparison with similar measurements performed under identical conditions for $\text{YBa}_2\text{Cu}_3\text{O}_x$. Both electrical resistance detection methods yielded the same T_c (onset) of 108 K; T_c (zero resistance) was achieved at 99 K (AC) and at 100 K (DC). These results support the hypothesis of a T_c -optimisation window for the trivalent lanthanide ions between Ho, Gd and Eu.

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References

- Asavaroengchai C, Metzger R M, Robinson D A, Morrobel-Sosa A, Thrasher J S, Alexander C Jr, Stanley D A and Maginnis M A 1987 *Superconductivity: Synthesis, Properties and Processing* ed W Hatfield (New York: Marcel-Dekker) submitted
- Bednorz J G and Müller K A 1986 *Z. Phys.* **B 64** 189
- Brown S E, Thompson J D, Wills J O, Aikin R M, Zirngiebl I E, Smith J L, Fisk Z and Schwartz R B 1987 *Phys. Rev.* **B 36** 2298
- Cava R J, Batlogg B, van Dover R B, Murphy D W, Sunshine S, Siegrist T, Remeika J P, Rietman E A, Zahurak S and Espinosa G P 1987 *Phys. Rev. Lett.* **58** 1676
- Fisk Z, Thompson J D, Zirngiebl I E, Smith J L and Cheong S-W 1987 *Solid State Commun.* submitted
- Hor P H, Meng R L, Wang Y Q, Gao L, Huang Z J, Bechtold J, Forster K and Chu C W 1987 *Phys. Rev. Lett.* **58** 1891
- Mei Y, Green S M, Reynolds G G, Wiczynski T, Luo H L and Politis C 1987 *Z. Phys.* **B 67** 303
- Morrobel-Sosa A, Robinson D A, Asavaroengchai C, Metzger R M, Thrasher J S, Alexander C Jr, Standley D A and Maginnis M A 1987 *Superconductivity: Synthesis, Properties and Processing* ed W Hatfield (New York: Marcel-Dekker)
- Robinson D A, Morrobel-Sosa A, Alexander C Jr, Thrasher J S, Asavaroengchai C and Metzger R M 1987 *Proc. NATO Workshop Inorganic and Organic Low-Dimensional Crystalline Materials (Minorca) 1987* ed P Delhaes (New York: Plenum)
- Stacy A M, Baddiung J V, Geselbracht M J, Ham W K, Holland G F, Hoskins R L, Keller S W, Millikan C F and zur Loye H-C 1987 *J. Am. Chem. Soc.* **108** 2528
- Takagi H, Uchida S-I, Kishio K, Kitazawa K, Fueki K and Tanaka S 1987 *Japan. J. Appl. Phys.* **26** L320
- Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908

THE QUEST FOR UNIMOLECULAR DEVICES¹⁰¹

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ABSTRACT. — We review here the progress made towards the goal of truly unimolecular devices, that is, electronic or other devices, whose active principle is based on the manipulation of the molecular geometry, or the molecular conformation, of a single organic molecule, or small cluster. This quest is at the forefront of a nascent field of research, called "molecular electronics", which aims to fill a future gap in conventional "inorganic" microelectronics: as devices based on silicon or gallium arsenide or germanium get smaller and smaller, because of the need for faster electronic circuits, the fabrication difficulties will rise rapidly, and, at the nanometer level, organic molecules, with the tunability of their molecular orbitals, should offer significant advantages, along with new technological challenges. The issue of the potential speed of organic rectifiers and transistors can be resolved by the use of strong oxidizing and reducing molecules, through which electronic transport can be very rapid. At present one cannot routinely address a group of several isolated single molecules: as yet there are no "molecular wires". However, one can use the tip of a scanning tunneling microscope to address a single molecule, and thus several candidates for molecular electronic devices can finally be studied. The review focusses mainly on the efforts to realize the Aviram-Ratner unimolecular rectifier, and chronicles the progress of the Organic Rectifier Project.

1. Introduction

There are two current definitions of "molecular electronics" (ME)¹:

(i) the "wider" definition, which includes the interesting electrical behaviour (conductivity, superconductivity, etc.) of all known lower-dimensional systems, LB films, and clusters, and

(ii) the "stricter and narrower" definition, which focusses on the properties of the single molecule. These two definitions are discussed in Section 2.

Examples of "bulk" molecular devices are presented in Section 3. Efforts to mimic intramolecular electron transfer in biosynthetic molecules are reviewed in Section 4. "Truly unimolecular" electronic device proposals are reviewed in Section 5; device assembly ideas are presented in Section 6. The ideas for "connecting" to such molecular devices are discussed in Section 7.

Sections 8-9 chronicle the progress made by our own group ["the Organic Rectifier Project" (ORP)] towards the realization of the organic rectifier, a proposal advanced in 1973 by Ari Aviram, Mark A. Ratner and coworkers²⁻⁴ that a single organic molecule of the type D- σ -A could be a rectifier of electrical current. This molecule D- σ -A would do so, because the D end is a good organic one-electron donor, σ is a covalent saturated ("sigma") bridge, and A is a good organic one-electron acceptor. The driving force for the ORP, which may be one of the key experiments in ME, is that the

working thickness promised by such a D- σ -A device is of the order of one or two molecular lengths, i. e. about 5 nm: such a small size is predicted to be unattainable, even by the rosiest forecasts for silicon or gallium arsenide technology. The progress of the ORP⁵⁻²⁵ has been reviewed often before^{6, 9, 11, 17, 20-22, 24, 26, 27}, but new results are incorporated in this review.

As discussed in Section 9, the rectification by a single organic molecule, or by an organized Langmuir-Blodgett (LB)²⁸⁻³⁴ monolayer of such molecules, has not yet been demonstrated by our group. The revolutionary scanning tunneling microscope³⁵ has an obvious potential for confirming the Aviram Ansatz; (STM); the early and disappointing efforts to detect rectification by an ad hoc modification of the STM^{21, 22, 24} will be reviewed; our own continuing efforts will be mentioned briefly. We mention also the results of Sambles' group at Exeter and Ashwell's group at Cranfield, who may have achieved rectification by an LB film^{36, 37}.

2. Broad and narrow definitions of molecular electronics

The term ME has been popularized by the late Forrest L. Carter, who organized international workshops on ME devices in Washington in 1981³⁸, 1983³⁹, and 1986⁴⁰; this was followed by conferences in Varna, Bulgaria in 1986⁴¹, and in Hawaii in 1989, which outlined the present challenges⁴².

In the period 1983-1984, some unscientific proposals about self-assembling biological "computers" ("biochips") received unfortunate, undeserved and uncritical world-wide media attention; the critical reaction to such exaggerations almost drowned, in the ocean of righteous disbelief, the infant field of ME! A very sobering note outlined what technical accomplishments were still needed⁴³. Since then, more conservative chemists, physicists, and materials scientists have broadened the definition of ME, re-labelled some of their research areas as ME, and thus have given ME its present nascent respectability.

At present, two interpretations of ME exist. In its first, broader, definition, (*sensu lato*) ME includes *the investigation of all molecule-based electronic processes in lower-dimensional systems*, to wit, in approximate historical order:

- (A1) Intercalated graphites (C₆K, etc.)⁴⁴
- (A2) Intercalated 2-D chalcogenides (TaS₂, etc.)⁴⁵
- (A3) Charge-transfer salts (organic conductors and superconductors)⁴⁶
- (A4) Conducting low-dimensional polymers^{46,47}
- (A5) Inorganic linear-chain compounds⁴⁸
- (A6) Langmuir-Blodgett (LB) multilayers⁴⁴

These research areas have been studied world-wide for almost two decades, and relabelling them as ME may be a convenient short-hand, an attention-getting method for funding research proposals, or just a current fad.

In the second, more narrow definition, (*sensu stricto*) ME devices ("zero-dimensional devices") utilize *the electronic properties of single molecules or clusters*. Examples of proposals are:

- (B1) Aviram and Ratner's rectifier, which is the main subject of this review^{2,4}
- (B2) Aviram and Ratner's hydrogen atom switch^{3,4}
- (B3) Mitani's proton transfer system⁴⁹
- (B4) Carter's soliton switch⁵⁰
- (B5)* Fujihira's LB monolayer photodiode⁵¹

Of these, only the last (indicated by an asterisk) is an experimentally proven device.

As "passive" molecular connectors which may be useful to interrogate unimolecular ME devices, the following proposals have been brought forth:

- (C1) molecular wires and antennas, e. g. carotenes and other polyenes⁵²
- (C2) Aviram's linked thiophene "connects"⁵³
- (C3) Miller's "molecular spacers"⁵⁴
- (C4) molecular inclusion compounds, e. g. cyclodextrins⁵⁵ and calixarenes⁵⁶.

These ideas and potential devices, which represent the best present long-range hope for ME, should exhibit the inherent speed of intramolecular electron transfer (much less than 1 ns). It is very likely that ME can compete with present-day semiconductor electronics only if ME can couple the advantages of *molecular size and fast intramolecular electron transfer* (faster than 1 ns); there is little use in making a small but slow device.

3. Molecular devices that depend on bulk properties

First, we will discuss some "bulk" molecular devices, even though they are molecular devices only in the larger sense

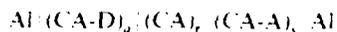
(i. e. because of the band structure of the solids, or because of phase change properties, or other bulk effects)

3.1. BULK ORGANIC RECTIFIERS

After the discovery of the junction diode and the transistor, it was of some academic interest to see whether organic molecules could function in bulk pn rectifiers (diodes) or as npn transistors. This would occur if a film or crystal of an organic electron donor were brought in contact with that of an organic electron acceptor. This was indeed verified in the 1960's⁵⁷.

3.2. MULTILAYER LB ORGANIC RECTIFIERS

Kuhn *et al.*⁵⁸ showed that one can obtain a pn (or DA) rectifier in a LB multilayer sandwich



where \cdot denotes an interface boundary, Al denotes a bulk Al contact, (CA-D)_q denotes the electron donor system D [= q LB monolayers of cadmium arachidate (CA) randomly doped in the ratio 5:1 with suitable organic π electron donors], (CA)_r denotes a spacer layer of r undoped monolayers of CA, and (CA-A)_s denotes the electron acceptor system A [= s LB monolayers of CA randomly doped with suitable organic π electron acceptors A]. This work was repeated and confirmed by Sugi *et al.*⁵⁹, who observed rectification properties, but *only* if $q \geq 3$, $r \geq 1$, and $s \geq 3$. In these LB films, the nearest-neighbor distance between D and A in successive layers cannot be controlled.

3.3. A PHASE-CHANGE ORGANIC SWITCH

In 1979 a fast switch was discovered by Potember in CuTCNQ⁶⁰. This was due to the thermodynamic metastability (in crystals or amorphous powders) of the violet, low-conductivity ionic state (IS) Cu⁺TCNQ⁻(c), relative to the yellow, low-conductivity, neutral state (NS) Cu(0)TCNQ(0)(c), with, presumably, an intermediate, mixed-valent, higher-conductivity state (CS); one could switch between the two states IS \leftrightarrow CS either with an applied voltage over a certain threshold value, or by a moderate laser beam, while heat will restore the IS. This is found also in AgTCNQ, and in a few other related systems⁶¹. The switching rate is quite fast, and can be even used for optical data storage⁶², but has not been incorporated in commercial devices.

3.4. A MOLECULE-BASED TRANSISTOR USING CONDUCTING POLYMERS

Wrighton *et al.* developed a "molecule-based transistor" which uses conducting polymers: either chemically doped polyaniline layers deposited on Au interdigitated electrodes⁶³ or a 50-100 nm "gate" polyaniline polymer between two Au electrodes shadowed with SiO₂; this device still has a rather slow switching rate (10 kHz), due to the slowness of ionic conduction, and a gain of almost 1,000⁶⁴. Recently Stubb *et al.* showed that a single Langmuir-Blodgett monolayer can be used in a "molecule-based" transistor⁶⁵.

3.5. PHASE-CHANGE OPTICAL MEMORIES

There are three established technologies for mass information storage and retrieval^{66,68}:

(i) ferrite, iron oxide and chromium oxide-based magnetic memories, disks and tapes (MM): these are erasable, or write many, read many (WORM) media.

(ii) Si and GaAs-based semiconductor computer memories (SM): these can be considered as very fast write many, read many (FWORM) media.

(iii) Al pits on polycarbonate-based laser-readable compact disk (CD) technology, this is a permanent, or write once, read many (WORM) medium.

The present limitations in storage density, access time, and cost of the above three techniques have spurred an extensive search for alternative storage strategies. For instance, magneto-optical recording will provide WORM capabilities in CD, but with no increase in storage density. Alternative methods of storing WORM data on CD-type surfaces depend on phase-change systems (opaque to transparent, etc.) which can use inorganic substrates (e. g. Te) or organic substrates, or systems which depend on local melting and moving aside an organic film (e. g. phthalocyanines⁷⁰). The need to find WORM optically addressable media is acutely felt, and many organic systems are being considered: these may show a cost advantage.

3.6. SPIN TRANSITION IN LB FILMS

The groups of Barraud and Kahn have demonstrated hysteretic bistability in an LB film of 200 monolayers of Fe(tris-alkylated-1,10-phenanthroline)₂(NCS)₂⁷¹.

4. Biosynthetic electron transfer molecules

4.1. UNDERSTANDING INTRAMOLECULAR ELECTRON TRANSFER

Taube pioneered the understanding intramolecular electron transfer in solution involving binuclear transition metal complexes, both D-σ-A and D-π-A⁷². More recently, efforts have been made to control the electron transfer in solution between D-σ=Creutz-Taube ion [Ru(bpy)₃]²⁺ (bpy is 2,2'-bipyridine) and A = methylviologen⁷³. Miller, Closs *et al.*⁷²⁻⁷³ showed that the intramolecular electron transfer rate through a molecule D-σ-A at first increases steadily with an increasing I_D-A_A (where I_D is the ionization potential of the donor moiety D, A_A is the electron affinity of the acceptor moiety A). Then, if I_D-A_A is increased further, the electron transfer rate decreases, because of an increase in the Franck-Condon reorganization (because now the geometries of D⁺ and A⁻ are quite different from the geometry of D and A respectively)^{73,74} (Marcus "inverted region"⁷⁵).

4.2. POTENTIAL ARTIFICIAL PHOTOSYNTHETIC MOLECULES D-σ-A

Several large research groups have tried to make artificial photosynthetic molecules, of the type D-σ-A, where D is an electron donor, such as a porphyrin, phthalocyanine, or related molecule, σ is a covalent "sigma" bridge, i. e. a saturated linkage, such as one or several [2.2.2]-bicyclooctane rings, and A is the electron acceptor (usually *p*-benzoquinone) one should mention the groups of Mauzerall (Rockefeller)⁷⁶, Weedon and Bolton (Western Ontario)⁷⁷, Dervan and Hopfield (Caltech)⁷⁸, Mataga (Osaka)⁷⁹, Gust (Arizona State)⁸⁰, Staab (Heidelberg)⁸¹, and Verhoeven (Amsterdam)⁸². The results so far have shown a rapid charge-transfer reaction (CTR), but also a very rapid recombination of the charge-separated state by a back charge transfer reac-

tion (BCTR). It is hoped, in some quarters, that if one organizes such D-σ-A molecules in LB multilayers or other assemblies, the BCTR may be suppressed.

4.3. POTENTIAL ARTIFICIAL PHOTOSYNTHETIC MOLECULES D-π-A

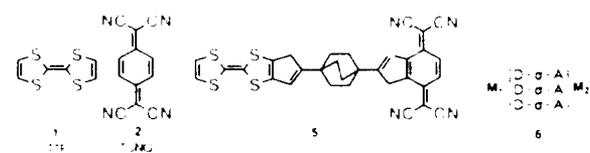
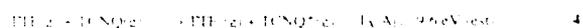
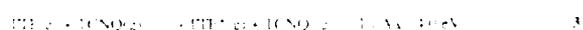
Nature produces a constant and abundant supply of carotenes as sacrificial anti-oxidants in living organisms: these carotenes have discussed either as "molecular antennas"⁸³ or as "molecular wires"⁸⁴. Carotenes have been used as the "π" bridge π between D and A, to yield D-π-A structures (D = Zn porphyrin, π = carotene, A = anthraquinone). Alas, both CTR and BCTR occurred at comparable rates, i. e. within a few ps of the laser excitation⁸⁵.

5. Truly unimolecular devices

Having discussed human efforts to mimic Mother Nature in photosynthesis, we turn to ideas to achieve unimolecular electronic devices, or zero-dimensional devices.

5.1. PROPOSED D-σ-A RECTIFIER

The Ansatz of Aviram and Ratner^{2,4} starts from the discovery of highly conducting lower-dimensional organic charge-transfer systems based on good one-electron donors (D) such as tetrathiafulvalene (TTF, 1) and good organic one-electron acceptors (A) such as 7,7,8,8-tetracyanoquinodimethan (TCNQ, 2). Good donor molecules (*i. e.* molecules with relatively low gas-phase first ionization potentials I_D) are, at the same time, poor acceptors (they have low electron affinity A_A); good acceptors (*i. e.* molecules with a relatively high first electron affinity A_A), are, at the same time, rather poor donors (have high I_D) thus the gas-phase energy required for reaction 3 (both components at infinite separation) is about 4 eV, while reaction 4 would need over 9 eV:

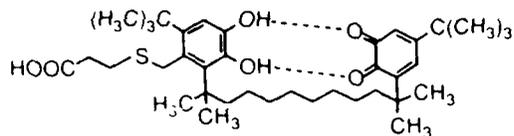


Thus, if one makes a D-σ-A molecule like 5, and assembles it somehow between two metal electrodes M₁ and M₂, as in 6 (discussed as M₁-D-σ-A-M₂ in Section 8 below), then the direction of easy electron flow is from M₂ to M₁ because it utilizes the zwitterionic state D⁺-σ-A⁻ (while the electron flow from M₁ to M₂ would be inefficient, because the barrier to form the zwitterion D⁻-σ-A⁺ would be several eV higher). Using terms popularized by Hoffman³⁷, the Aviram-Ratner device can work if the tunneling of electron from A to D is through the bond system, and will fail if the tunneling between the metal electrodes M₁ and M₂ is predominantly through space. Molecule 5 was never synthesized, and the idea languished until the ORP started in earnest, as is discussed in Sections 8 and 9 below.

5.2. PROPOSED H ATOM AND PROTON TRANSFER SWITCHES

Aviram has also proposed an intramolecular hydrogen atom transfer switch, based on H bonding in *ortho*-quinone-

catechol systems^{3,4}. It has been confirmed that there is intramolecular H atom transfer in such a system^{84,85}:



Mitani is working toward a proton transfer switch⁴⁹

5.3. PROPOSED SOLITON SWITCH

Carter⁵⁰ proposed that soliton motion in polyacetylenes could be harnessed in various switches, gates, and logic circuits. However, apart from the difficulties of synthesizing or addressing such molecules, soliton switches are expected to be relatively slow devices.

5.4. FUJIHIRA'S LB PHOTODIODE

Fujihira and co-workers have demonstrated that a single LB monolayer can function as a photodiode⁵¹; *this is probably the first truly unimolecular device*. They synthesized a D- σ 1-A- σ 2-S molecule, where D = electron donor = ferrocene, σ 1 = $(\text{CH}_2)_{11}$ chain, A = final electron acceptor = viologen, σ 2 = $(\text{CH}_2)_6$ chain, S = sensitizer = pyrene. This molecule was transferred as an LB monolayer onto a semitransparent Au electrode (with the viologen, or A, part of molecule closest to Au); this electrode was used as a window of an electrochemical cell which also contained a 0.1 M KCl solution and a Pt counter electrode. Under bias, an electron is transferred from solution to the ferrocene end of the LB film, and then to the ground state of the pyrene molecule. Light at 330 nm excited the pyrene radical cation from the ground state to an excited state, from which the electron is transferred to the viologen, thus completing the circuit. A photocurrent of 2 nA at 0.0 V vs SCE was observed only when the light was turned on⁵¹.

5.5. PROPOSED KETO-ENOL SWITCH

Sixl focussed interest on the photochromism of N-salicylideneaniline, where the enol configuration can be converted to the *trans*-keto conformation by using light of frequency ν_1 , and converted back by either heat or by light of frequency ν_2 . In this case keto-enol tautomerism is accompanied by an intramolecular rotation⁸⁶.

5.6. CONDUCTIVITY CHANGE IN LB FILMS DUE TO LIGHT-INDUCED CONFORMATIONAL CHANGE

Kawabata et al. have showed recently that a light-induced *cis-trans* conformational change in azobenzene could affect the electrical conductivity of a conductive LB film⁸⁷.

5.7. POTENTIAL CONFORMATIONAL CHANGE SYSTEMS

The idea of using organic molecules which undergo conformational changes in optical storage devices is widespread. Birge⁸⁸ has studied the primary step in the photocycle of bacteriorhodopsin (the light-harvesting protein of Halobacterium halobium), in which the bacteriorhodopsin containing all-*trans* retinal (bR 568) can be converted (at 77 K) with

two-photon illumination at 540 nm and 635 nm into K 610 or bathorhodopsin; at lower laser powers, the same two-photon illumination scheme can interrogate which molecules have converted to K 610, and which remain in the bR 568 state. The K 610 state may consist of a *cis*-retinal segment. The harnessing of such *cis-trans* isomerizations (also involved in the physiology of the visual pigments) may some day yield interesting molecular devices.

6. Device assembly ideas

6.1. MACROSCOPIC CONNECTIONS-LB FILMS AND POLYDIACETYLENES

Before the proposed unimolecular devices can be used as such, one must confront the serious issues of controlled assembly, of device interrogation, and of device resetting at the molecular level. In this section we deal with bulk molecular devices. If one cannot address a single molecule, one can perhaps address a monolayer of identical molecules transferred to a suitable (metal) substrate by the Langmuir-Blodgett (LB) film method²⁸⁻³⁴; then many identical molecules can be addressed electrically, provided that electrical short circuits through defects do not occur. However, LB monolayers are only weakly physisorbed to surfaces, and thus can desorb with time. This difficulty can be circumvented, if a photopolymerizable diacetylene⁸⁹ group is included in the monolayer-forming molecule, and if the molecular geometry is so engineered, as to yield topotactic polymerization; this can result in a very robust, yet electroactive, polymer.

6.2. MACROSCOPIC CONNECTIONS-THE SILYL BRIDGE

An alternate connection strategy, devised by Murray⁹⁰ to study the electrochemistry at the electrode surface more closely, consists of derivatizing an oxide-coated metal electrode surface with trichlorosilyl groups, then reacting this surface with the desired molecule which has a terminal alcohol group; this, however, does not usually give full monolayer coverage on the metal. The reverse strategy, advanced by Sagiv, of silanizing the molecule and attaching it to an oxide and hydroxyl-group-covered metal surface, claims to achieve full monolayer coverage⁹¹.

6.3. PROPOSED MACROSCOPIC CONNECTIONS-CYCLODEXTRINS AND CALIXARENES

The existence of cavities of precisely controlled size within cyclodextrins and calixarenes allows the inclusion of small electroactive molecules within these cavities, and yet provide well-formed macroscopic crystals with the desired inclusions precisely oriented within them^{55,56}.

7. How to connect to a unimolecular electronic device

7.1. PROPOSED MOLECULAR WIRES

The carotenes and other conjugated linear polyenes have been touted as "molecular wires" or as "molecular antennas"⁵², and certainly will provide fast electronic access to single molecules. These polyenes are, unfortunately, very susceptible to air oxidation (as is the simplest conducting polymer, doped polyacetylene).

7.2. PROPOSED SPIRO-LINKED THIOPHENE INTERCIRCUIT CONNECTIONS

Aviram has proposed⁵³ a spiro-linked polythiophene system as a possible interconnection between conducting "molecular wires" based on *n* or *p*-doped polythiophene.

7.3. MOLECULAR SPACERS

Miller et al. have shown how several successive Diels-Alder condensation reactions can yield insulating, yet sturdy, LB film-forming oligomers of controlled length.⁵⁴

7.4. SCANNING TUNNELING MICROSCOPY

The recent advent of affordable scanning tunneling microscopy (STM)⁵⁵ should let us address electronically a single molecule. If this becomes easily controllable and reproducible, then a real revolution in ME devices should be "just around the corner".

8. Review of the organic rectifier project

This section reviews the progress made by the ORP towards the synthesis and characterization of the Aviram-Ratner rectifier **6** (M_1 -D- σ -A- M_2): the efforts to detect rectification are reviewed in Section 9.

8.1. STRATEGIES FOR ASSEMBLY OF D- σ -A DEVICES

As discussed above, to address a single molecule electrically, one needs a "molecular wire" (e.g. a polyacetylene strand) or a "molecular antenna" (e.g. the conjugated portion of β -carotene), neither of which can be easily connected to an external potential source, at present. Until the recent advent of the STM, one could not connect a single molecule to an external circuit. Therefore, when the ORP was initiated, in about 1981, to realize the Aviram-Ratner rectifier, one had to content oneself with assemblies of molecules. The three techniques that showed promise were (i) the LB technique²⁵⁻³¹, and the technique of covalently bonding molecules to electrode surfaces, either by (ii) silanizing a hydroxyl-coated electrode, then attaching molecules covalently³⁰, or (iii) by silanizing the molecule, and attaching it directly by spin-coating by the oleophobic method³² to a hydroxyl-coated electrode³¹. As discussed above, good monolayer coverage is claimed for the latter method³¹, but not for the former method³⁰.

The ORP was committed to the LB technique. Then, of course, one then needs LB films that are defect-free in the lateral dimension, at least to within the area probed electrically. Of course, LB monolayers do have many microscopic and macroscopic defects³³.

8.2. ELECTRONIC AND SYNTHETIC CRITERIA

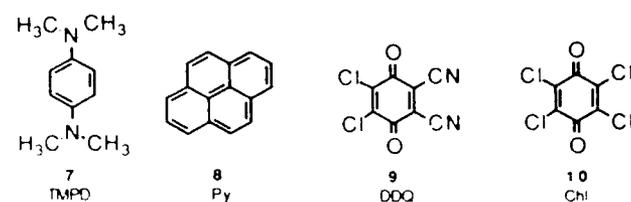
There are several interlocking criteria that must be satisfied for the rational synthesis of suitable D- σ -A systems:

(i) I_D for the donor end D must be as small, and as close as possible to the work function ϕ of the metal layer M_1 . Typical values are listed in Table I.

(ii) A_A for the acceptor end (Table I) must be as large as possible, and as close as possible to the work function ϕ of the metal layer M_2 . It is clear from Table I that requirements (i) and (ii) can be met only approximately.

Table I. -- Experimental ionization potentials I_D for selected good donors D, experimental electron affinities A_A for selected good acceptors A, and work functions ϕ for selected metals M_1 , M_2 .²⁰

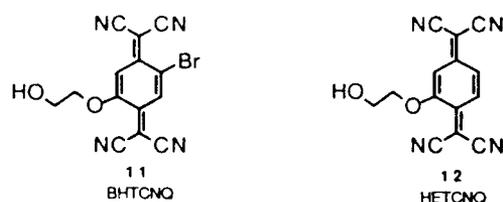
I_D eV	A_A eV	ϕ eV			
TMPD (7)	6.25	DDQ (9)	3.13	Al	3.74
TTF (1)	6.83	TCNQ (2)	2.8	Au	4.58
Pyrene (8)	7.41	Chloranil (10)	2.76	Pt	5.29



(iii) In a molecule in which the "sigma" bridge has already been built, it is extremely difficult to convert, in situ, by chemical synthesis, a weak donor into a strong donor, or a weak acceptor into a strong acceptor. Therefore, instead, one must synthesize a series of mono-substituted strong donors, and mono-substituted strong acceptors, which can be joined by some coupling reaction which can avoid the usual, and undesirable, formation of ionic charge-transfer complexes, such a coupling reaction is the urethane, or carbamate coupling reaction, pioneered for a (- σ -TTF- σ -TCNQ)-_n copolymer by Hertler³⁴ and adapted to monofunctional derivatives by Baghdadchi³⁵.

(iv) The molecules must pack efficiently into self-assembling monolayers. If the designed molecule does not form Pockels-Langmuir (PL)¹⁶⁻²⁵ self-assembling monolayers at the air-water interface, then either long aliphatic "greasy tails" must be added to form a hydrophobic tail, or an ionic, hydrophilic "head" should be added. The molecules should be fairly flat, so as to form compact films, yet flexible enough, so as transfer well (by the vertical dipping method) as LB films.

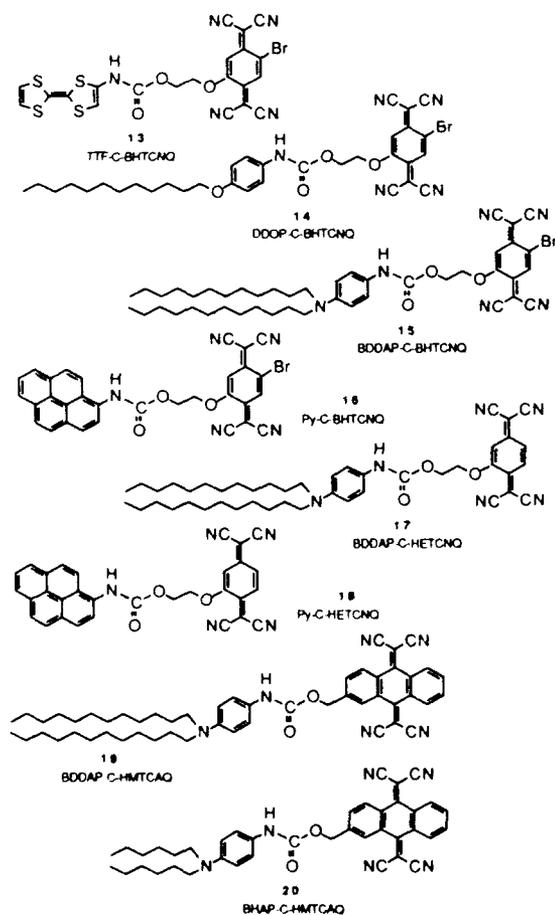
(v) The synthesis of the acceptor should be relatively easy, and should occur in high yield. The acceptor used in the early work of the ORP was BHTCNQ, **11**, whose synthesis^{34, 35} contained a very inefficient, low-yield step. A new, better monofunctionalized TCNQ acceptor, prepared in high yield, was HETCNO, **12**.¹⁸



(vi) The electron transfer through the D- σ -A molecule, and through its hydrophobic or hydrophilic tails, must be fast: as said above, a molecular device that is small but slow is not predicted to be useful. That electron transfer is fast through properly designed molecules, e.g. the photosynthetic reaction center, is well known. The work of Miller et al.,^{73, 74} reviewed above, shows that a balance must be struck between the requirements implied by the ionization potentials and electron affinities of Table I, and the resulting I_D - A_A values, and those of the Franck-Condon factor.

Table II. — Pressure-Area isotherm data for Pockels-Langmuir films. Π_c and A_c are the pressure and molecular area, respectively, at the collapse point. \S indicates that the film makes Z-type LB multilayers (substrate at 22°C, film at 5°C)

Molecule	No.	Type	T K	Π_c mN m	A_c \AA^2	Ref
TTF-C-BHTCNQ	13	strong D strong A	292	12.7	134 ± 50	6
DDOP-C-BHTCNQ	14	weak D strong A	292	20.2	50 ± 1	5
BDDAP-C-BHTCNQ	15	medium D strong A	293	47.3	57 ± 1	16
Py-C-BHTCNQ	16	medium D strong A	283	28.2	53 ± 1	7
BDDAP-C-HETCNQ	17	medium D strong A	293	40.0	44 ± 1	16
Py-C-HETCNQ	18	medium D strong A	293	46		16
BDDAP-C-HMTCAQ	19	medium D weak A	293	22.3	58 ± 1	16
BHAP-C-HMTCAQ	20	medium D weak A	293	35.8	42 ± 1	17
DDOP-C-ENP	\S 21	weak D weak A	278	23.7	38 ± 1	25
TDDOP-C-ENP	\S 22	weak D weak A	278	34.0	76 ± 1	25
TDDOP-C-HETCNQ	\S 23	weak D strong A	283	47.5	54 ± 1	25
MTDAP-C-ENP	\S 24	weak D weak A	278	16.5	63 ± 1	24



(vii) The device **6** must have a finite tolerance for high voltages or heating.

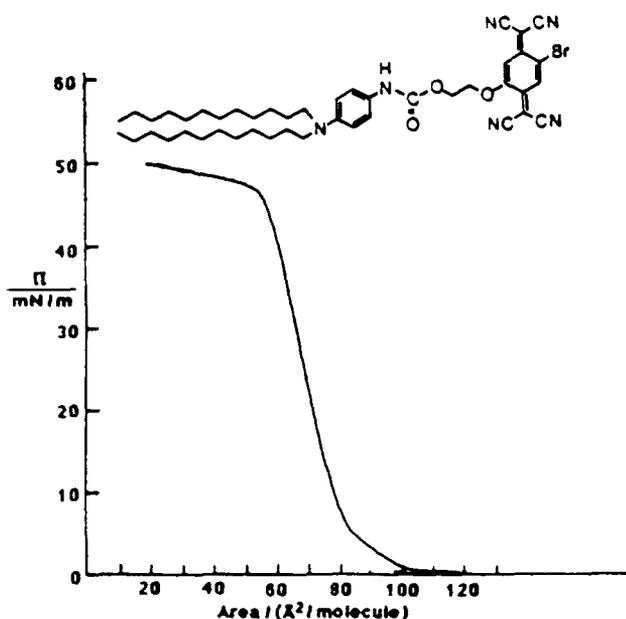
8.3. LANGMUIR-BLODGETT FILMS

We present in Table II an updated catalog of molecules (**13-24**) prepared by the ORP, which form PL monolayers at the air-water interface, and which transfer well onto Al or glass or other slides as LB monolayers. TTF-C-BHTCNQ, **13**, was difficult to purify; the "neutral" form seemed to deposit "pancake-style" onto the water, and synthetic difficulties forced its abandonment. The strongest films (highest collapse pressure, most vertical pressure-area isotherm) were obtained with BDDAP-C-BHTCNQ, **15** (Fig. 1). The acceptor HMTCAQ used in **19** and **20** was easy to prepare¹⁰, but is well known to be a weak two-electron acceptor, with a highly non-planar geometry²³.

Molecules **21-24** are model systems for a related project, which aims to incorporate D- σ -A systems into LB-film-forming diacetylenes, which may be polymerized in situ on the film balance, for the purpose of preparing new systems with promise as non-linear optical devices. Interestingly, **21-24** form Z-type multilayers on a glass substrate (the film sub-phase is held at 5°C but the slide is at room temperature). An attempt was made to see whether any second harmonic signals could be detected from Z multilayers of **23**, but the result was negative, maybe because the Z-type multilayers may have reorganized with the time elapsed between deposition and measurement⁹⁷.

8.4. ELECTROVOLTAISMETRY

One donor (DMAP-C-Me, **25**), several acceptors (**2**, **11**, **12**, and HMTCAQ, **26**) and several D- σ -A molecules (**14**,



17, 18, 21, 22 and 23) were characterized by cyclic voltammetry (CV). The results, summarized in Table III, confirm that the carbamate linkage does preserve the oxidation (reduction) potentials of the D(A) ends of the D- σ -A molecules.

8.5. CRYSTAL STRUCTURES OF MODEL DONOR, ACCEPTOR, AND D- σ -A MOLECULES

A few crystal structures have been solved: for the donor DMAP-C-Me, **25**¹² (Fig. 3) for the acceptor BHTCNQ, **11**¹⁴ (Fig. 4), and for the methyl ester (AETCNQ, **27**) of the acceptor HETCNQ, **12**¹⁵ (Fig. 5). The small difference in conformation between AETCNQ and BHTCNQ can be attributed to crystal packing forces, rather than to intramole-

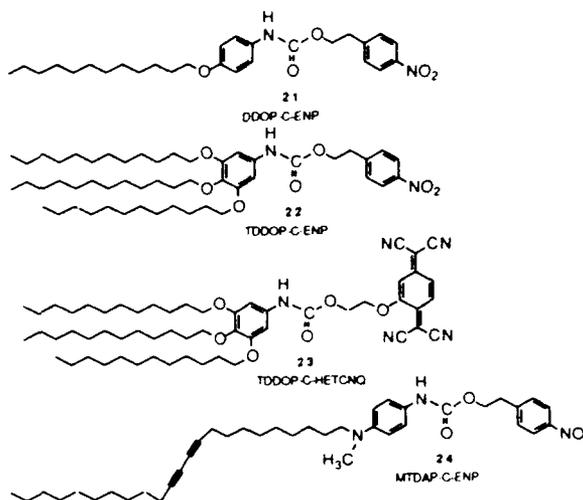


Figure 1. — Pressure-area isotherm of BDDAP-C-BHTCNQ, **15**, at 293 K [15]

cular effects. Naturally, amphiphilic molecules that form LB films will not usually crystallize, because of the usual aliphatic "tails" added to them. However, we have solved the structures of two D- σ -A molecules which do not form PL or LB films: Ph-C-BHTCNQ, **28**⁷ (Fig. 6), and DMAP-C-HMTCAQ, **29**²³ (Fig. 7). Both structures show an extended carbamate linkage; in Ph-C-BHTCNQ, the dihedral angle between the phenyl ring and the six-membered central ring of BHTCNQ is only 8°. This gives hope that in LB films of related D- σ -A molecules the carbamate linkage will also be extended.

Table III. — Solution cyclic voltammetric potentials²⁶⁻²⁷. All data were obtained at a Pt electrode, and are given in Volts vs SCE.

Molecule	No.	Oxid. (1) D → D ^{•+}		Oxid. (2) D ^{•+} → D ²⁺		Red. (1) A → A ^{•-}		Red. (2) A ^{•-} → A ²⁻		Ref.
		E _p	E _{1,2}	E _p	E _{1,2}	E _p	E _{1,2}	E _p	E _{1,2}	
<i>Donor</i>										
DMAP-C-Me	25 ^a	0.58	0.55							13
<i>Acceptors</i>										
TCNQ	2 ^b					0.19		-0.35		98
TCNQ	2 ^c					0.11	0.13	-0.46	-0.43	25
BHTCNQ	11 ^b						0.305		-0.170	8
HETCNQ	12 ^b						0.107		-0.398	18
HMTCAQ	26 ^b							-0.372	-0.333	10
<i>D-σ-A</i>										
DDOP-C-BHTCNQ	14 ^d		1.21				0.25		-0.07	8
BDDAP-C-HETCNQ	17 ^e	0.66i		1.10		0.02		-0.49i		99
Py-C-HETCNQ	18 ^e	1.04	1.01	1.18	1.15	0.11	0.08	-0.32	-0.35	99
BHAP-C-HMTCAQ	20 ^e	0.63	0.60					-0.39	-0.36	99
TDDOP-C-HETCNQ	23 ^e	1.02i				0.10	0.07	-0.50	-0.47	25
DDOP-C-ENP	21 ^e	1.42	1.39			-1.16	-1.13			25
TDDOP-C-ENP	22 ^e	1.17i				-1.12	-1.15			25
MTDAP-C-ENP	24 ^e	0.57	0.54			-1.09	-1.06			99

^a Solvent: CH₃CN. Reference electrode: SCE. A peak at 0.37 V (return scan) grows with successive cycles, and is indicative of dimer or polymer formation.¹³ ^b Solvent: CH₃CN. Reference electrode: SCE. ^c Solvent: CH₂ClCH₂Cl. Reference electrode: Ag|AgCl. An offset correction of 0.15 V has been applied to convert the values to V vs. SCE. ^d Solvent: CH₃CN. Reference electrode: Ag|AgNO₃. An offset correction of 0.320 V has been applied to convert the values to V vs. SCE. ^e Solvent: CH₂ClCH₂Cl. Reference electrode: Ag|AgCl. An offset correction of 0.19 V has been applied to convert the values of V vs. SCE.

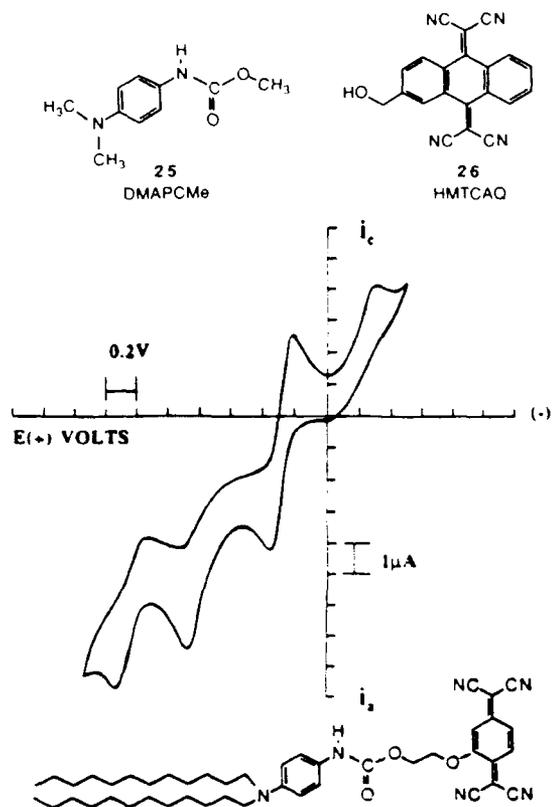


Figure 2. - Cyclic voltammogram of BDDAP-C-HETCNQ. 17

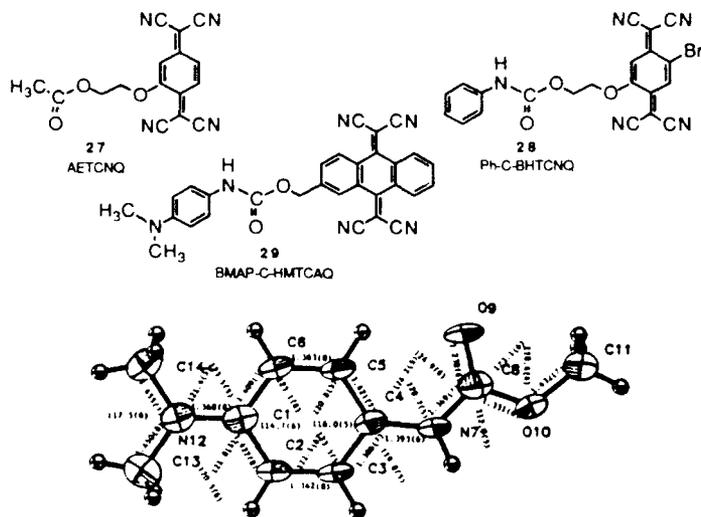


Figure 3. - ORTEP-II plot of the crystalline structure of DMAP-C-Me, 25.¹² Space group $Pbca$ ($\# 61$), $a = 13.926$, $b = 9.999$, $c = 14.854$ Å, $Z = 8$, $R = 5.9\%$ for 786 reflections

8.6. MOLECULAR ORBITAL CALCULATIONS

As reported previously²¹ semi-empirical molecular orbital (MO) calculations, using the MNDO algorithm, with full geometry optimization, in program MOPAC, have been performed on D- σ -A molecules, to predict their geometry, and also their HOMO and LUMO energies. The structure as drawn by program ORTEP-II using typical van der Waals

atomic radii (1.2 Å for H, 1.7 Å for C, 1.5 Å for O, 1.35 Å for F, and 1.65 Å for S) are shown in Figures 8-12 (the van der Waals shape is viewed from the A end of the molecule). Also given are the HOMO ($-I_D$) and LUMO ($-A_A$) energies, and also the differences I_D-A_A and I_A-A_D discussed in Equations 3 and 4 above.

Overall, the MNDO structures are extended, as expected, but there are some small surprises: (i) while the data of Table II suggest that in a PL film Py-C-BHTCNQ is a relatively flat molecule, Figure 11 introduces a twist in the carbamate linkage; (ii) while the data of Table II suggest a well-packed BDDAP-C-BHTCNQ molecule, Figure 10 shows a conformer in which the bis-hexyl "tails" are not well aligned with each other; (iii) while the crystal structure of BMAP-C-HMTCAQ²³ shows that both dicyanomethylene substituents on the anthracene ring deviate from the plane in the same direction, MNDO gave them a "corkscrew" twist in Figure 12. The MNDO ionization energies I_D are probably 1 to 2 eV high, as expected from a Koopman's theorem calculation; the size of the difference $(I_D-A_A)-(I_A-A_D)$ is as large as expected, but some of the I_D values are not as low as hoped.

8.7. FOURIER TRANSFORM INFRARED SPECTRA OF D- σ -A MONOLAYERS

Grazing-angle Fourier transform infrared (FTIR) spectra of monolayers of BDDAP-C-HMTCAQ, BDDAP-C-BHTCNQ, and TDDOP-C-HETCNQ, have been measured, and reported previously^{20, 22, 24}. The C-H stretch bands are well resolved, even for a single monolayer, and a broad structure at about 3500 cm^{-1} is seen for "fresh" samples, but disappears for samples older than about 60 days; this may be water trapped between the LB film layer and the aluminium layer, but the identification is not certain (the films were not studied in vacuum).

9. Rectification attempts

We discuss here seven attempts, by the ORP and by others, to detect rectification.

In the *first* experiment⁴, a 2 mm diameter droplet of Hg was used to probe the conductivity across a single monolayer LB film deposited on either Pt or conducting tin oxide glass; the sandwiches:

- (i) Pt|DDOP-C-BHTCNQ|Hg,
- (ii) Pt|Py-C-BHTCNQ|Hg, and

(iii) conducting SnO_2 glass|DDOP-C-BHTCNQ|Hg were thus tested; in all cases the background conductivity of the solid support was measured, presumably because of microscopic pinholes in the LB film, which may have been formed, in part, by the damage that the Hg drop can do on the film surface⁴.

In the *second* experiment²⁰, in the hope that maybe defects may be avoided, statistically, in a domain of the order of about $0.5 \text{ mm} \times 0.5 \text{ mm}$, if one searched through enough samples, the left-hand half of fifteen glass microscope slides was coated (using a mask) with five parallel fingers of Al at least 500 nm thick, 3.5 mm long, and 1.6 mm wide. Then the fifteen slides were coated with a single LB monolayer of BDDAP-C-BHTCNQ, 15, at room temperature. Then the slides were coated again with five fingers of Al, but this time on the right hand side of the slide, so that the vertical overlap

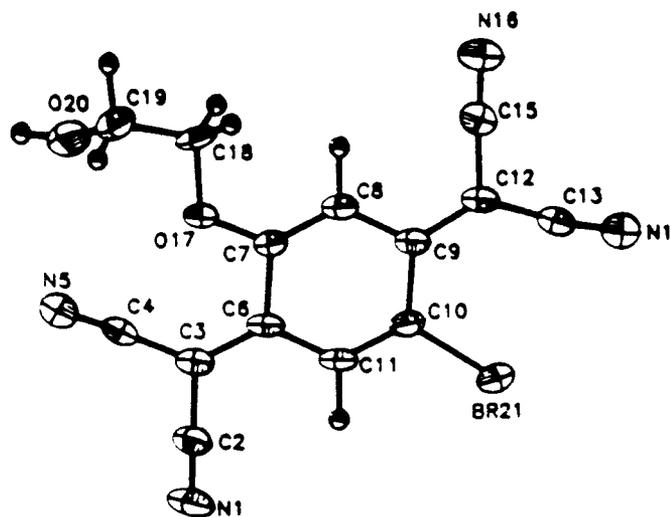


Figure 4. — ORTEP-II plot of BHTCNQ, 11^{14} . Space group $P2_1$, n ($n \neq 14$), $a = 9.258$, $b = 13.618$, $c = 10.947$ Å, $\beta = 92.14^\circ$, $Z = 4$, $R = 3.9\%$ for 1395 reflections.

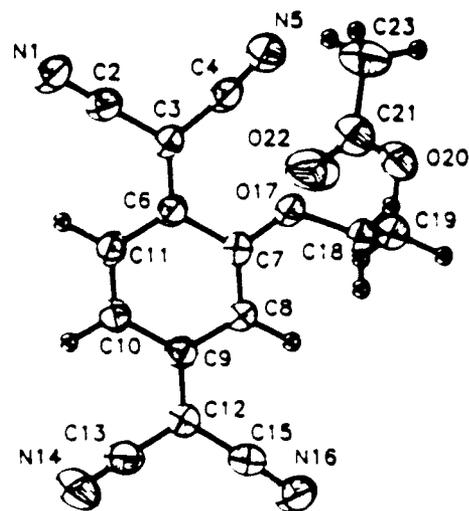


Figure 5. — ORTEP-II plot of AETCNQ, 27^{15} . Space group $P1$ bar ($n \neq 2$), $a = 7.165$, $b = 9.058$, $c = 13.244$ Å, $\alpha = 70.06^\circ$, $\beta = 87.14^\circ$, $\gamma = 68.22^\circ$, $Z = 2$, $R = 3.4\%$ for 1143 reflections.

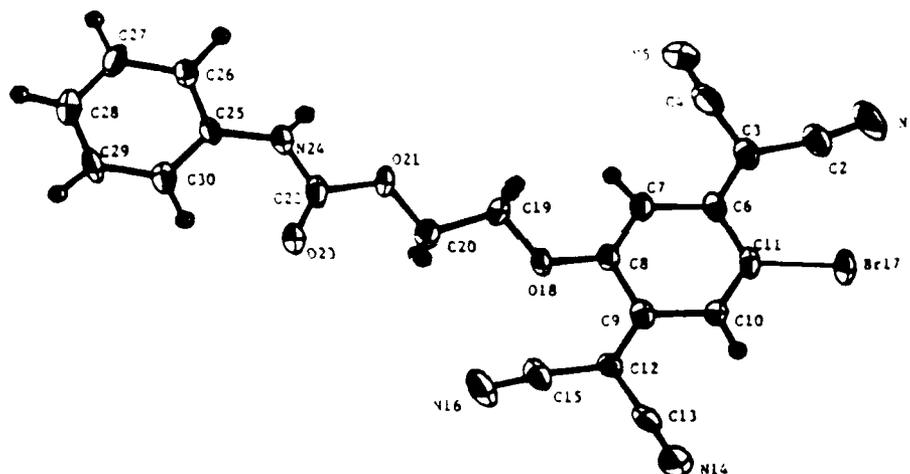


Figure 6. — ORTEP-II plot of the crystalline structure of Ph-C-BHTCNQ, 28^{17} . Space group $P2_1$, n ($n \neq 14$), $a = 8.310$, $b = 9.278$, $c = 25.383$ Å, $\beta = 96.15^\circ$, $Z = 4$, $R = 7.9\%$ for 2229 reflections.

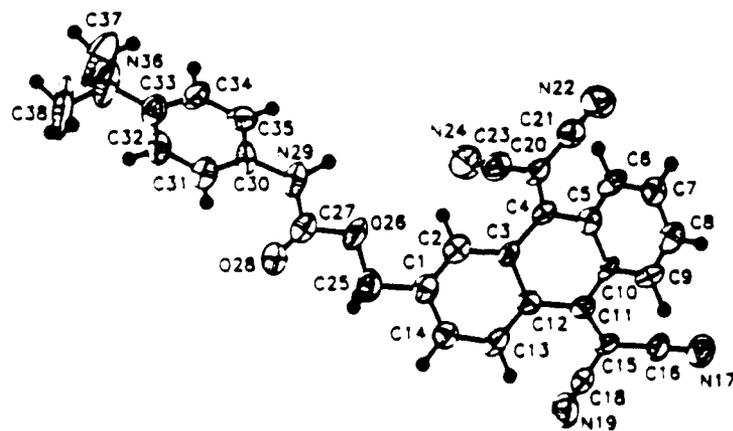


Figure 7. — ORTEP-II plot of the crystalline structure of DMAP-C-HMTCAQ, 29^{23} . Space group $P1$ bar ($n \neq 2$), $a = 8.748$, $b = 10.989$, $c = 13.541$ Å, $\alpha = 90.67^\circ$, $\beta = 99.15^\circ$, $\gamma = 98.62^\circ$, $Z = 2$, $R = 12.7\%$ for 1839 reflections.

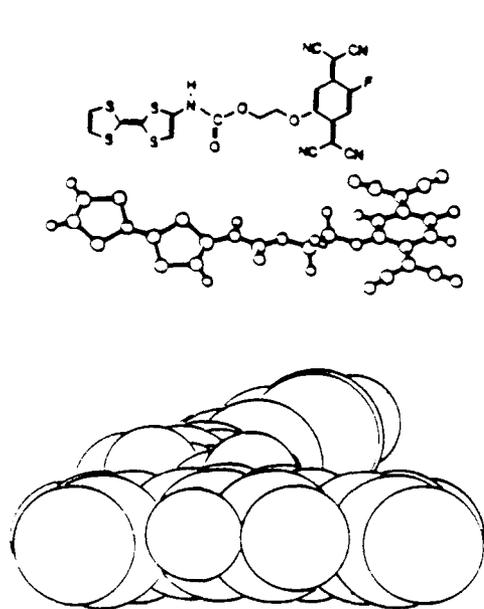


Figure 8. Structure (top), MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) for TTF-C-FHTCNQ, a variant of TTF-C-BHTCNQ, **13**. $I_D = 8.197$ eV, $A_A = 2.975$ eV, $I_D - A_A = 5.222$, $I_A - A_D = 9.447$ eV.²¹

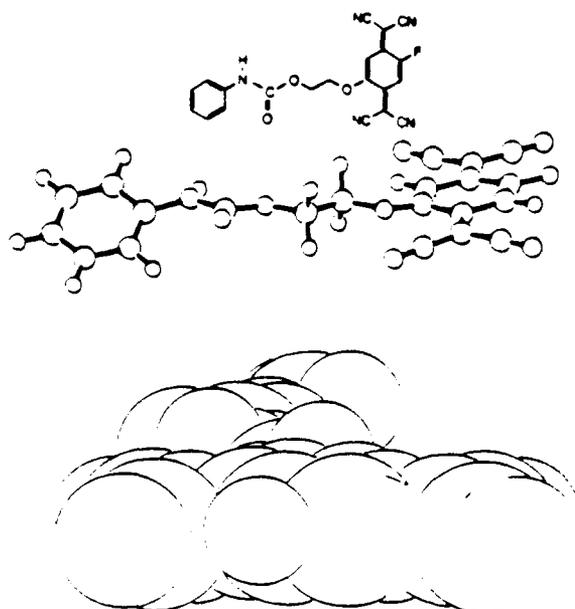


Figure 9. Structure (top), MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) for Ph-C-FHTCNQ, a variant of Ph-C-BHTCNQ, **28**. $I_D = 9.141$ eV, $A_A = 2.941$ eV, $I_D - A_A = 6.200$ eV, $I_A - A_D = 9.493$ eV.²¹

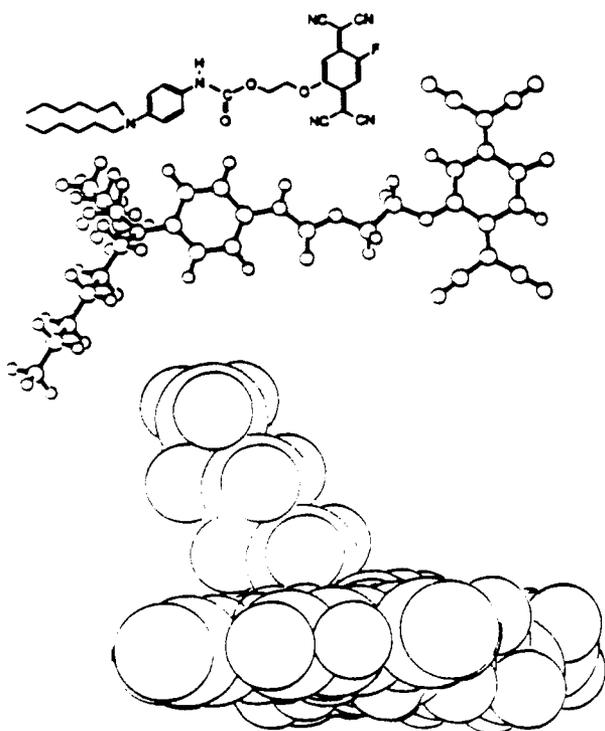


Figure 10. Structure (top), MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) for BHAP-C-FHTCNQ, a variant of BDDAP-C-BHTCNQ, **15**. $I_D = 8.767$ eV, $A_A = 2.936$ eV, $I_D - A_A = 5.831$, $I_A - A_D = 9.461$ eV.²¹

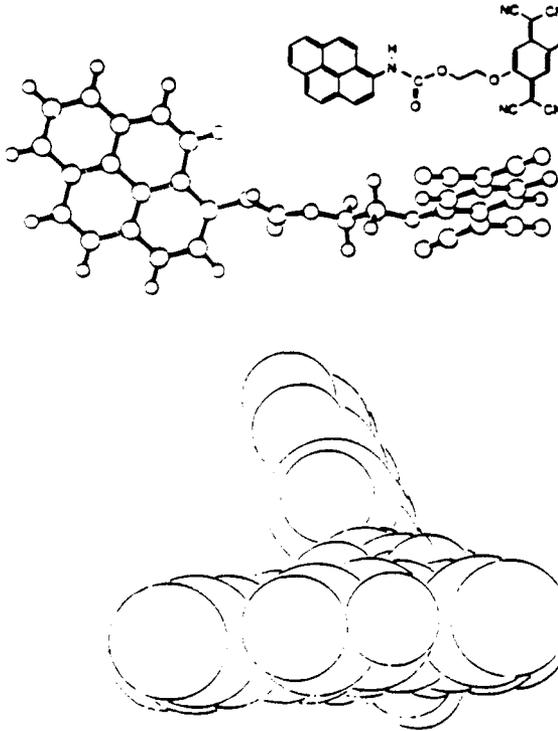


Figure 11. Structure (top), MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) for Py-C-FHTCNQ, a variant of Py-C-BHTCNQ, **16**. $I_D = 8.192$ eV, $A_A = 2.957$ eV, $I_D - A_A = 5.235$ eV, $I_A - A_D = 8.347$ eV.²¹

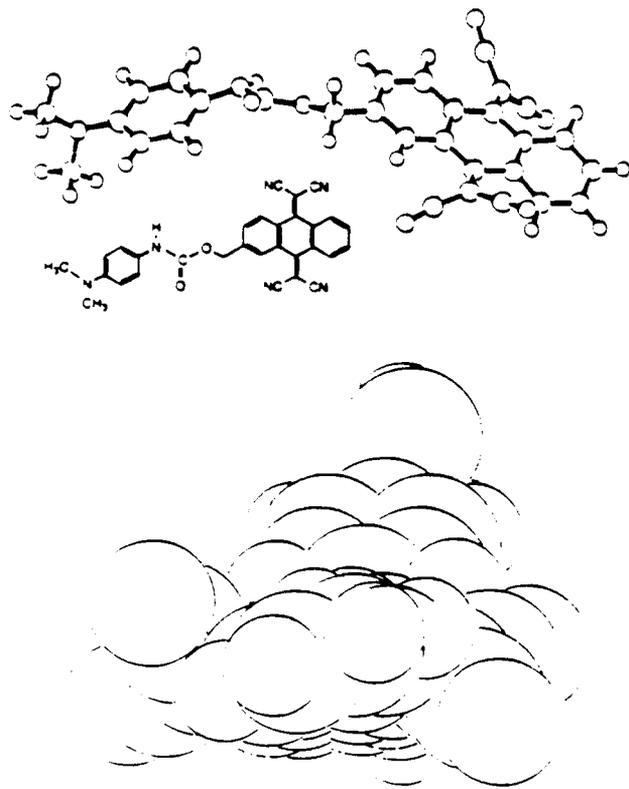


Figure 12. - MNDO conformation (top), structure (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) of BMAP-C-HMTCAQ. **29:** $I_D = 9.052$ eV, $A_A = 2.627$ eV, $I_D - A_A = 6.425$, $I_A - A_D = 9.220$ eV.²¹

Al|BDDAP-C-BHTCNQ|Al would be in an area of only about $0.5 \text{ mm} \times 0.5 \text{ mm}$. Of the 75 junctions thus prepared, many were open circuits; the rest were short circuits. Thus, a defect-free domain of BDDAP-C-BHTCNQ had not been found.

In the *third* experiment, Aviram, Joachim, and Pomerantz reported in 1988⁸⁴ (and later retracted⁸⁵) that rectification had been observed in a modified STM, for the molecule shown in Section 5.2 above, which had been originally designed as internal hydrogen atom transfer switch (and not as a rectifier). The claim for molecular rectification was later retracted⁸⁵.

In the *fourth* experiment, Dr. Pomerantz studied with his modified STM, an LB monolayer of BDDAP-C-BHTCNQ, **15**, deposited on a Au|Ag|mica substrate, using an atomically sharp W tip, as the couple W|BDDAP-C-BHTCNQ|Au. Large "rectification" currents were observed^{21,22}, but later control experiments by Dr. Pomerantz showed that this "rectification effect", with very large currents, could occur *in the absence of any molecule*. Disclaimers for the preliminary results were issued^{21,22}.

Recently, in a *fifth* experiment, Sambles et al. at the University of Exeter found that a monolayer of BDDAP-C-BHTCNQ, sandwiched between Pt and Mg electrodes, behaved as a rectifying LB film³⁶.

Later, Sambles' and Ashwell's group found, in a *sixth* experiment, that an LB film of Z- β -(1-hexadecyl-4-quinolinium)- α -cyano-4-styryldicyanometanide (C₁₆H₃₃-Q3CNQ, **77**), a D- π -A molecule, similarly sandwiched between Pt and Mg electrodes (the latter shadowed with Ag) also showed macroscopic rectification behavior³⁷. However it has not yet been excluded that the observed I-V curves are not due to dipolar association (e.g. between Mg and TCNQ) or to other Schottky barriers³⁷.

The ORP has recently acquired a STM (Digital Instrument Nanoscope II) of its own, and, in a *seventh* experiment, has studied monolayer LB films of BDDAP-C-HETCNQ and Py-C-HETCNQ, transferred onto highly oriented pyrolytic graphite (Union Carbide grade ZYA) by a horizontal lifting technique. Pt Ir "nanotips" (Digital Instruments) were used. At low set-point currents, some asymmetries in the current-voltage plots can be seen. In preliminary work with BDDAP-C-HETCNQ and Py-C-HETCNQ, the image of graphite is replaced by what seems to be an image of the film¹⁰⁰.

Conclusion

We have outlined here several topics in ME, and hope to have convinced the reader that many exciting prospects exist in this infant field.

REFERENCES

- Metzger R. M., in "Lower-Dimensional Systems and Molecular Electronics", Metzger R. M., Day P., Papavassiliou G. C. Eds., NATO ASI Series, Plenum, New York, 1991, p. 691
- Aviram A., Freiser M. J., Seiden P. E., Young W. R., U. S. Patent US-3,953, 874, 27 April 1976
- Aviram A., Ratner M. A., *Chem. Phys. Lett.*, 1974, **29**, 277.
- Aviram A., Seiden P. E., Ratner M. A., in "Molecular Electronic Devices", Carter F. L. Ed., Dekker, New York, 1982, p. 5.
- Metzger R. M., Panetta C. A., *J. Phys. Les Ulis, Fr., Colloque*, 1983, **44**, C3-1605.
- Metzger R. M., Panetta C. A., in "Molecular Electronic Devices", Vol. II, Carter F. L. Ed., Dekker, New York, 1987, p. 1.
- Panetta C. A., Baghdadchi J., Metzger R. M., *Mol. Cryst. Liq. Cryst.*, 1984, **107**, 103.
- Metzger R. M., Panetta C. A., Heimer N. E., Bhatti A. M., Torres E., Blackburn G. F., Tripathy S. K., Samuelson L. A., *J. Mol. Electronics*, 1986, **2**, 119.
- Metzger R. M., Panetta C. A., Miura Y., Torres E., *Synth. Metals*, 1987, **18**, 797.
- Torres E., Panetta C. A., Metzger R. M., *J. Org. Chem.*, 1987, **52**, 2944.
- Metzger R. M., Panetta C. A., in "Proceedings of the Eighth Winter Conference on Low-Temperature Physics, Cuernavaca, Mexico", 1987, 81.
- Laidlaw R. K., Miura Y., Panetta C. A., Metzger R. M., *Acta Cryst.*, 1988, **C44**, 2009.
- Laidlaw R. K., Miura Y., Grant J. L., Cooray L., Clark M., Kispert L. D., Metzger R. M., *J. Chem. Phys.*, 1987, **87**, 4967.
- Laidlaw R. K., Baghdadchi J., Panetta C. A., Miura Y., Torres E., Metzger R. M., *Acta Cryst.*, 1988, **B44**, 645.
- Miura Y., Laidlaw R. K., Panetta C. A., Metzger R. M., *Acta Cryst.*, 1988, **C44**, 2007.
- Metzger R. M., Schumaker R. R., Cava M. P., Laidlaw R. K., Panetta C. A., Torres E., *Langmuir*, 1988, **4**, 298.
- Metzger R. M., Panetta C. A., in "Organic and Inorganic Lower-Dimensional Materials", NATO ASI Series, Vol. B168,

- Delhaes P., Drillon M. Eds., Plenum, New York, 1988, p. 271.
- ¹⁸ Miura Y., Torres E., Panetta C. A., Metzger R. M., *J. Org. Chem.*, 1988, **53**, 439.
- ¹⁹ Miura Y., Panetta C. A., Metzger R. M., *J. Liquid Chrom.*, 1988, **11**, 245.
- ²⁰ Metzger R. M., Panetta C. A., *J. Mol. Electronics*, 1989, **5**, 1.
- ²¹ Metzger R. M., Panetta C. A., *J. Chem. Phys.*, 1988, **85**, 1125.
- ²² Metzger R. M., Panetta C. A., *Synth. Met.*, 1989, **28**, C807.
- ²³ Metzger R. M., Laidlaw R. K., Torres E., Panetta C. A., *J. Cryst. Spectr. Res.*, 1989, **19**, 475.
- ²⁴ Metzger R. M., Panetta C. A., in "Molecular Electronics Science and Technology", Aviram A., Bross A. Eds., New York Engineering Foundation, 1990, p. 293.
- ²⁵ Metzger R. M., Wiser D. C., Laidlaw R. K., Takas M. A., Mattern D. L., Panetta C. A., *Langmuir*, 1990, **6**, 1515.
- ²⁶ Metzger R. M., Panetta C. A., in "Lower-Dimensional Systems and Molecular Electronics", Metzger R. M., Day P., Papavassiliou G. C. Eds., NATO ASI Series, Plenum, New York, 1991, p. 641.
- ²⁷ Metzger R. M., Panetta C. A., in "Advanced Organic Solid State Materials", Chiang L. Y., Cowan D. O., Chaikin P. Eds., Materials Research Society Symposium Proceedings Series, 1990, **173**, 531.
- ²⁸ See e.g. Gaines Jr. G. L., "Insoluble Monolayers at Liquid - Gas Interfaces", Interscience, New York, 1966.
- ²⁹ Blodgett K. B., *J. Am. Chem. Soc.*, 1935, **57**, 1007.
- ³⁰ Blodgett K. B., Langmuir I., *Phys. Rev.*, 1937, **51**, 964.
- ³¹ Kuhn H., Möbius D., Bücher H., in "Techniques of Chemistry, Vol. I - Physical Methods of Chemistry - Part V - Determination of Thermodynamic and Surface Properties", Weissberger A., Rossiter B. W. Eds., Wiley-Interscience, New York, 1972, p. 577.
- ³² Kuhn H., *Pure Appl. Chem.*, 1979, **51**, 341.
- ³³ Kuhn H., *Pure Appl. Chem.*, 1981, **53**, 2105.
- ³⁴ See e.g. *Thin Solid Films*, Vols. 68, 1980, 99, 1983, 132-134, 1985, 159-160, 1987.
- ³⁵ Binnig G., Rohrer H., Gerber Ch., Weibel E., *Phys. Rev. Lett.*, 1982, **49**, 57.
- ³⁶ Geddes N. J., Sambles J. R., Jarvis D. J., Parker W. G., Sandman D. J., *Appl. Phys. Lett.*, 1990, **56**, 1916.
- ³⁷ Ashwell G. J., Sambles J. R., Martin A. S., Parker W. G., Szablewski M., *J. Chem. Soc. Chem. Commun.*, 1990, 1374.
- ³⁸ Carter F. L. Ed., "Molecular Electronic Devices", Dekker, New York, 1982.
- ³⁹ Carter F. L. Ed., "Molecular Electronic Devices II", Dekker, New York, 1987.
- ⁴⁰ Carter F. L., Siatkowski R. E., Wohltjen H. Eds., "Molecular Electronic Devices, Proceedings of the 3rd International Symposium", North-Holland, Amsterdam, 1988.
- ⁴¹ Borissov M. Ed., "Molecular Electronics - IVth International School on Condensed Matter", World Scientific, Singapore, 1987.
- ⁴² Aviram A. Ed., "Molecular Electronics - Science and Technology", New York Engineering Foundation, 1990.
- ⁴³ Haddon R. C., Lamola A. C., *Proc. Natl. Acad. Sci. U.S.A.*, 1985, **82**, 1874.
- ⁴⁴ Davidov D., Selig H. Eds., "Graphite Intercalation Compounds", *Synth. Metals*, 1988, **23**.
- ⁴⁵ Acrivos J. V., *NATO ASI Ser.*, 1984, **C130**, 479.
- ⁴⁶ For the proceedings of a recent conference, see "Advanced Organic Solid State Materials", Chiang L. Y., Cowan D. O., Chaikin P. Eds., Materials Research Society Symposium Proceedings Series, 1990, **173**, 531.
- ⁴⁷ Skotheim T. A. Ed., "Handbook of Conducting Polymers", Vol. I and II, Dekker, New York, 1986.
- ⁴⁸ Relevant articles in Miller J. S. Ed., "Extended Linear-Chain Compounds", Vols. I, II, and III, Plenum, New York, 1982, 1983.
- ⁴⁹ Inabe T., Hoshino N., Mitani T., Maruyama Y., *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2245.
- ⁵⁰ Carter F. L., in Carter F. L. Ed., "Molecular Electronic Devices", Dekker, New York, 1982, p. 51.
- ⁵¹ Fujihira M., Nishiyama K., Yamada H., *Thin Solid Films*, 1985, **132**, 77.
- ⁵² Lehn J.-M., *Angew. Chem. Intl. Ed. Engl.*, 1988, **27**, 89.
- ⁵³ Aviram A., *J. Am. Chem. Soc.*, 1988, **110**, 5687.
- ⁵⁴ Kenny P. W., Miller L. L., Rak S. F., Jozefiak T. R., Christopfel W. C., Kim J. H., Uphaus R. A., *J. Am. Chem. Soc.*, 1988, **110**, 4445.
- ⁵⁵ Szejtli J., "Cyclodextrin Technology", Kluwer, Dordrecht, 1988.
- ⁵⁶ Vicens J., Böhmer V. Eds., "Calixarenes a Versatile Class of Macrocyclic Compounds", Kluwer, Dordrecht, Holland, 1990.
- ⁵⁷ Meinhard J. E., *Appl. Phys. Lett.*, 1964, **35**, 3059.
- ⁵⁸ Polymeropoulos E. E., Möbius D., Kuhn H., *Thin Solid Films*, 1980, **68**, 173.
- ⁵⁹ Sugi M., Sakai K., Saito M., Kawabata Y., Izima S., *Thin Solid Films*, 1985, **132**, 69.
- ⁶⁰ Potember R. S., Poehler T. O., Cowan D. O., *Appl. Phys. Lett.*, 1979, **34**, 405.
- ⁶¹ Potember R. S., Hoffman R. C., Hu H. S., Cocchiaro J. E., Viands C. A., Murphy R. A., Poehler T. O., *Polymer*, 1987, **28**, 574.
- ⁶² Potember R. S., Hoffman R. C., Benson R. C., Poehler T. O., *J. Phys., Les Ulis*, 1983, **44**, C3-1597.
- ⁶³ White H. S., Kittleson G. P., Wrighton M. S., *J. Am. Chem. Soc.*, 1984, **106**, 5375.
- ⁶⁴ Turner Jones E. T., Chyan O. M., Wrighton M. S., *J. Am. Chem. Soc.*, 1987, **109**, 5526.
- ⁶⁵ Paloheimo J., Kuivalainen P., Stubb H., Vuorimaa E., Yli-Lahti P., *Appl. Phys. Lett.*, 1990, **56**, 1157.
- ⁶⁶ Ryu H., Akagane K., Kori H., *Chem. Economy and Eng. Rev.*, 1986, **18(12)**, 26.
- ⁶⁷ Slonim J., Mole D., Bauer M., *Library Hi-Tech*, 1985, **3(4)**, 27.
- ⁶⁸ Kalanaraman P. S., Kuder J. E., Jones R. S., in "Functional Polymers", Bergbreiter D. E., Martin C. R. Eds., Plenum, New York, 1989, p. 173.
- ⁶⁹ Nikles D. E., Forbes C. E., Goldberg H. A., Johnson R. E., Kohn R. S., Onorato F. J., *Proc. Soc. Photo-optical Instrum. Engineers*, 1989, **107B**, 43.
- ⁷⁰ Coronel P., Barraud A., Claude R., Kahn O., Ruau-del-Teixier A., Zarembowitch J., *J. Chem. Soc. Chem. Commun.*, 193, 1989.
- ⁷¹ Taube H., *Pure Appl. Chem.*, 1975, **44**, 26.
- ⁷² Meyer T. J., in "Photochemical Energy Conversion", Norris Jr. J. R., Meisel D. Eds., Elsevier, New York, 1989, p. 75.
- ⁷³ Calcaterra L. T., Closs G. L., Miller J. R., *J. Am. Chem. Soc.*, 1983, **105**, 670.
- ⁷⁴ Miller J. R., Calcaterra L. T., Closs G. L., *J. Am. Chem. Soc.*, 1984, **106**, 3047.
- ⁷⁵ Marcus R. A., *Disc. Faraday Soc.*, 1960, **29**, 21.
- ⁷⁶ Lindsay J., Mauzerall D., Linschitz H., *J. Am. Chem. Soc.*, 1983, **105**, 6528.
- ⁷⁷ McIntosh A. R., Bolton J. R., Conolly J. S., Marsh K. L., Cook D. R., Ho T.-F., Weedon A. C., *J. Phys. Chem.*, 1986, **90**, 5640.
- ⁷⁸ Joran A. D., Leland B. A., Geller G. G., Hopfield J. J., Dervan P. B., *J. Am. Chem. Soc.*, 1984, **106**, 6090.
- ⁷⁹ Nishitani S., Kurata N., Sakata Y., Misumi S., Karen A., Okada T., Mataga N., *J. Am. Chem. Soc.*, 1983, **105**, 7771.
- ⁸⁰ Moore T. A., Gust D., Mathis P., Mialocq J.-C., Chachaty C., Bensasson R. V., Land E. J., Dozzi D., Lidell P. A., Lehman W. R., Nemweth G. A., Moore A. L., *Nature*, 1984, **307**, 630.
- ⁸¹ Krieger C., Weiser J., Staab H. A., *Tetrahedron Lett.*, 1985, **26**, 6050.
- ⁸² Hush N. S., Paddon-Row M. N., Cotsaris E., Oevering H., Verhoeven J. W., Heppener M., *Chem. Phys. Lett.*, 1985, **117**, 8.
- ⁸³ Wasielecki M. R., Johnson D. G., Svec W. A., Kersey K. M., Cragg D. E., Minsek D. W., in "Photochemical Energy Conversion", Norris Jr. J. R., Meisel D. Eds., Elsevier, New York, 1989, p. 135.
- ⁸⁴ Aviram A., Joachim C., Pomerantz M., *Chem. Phys. Lett.*, 1988, **146**, 490.

- ⁸⁵ Aviram A., Joachim M., Pomerantz M., *Chem. Phys. Lett.*, 1989, **162**, 416.
- ⁸⁶ Sixl H., Higelin D., in Carter F. L. Ed., "*Molecular Electronic Devices II*", Dekker, New York, 1987, p. 27.
- ⁸⁷ Tachibana H., Nakamura T., Matsumoto M., Komizu H., Manda E., Niino H., Yabe A., Kawabata Y., *J. Am. Chem. Soc.*, 1989, **111**, 3080.
- ⁸⁸ Birge R. R., Cooper T. M., *Biophys. J.*, 1983, **42**, 61.
- ⁸⁹ Wilson E. G., *Mol. Cryst. Liq. Cryst.*, 1985, **121**, 271.
- ⁹⁰ Murray R. W., *Acc. Chem. Res.*, 1980, **13**, 135.
- ⁹¹ Maoz R., Netzer L., Gun J., Sagiv J., *J. Chim. Phys.*, 1988, **85**, 1059.
- ⁹² Bigelow W. C., Pickett D. L., Zisman W. A., *J. Colloid Sci.*, 1946, **1**, 513.
- ⁹³ Peterson I. R., *J. Chim. Phys.*, 1988, **85**, 997.
- ⁹⁴ Hertler W. R., *J. Org. Chem.*, 1976, **41**, 1412.
- ⁹⁵ Baghdadchi J., *Ph. D. dissertation*, Univ. of Mississippi, Dec. 1982.
- ⁹⁶ Wu X. -L., Parakka J. L., Metzger R. M., Unpublished results.
- ⁹⁷ Cephalas A. C., private communication.
- ⁹⁸ Anderson J. R., Jorgensen O., *J. Chem. Soc. Perkin Trans. I*, 1979, 3095.
- ⁹⁹ Takassi M. A., *Ph. D. Dissertation*, University of Mississippi, Aug. 1989.
- ¹⁰⁰ Wu X. -L., Metzger R. M., Unpublished results.
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Monolayers and Z-Type Multilayers of Donor- σ -Acceptor Molecules with One, Two, and Three Dodecoxy Tails[†]

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Pockels-Langmuir and Langmuir-Blodgett monolayer films have been found for the 2-(4-nitrophenyl)ethyl esters of *N*-(4-dodecoxyphenyl)carbamic acid (DDOP-C-ENP, 7) and *N*-(3,4,5-tridodecoxyphenyl)carbamic acid (TDDOP-C-ENP, 9) and also for the (2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane ester of *N*-(3,4,5-tridodecoxyphenyl)carbamic acid (TDDOP-C-HETCNQ, 10). However, monolayers were not formed for the 2-(4-nitrophenyl)ethyl esters of *N*-(3,5-didodecoxyphenyl)carbamic acid (BDDOP-C-ENP, 8). The pressure-area isotherms vary greatly depending on the number of dodecoxy groups attached to these donor- σ -acceptor molecules. The film strength improves dramatically by lowering the subphase temperature. The molecular area appears to be defined by the acceptor end for DDOP-C-ENP, 7, but by the dodecoxy donor end (for both TDDOP-C-ENP, 9, and TDDOP-C-HETCNQ, 10). Noncentrosymmetric Z-type LB multilayers are obtained for DDOP-C-ENP, TDDOP-C-ENP, and TDDOP-C-HETCNQ. This suggests some interesting nonlinear optical properties for these multilayers.

1. Introduction

A recent report from these laboratories discusses the formation of monolayer films of molecules of the type

D- σ -A, where D is an organic one-electron donor, σ is a covalent σ bridge, and A is an organic one-electron acceptor.¹ These molecules are of interest in the construction of unimolecular organic rectifiers,²⁻¹³ which are

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(1) Metzger, R. M.; Schumaker, R. R.; Cava, M. P.; Laidlaw, R. K.; Panetta, C. A.; Torres, E. *Langmuir* 1988, 4, 298-304.

(2) Metzger, R. M.; Panetta, C. A. *J. Phys., Colloq.* 1983, 44, C3-1605-C3-1611.

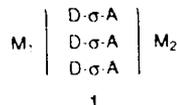
(3) Metzger, R. M.; Panetta, C. A. In *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1987; pp 5-25.

(4) Panetta, C. A.; Baghdadchi, J.; Metzger, R. M. *Mol. Cryst. Liq. Cryst.* 1984, 107, 103-113.

(5) Metzger, R. M.; Panetta, C. A.; Heimer, N. E.; Bhatti, A. M.; Torres, E.; Blackburn, G. F.; Tripathy, S. K.; Samuelson, L. A. *J. Mol. Electron.* 1986, 2, 119-124.

(6) Metzger, R. M.; Panetta, C. A.; Miura, Y.; Torres, E. *Synth. Met.* 1987, 18, 797-802.

based on the idea¹⁴⁻¹⁸ that electrical current path will be unsymmetrical within molecules D- σ -A, because the zwitterionic state D⁺- σ -A⁻ is much lower in energy than the state D⁻- σ -A⁺. If these D- σ -A compounds can be organized as a monolayer between two conventional metal films M₁ and M₂ as ordered structures M₁|D- σ -A|M₂, 1, then the asymmetry of the molecular orbitals of the D- σ -A molecules would ensure that electron transfer is preferred in one direction over the other.



The present efforts²⁻¹³ to synthesize and test the organic rectifier concept assume that the best technique for its assembly is the Langmuir-Blodgett film technique.¹⁹⁻²⁵ For this, the D- σ -A molecule must be an amphiphilic molecule; i.e., either the D end or the A end must be made hydrophilic and the opposite end hydrophobic. On a Langmuir trough, or Pockels-Langmuir-Adam-Wilson-McBain balance, or film balance, the amphiphilic molecules self-assemble as a monolayer (hereinafter called¹ a "Pockels-Langmuir" (PL) monolayer in honor of Agnes Pockels (1862-1935)²⁶ and Irving Langmuir (1881-1957)). The monolayer must transfer well (i.e., with a transfer ratio close to 1.00) to a solid substrate, thus forming a Langmuir-Blodgett (LB) film (named after Langmuir and Kathleen Blodgett (1898-1979)).²⁰⁻²⁵ As reported elsewhere,^{1,10-12} we have prepared several such molecules (1-6), shown in Figure 1: all of them form both PL and LB films.

Recently, indications^{11,12,17,18} that two such molecules (including BDDAP-C-BHTCNQ, 4) did exhibit rectification, when deposited on a Au|Ag|mica support, and probed by scanning tunneling microscopy, were later found to be due to some unexplained artifact of the W tip|Au|Ag|mica couple.²⁷

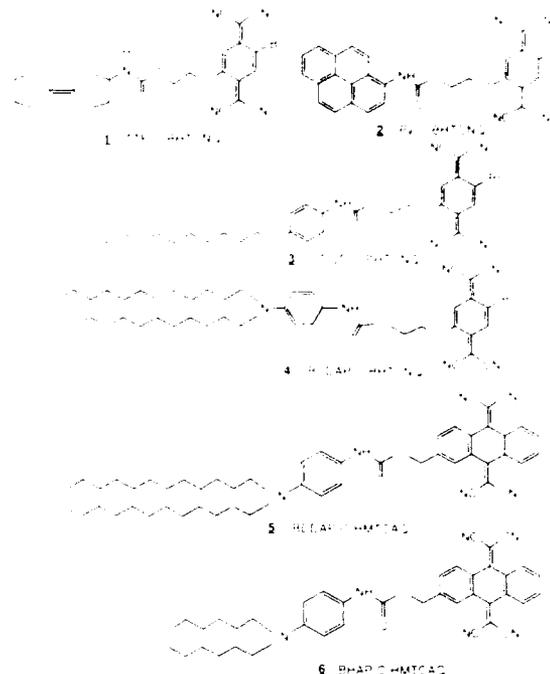


Figure 1. Structures of D- σ -A molecules that do form PL monolayers, from ref 1 and 11.

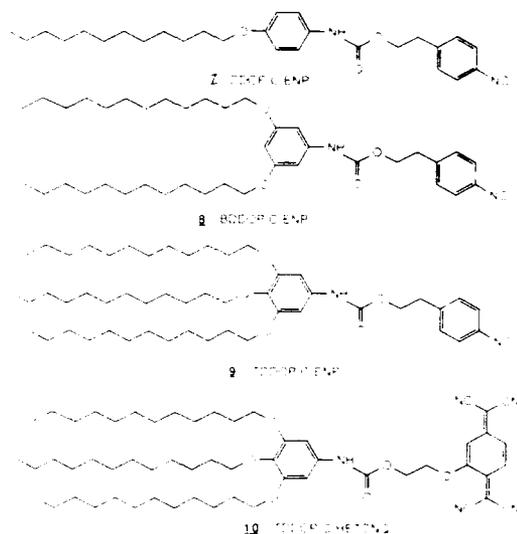


Figure 2. Structures of D- σ -A molecules reported in this study.

Here we report on PL and LB film formation of four novel D- σ -A compounds (Figure 2): (i) the 2-(4-nitrophenyl)ethyl ester of *N*-(4-dodecoxyphenyl)carbamic acid (DDOP-C-ENP, 7), (ii) the 2-(4-nitrophenyl)ethyl ester of *N*-(3,5-didodecoxyphenyl)carbamic acid (BDDOP-C-ENP, 8), (iii) the 2-(4-nitrophenyl)ethyl ester of *N*-(3,4,5-tridodecoxyphenyl)carbamic acid (TDDOP-C-ENP, 9), and (iv) the (2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane ester of *N*-(3,4,5-tridodecoxyphenyl)carbamic acid (TDDOP-C-HETCNQ, 10). The donor ends of 7-10 are in fact rather weak electron donors, similar to the donor end of DDOP-C-BHTCNQ, 3; the acceptor end of 7-9 is again a weak electron acceptor, useful only as a readily accessible model acceptor group. The acceptor end of 10 is the strong one-electron acceptor TCNQ.^{28,29} Preliminary data for 10 have been presented elsewhere.¹¹

(7) Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* 1987, 52, 2944-2945.

(8) Metzger, R. M.; Panetta, C. A. Proc. of the Eighth Winter Meeting on Low-Temp. Physics, Cuernavaca Mexico, 1987, pp 81-100.

(9) Metzger, R. M.; Panetta, C. A. In *Organic and Inorganic Lower-Dimensional Materials*; Delhaes, P., Drillon, M., Eds.; Plenum: New York, 1988; pp 271-286.

(10) Metzger, R. M.; Panetta, C. A. *J. Mol. Electron.* 1989, 5, 1-17.

(11) Metzger, R. M.; Panetta, C. A. *J. Chim Phys.* 1988, 85, 1125-1134.

(12) Metzger, R. M.; Panetta, C. A. *Synth. Met.* 1989, 28, C807-C814.

(13) Miura, Y.; Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* 1988, 53, 439-440.

(14) Aviram, A.; Freiser, M. J.; Seiden, P. E.; Young, W. R. US Patent 3,953,874, April 27, 1976.

(15) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* 1974, 29, 277-283.

(16) Aviram, A.; Seiden, P. E.; Ratner, M. A. In *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982; p 5.

(17) Aviram, A.; Joachim, C.; Pomerantz, M. *Chem. Phys. Lett.* 1988, 146, 490-495.

(18) Aviram, A.; Joachim, C.; Pomerantz, M. unpublished.

(19) See, e.g.: Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience Publishers: New York, 1966.

(20) Blodgett, K. B. *J. Am. Chem. Soc.* 1935, 57, 1007-1022.

(21) Blodgett, K. B.; Langmuir, I. *Phys. Rev.* 1937, 51, 964-982.

(22) Kuhn, H.; Möbius, D.; Bücher, H. In *Techniques of Chemistry, Vol I-Physical Methods of Chemistry-Part V-Determination of Thermodynamic and Surface Properties*; Weissberger, A., Rossiter, B. W., Eds.; Wiley-Interscience: New York, 1972; pp 577-702.

(23) Kuhn, H. *Pure Appl. Chem.* 1979, 51, 341-352.

(24) Kuhn, H. *Pure Appl. Chem.* 1981, 53, 2105-2122.

(25) See, e.g.: *Thin Solid Films* 1980, 68; 1983, 99; 1985, 132-134.

(26) See biographical note in: Derrick, M. E. *J. Chem. Ed.* 1982, 59, 1030-1031.

(27) Pomerantz, M.; Aviram, A., private communication.

(28) Acker, D. S.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Melby, L. R.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* 1960, 82, 6408-6409.

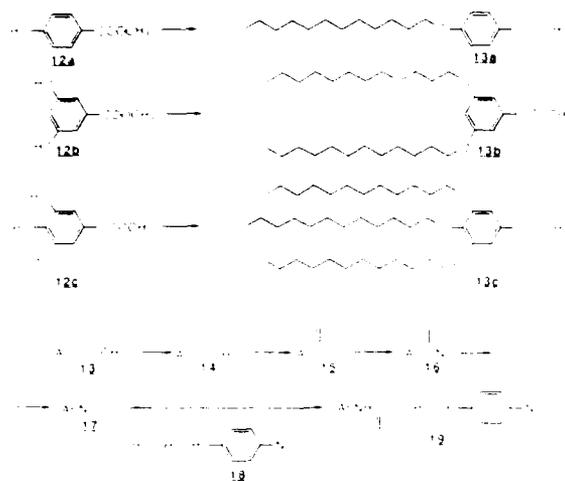
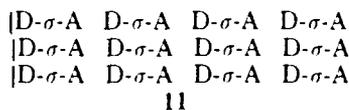


Figure 3. Synthetic scheme.

Our rationale in choosing these D- σ -A molecules was to see if stronger films would result when the cross-sectional area of the alkyl tails better matched that of other portions of the molecule. Thus BDDAP-C-BHTCNQ, **4**, with a TCNQ acceptor and two alkyl tails, forms more rigid PL monolayers than DDOP-C-BHTCNQ, **3**, which also has a wide TCNQ acceptor but only one alkyl tail.¹⁰ On this basis, we might expect DDOP-C-ENP, **7** (one tail), to make the weakest film, with BDDOP-C-ENP, **8** (two tails), TDDOP-C-ENP, **9**, or TDDOP-C-HETCNQ, **10** (three tails), forming better ones. We have found that monolayer formation does indeed depend strongly on the number of tails, but the relationship is complex.

In addition, we report that LB multilayers formed from these compounds are of the "Z type"; i.e., they are non-centrosymmetric, with a head-to-tail packing as in **11** below (where the bars indicate the solid substrate, e.g., glass). These multilayers may be expected to have unusual nonlinear optical (NLO) properties, such as frequency doubling.



2. Experimental Section

Synthesis. Summary. As shown in Figure 3, the syntheses started from the phenols **12**, which were activated by the trident tris(3,6-dioxahexyl)amine (TDA, tris[2-(2-methoxyethoxy)ethyl]amine) as a phase-transfer catalyst, as described by Soula.³⁰ The resulting alkoxy esters **13** were saponified to give the alkoxy acids **14**, which were converted to the acyl chlorides **15** with thionyl chloride. Treatment with sodium azide in tetrahydrofuran/acetone gave the acyl azides, and Curtius rearrangement in benzene at the reflux temperature gave the isocyanates **17**. These were coupled with 4-nitrophenethyl alcohol, **18**, in benzene in the presence of the catalyst dibutyltin dilaurate⁹ to give the carbamate products **19** (i.e., **7-10**). The acceptor HETCNQ used to obtain **10** has been described elsewhere.¹³

Synthetic Details. Melting temperatures were determined on a Mel-Temp apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on Whatman silica gel plates; R_f values are given for development with CH_2Cl_2 and inspection under ultraviolet light. NMR spectra were determined (in

CDCl_3 with TMS as the internal standard) with a Perkin-Elmer R24B spectrometer, except for **7**, which was determined on a Varian XL-300 instrument. Mass spectra (MS) were determined with a Hewlett-Packard 5895 GC/MS instrument (heated probe); parent (M^+) and base (100%) peaks are given. IR spectra were determined with a Beckman Acculab-1 spectrometer; weak peaks are not given. Microanalyses were performed by Desert Analytics, Tucson, AZ. Starting materials were obtained from Aldrich Chemical Co., except for **12a**, which was prepared by Fischer esterification of *p*-hydroxybenzoic acid.

General Procedure for Alkylation of Phenols 12. The phenol (10 mmol) and 1-bromododecane (5% excess) were suspended in 60 mL of toluene in a round-bottom flask fitted with a Dean-Stark trap. After the mixture was heated to the reflux temperature for 1.5 h to remove water, crushed anhydrous potassium carbonate (10% excess) was added. Then TDA (about 5%) was added, and the mixture was heated to the reflux temperature. If the reaction seemed incomplete by TLC analysis after 1 or 2 days, an additional charge of K_2CO_3 was added. Reactions were typically stopped after 3-4 days. The mixture was cooled and washed with water 3 times, and the aqueous layers were back-extracted with hexanes. The combined organic layers were dried over MgSO_4 and filtered, and the solvents were removed by rotary evaporation to give crude product.

Methyl 4-Dodecoxybenzoate (13a). The light-orange product was crystallized from 10 mL of MeOH to give a shiny white solid in 60% yield; mp 54-56.5 °C; TLC 0.56; $^1\text{H NMR}$ δ 7.9 (d, 2 H, Ar-H), 6.85 (d, 2 H, Ar-H), 4.2-3.8 (5 H, O-CH), 2.1-0.6 (23 H, alkyl); MS m/e 320 (M^+ , 11%), 57 (100%); IR (KBr) 2960, 2920, 2860, 1720, 1605, 1505, 1455, 1430, 1315, 1280, 1255, 1190, 1170, 1105, 1020, 840, 760 cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_3$: C, 74.96; H, 10.06. Found: C, 74.88; H, 10.33.

Methyl 3,5-Didodecoxybenzoate (13b). The crude product was crystallized from 12 mL of EtOAc to give a 77% yield of a waxy, off-white solid; mp 62-65.2 °C; TLC 0.67; $^1\text{H NMR}$ δ 7.1 (d, 2 H, *o*-Ar-H, $J = 3$ Hz), 6.55 (br s, 1 H, *p*-Ar-H), 4.2-3.7 (7 H, O-CH), 2.0-0.6 (46 H, alkyl); MS, m/e 505 (M^+ , 1%), 336 ($M-\text{C}_{12}\text{H}_{25}$, 1%), 69 (100%); IR (KBr) 2920, 2850, 1720, 1600, 1465, 1440, 1390, 1325, 1235, 1160, 1050 cm^{-1} .

Anal. Calcd for $\text{C}_{32}\text{H}_{56}\text{O}_4$: C, 76.14; H, 11.18. Found: C, 75.93; H, 11.49.

Methyl 3,4,5-Tridodecoxybenzoate (13c). The crude oil was triturated twice with CH_3OH to remove incompletely alkylated starting material; the methanol was back-extracted with hexanes and the extract added to the crude product (78%). This was crystallized twice from 1:3 *i*-PrOH:EtOH, with cooling on ice, to give a 38% yield of cream-colored powder; mp 39-42.5 °C; TLC 0.66; $^1\text{H NMR}$ δ 7.15 (s, 2 H, Ar-H), 4.2-3.8 (9 H, O-CH), 2.1-0.7 (69 H, alkyl); MS, m/e 689 (M^+ , 1%), 57 (100%); IR (KBr) 2920, 2850, 1715, 1585, 1460, 1435, 1330, 1215, 1120 cm^{-1} .

Anal. Calcd for $\text{C}_{44}\text{H}_{80}\text{O}_5$: C, 76.69; H, 11.70. Found: C, 77.06; H, 11.97.

General Procedure for Saponification of Esters 13. The ester was dissolved in EtOH; for **14b** and **14c**, about 20% tetrahydrofuran was added as a cosolvent. A 2.5-fold excess of NaOH was added as a 2.5 M aqueous solution. The solution was heated for several hours on steam and then cooled and partitioned between CH_2Cl_2 and 5% HCl (aqueous). The aqueous layer was extracted twice with CH_2Cl_2 , and the combined organic layers were dried over MgSO_4 and filtered. The solvents were removed by rotary evaporation.

4-Dodecoxybenzoic Acid (14a). The crude product (90%) was crystallized from 50 parts hexanes to give a white solid in two crops: 85% mp 93-140 °C (liquid crystal, lit.³² mp 95-137 °C); TLC 0.05; $^1\text{H NMR}$ δ 8.9 (br s, 1 H, COOH), 8.0 (d, 2 H, Ar-H), 6.85 (d, 2 H, Ar-H), 4.0 (t, 2 H, O-CH), 2.0-0.7 (23 H, alkyl); MS m/e 306 (M^+ , 3%), 57 (100%); IR (KBr) 2920, 2850, 2640 (br), 1680, 1600, 1570, 1510, 1465, 1430, 1330, 1300, 1260, 1170, 1125, 1060, 990, 965, 935, 845, 770, 710, 690, 640 cm^{-1} .

3,5-Didodecoxybenzoic Acid (14b). The crude product (quantitative) was crystallized from 8 parts EtOH to give a white solid (85%); mp 65-66 °C; TLC 0.44; $^1\text{H NMR}$ δ 9.3 (br s, 1 H,

(29) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370-3374.

(30) Soula, G. *J. Org. Chem.* **1985**, *50*, 3717-3721.

(31) Francis, T.; Thorne, M. P. *Can. J. Chem.* **1976**, *54*, 24-30.

(32) Bennett, G. M.; Jones, B. *J. Chem. Soc.* **1939**, 420-424.

COOH), 7.2 (d, 2 H, *o*-Ar-H, $J = 3$ Hz), 6.65 (br s, 1 H, *p*-Ar-H), 3.95 (t, 4 H, O-CH), 2.1-0.7 (46 H, alkyl); MS m/e 490.5 (M^+ , 6%), 57 (100%); IR (KBr) 2920, 2850, 2640 (br), 1690, 1590, 1465, 1440, 1420, 1380, 1350, 1300, 1270, 1240, 1170, 1050, 940, 880, 835, 770, 740, 730, 720, 670 cm^{-1} .

Anal. Calcd for $C_{31}H_{54}O_4$: C, 75.87; H, 11.09. Found: C, 76.32; H, 11.41.

3,4,5-Tridodecoxybenzoic Acid (14c). The crude product (quantitative) was crystallized from 25 parts EtOH to give a white solid (76%): mp 57.5-59 °C; TLC 0.10; 1H NMR δ 8.1 (br s, 1 H, COOH), 7.2 (s, 2 H, Ar-H), 4.0 (t, 6 H, O-CH), 2.0-0.7 (69 H, alkyl); MS m/e 675 (M^+ , 1%), 57 (100%); IR (KBr) 2920, 2850, 1675, 1575, 1460, 1425, 1375, 1325, 1270, 1220, 1115 cm^{-1} .

Anal. Calcd for $C_{43}H_{78}O_5$: C, 76.50; H, 11.65. Found: C, 76.58; H, 12.09.

General Procedure for Curtius Rearrangement and Coupling. The substituted benzoic acid 14 (1 mmol) was dissolved in 20 mL of benzene. Thionyl chloride (1 mL) was added, and the solution was heated to the reflux temperature overnight. A drop of the solution was removed for IR analysis, which showed loss of the carbonyl peak for 14 at 1675-1690 cm^{-1} and the appearance of the acyl chloride carbonyl peak(s) for 15 at 1735-1765 cm^{-1} . The benzene was removed by rotary evaporation, and the acyl chloride 15 was dissolved in 6 mL of dry tetrahydrofuran and 2 mL of acetonitrile. Sodium azide (1.5 equiv) was added, and the mixture was stirred overnight at room temperature. The mixture was then diluted with CH_2Cl_2 and filtered, and the solvents were removed by rotary evaporation. IR analysis showed that acyl chloride remained, so the NaN_3 treatment was repeated. The resulting product showed loss of the acyl chloride peak for 15 and the appearance of carbonyl (1690 cm^{-1}) and azide (2130-2150 cm^{-1}) peaks for acyl azide 16. The acyl azide 16 was dissolved in 20 mL of benzene in a dry round-bottom flask protected with a $CaSO_4$ drying tube and heated to the reflux temperature overnight. A drop of the solution was removed for IR analysis, which showed no carbonyl or acyl azide peaks but an isocyanate peak for 17 at 2260-2280 cm^{-1} (TLC: 17a, 0.70; 17b, 0.76; 17c, 0.85). 4-Nitrophenethyl alcohol (18) (1 mmol) was dissolved in benzene, or HETCNQ¹³ was dissolved in dry THF, and added to the solution of isocyanate 17, followed by about 20 μL of dibutyltin dilaurate. After 1-2 days, TLC showed a substantial conversion to product. The solvent was removed by rotary evaporation to give the crude carbamate product.

2-(4-Nitrophenyl)ethyl N-(4-Dodecoxyphenyl)carbamate (DDOP-C-ENP, 7). The cream-colored crude product was crystallized twice from EtOH to give a 30% yield of white powder: mp 126-127 °C; TLC 0.20; 1H NMR δ 8.2 (d, 2 H, Ar-NO₂), 7.4 (d, 2 H, Ar-NO₂), 7.25 (br s, 2 H, Ar-OR), 6.8 (d, 2 H, Ar-OR), 6.45 (br s, 1 H, NH), 4.4 (t, 2 H, COO-CH₂), 3.9 (t, 2 H, ArO-CH₂), 3.1 (t, 2 H, Ar-CH₂), 1.8 (m, 2 H, ArOCH₂-CH₂), 1.5-1.2 (br, 18 H, alkyl), 0.9 (t, 3 H, CH₃); MS m/e 470.5 (M^+ , 12%), 135 (100%); IR (KBr) 3340 (NH), 2920, 2850, 1680, 1590, 1520, 1460, 1410, 1340, 1285, 1225, 1160, 1075, 815 cm^{-1} .

Anal. Calcd for $C_{27}H_{38}O_5N_2$: C, 68.91; H, 8.14; N, 5.95. Found: C, 68.75; H, 8.30; N, 6.08.

2-(4-Nitrophenyl)ethyl N-(3,5-Didodecoxyphenyl)carbamate (BDDOP-C-ENP, 8). The crude syrup was purified by column chromatography on Florosil, with CH_2Cl_2 in hexanes as eluant. A gum was obtained in 72% yield. This was crystallized by dissolving the gum in 5 mL of CH_2Cl_2 , adding 50 mL of EtOH, and allowing the mixture to concentrate by evaporation over many days. A first crop of brown gummy material was discarded; the second crop represented a 56% yield of white solid: mp 47.5-51.5 °C; TLC 0.50; 1H NMR δ 8.0 (d, 2 H, Ar-NO₂), 7.3 (d, 2 H, Ar-NO₂), 6.45 (br s, 3 H, *o*-Ar-OR + NH), 6.1 (br s, 1 H, *p*-Ar-OR), 4.4 (t, 2 H, COO-CH₂), 3.9 (t, 4 H, ArO-CH₂), 3.1 (t, 2 H, Ar-CH₂), 2.0-0.7 (46 H, alkyl); IR (KBr) 3310 (NH), 2920, 2850, 1695, 1605, 1515, 1460, 1430, 1380, 1340, 1310, 1255, 1230, 1155, 1090, 1050, 820 cm^{-1} .

Anal. Calcd for $C_{39}H_{62}O_6N_2$: C, 71.52; H, 9.54; N, 4.28. Found: C, 71.45; H, 9.80; N, 4.19.

2-(4-Nitrophenyl)ethyl N-(3,4,5-Tridodecoxyphenyl)carbamate (TDDOP-C-ENP, 9). The crude yellow oil solidified on standing. It was crystallized from 1:10 *i*-PrOH:EtOH and then twice from acetic acid to give a cream-colored solid: 39% yield, mp 60.5-64.5 °C; TLC 0.44; 1H NMR δ 8.1 (d, 2 H, Ar-NO₂), 7.3 (d, 2 H, Ar-NO₂), 6.5 (br s, 3 H, *o*-Ar-OR + NH), 4.35 (t, 2 H, COO-CH₂), 3.9 (t, 6 H, ArO-CH₂), 3.05 (t, 2 H, Ar-CH₂), 2.0-0.7 (69 H, alkyl); IR (KBr) 3380 (NH), 2920, 2850, 1690, 1595, 1520, 1465, 1430, 1380, 1340, 1295, 1235, 1120, 1085, 1050 cm^{-1} .

Anal. Calcd for $C_{51}H_{86}O_7N_2$: C, 72.99; H, 10.33; N, 3.34. Found: C, 73.41; H, 10.77; N, 3.24.

N-(3,4,5-Tridodecoxyphenyl)carbamate of 2-(2'-Hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane (TDDOP-C-HETCNQ, 10). TLC showed incomplete conversion to product, so the mixture was allowed to sit 2 weeks before workup. The crude oil was triturated with 80% methanol to remove unreacted HETCNQ. The remainder was taken into 125 parts of hot ethanol and cooled to give a dark gum (40% yield). This was chromatographed on TLC-mesh silica gel; elution with 1% THF in CH_2Cl_2 gave a 15% yield of material pure to TLC (0.10). Crystallization from CH_3CN gave a 7% yield of a puce solid: mp 67.5-70.5 °C; IR (KBr) 3360 (NH), 2920, 2850, 2200, 1725, 1595, 1530, 1500, 1455, 1420, 1375, 1275, 1230, 1210, 1170, 1110, 990, 800 cm^{-1} .

Anal. Calcd for $C_{57}H_{86}N_5O_6$: C, 73.12; H, 9.15; N, 7.47. Found: C, 73.79; H, 9.62; N, 6.66.

The compound blackened on standing in air; wafting bromine vapors over a solution, which typically restores the orange color of darkened TCNQs, in this case apparently formed a new compound (TLC 0.15), perhaps by bromination of the anilide ring.

Characterization. Cyclic Voltammetry. Cyclic voltammograms were obtained by using a Bioanalytical Systems CV-27 cyclic voltammograph with a Houston Instruments Omni-graphic X-Y recorder; all measurements were performed in CH_2ClCH_2Cl solvent that was 0.1 M in $(NH_4)_4PF_6$ by using a three-electrode cell, with a Pt disk working electrode, a Pt wire auxiliary electrode, and a Ag|AgCl electrode. The emf data were converted to volts vs the saturated calomel electrode (SCE) by adding 0.15 V to the data vs Ag|AgCl.

Pockels-Langmuir Monolayers. As indicated elsewhere¹ a Lauda FW-1 film balance (Langmuir trough) was used to obtain pressure-area (Π -A) isotherms; LB films were prepared by using a Joyce-Loebl vertical film dipping mechanism. The film balance was housed in a special room equipped with a HEPA filter to provide dust- and oil-free air under positive pressure. A Millipore Milli-Q Z040 system, supplied with house deionized water, provided pyrogen-free water for the aqueous subphase, with a resistivity of 18 M Ω cm. The temperature of the subphase (5-35 °C) was controlled to 0.1 °C by a Lauda RM6 variable-temperature bath. A Brinkmann BR 1101 XY recorder provided a graph of the Π -A curves. The compounds to be studied were weighed on a Mettler M5SA microbalance and dissolved in reagent-grade deuteriochloroform. The solutions were spread on the subphase ("cast") with a Hamilton 100- μL syringe. With the syringe held above the subphase, small drops were dispersed at the air-water interface, as the syringe was passed over the subphase. Typical quantities of solution were 20 μL containing approximately 10^{17} molecules. To ensure quantitative transfer, the syringe was rinsed twice with solvent, and the wash solvent was spread over the subphase. The microscope slides used for LB studies were soaked in soap and Milli-Q water for 1 day and rinsed with Milli-Q water before use.

Molecular Areas of PL Monolayers. As discussed previously,¹ one can define molecular areas from a pressure-area isotherm in three ways: A_0 is the area per molecule at extrapolated zero differential surface tension; A_c is the minimum area per molecule at the collapse point, i.e., at the point in the Π -A isotherm where the pressure is the maximum reversible pressure (or "collapse pressure" Π_c); and A_m is the area at the mid-point pressure $\Pi_m = 0.5\Pi_c$.

LB Monolayers and Multilayers on Glass. Glass microscope slides were pre-cleaned with soapy water and rinsed with

(33) Riddle, M. B.; Rickert, S. H.; Lando, J. B. *Thin Solid Films* 1985, 134, 121-134.

(34) Daniel, M. F.; Lettington, O. C.; Small, S. M. *Thin Solid Films* 1983, 99, 61-69.

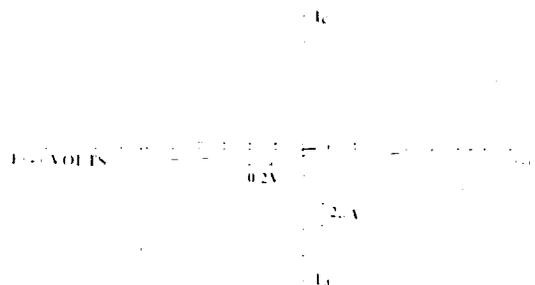


Figure 4. Cyclic voltammogram for DDOP-C-ENP (7): solvent, $\text{CH}_2\text{ClCH}_2\text{Cl}$; supporting electrolyte, $(\text{C}_4\text{H}_9)_4\text{NPF}_6$; reference electrode, Ag|AgCl ; sensitivity, $2 \mu\text{A}$; division; scan speed, 0.1 V/s .

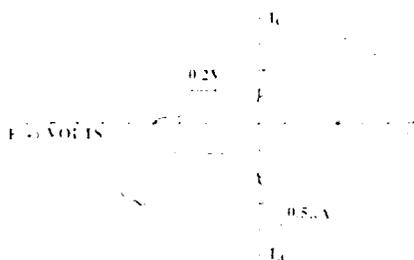


Figure 5. Cyclic voltammogram for TDDOP-C-HETCNQ (10): solvent, $\text{CH}_2\text{ClCH}_2\text{Cl}$; supporting electrolyte, $(\text{C}_4\text{H}_9)_4\text{NPF}_6$; reference electrode, Ag|AgCl ; sensitivity, $2 \mu\text{A}$; division; scan speed, 0.1 V/s .

Table I. Half-Wave Solution Potentials $E_{1/2}$ ^a

	$E_{1/2}^{\text{ox}}$	$E_{1/2}^{\text{red}}$
DDOP-C-ENP (7)	1.39 rev	-1.13
BDDOP-C-ENP (8)	1.67 irr	-1.09
TDDOP-C-ENP (9)	1.14 irr	1.12
TDDOP-C-HETCNQ (10)	0.99 irr	0.07, -0.47
TCNQ		0.02, -0.55

^a In V versus SCE, quoted as oxidation peak -0.030 V or as reduction peak $+0.030 \text{ V}$ and measured in $\text{CH}_2\text{ClCH}_2\text{Cl}$ solution with $0.1 \text{ M } (\text{C}_4\text{H}_9)_4\text{NPF}_6$ supporting electrolyte. $E_{1/2}^{\text{ox}}$ refers to the irreversible oxidation of the donor (anisole) moiety; $E_{1/2}^{\text{red}}$ refers to the reversible reduction of the acceptor (*p*-nitrophenol or TCNQ) moiety (the TCNQ moiety has two reduction waves).

Milli-Q water; they were then dipped at an intermediate speed (0.2 mm/s) while maintaining a constant film pressure of approximately $0.75 \Pi_c$. To monitor the film transfer ratios more closely, a digital voltmeter, connected to the output of the X-Y recorder, was used to follow the barrier movement (when this barrier was held electronically at constant film pressure). The transfer was conducted with the film held at the lowest temperature (278.2 K for 7 and 9; 277.7 K for 10) but with the substrate kept at room temperature.

LB Film Thickness Monitored by X-ray Diffraction. The thicknesses of several LB multilayer films, on glass microscope slides, were monitored by X-ray diffraction ($\text{Cu K}\alpha$ radiation) using a Phillips Model 3100 X-ray powder diffractometer. The estimates of crystallite size, L , were obtained by using the Scherrer line-width equation:³⁵ $u = 0.94\lambda / (L \cos \theta)$ (where θ is the Bragg angle and u is the line width at half height).

LB Film Thickness Monitored by Ellipsometry. A Rudolph Research Auto-EL-III automatic ellipsometer, with a small He-Ne laser source, microspot optics, and a XY stage adjustable to $\pm 0.001 \text{ in.}$ was used to monitor the film thickness at about 20 spots over a silicon substrate and to obtain a histogram of the computed values, measured for the bare substrate and for substrate with LB films, measured by a micrometer at the same spots.

(35) Cf. Warren, B. E. *X-Ray Diffraction*; Addison-Wesley: Reading, PA, 1969; p 253.

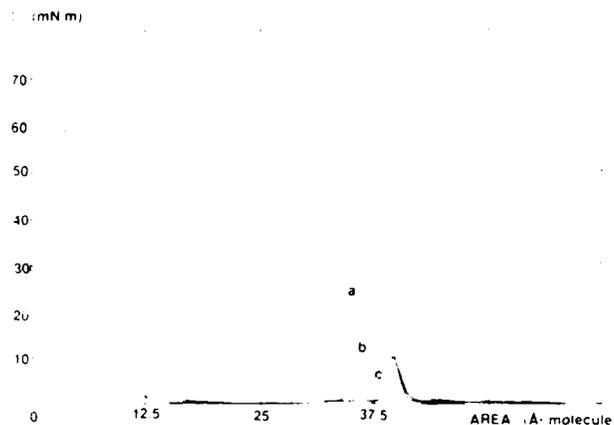


Figure 6. Pressure-area isotherm for DDOP-C-ENP (7): (a) at 278.2 , (b) at 293.2 , and (c) at 306.3 K .

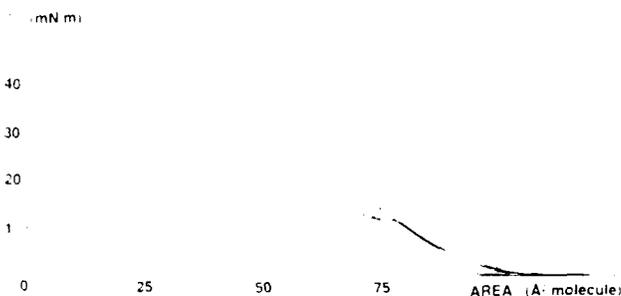


Figure 7. Pressure-area isotherm for BDDOP-C-ENP (8): (a) at 279.1 , (b) at 293.2 , and (c) at 306.3 K .

Calculated Molecular Geometry. The optimal molecular geometry of 9 was computed by using the MNDO algorithm of the computer program MOPAC (Version 4.02) on the Alabama Supercomputer Authority Cray X/MP-24 computer. The estimate of molecular packing area and thickness of 9 was obtained by first plotting the computed geometry by using the program ORTEP-II, using the computed coordinates, and accosting several molecules with the SYBYL software system on an Evans and Sutherland PS-300 terminal driven by a MicroVAX-II.

Infrared Studies of LB Multilayers. The transmittance spectra were measured in the range $4000\text{--}2000 \text{ cm}^{-1}$ (the latter is a silica absorption edge) by using a BioRad FTS-40 spectrophotometer at ambient temperature under purge N_2 gas. Also, the grazing angle reflectance of a glass slide covered by Al and by three monolayers of 9 was measured with a Bruker IFS-88 FT IR spectrometer, equipped with a Specac grazing-angle accessory; this preliminary spectrum is given as Figure 6 of ref 11 and is not reproduced here.

3. Results

Cyclic Voltammetry. Figures 4 and 5 show the cyclic voltammograms for 7 and 10, respectively. The data for 7, 8, 9, and 10 are reported in Table I. The oxidation wave for the donor parts is irreversible for 8–10 but reversible for 7. The reduction waves for 7–9 are (as they should be) the same to within the experimental error of $\pm 0.02 \text{ V}$. As expected for the TCNQ-bearing molecule 10, two reduction waves appear, shifted slightly (relatively to pure TCNQ) to more negative voltages. No significant impurity was detected in any of the compounds.

PL Monolayers. Figures 6–9 show the Π -A isotherms for 7–10, respectively. The monolayer data are given in Table II. The formation of monolayers was determined on the basis of the measured area per molecule. Since it is fairly obvious from Figures 8–10 that the differential surface tension regime between $\Pi = 0$ and $\Pi = \Pi_c$ corresponds to that of a "two-dimensional fluid" (rather than a two-dimensional incompressible solid), we present

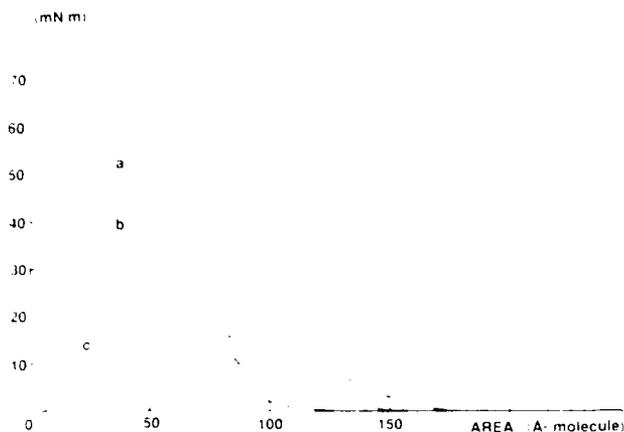


Figure 8. Pressure-area isotherm for TDDOP-C-ENP (9): (a) at 278.2, (b) at 293.2, and (c) at 306.2 K. Small dots indicate the points (Π_c, A_c) .

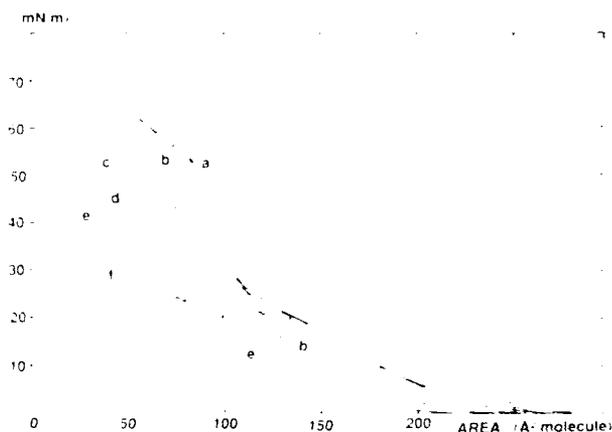


Figure 9. Pressure-area isotherm for TDDOP-C-HETCNQ (10): (a) at 277.7, (b) at 282.8, (c) at 288.6, (d) at 293.4, (e) at 297.7, and (f) at 303.1 K (these curves supersede those quoted in ref 11). Small dots indicate the points (Π_c, A_c) .

in Table II also a value of the isothermal compressibility, defined as $\kappa = -(1/A_c)(\partial A/\partial \Pi)_T$, and measured as the slope of the Π - A isotherms at $\Pi = 0.5\Pi_c$.

The shape of the Π - A isotherms for DDOP-C-ENP (7, Figure 6) is rather peculiar at both 306.3 and 293.2 K: the monolayer forms and then, under further compression, the differential surface tension drops to zero. It may be that some other collective ordering mode sets in, so that the molecules aggregate as isolated "islands" with no lateral cohesion. One is led to think of liquid crystals, Scheibe-Jelly aggregates, micelles, etc., but from the present data it is not safe to speculate too far. By lowering the temperature to 278.2 K, one sees that the pressure for areas below A_c no longer drops to zero but sinks to about half of Π_c . This behavior has been seen before, for brassidic acid,³³ where this region was termed the "post-collapse region", and the amount of decline of the differential surface tension was considered as a measure of the relative toughness of the PL film. It is quite clear that for 7 the toughness, as well as the critical surface pressure Π_c , is increased by reducing the aqueous subphase temperature. The area per molecule A_c is fairly temperature-independent, so one can safely assume that this is indeed a monolayer, but its strength and toughness are extremely sensitive to temperature. Since the slope of the Π - A curve is not steep, we have a two-dimensional fluid rather than a two-dimensional solid: there is a slight temperature dependence to the film compressibility. Although it is not quite certain that the *p*-nitro-

phenyl group is the hydrophilic end of the molecule, one can safely assume that the dodecoxy group is hydrophobic. The molecular area of 38 \AA^2 is quite reasonable, if one assumes that the van der Waals width (W) of the benzene ring (or either end of DDOP-C-ENP) is 6 \AA and that the molecule has a length L of about 6 \AA , across the benzene rings, with all substituents folded into an approximately extended geometry.

A different situation exists for BDDOP-C-ENP, 8 (Figure 7). At all temperatures an initial rise in Π is observed, until a plateau is reached. The area A_c does not correlate well with the area of 8, and the flatness of Π , as the area is reduced, indicates that no monolayer is formed at all, but rather a peculiar clustering into aggregates, which are not monolayers. This has been observed for films of 4-cyano-4'-*n*-pentyl-*p*-terphenyl (where, however, monolayers do form and the constant Π independent of A is shown only at 293.2 K, but a more usual Π - A curve appears at 281.2 K).³⁴ One possibility is that the molecules of 8 cluster on a slant (thus explaining the "large" A_c) and then "ride on each other" with no extensive property such as a characteristic film pressure.

The situation changes again for TDDOP-C-ENP, 9 (Figure 8). This time the area per molecule A_c is very temperature-dependent, and the collapse pressure increases to a reasonable value only at 278.2 K. In fact, the situation at 306.2 K is reminiscent of DDOP-C-ENP, 7, while at 293.2 and 278.2 K true monolayer behavior seems to have been reasserted. The area per molecule at the lowest temperature, 76 \AA^2 , is 38 \AA^2 larger than that of 7; since the area per molecule A_c of cadmium arachidate is about 20 \AA^2 , and there are two more alkyl chains for 9 than for 7, we observe some deviation from additivity of molecular areas ($38 + 20 + 20 = 78 \text{ \AA}^2 > 76 \text{ \AA}^2$).

The strong electron acceptor end of 10 makes the pressure-area isotherm change again (Figure 9). The film strength improves dramatically with decreasing temperature (as was the case for 9). At the highest temperature (297.7 K), there is only one ordering transition at fairly low Π_c , but, as the temperature is lowered, two ordering transitions set in: at the lowest temperature (277.7 K) only one transition remains, at a fairly high Π_c . One may want to speculate whether the intermediate ordering transitions are due to uncoiling of the three dodecoxy groups. The minimum area at collapse, A_c , of 10 is very similar to that of 9: this indicates that the limiting area is due not to the TCNQ end but to the three bulky chains on the donor end. Indeed, the previously measured A_c for TCNQ-bearing D- σ -A molecules was between 50 and 58 \AA^2 .^{1,10,11}

Transfer Ratios and Z-Type Deposition. The LB film transfers were carried out at a film pressure held constant at about three-quarters of the measured Π_c and, as stated above, at the lowest possible subphase temperature (but, since a glass slide at room temperature is moved through the PL monolayer, there is an unavoidable temperature gradient). For 7, the barrier moves in slowly over a 2-h period even when no films are being transferred (i.e., the PL film is marginally stable); nevertheless, by keeping the pressure at $0.75\Pi_c$, and the area above A_c , LB transfer becomes possible. For 8 and 9, the barrier does not creep appreciably by itself, and transfer is performed at about $0.75\Pi_c$.

For the molecules 7, 9, and 10, which did transfer as LB films, transfer ratios close to 1.0 were observed when the slide was *withdrawn* from the subphase, with the polar end of the first LB monolayer adhering to the glass substrate, whereas the transfer ratio was close to zero when

Table II. Monolayer Data from Pressure-Area (Π -A) Isotherms for 7-10 at Water Subphase Temperature T^a

molecule	T , K	Π_c , mN m	A_c , Å ²	A_m , Å ²	A_0 , Å ²	κ , m/mN	PL	LB	Z
DDOP-C-ENP (7)	278.2	23.7	38	40	42	0.019	Y	Y	Y
	293.2	20.0	38	40	41	0.017	Y	Y	
	306.3	10.4	39	39	41	0.024	Y	Y	
BDDOP-C-ENP (8)	279.1	14.3	(75)	(85)	(95)	0.047	N	N	N
	293.2	13.8	(73)	(82)	(91)	0.048	N	N	N
	306.3	12.6	(79)	(87)	(96)	0.045	N	N	N
TDDOP-C-ENP (9)	278.2	34.0	76	82	89	0.066	Y	Y	Y
	293.2	11.5	99	117	132	0.037	Y	Y	
	306.2	15.2	107	130	151	0.033	Y	Y	
TDDOP-C-HETCNQ (10)	277.7	55.5	75	107	227		Y	Y	Y
	282.8	52.5	83	125	188		Y	Y	
	288.6	47.5	65	115	278		Y	Y	
	293.4	43.0	73	121	254		Y	Y	
	297.7	20.0	96	128	207		Y	Y	
	303.1	19.3	132	164	235		Y	Y	

^a The estimated precision in Π is ± 0.1 mN m; the estimated precision in the area per molecule (A_c , A_m , A_0) is $\pm 5\%$, except where indicated. As indicated in the text, Π_c indicates the differential surface pressure at the collapse point; A_c , A_m , and A_0 are the molecular areas at the collapse point, at $\Pi = 0.5\Pi_c$, and at the extrapolated zero pressure, respectively; finally, κ is an estimate of the isothermal compressibility at $0.5\Pi_c$. A Y under PL indicates that a Pockels Langmuir monolayer at the air-water interface does form (N means no). A Y under LB indicates that a Langmuir-Blodgett film was transferred to a glass substrate (microscope slide). A Y under Z indicates that the multilayers are of the Z-type (PL films transfer to microscope glass only during upstroke, i.e., withdrawal of slide from the subphase). The data for TDDOP-C-HETCNQ (10) supersede those reported in ref 10.

the slide was dipped downward into the subphase (Z-type deposition).

FTIR Spectra. The FTIR spectra of a 15-multilayer film of **7** failed to show characteristic bands. This indicates that the LB monolayers are extremely disordered and are more typical of a fluid with a low degree of orientation within the film, rather than of a two-dimensional solid (as one sees, e.g., for FTIR spectra of multilayers of cadmium arachidate). However, a 15-multilayer LB film of **9** (TDDOP-C-ENP), transferred to a microscope slide at 278 K, but studied at room temperature, showed two weak and broad bands peaked at 2925 ± 2 and at 2855 ± 2 cm^{-1} , which are characteristic C-H stretch frequencies (we have observed much sharper signals, at the same frequencies, for 15 monolayers of the molecule **4**, BDDAP-C-BHTCNQ,¹¹ which forms PL monolayers with a much steeper Π -A isotherm than does **9**, TDDOP-C-ENP). Thus, we can claim that an intermediate degree of order exists within LB films of TDDOP-C-ENP.

LB Film Thickness Monitored by X-ray Diffraction. For a multilayer of cadmium arachidate transferred onto a glass slide, nine X-ray diffraction (Cu K α) peaks were observed, of which the lowest angle is at $2\theta = 1.62^\circ$, giving a repeat distance (two monolayer thicknesses) of 54.5 Å. The Scherrer line-width equation gave a correlation length of 235 Å.

A multilayer of **7**, transferred to a glass substrate, gave only one X-ray diffraction peak (Cu K α) at $2\theta = 2.16^\circ$, giving a repeat distance of 40.9 Å. The Scherrer line-width equation gave a correlation length of 438 Å.

A LB multilayer of **9** on glass yielded a single diffraction peak at $2\theta = 1.94^\circ$ (repeat distance of 45.5 Å). The Scherrer correlation length was 473 Å.

LB Film Thickness Monitored by Ellipsometry. By use of the literature value for the refractive index of cadmium arachidate ($n = 1.542$), the thickness for two LB layers of cadmium arachidate on Si was obtained as 53 ± 8 Å (uncertainty = width of distribution of thickness values at half the peak of the distribution), whence the thickness per monolayer becomes 27 ± 4 Å. For 40 LB layers of **7** on Si, the refractive index was $n = 1.585$, and the measured film thickness was 1300 ± 150 Å, whence the monolayer thickness is 33 ± 4 Å.

Calculated Molecular Geometry. A MNDO geometry-optimized structure of **7** was obtained. The com-

Figure 10. ORTEP-II plot of the MNDO-computed geometry of **7** obtained by using van der Waals atomic radii (1.2 Å for H, 1.7 Å for C, 1.5 Å for N, 1.4 Å for O).

puted dipole moment was 5.992 D. The highest occupied molecular orbital has energy -9.172 eV; the lowest unoccupied molecular orbital has energy -1.117 eV. This correlates well with similar calculations reported elsewhere:¹¹ the HOMO should be localized mainly on the donor end of the molecule, and the LUMO should be localized on the acceptor. As expected, the LUMO of **7** implies a lower electron affinity for ENP than, e.g., TCNQ (for which LUMO energies in related D- σ -A molecules are about -2.95 eV).¹¹ The MNDO-optimized geometry did yield an extended configuration (as MNDO tends to do), but there was a significant twist in the ethyl carbon atoms linked to the nitrophenyl, namely around the atom indicated in boldface in the group $\text{OCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2$. An ORTEP-II plot, obtained by using van der Waals atomic radii, is given in Figure 10. The molecular length of the bent molecule is 30 Å; when "unfolded" (not shown), the molecular length becomes 39 Å. The molecular cross section of the ENP end (Figure 10) is only about 23 Å² (nitro group eclipsed with phenyl ring) or 33 Å² (nitro group bent as shown).

4. Discussion

While the acceptor ENP of molecules **7**, **8**, and **9** is fairly weak, compared to the TCNQ acceptor of **10**, it was sufficiently polar to let **7** and **9** (but not **8**) form mono-

layers. The monolayers can be transferred to a glass substrate, if the PL monolayer is held at low temperature, but the films probably are not well ordered.

The large intralayer Scherrer correlation length is surprising, but the difficulties in observing good FTIR spectra indicate a low degree of interlayer registry. Clearly some further FTIR studies are needed.

The experimental molecular area of **7** (38 \AA^2) correlates approximately with the "thickness" of the ENP ring, viewed as in Figure 10. The X-ray monolayer thickness of **7** agrees within two standard deviations with the ellipsometry result. The X-ray monolayer thickness of **7** and **9** is consistent with a Z-type deposition. The X-ray thickness of **7** correlates also very well with the "molecular length" of **7**: one must presume that under the conditions of the film balance all "kinks" are indeed taken out, and that the molecule assumes the most extended geometry it can.

The finding that Z-type monolayers are formed is surprising, and indicates that some of these molecules (particularly **10**) should be very interesting as noncentrosymmetric systems with aromatic rings and potentially very large transition dipoles, which should make them promising for nonlinear optical devices (frequency doublers).

These molecules seem polar enough to orient and pack as PL monolayers at the air-water interface, but not polar enough to produce the typical centrosymmetric Y-type layers formed, e.g., by LB multilayer films of cadmium arachidate.

Acknowledgment. We are grateful to Nippon Telephone and Telegraph for their initial support. We thank the Geology Department of the University of Alabama for the use of their X-ray powder diffractometer and the Alabama Supercomputer Authority for computer time on the Alabama Cray X-MP-2/4. Shankar Krishnamoorthy performed the ellipsometry measurements. Chinn-arong Asavaroengchai helped with the theoretical calculations. Dora Fracchiolla (NSF REU student in 1988) helped with some of the LB film work.

Registry No. **7**, 123126-34-1; **8**, 123126-35-2; **9**, 123126-36-3; **10**, 123126-37-4; **12a**, 99-76-3; **12b**, 2150-44-9; **12c**, 99-24-1; **13a**, 40654-49-7; **13b**, 123126-38-5; **13c**, 123126-39-6; **14a**, 2312-15-4; **14b**, 123126-40-9; **14c**, 117241-31-3; **15a**, 50909-50-7; **15b**, 123126-41-0; **15c**, 117241-33-5; **16a**, 123126-42-1; **16b**, 123126-43-2; **16c**, 123126-44-3; **17a**, 123126-45-4; **17b**, 123126-46-5; **17c**, 123126-47-6.

Langmuir–Blodgett Films of Potential Donor–Sigma–Acceptor Organic Rectifiers*

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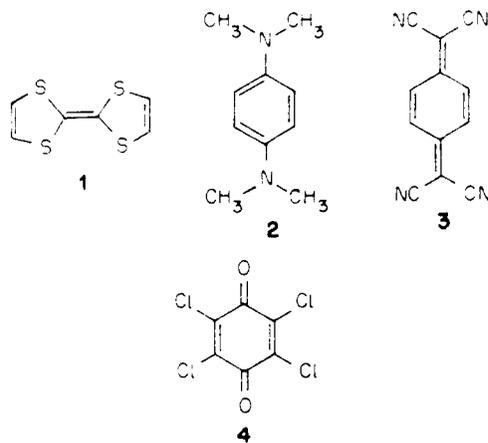
Department of Chemistry, University of Mississippi, University, Mississippi 38677, USA

The Organic Rectifier Project (ORP) at the Universities of Mississippi and Alabama aims at the realization of a one-molecule-thick rectifier of electrical current, which could be part of a 5 nm-thick electronic device. Such a device, suggested in 1973 by Aviram, relies on the asymmetry of molecules D- σ -A, where D is a good one-electron donor (but poor acceptor), A is a good one-electron acceptor (but poor donor) and σ is a covalent bridge that insulates the molecular orbitals of D from those of A. Six molecules have been found to self-assemble as monolayers; four contain the TCNQ moiety; three contain 'greasy' dodecyl groups on the donor end (which helps in monolayer formation), but one contains only hexyl groups. All of them can be transferred to a glass, conducting tin oxide or Al substrate as Langmuir–Blodgett films. In preliminary trials, no rectification was observed. Recent FTIR data for LB films as a function of aging are presented.

INTRODUCTION

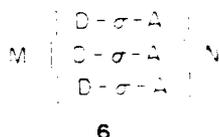
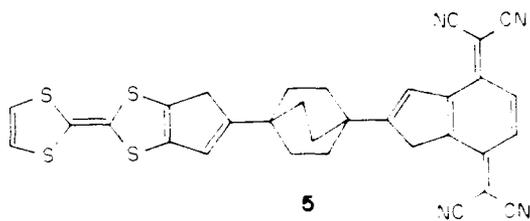
This paper outlines progress of the Organic Rectifier Project (ORP) towards the synthesis of molecules of the type D- σ -A, which, in defect-free organized assemblies, may be rectifiers of electrical current; here D is a strong one-electron organic donor, such as TTF (tetrathiafulvalene, **1**) or TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine, **2**), σ is a covalent sigma bridge and A is a strong one-electron acceptor, such as TCNQ (7,7,8,8-tetracyanoquinodimethane, **3**) or chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone, **4**). In 1973, Aviram and co-workers^{1–3} proposed that D- σ -A molecules, such as the Gedankenmolekül **5**, sandwiched as an oriented monolayer between ordinary metallic thin films M and N, as in **6**, would rectify alternating electrical current. The obvious advantage of such a device is its small thickness:

the molecule **5** (never synthesized) should be only 2 nm thick. If very thin conventional films M, N (1.5 nm each) can be used, then a 5 nm thick device becomes possible, much thinner than the working direction of conventional Si or GaAs devices (1–3 μ m).



*Supported in part by NSF-DMR Grant 84-17563.

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The incremental results of the Organic Rectifier Project have been reported elsewhere.⁴⁻²⁰ The present review follows closely another review, prepared for a different audience six months ago [13].

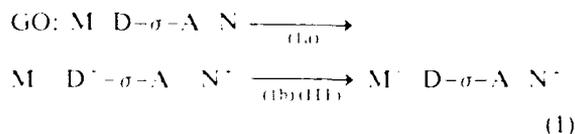
THEORETICAL, SYNTHETIC AND ASSEMBLY CRITERIA

In this section are summarized the design criteria that have evolved in the ORP.⁴⁻²⁰

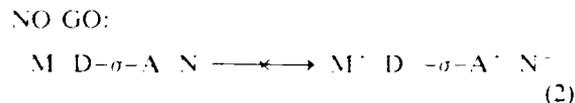
Simplified mechanism

If device **6** is successfully assembled, then the mechanism for rectification is given by Eqns (1)-(3).^{1-4,6,9,10,13}

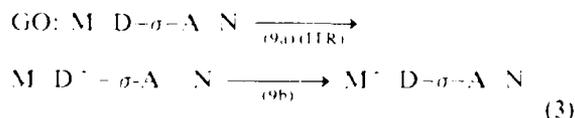
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Reverse bias:

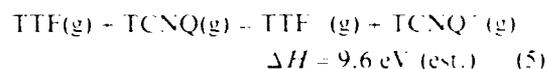
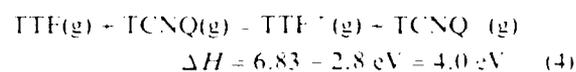


Reverse bias:



Under vanishing or moderate forward electrical bias, the electron transfer (ET) can occur² by elastic, through-space (TS)²¹ tunneling through a

chemisorptive barrier from D to M, and from N to A [Eqn (1a)]; the zwitterionic molecular state $D^+-\sigma-A$ forms; this is followed² by through-bond (TB)²¹ inelastic tunneling [called ITF, Eqn (1b), or forward inelastic tunneling] from A⁻ to D⁺; this yields charge separation. Under reverse electrical bias, the formation of zwitterion $D^+-\sigma-A^+$ [Eqn (2)] is very unlikely, because good organic one-electron donors are very poor acceptors, and good acceptors are poor donors. Indeed, in the gas phase, the energy required to form the ions TTF⁺(g), TCNQ⁻(g) at infinite mutual separation is, experimentally, 4.0 eV;^{22,23} in contrast, the energy required to form the ion pair TTF⁺(g), TCNQ⁻(g) is estimated at 9.6 eV;^{24,25}

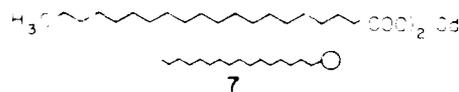


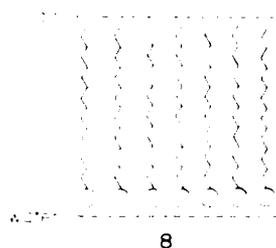
However, under large reverse electrical bias, another reaction channel opens [Eqn (3a)]: a zwitterion $D^+-\sigma-A^+$ forms first, followed by charge separation from M to N; this is reverse, or 'uphill' tunneling ITR, and is much less likely than ITF.² Of course, tunneling here is between states of different energies, so one sees these as elastic processes between virtual states of equal energy, followed by inelastic 'through-bond' processes.

Langmuir-Blodgett films

The ORP has concentrated on molecules $D-\sigma-A$ which self-assemble at the air-water interface as 'Pockels-Langmuir (PL) monolayers (this name^{13,14} honors Irving Langmuir (1881-1957) and Fraulein Agnes Pockels²⁶). Such PL monolayers can, usually, be transferred to glass or metal or other solid substrates by the Langmuir-Blodgett (LB) technique pioneered by Langmuir and by Katharine B. Blodgett (1898-1979).²⁷⁻³¹ The typical molecule that forms excellent PL and LB films is cadmium arachidate, or cadmium eicosanoate, $\text{Cd}(\text{n-C}_{19}\text{H}_{39}\text{COO})_2$ (**7**).

At the air-water interface a PL monolayer of cations **7** (shaped like tadpoles) points with the





carboxylate ends toward the water subphase, as in **8**; the cadmium counterions are in the subphase, coordinated fairly closely with the carboxylate head group. Usually, such work is carried out today by using an automated Langmuir trough or film balance.

The LB technique consists of slowly inserting a macroscopic metal, glass, silicon or other substrate through the monolayer into the subphase, either on insertion into the water or on slow withdrawal from the water; the PI monolayers transfer quantitatively to the substrate with little or no distortion; thus are formed the LB monolayers. If the substrate is dipped several times through the monolayer, LB multilayers can be transferred to the substrate.²⁷⁻³²

Other techniques for monolayer coverage of metals

Another method of transferring self-assembling monolayers to substrates without using a Langmuir trough is the Bigelow oleophobic (BO) film-casting technique.³³⁻³⁶ The forces binding an LB or BO monolayer to the substrate are usually weak physisorptive or chemisorptive forces. Better adhesion is achieved by direct covalent bonding to a surface. Bonding to silanized metal surfaces rarely achieves monolayer coverage.³⁷ Also, attaching silanized molecules to oxide-bearing metal surfaces produces compact monolayers,³⁸ as does attaching molecules bearing disulfide bonds to gold surfaces.³⁹ Another method of providing 'strong' films is to polymerize LB films containing diacetylene linkages *in situ* using ultraviolet radiation.⁴⁰

Despite the existence of these other potential techniques for assembling an organic M-D- σ -A-N rectifier, we concentrate below on D- σ -A molecules that will self-assemble as PI and LB monolayers.

Synthetic and device assembly criteria

The criteria for the synthesis and assembly of an M-D- σ -A-N device **6** have been discussed before^{1,6,9,10,13} and can be enunciated as follows.

(1) The donor D must have a relatively low ionization potential, I_D (< 7.5 eV); it should be a fairly flat molecule, to provide good lateral packing.

(2) The acceptor A must have a relatively high electron affinity, A_A (> 2 eV), and should also be a fairly flat molecule, to allow for compact packing.

(3) The σ bridge must be at least partially saturated (not conjugated). It must also be long enough (more than three carbon-like atoms) to prevent extensive ground-state mixing of the donor molecular orbitals with the acceptor molecular orbitals, yet short enough (less than nine carbon-like atoms) or rigid enough to prevent the curling of the D end over the A end of the molecule. Five or six carbon atoms seems to be the optimal length. The σ bridge must also be flat enough to provide good lateral LB film packing.

(4) The I_D and A_A values of D and A must approach as closely as possible the work functions of the metals M and N^{22,23,41-45} (see Table I). Unfortunately, one cannot hope for a perfect match, even for the best donors and acceptors known to date.

(5) The organic coupling reaction (6), leading to the linked D- σ -A, must be more probable, or faster, than the competing charge transfer (CT) salt formation (7):



As described below, the ester and carbamate coupling reactions have been found to be acceptable. Many other coupling reactions are not feasible because of the high reactivity of TCNQ.

Table 1. Ionization potentials, I_D , for the donors (D), electron affinities, A_A , for the acceptors (A) and work functions, ϕ , for the metals (M, N)

	I_D (eV)		A_A (eV)		ϕ (eV)
TMPD	6.25 ¹⁷	DDQ	3.13 ⁴³	Al	3.74 ⁴¹
TFE	6.83 ¹⁷	TCNQ	2.80 ¹⁹	Au	4.58 ⁴¹
Pyrene	7.41 ¹⁸	Chloranil	2.76 ⁴⁰	Pt	5.29 ⁴¹

(6) The Franck-Condon reorganization of the molecular geometry of D to D⁺ and of A to A⁻ must be small, i.e. fast, so that the overall electron transfer (ET) within D-σ-A (fast owing to the large difference I_D-I_A) does not slow down because of the Franck-Condon factor.⁴⁶⁻⁴⁸ Under the right conditions, ET through the molecule can be faster than 1 ns.⁴⁷⁻⁵⁰ It is important, of course, to achieve a fast ET process, since a small but slow molecular electronic device has no advantage over the larger but very fast conventional (Si or GaAs) electronic device.

(7) The D-σ-A molecule must pack in PL monolayers. For this, one end must be hydrophobic and the other hydrophilic. In the PL monolayer, one must prevent the packing of D-σ-A over A-σ-D (which would cancel dipole moments and destroy the directionality of the device **6**). The lateral π-π attractive interactions, and possibly even a mixed-valence ground state (which exists in the quasi-one-dimensional salt TTF-TCNQ) may help reduce the cost of ionization of D-σ-A to D⁺-σ-A⁻ from 4 eV to possibly 1-2 eV.

(8) The monolayers must be close-packed and defect-free over the region of overlap of metal layer M atop D-σ-A atop metal layer N (to prevent electrical shorting of metal layer M when it is deposited atop metal layer N). When LB films of cadmium arachidate are transferred on to hydrophobic, oxide-free metals (Pt, Au, Ag) they have relatively large defects (probably at domain boundaries),⁵¹ and may have a disordered, fan-like structure.⁵² Over hydrophilic, oxide-covered metals (Al, Sn) or glass or quartz, the defects in the cadmium arachidate LB films seem smaller, allowing for a percolative current *j* across the film and through disclinations⁵³ (the voltage dependence of *j* is log *j* = *aV*¹⁻⁴⁵⁴ and not log *j* = *bV*¹⁻²⁵⁵). One way of achieving freedom from defects on the scale of a few microns would be to use a thin interdigitated layer M, where the film perfection is sampled on several small disks of radius 3 μm (these disks would be connected to macroscopic electrodes). Some crude, preliminary and negative results (on the mm scale) are described below.

(9) At an M-N distance of, typically, 2 nm, TB tunneling must be much more likely than TS tunneling [the latter is undirected, and depends only on barrier height and distance, i.e. it is equally likely from M to N as it is from N to M; TB tunneling shows the desired 'chemical' selec-

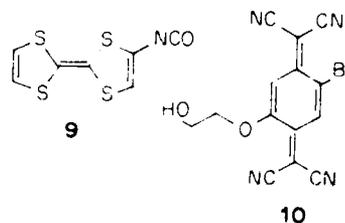
tivity of making reaction (1) much more likely than reactions (2) and (3)]. In inelastic electron tunneling spectroscopy (IETS)⁵⁶ through *random* films of insulators placed between superconducting Pb and normal Al electrodes at 4.2 K, the ratio TB:(TB + TS) is only 0.01. For the organic rectifier, this ratio (for compact monolayers) must be much closer to 1.0. One should remember that even in compact monolayers of cadmium arachidate, a 'background' conductivity, independent of the number of monolayers, was always present; this was presumably due to TS tunneling processes.⁵⁵

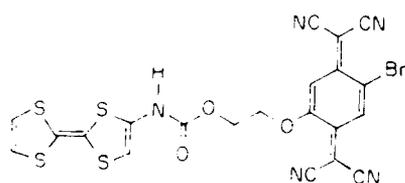
(10) Heating the monolayer above its chemical decomposition temperature (conservatively estimated as 100 °C) should be avoided, both while laying down the second metal layer N atop M atop D-σ-A as a sputtered or evaporated film, and also during the TB tunneling process in the device **6**, which will be exothermic, and will therefore require some mechanism for heat dissipation. Similarly, high voltages that may cause dielectric breakdown must be avoided.

RESULTS

Coupling reactions

In 1976 Hertler⁵⁷ prepared carbamate, or urethane, polymers of TTF with TCNQ if one reacts the 2,2'-bisisocyanate of TTF with a 2,5-dihydroxyethoxy-TCNQ; the resulting insoluble black polymer was semiconducting, not metallic. However, the utility of Hertler's contribution was to show that carbamates of strong donors with strong acceptors could be prepared, and that reaction (6) was preferred over reaction (7) for carbamates. Baghdadchi prepared the monoisocyanate of TTF, **9**, and coupled it with Hertler's 2-bromo-hydroxyethoxy-TCNQ (BHTCNQ), **10**,⁴⁷⁻⁵⁷ to yield to carbamate **11** of TTF with TCNQ. However, two forms were found, of which one seemed zwitterionic and the





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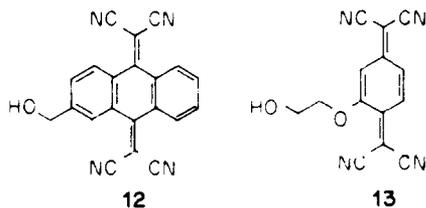
other neutral (as evidenced by the infrared CN stretching frequencies). Neither product could be isolated in acceptable purity.

Esters of TTF with BHTCNQ, **10**, were also prepared, using the 2-acyl chloride of TTF, but, again, two products were obtained. The neutral form of the TTF carbamate with BHTCNQ did form LB monolayers, but with the wrong geometry (probably with the molecule lying almost flat on the water subphase, rather than normal to it).

Since that time, most of our efforts have been concentrated on the carbamate coupling, although one may conceive of other possible coupling reactions.

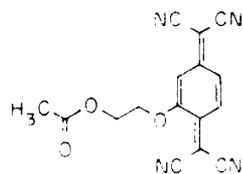
Acceptors

Most of the work has been carried out with Hertler's BHTCNQ, **10**, the crystal structure of which was recently determined.¹⁷ Its electron affinity is estimated by cyclic voltammetry as 2.9 ± 0.2 eV.¹⁷ However, its very inefficient synthesis spurred a search for a better, or more accessible acceptor. The anthraquinone analog **12** has been prepared in excellent yield,¹¹ but the molecule is severely bent, and **12** is a weak



12

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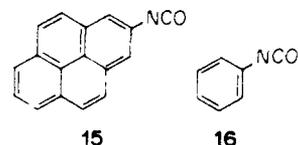


14

two-electron acceptor, rather than a strong one-electron acceptor. In a major breakthrough, the synthesis of **13** has been accomplished in high yield,¹⁵ and the crystal structure of its methyl ester, **14** has been determined.¹⁶

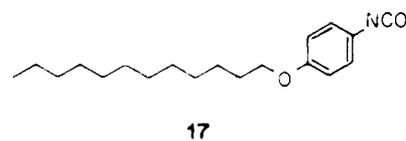
Donors

After the early work on TTF isocyanate (a strong donor),⁴ the isocyanate of pyrene, **15** (a medium donor), was prepared; later, various derivatives of phenyl isocyanate, **16** (a weak donor), were prepared; adding a dodecyloxy group gave the weak donor **17**; adding the dimethylamino group gave the medium donor DMAP-NCO, **18**. The crystal structure of its methyl carbamate, DMAPCMe, **19**, was determined;¹⁹ its calculated (AM1) ionization potential (7.17 eV) and cyclic voltammetry showed that **19** is a donor weaker than TMPD or TTF but stronger than pyrene.¹² There is extensive hydrogen bonding in the crystal of DMAPCMe,¹⁹ in solution¹² and also in the solution of its electrochemically generated radical anion.¹² The bisdodecyl and the bishexyl derivatives of **18** have also been synthesized.

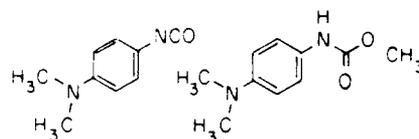


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Crystal structures of donor-sigma-acceptor molecules

To test the proposition that the σ bridge allows for an extended structure of the D- σ -A adducts, crystal structures have been determined for

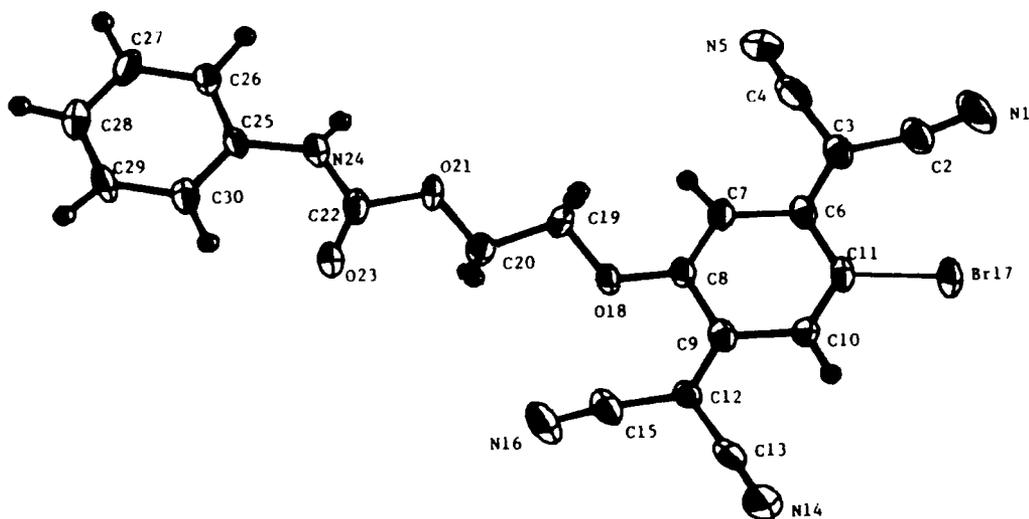


Figure 1. ORTEP plot of phenyl-C-BHTCNQ, **20** (monoclinic, space group $P2_1/n$, a 8.310 Å, b 9.278 Å, c 25.383 Å, β 95.15°, Z 4, R 7.9%).

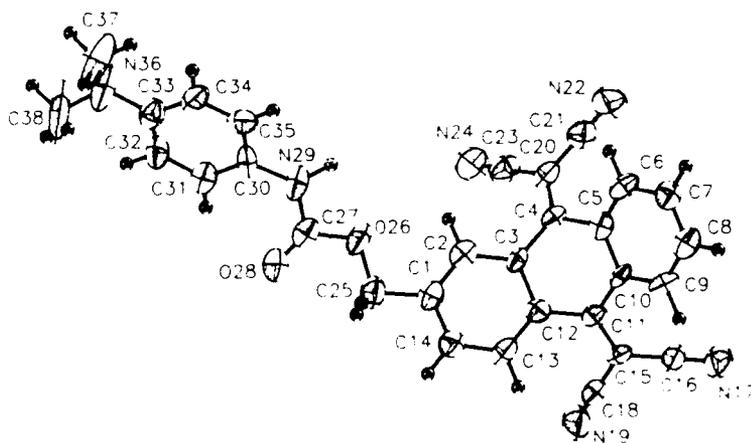
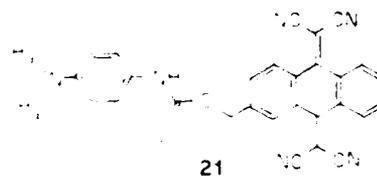
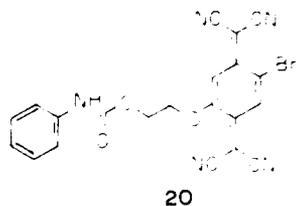


Figure 2. ORTEP plot of DMAP-C-HMTCAQ, **21** (triclinic $P1$, a 8.748 Å, b 10.989 Å, c 13.541 Å, α 90.67°, β 99.15°, γ 98.62°, Z 2, R 12.7%).

phenyl-C-BHTCNQ, **20**, (Fig. 1),²⁷ and for DMAP-C-HMTCAQ, **21** (Fig. 2).³⁰ Of course, in both cases the molecules do not form LB films,

but the crystal structure reveals an extended conformation: the crystals belong to the centrosymmetric space group $P1$; the molecules pack in the crystal so that D - a - A packs almost over A - a - D .



Pockels–Langmuir and Langmuir–Blodgett films

It was found that only certain D- σ -A molecules, **22–26**, form monolayers at the air–water interface; the data are given in Table 2, and the rele-

vant pressure–area isotherms are shown in Figs 3–7.

The collapse pressure Π_c is defined as the differential surface tension, which, if exceeded, leads to the collapse of the film, and to the irreversible 'riding of ice floes over each other.' The area per

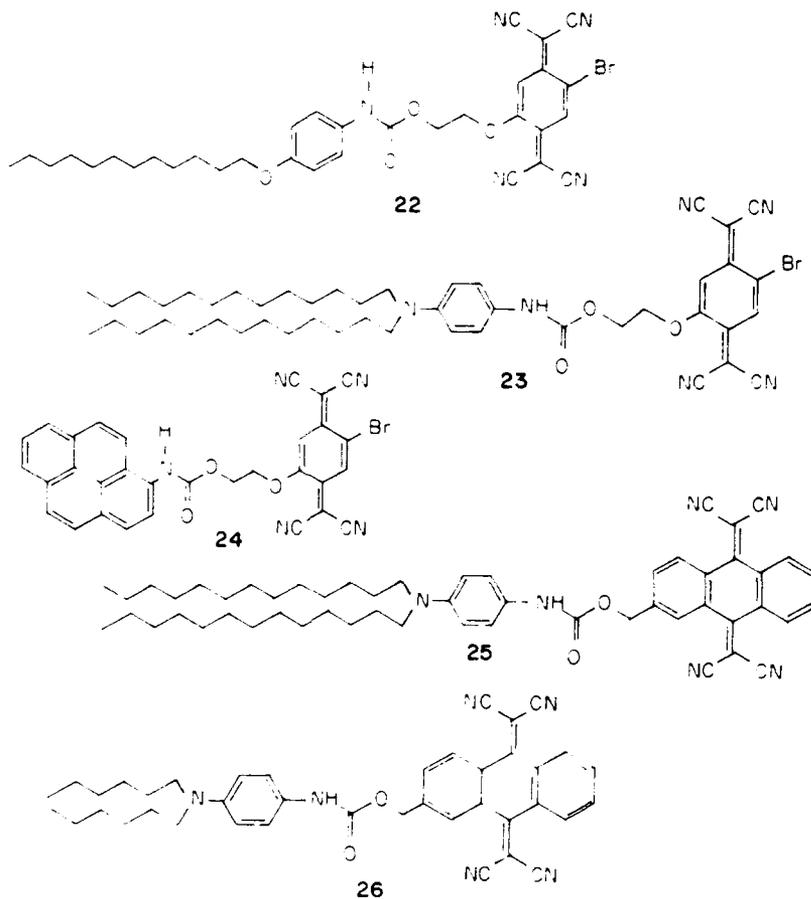


Table 2. Molecular areas and collapse pressures for PL monolayers

Molecule	No	T (K)	Π_c (mNm ⁻¹)	A_c (Å ²)	A_m (Å ²)	A_0 (Å ²)	Ref.
TTF C BHTCNQ	11	292	12.7	134 ± 50			6
DDOP C BHTCNQ	22	292	20.2	50	55	60	6, 14
BDDAP C BHTCNQ	23	293	47.3	57	69	82	14
		303	45.9	54	70	82	
Py C BHTCNQ	24	283	28.2	53	60	66	14
BDDAP C HMTCAQ	25	293	22.3	58	71	83	14
BHAP C HMTCAQ	26	293	35.8	42	47	53	13

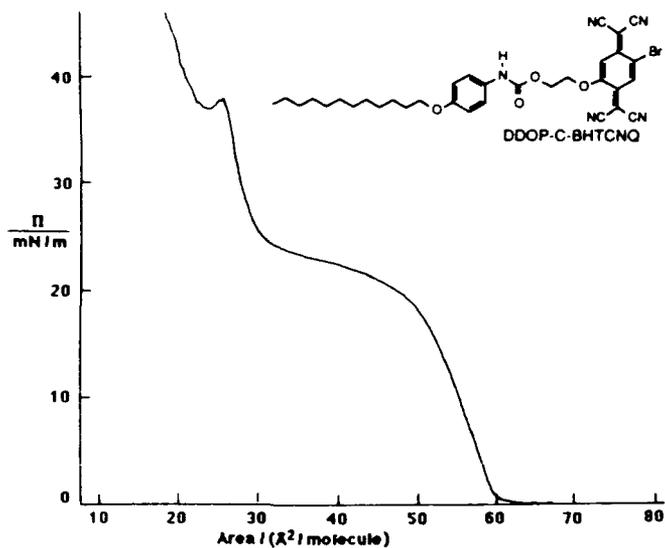


Figure 3. Pressure-area isotherm for DDOP-C-BHTCNQ, 22.^{6,14}

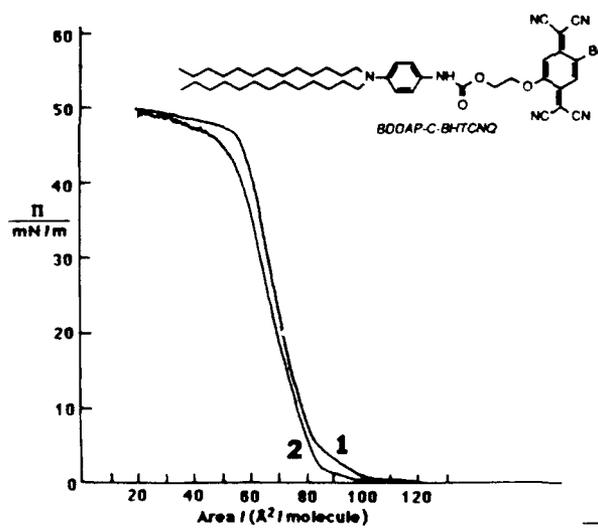


Figure 4. Pressure-area isotherm for BDDAP-C-BHTCNQ, 23, at (1) 293 K and (2) 303 K.⁶

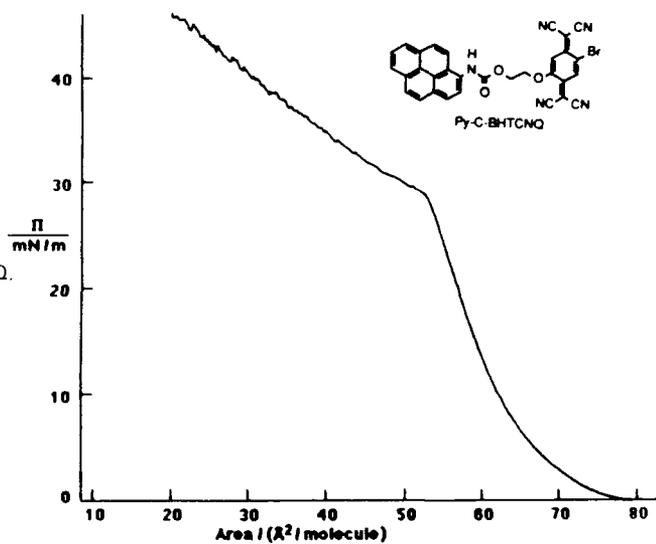


Figure 5. Pressure-area isotherm for Py-C-BHTCNQ, 24.¹⁴

molecule can be defined in several ways: the area at the collapse point is A_c , and is the smallest; the area per molecule at zero pressure, A_0 , is the point in the Π - A isotherm obtained when the steepest part of the curve is extrapolated linearly to zero pressure; A_m is defined as the mid-point between A_c and A_0 . Of all these points, A_m gives what probably is the best estimate of the lateral dimensions of the molecule in a well packed film.

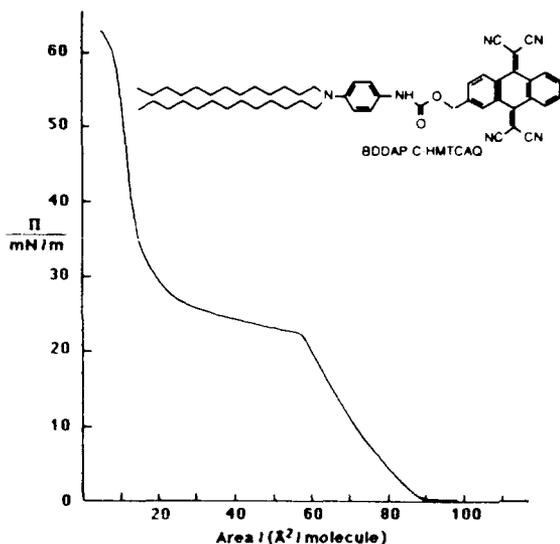


Figure 6. Pressure-area isotherm for BDDAP-C-HMTCAQ, **25**.¹²

The slope of the Π - A isotherm in the thermodynamically reversible monolayer regime ($\Pi \leq \Pi_c$ and $A \geq A_c$), helps to determine the fluidity or rigidity within the film. For cadmium arachidate, the slope is almost vertical, because the film is almost crystalline in its two-dimensional packing. For the molecules **22-26** (Figs 3-7) the slope indicates a more fluid-like environment, in which the molecules probably do not pack as rigidly as they would in a crystal. Of these, only Py-C-BHTCNQ, **24**, lacks an alkyl 'greasy chain'; DDOP-C-BHTCNQ, **22**, BDDAP-C-BHTCNQ, **23**, and BDDAP-C-HMTCAQ, **25** all have dodecyl groups that help provide a hydrophobic region in the molecule (if the dodecyl groups are replaced by methyl groups, no monolayers are formed). The 'most rigid' of these films are the film of BDDAP-C-BHTCNQ, **23** (Fig. 4).

Since, however, the presence of long alkyl chains may retard the TB ET, it may be an advantage to have the shortest possible alkyl chain which still can provide monolayer formation. Thus we are pleased with the recent result that the bis(hexyl) chain in BHAP-C-HMTCAQ, **26**, was 'sufficient' to provide good PL monolayers. Work on similar molecules is continuing. A preliminary search for an intervalence band in the optical spectra of **22-26** has failed;¹² it may be that its oscillator strength is so weak that a more careful search for it should be made; it is also possible

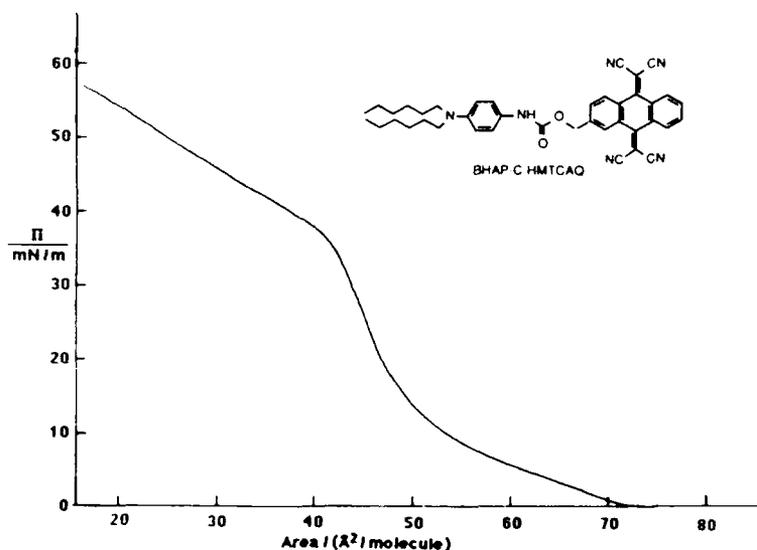


Figure 7. Pressure-area isotherm for BHAP-C-HMTCAQ, **26**.¹³

that a six-atom carbamate link is 'too long' and that an ester linkage (one atom shorter) is desirable.

Preliminary tests of rectification

Efforts were made to find rectification behavior in sandwiches of molecules **11**,^{4,6} **22**⁸ and **24**.⁸ For **11**, sandwiches Pt | **11** | Hg and SnO | **11** | Hg were electrical shorts.^{4,6} This was not surprising, since the large molecular *A*, for **11** indicated that it was 'sitting' with the longest axis almost parallel to the water subphase, and therefore almost parallel to the Pt or SnO substrate; if this is true, then the film thickness, probably only 6 Å, was so small that TS tunneling, or tunneling through defects, could not be avoided. For **22** and **24**, electrical shorts were observed in similar sandwiches.⁸ However, in the same laboratory, sandwiches *A* | **7** | Hg using monolayers of cadmium arachidate were not insulating,⁸ even though they had been prepared previously as high-resistance sandwiches in other laboratories.^{4,5} Therefore, it can be stated that a proper test of rectification of **22** or **24** had not been made.

More recently an effort was made to detect rectification by LB monolayers of BDDAP-C-BHTCNO, **23**, in a Al | **23** | Al sandwiches constructed as shown in Fig. 8, and explained below. Fifteen glass microscope slides (7.5 × 2.5 cm) were cleaned and coated, using a slitted brass mask, with five fingers each of shiny Al 3.5 mm long, 1.6 mm wide, and probably 100–500 nm thick (bottom strips). A single LB film was then transferred to each coated slide, overlapping the bottom strips. By using the same mask turned 180°, each slide received a second coating of five more fingers of Al of the same dimensions (top strips), but so that the top strips overlapped (through the intervening monolayer) with the bottom strips only within a disc region about 1.5 × 1.5 mm (see Fig. 3). Of course, the alignment of the D-σ-A molecules around the edges of the disc is poor, owing to the irregular contour of glass and Al that they must follow. Electrodes were attached to the long aluminium strips and through-film conductivity was monitored using a BAS CV-22 potentiostat for the 15 slides, i.e. for 75 Al | **23** | Al sandwiches. Many of these had infinite resistance, i.e. good contact was somehow not achieved. The rest of these sandwiches exhibited the linear, ohmic *I-V* characteristics of

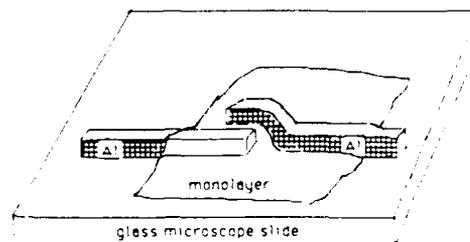


Figure 8. Schematic diagram of Al | **23** | Al sandwich used in a preliminary test of rectification. A monolayer of BDDAP-C-BHTCNO, **23**, was transferred as an LB film atop a glass microscope slide provided with five bottom strips of Al (left, shaded; for simplicity only one is shown). Then five top strips of Al (right, shaded; only one is shown) were deposited on the monolayer, but with small overlap with the bottom strip.

bulk Al, i.e. were electrical shorts. Even this 'refined crude experiment' was not a suitable test, or else there were too many defects in the monolayer. Naturally, more refined experiments are planned.

Fourier transform infrared (FTIR) spectra of **25**

Important structural information for LB films is provided by Fourier transform infrared (FTIR) spectroscopy.^{16,48,62} In a comparative test of several FTIR spectrometers, spectra of BDDAP-C-HMTCAQ(**25**) monolayers on Al-coated glass slides were obtained (Figs 9–17) in the grazing angle specular reflectance mode, at different times after the receipt of identical samples from the same batch, and their subsequent storage in air. Figures 9–11, 12–15 and 16 and 17 were obtained, in a flowing boil-off N₂ atmosphere, on Mattson, Nicolet and Bruker FTIR spectrometers, respectively. Table 3 lists the details of the instruments used, the sample age, the resolution, scan time, number of scans and the angle of incidence used (Nicolet stated 'Brewster's angle' but did not give its wavelength).

It is clear that LB monolayers have a finite lifetime on Al substrates; in fact, whereas the Mattson instrument saw the single monolayer easily (Fig. 9), the Nicolet instrument barely could (Figs. 13–15) and the Bruker instrument, not seeing it at all, used the monolayer slide as a 'blank' to determine the 'background' absorbance of Al for Figs 16 and 17. In Figs 12–14 a single monolayer is present, and one can resolve the aliphatic CH stretch bands at 2951, 2910 and

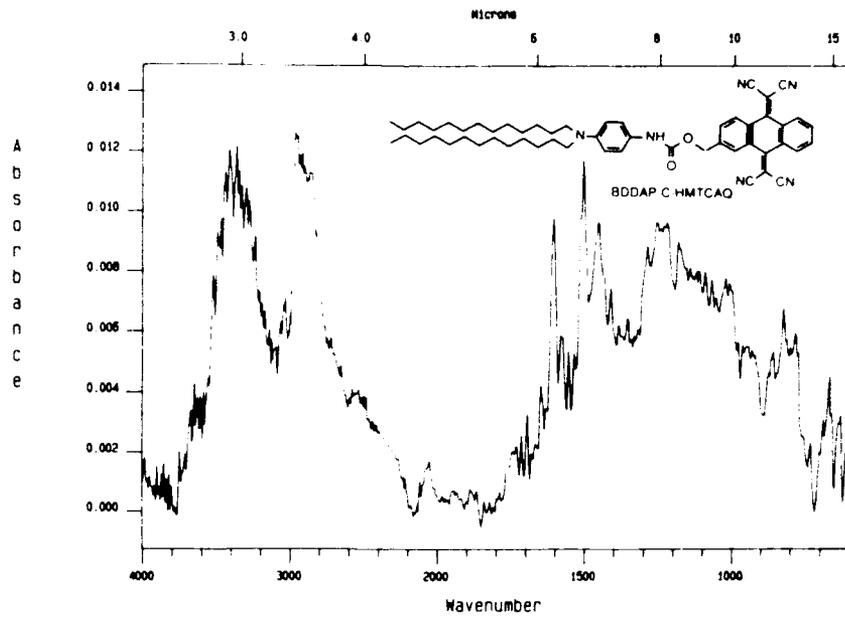


Figure 9. FTIR (Mattson) of one LB monolayer of BDDAP-C-HMTCAQ, 25 on Al

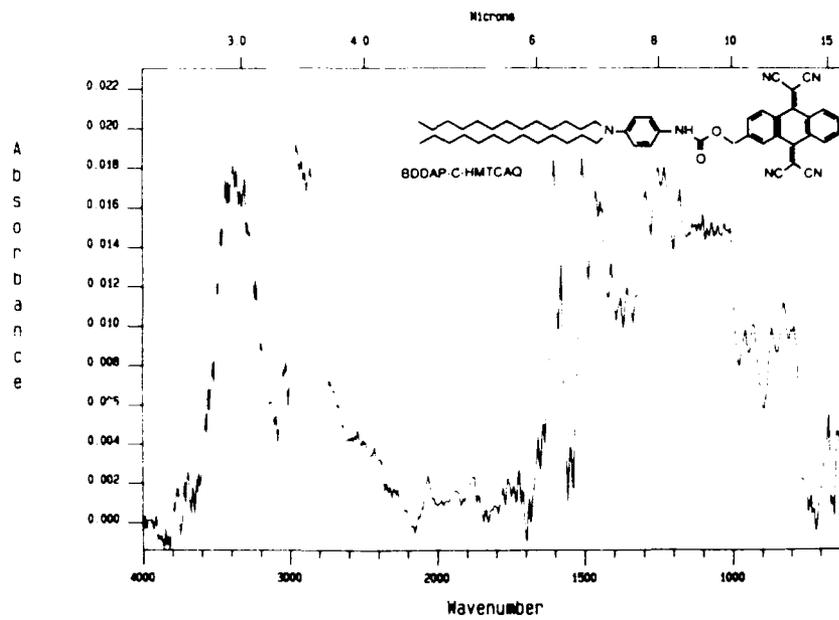


Figure 10. FTIR (Mattson) of four LB monolayers of BDDAP-C-HMTCAQ, 25, on Al

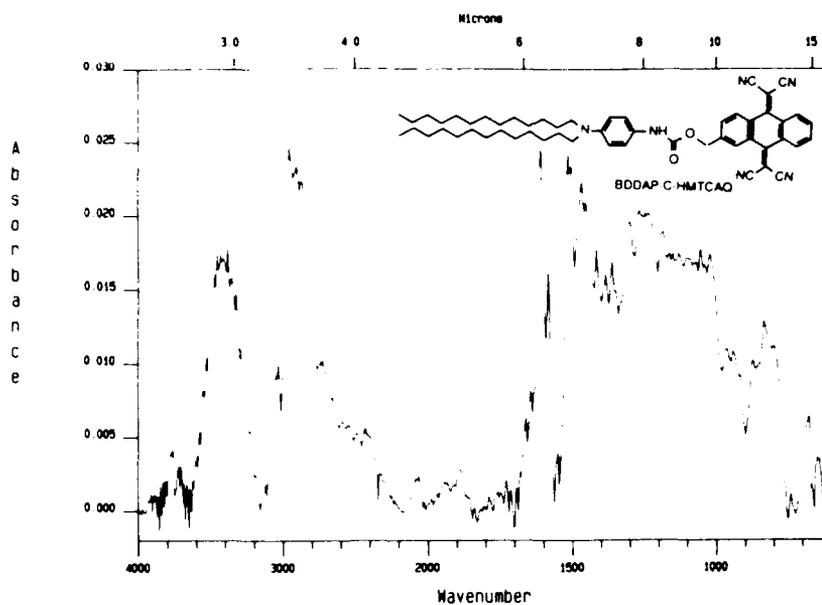


Figure 11. FTIR (Matteson) of sixteen LB monolayers of BDDAP-C-HMTCAQ, 25, on Al.

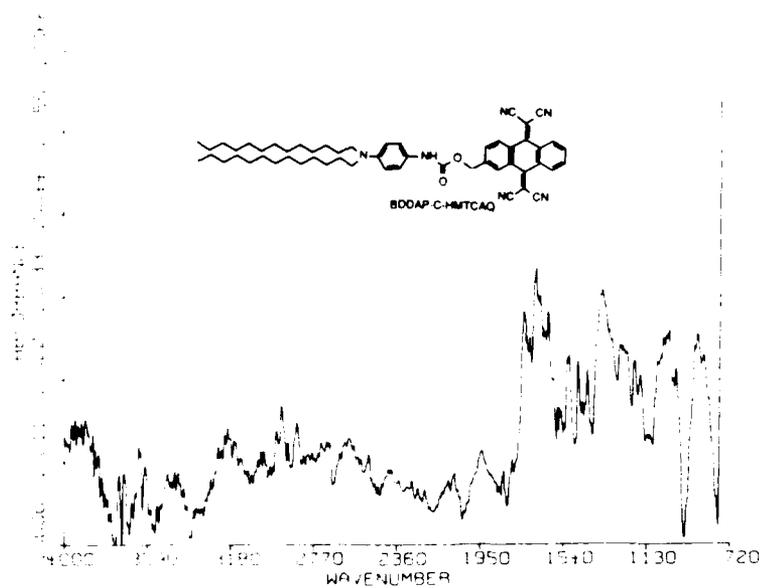


Figure 12. FTIR (Nicolet) of one LB monolayer of BDDAP-C-HMTCAQ, 25, on Al.

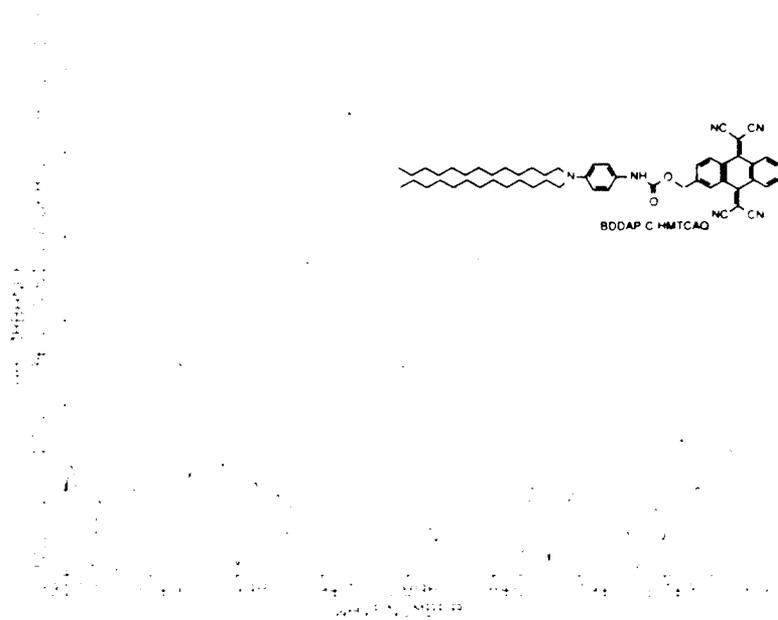


Figure 13. FTIR (Nicolet) of one LB monolayer of BDDAP-C-HMTCAQ (25) on Al, detail showing C-H stretch bands

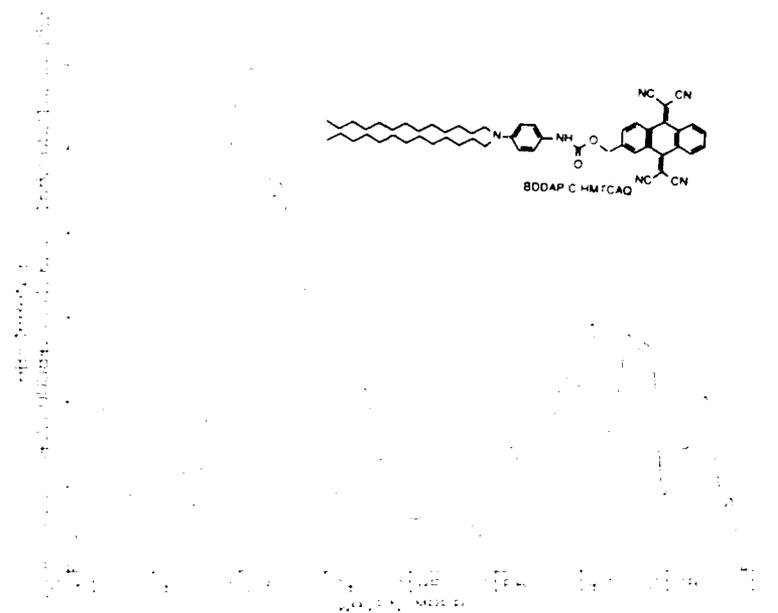


Figure 14. FTIR (Nicolet) of one LB monolayer of BDDAP-C-HMTCAQ (25) on Al, detail showing C-N band.

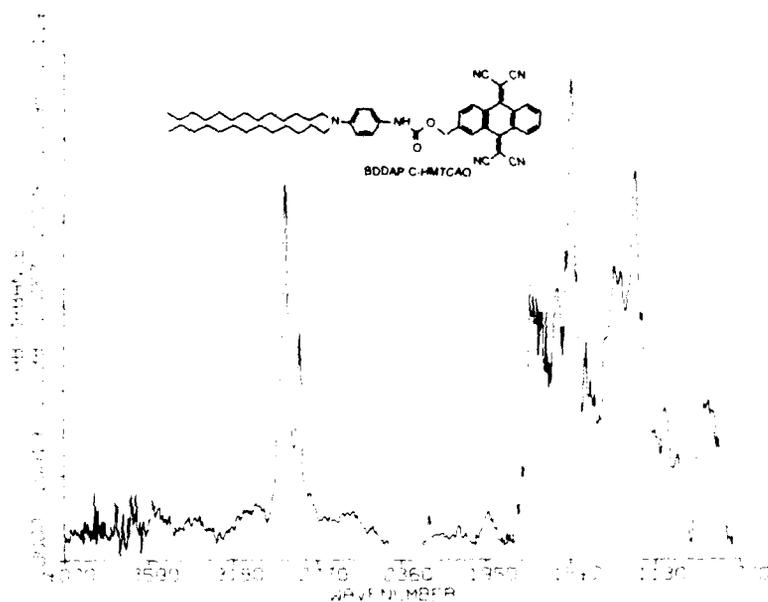


Figure 15. FTIR (Nicolet) of sixteen LB monolayers of BDDAP-C-HMTCAQ, 25, on Al.

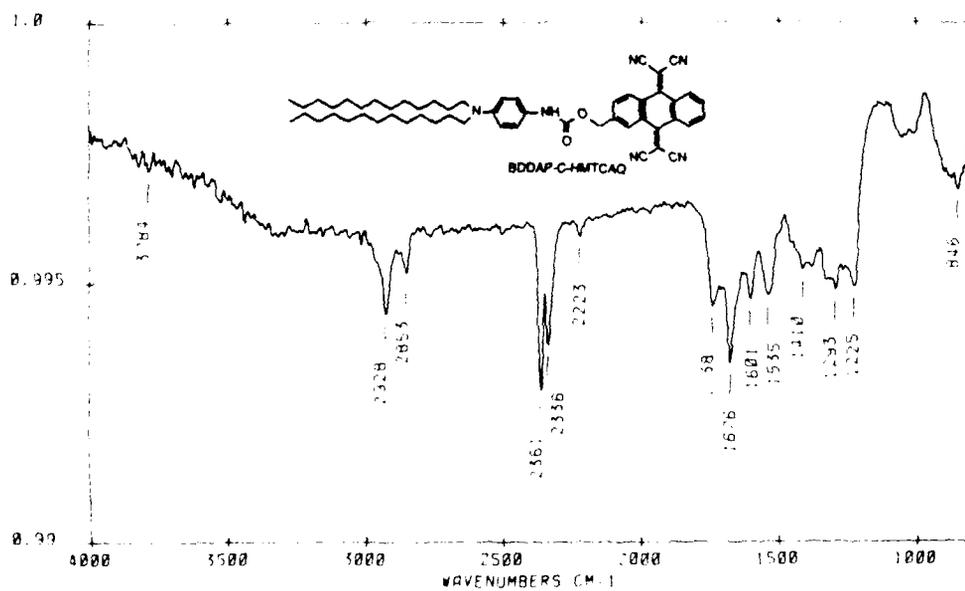


Figure 16. FTIR (Bruker) of four LB monolayers (minus spectrum of one monolayer) on Al of BDDAP-C-HMTCAQ, 25, on Al.

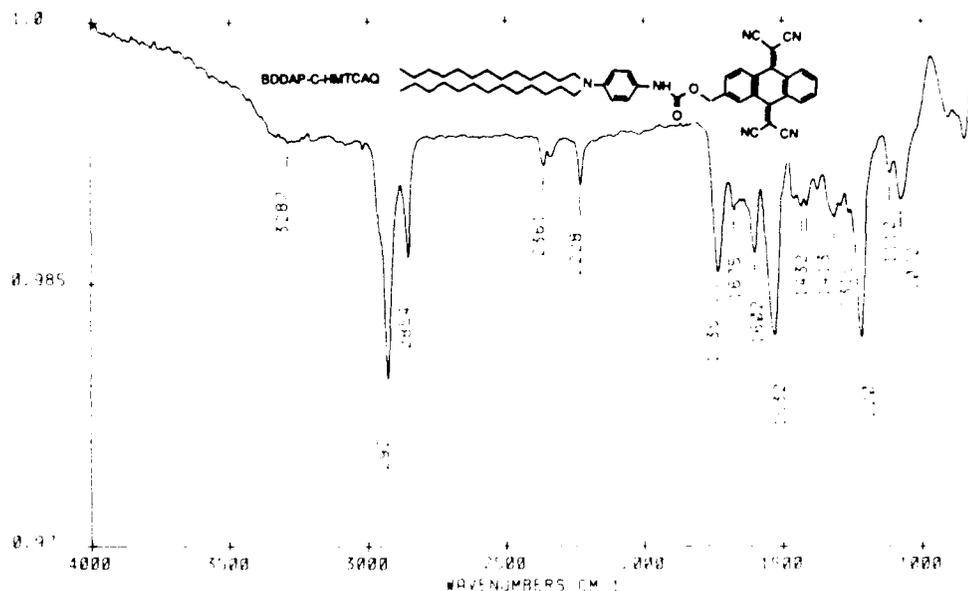


Figure 17 FTIR (Bruker) of sixteen LB monolayers (minus spectrum of one monolayer on Al) of BDDAP-C-HMTCAQ 25 on Al

Table 3. Sample age and instrumental conditions for FTIR measurements

Instrument	Figs	Sample age (months)	Resolution (cm ⁻¹)	No. of scans	Scan time (min)	Angle of incidence (° from normal)
Mattson Cygnus 100	9-11	1-13	8		6	82
Nicolet 60SXR	12-15	2-13	4	2048	9	N/a
Bruker IFS 88	16-17	1-83	8	1000	2	70

2849 cm⁻¹ and the much weaker CN stretch at 2221 cm⁻¹.

Similarly, Figs 11, 15 and 17 should all be the easily seen 16-monolayer spectrum. In practice, all three instruments do show the C-H stretch doublet (at 2927 and 2954 cm⁻¹) that is also seen in monolayers of cadmium arachidate; however, their absorbance is not the same. Also, the Mattson instrument does not resolve the doublet, as would be expected.

In all samples, the Mattson instrument observes a broad absorption peaked at 3475 cm⁻¹, which may be due to OH of water, either in the purge compartment or in the monolayers themselves; neither the Bruker nor the Nicolet instrument see this, presumably because the samples have aged and dried for a longer time. In conclusion, one can presume that FTIR spectroscopy can be used to

monitor sample evaporation, annealing and aging, and obtain data which should be useful in evaluating the quality of the LB films.

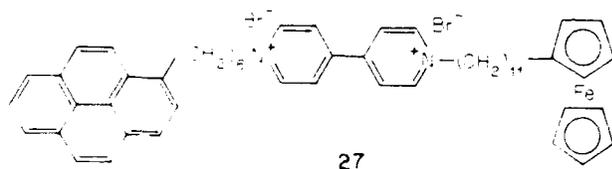
WORK OF OTHER GROUPS

Conceptually, our synthetic program is related to efforts by many groups to model the photosynthetic reaction center: linked D-σ-A systems (D = porphyrin, A = quinones) are under intensive study in several laboratories.⁶³⁻⁶⁸

It should be mentioned that Polymeropoulos *et al.*⁶⁹ and later Sugi *et al.*⁷⁰ prepared rectifiers based on seven or more monolayers of cadmium arachidate, three of them randomly doped (5:1) with an electron donor dye, one a pure cadmium arachidate layer and the other three doped (5:1)

with an electron acceptor dye. However, this device does not work if there are fewer than seven monolayers.

Recently, Fujihira *et al.*⁷¹ announced an IB photodiode using a single monolayer of molecule **27**, which consists of a donor D (ferrocene), a sensitizer S (pyrene) and an acceptor A (viologen), deposited as an LB film on a semitransparent gold electrode (with the viologen on the Au surface), and placed in 0.1 M potassium chloride solution, with a platinum counter electrode. The electron transfer is from solution to D, then to the ground state of S; on irradiation of the film at 330 nm, the electron is pushed to the excited state of S, S*, which is higher in energy than the LUMO of A, which finally acquires the electron and transfers it to the Au layer. A current of 2 nA (at 0.0 V versus SCE) was measured when light was on,⁷¹ and no current was registered with the light off. However, no subsequent full publication of these results has come to our attention.



Finally, Wrighton and co-workers have realized the 'molecule-based' transistor, which relies on either chemically doped polyaniline layers

deposited atop Au interdigitated electrodes⁷² or as a 50–100 nm 'gate' polyaniline polymer between two Au electrodes shadowed with SiO₂.⁷³ The device has been improved to the point where its switching rate is 10 kHz, and its gain is almost 1000.⁷³

CONCLUSIONS

We have demonstrated that IB films of D-*o*-A molecules can be synthesized; we are on our way to fabricating metal-organic-metal sandwiches which should give us a realistic test for the organic rectifier.

Acknowledgements

It is a pleasure to thank all of our collaborators past and present: Dr Jamil Baghdadi (now at BASF, Buffalo), Dr A. M. Bhatti (now at the University of Southern Mississippi), Prof Sukam Tripathy (GIEE, now University of Lowell), Prof Yojo Miura (Osaka City University), Profs Norman E. Heimer and Daniel L. Mattern (Mississippi), Profs M. P. Cava, J. L. Atwood and L. D. Kispert (Alabama), Drs R. Schumaker, J. L. Grant and R. K. Laidlaw (Alabama) and Mr Epitacio Torres (Mississippi). We are grateful to Mr David Presser of Mattson Instruments, Mr Ken Kempter and Dr Robert Rosenthal of Nicolet Analytical Instruments and Mr Jurgen Gast of Bruker Analytische Messtechnik for measuring the FTIR spectra. The work would not have been possible without the generous support of the National Science Foundation and the Office of Naval Research.

REFERENCES

1. A. Aviram, M. L. Freiser, P. E. Seiden and W. R. Young, *US Pat.* 3953874 (1976).
2. A. Aviram and M. A. Ratner, *Chem. Phys. Lett.* **29**, 277 (1974).
3. A. Aviram, P. E. Seiden and M. A. Ratner, in *Molecular Electronic Devices*, edited by E. L. Carter, p. 5. Marcel Dekker, New York (1982).
4. R. M. Metzger and C. A. Panetta, *J. Phys. (Les Ulis, Fr.) Colloq.* **44**, C3-1605 (1983).
5. J. Baghdadi, PhD Dissertation, University of Mississippi (1982).
6. R. M. Metzger and C. A. Panetta, in *Molecular Electronic Devices*, Vol. II, edited E. L. Carter, pp. 5-25. Marcel Dekker, New York (1987).
7. C. A. Panetta, J. Baghdadi and R. M. Metzger, *Mol. Cryst. Liq. Cryst.* **107**, 103 (1984).
8. R. M. Metzger, C. A. Panetta, N. E. Heimer, A. M. Bhatti, E. Torres, G. E. Blackburn, S. K. Tripathy and E. A. Samuleson, *J. Mol. Electron.* **2**, 119 (1986).
9. R. M. Metzger, C. A. Panetta, Y. Miura and E. Torres, *Synth. Met.* **18**, 797 (1987).
10. R. M. Metzger and C. A. Panetta, in *Proceedings of the Eighth Winter Conference on Low-Temperature Physics, Cuernavaca, Mexico, January 1987*, pp. 81-100.
11. E. Torres, C. A. Panetta and R. M. Metzger, *J. Org. Chem.* **52**, 2944 (1987).
12. R. K. Laidlaw, Y. Miura, J. L. Grant, I. Cooray, M. Clark, L. D. Kispert and R. M. Metzger, *J. Chem. Phys.* **87**, 4967 (1987).
13. R. M. Metzger and C. A. Panetta, in *Proceedings of the NATO Advanced Workshop on Inorganic and Organic Lower-Dimensional Materials*, edited by P. Delhaes, Plenum Press, New York, pp. 271-286.
14. R. M. Metzger, R. R. Schumaker, M. P. Cava, R. K. Laidlaw, C. A. Panetta and E. Torres, *Langmuir*, **4**, 298 (1988).
15. Y. Miura, E. Torres, C. A. Panetta and R. M. Metzger, *J. Org. Chem.* **53**, 439 (1988).
16. Y. Miura, R. K. Laidlaw, C. A. Panetta and R. M. Metzger, *Acta Crystallogr., Sect. C* in press.
17. R. K. Laidlaw, J. Baghdadi, C. A. Panetta, Y. Miura, E. Torres and R. M. Metzger, *Acta Crystallogr., Sect. B*

- B44**, 675 (1988).
18. Y. Mizuta, C. A. Parrella and R. M. Metzger, *J. Vac. Technol.*, in press.
 19. R. K. Laidlaw, Y. Mizuta, C. A. Parrella and R. M. Metzger, *J. Vac. Technol.*, Sect. C, in press.
 20. R. M. Metzger, R. K. Laidlaw, E. Torres, and C. A. Parrella, *J. Crystalline Spectrosc. Res.*, in press.
 21. R. Hoffmann, *Acc. Chem. Res.* **4**, 1 (1971).
 22. R. Geiger, E. Schmidt, D. O. Cowan and E. P. Irtzaris, *J. Electron Spectrosc.* **2**, 207 (1973).
 23. R. N. Compton and C. D. Cooper, *J. Chem. Phys.* **66**, 4325 (1977).
 24. Z. G. Soos, *Chem. Phys. Lett.* **63**, 179 (1979).
 25. E. Herman and E. P. Barr, *Phys. Rev. Lett.* **33**, 924 (1974).
 26. See, e.g., G. F. Gantner, *Evaporation Monolayers at Liquid-Gas Interfaces*, Interscience, New York (1966).
 27. K. B. Boddeger, *J. Am. Chem. Soc.* **57**, 1907 (1935).
 28. K. B. Blodgett and E. F. Evans, *Phys. Rev.* **51**, 964 (1937).
 29. H. Kuhn, D. Mohr and H. Bacher, in *Techniques of Chemistry, Vol. I, Physical Methods of Chemistry, Part I, Determination of Thermodynamic and Surface Properties*, edited by V. Weissberger and B. W. Rossiter, pp. 577-702, Wiley-Interscience, New York (1972).
 30. H. Kuhn, *Pure Appl. Chem.* **51**, 341 (1979).
 31. H. Kuhn, *Pure Appl. Chem.* **53**, 2105 (1981).
 32. See, e.g., *Thin Solid Films* **68** (1980); **99** (1983); **132**, **134** (1985).
 33. W. C. Bigelow, D. I. Pickett and W. A. Zisman, *J. Colloid Sci.* **1**, 513 (1946).
 34. I. Netzer, R. Iscovici and J. Sagiv, *Thin Solid Films* **99**, 235 (1983).
 35. I. Netzer, R. Iscovici and J. Sagiv, *Thin Solid Films* **100**, 67 (1983).
 36. I. Gorn, R. Iscovici and J. Sagiv, *J. Colloid Interface Sci.* **101**, 201 (1984).
 37. R. W. Murray, *Acc. Chem. Res.* **13**, 135 (1980).
 38. R. Maoz and J. Sagiv, *Thin Solid Films* **132**, 135 (1985).
 39. R. G. Nuzzo, F. A. Fusco and D. A. Allara, *J. Am. Chem. Soc.* **109**, 2358 (1987).
 40. G. Wegner, *Z. Naturforsch., Teil B* **24**, 829 (1969).
 41. M. Balle and E. F. Evans, *Mol. Cryst.* **3**, 357 (1968).
 42. E. Clar, E. M. Robertson, R. Schloegl and W. Schmidt, *J. Am. Chem. Soc.* **103**, 1320 (1981).
 43. E. C. M. Chen and W. T. Wentworth, *J. Chem. Phys.* **63**, 3183 (1975).
 44. C. D. Cooper, W. E. Fry and R. N. Compton, *J. Chem. Phys.* **69**, 2367 (1978).
 45. D. R. Coe, ed., *American Institute of Physics Handbook*, 2nd ed., pp. 9-147, 9-149.
 46. R. A. Marcus, *Discuss. Faraday Soc.* **29**, 21 (1960).
 47. E. T. Calcaterra, G. E. Cross and J. R. Miller, *J. Am. Chem. Soc.* **105**, 670 (1983).
 48. J. R. Miller, E. T. Calcaterra and G. E. Cross, *J. Am. Chem. Soc.* **106**, 3047 (1984).
 49. N. S. Hulse, M. S. Pridon, R. W. F. Coats, H. Overberg, J. W. Verhoeven and M. Heppener, *Chem. Phys. Lett.* **117**, 8 (1985).
 50. P. J. Dutton, R. C. Prince, D. M. Lude, K. M. Petty, K. J. Kantmann, K. J. Netzel and P. M. Ritzberg, *Bioelectrochem. Comp. Bio.* **28**, 213 (1977).
 51. E. R. Peterson and G. J. Russell, *Thin Solid Films* **134**, 143 (1985).
 52. S. Garoff, H. W. Deckman, E. H. Dunsman, M. S. Alster and E. M. Bloch, *J. Phys. (Les Lett. Fr.)* **47**, 70 (1986).
 53. E. R. Peterson, *J. Mol. Electron.*, submitted for publication.
 54. G. G. Roberts, P. S. Vincent, and W. A. Barlow, *J. Phys. C* **11**, 2077 (1978).
 55. B. Mann and H. Kuhn, *J. Appl. Phys.* **42**, 4398 (1971).
 56. P. K. Hansma, (Ed.), *Luminescence Spectroscopy, Characterization, Applications, and New Techniques*, Plenum Press, New York (1982).
 57. W. R. Hertler, *J. Org. Chem.* **41**, 1412 (1976).
 58. N. F. Schenck, M. D. Porter, J. B. Bogle and D. J. Allara, *Chem. Phys. Lett.* **132**, 93 (1986).
 59. W. G. Golden, D. D. Saperstein, M. W. Severson and J. Overland, *J. Phys. Lett.* **132**, 574 (1984).
 60. I. Rabolt, M. Jurich and U. D. Swallen, *Appl. Spectrosc.* **39**, 269 (1985).
 61. I. F. Rabolt, E. C. Burns, N. E. Schlotter and U. D. Swallen, *J. Chem. Phys.* **78**, 946 (1983).
 62. U. D. Swallen and I. F. Rabolt, in *Linear Transform Infrared Spectroscopy*, Vol. 4, pp. 287-314, Academic Press, New York (1985).
 63. J. Lindsay, D. Mauzerall and H. Linschütz, *J. Am. Chem. Soc.* **105**, 6528 (1983).
 64. A. R. McIntosh, J. R. Bolton, J. S. Connolly, K. E. Marsh, D. R. Cook, T. -E. Ho and A. C. Weedon, *J. Phys. Chem.* **90**, 5640 (1986).
 65. A. D. Joran, B. A. Leland, G. G. Geller, J. J. Hopfield and P. B. Dervan, *J. Am. Chem. Soc.* **106**, 6090 (1984).
 66. S. Nishitani, N. Kurata, Y. Sakata, S. Misumi, A. Kari, T. Okada and S. Mataga, *J. Am. Chem. Soc.* **105**, 7771 (1983).
 67. E. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachat, R. V. Bensasson, E. J. Land, D. Dozi, P. A. Liddell, W. R. Lehman, G. A. Nemeth and A. U. Moore, *Nature (London)* **307**, 630 (1984).
 68. C. Krieger, J. Weiser and H. A. Staab, *Tetrahedron Lett.* **26**, 60550 (1985).
 69. E. E. Polymeropoulos, D. Moebius and H. Kuhn, *Thin Solid Films* **58**, 173 (1980).
 70. M. Suen, K. Sakai, M. Saito, Y. Kawabata and S. Iijima, *Thin Solid Films* **132**, 69 (1985).
 71. M. Fujihira, K. Nishiyama and H. Yamada, *Thin Solid Films* **132**, 77 (1985).
 72. H. S. White, G. P. Kittleson and M. S. Wrighton, *J. Am. Chem. Soc.* **106**, 5375 (1984).
 73. E. J. Turner Jones, O. M. Chyan and M. S. Wrighton, *J. Am. Chem. Soc.* **109**, 5526 (1987).

LANGMUIR-BLODGETT FILMS OF DONOR-SIGMA-ACCEPTOR

MOLECULES AND PROSPECTS FOR ORGANIC RECTIFIERS §

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INTRODUCTION

Our goal is to assemble and test a unimolecular rectifier of electrical current, which could be part of a very thin (nm thick) electronic device. This idea, originated by Aviram in 1973, depends on the asymmetry of molecules D- σ -A, where D is a good one-electron donor (but poor acceptor), A is a good one-electron acceptor (but poor donor), and σ is a covalent bridge that keeps the molecular orbitals of D separate from those of A. We have found five molecules which self-assemble as monolayers; three contain the TCNQ moiety; three contain "greasy" dodecyl groups on the donor end (which helps in monolayer formation), but one contains only hexyl groups. All of them can be transferred to a glass or Al substrate as Langmuir-Blodgett films. Recent FTIR data for a single monolayer are presented.

THE ORGANIC RECTIFIER - THEORETICAL, SYNTHETIC, AND ASSEMBLY CRITERIA

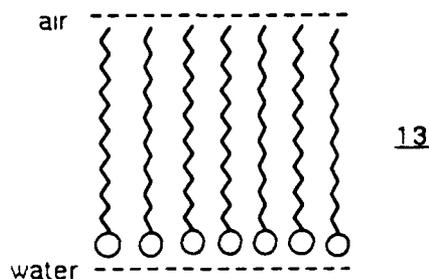
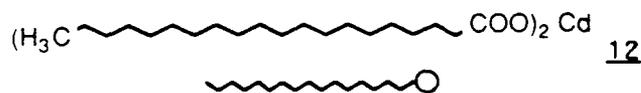
This is a progress report on the Organic Rectifier Project, i.e. on our efforts to synthesize molecules of the type D- σ -A, which may be potential rectifiers of electrical current. Here D = strong one-electron organic donor, such as TTF (tetrathiafulvalene, 1), or TMPD (N,N,N',N'-tetramethyl-para-phenylenediamine, 2), σ = covalent sigma bridge, A = strong one-electron acceptor, such as TCNQ (7,7,8,8-tetracyanoquinodimethane, 3) or chloranil (2,3,5,6-tetrachloro-para-benzoquinone, 4). Aviram and co-workers predicted in 1973 [1-3] that D- σ -A molecules, such as the proposed molecule 5, sandwiched as an oriented monolayer between ordinary metallic thin films M and N, as in 6, would act as a rectifier of electrical current. The obvious advantage of such a device is its small thickness: the molecule 5 should be only 2 nm thick. If very thin conventional films M, N (1.5 nm each) can be used, then a 5 nm thick device becomes possible, much thinner than the working direction of conventional Si or GaAs devices (1 to 3 μ m).

The incremental results of the Organic Rectifier Project have been reported elsewhere [4-15]. Here we summarize the design criteria that have evolved, and discuss the implications of our most recent results.

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Langmuir-Blodgett Films

So far, our efforts have been centered upon molecules D- σ -A which self-assemble at the air-water interface as "Pockels-Langmuir" monolayers (our term for such monolayers, honoring Irving Langmuir (1881-1957) and Agnes Pockels). [22]. Such monolayers can, usually, be transferred to glass or metal or other substrates by the Langmuir-Blodgett (LB) technique pioneered by Langmuir and by Katharine B. Blodgett (1898-1979) [23-26]. The typical molecule that forms excellent PL and LB films is cadmium arachidate, $\text{Cd}(n\text{-C}_{19}\text{H}_{39}\text{COO})_2$, **12**.



At the air-water interface a PL monolayer of cations **12** (shaped like tadpoles) points with the carboxylate ends toward the water subphase, as in **13**: the cadmium counterions are in the subphase, coordinated rather closely with the carboxylate head group. Usually, such work is done today by using an automated Langmuir trough or film balance.

The LB technique consists of slowly inserting a macroscopic metal, glass, silicon, or other substrate through the monolayer into the subphase; either upon insertion into the water, or upon slow withdrawal from the water, the PL monolayers transfer quantitatively to the substrate with little or no distortion: thus are formed the LB monolayers. If the substrate is dipped several times through the monolayer, LB multilayers can be transferred to the substrate [23-28].

Other techniques for monolayer coverage of metals

Another method of transferring self-assembling monolayers to substrates without using a Langmuir trough is the Bigelow oleophobic (BO) film-casting technique [29-32]. The forces binding an LB or BO monolayer to the substrate are usually weak physisorptive or chemisorptive forces. A better adhesion is by direct covalent bonding to a surface. Bonding to silanized metal surfaces rarely achieves monolayer coverage [33]. Also, attaching silanized molecules to oxide-bearing metal surfaces produces compact monolayers [34], as does attaching molecules bearing disulfide bonds to gold surfaces [35]. Another method of providing "strong" films is to polymerize LB films containing diacetylene linkages in situ using ultraviolet radiation [36].

Despite the existence of these other potential techniques for assembling an organic M | D- σ -A | N rectifier, we concentrate below on D- σ -A molecules that will self-assemble as PL and LB monolayers.

Synthetic and device assembly criteria

The criteria for successful synthesis of candidate D- σ -A molecules and for their assembly into the organic rectifier **6** have been stated before [4,5,8,10,16] and can be summarized as follows:

(1) The donor D must have a low ionization potential I_D (<7.5 eV) and be fairly flat.

(2) The acceptor A must have a high electron affinity A_A (>2 eV) and must be fairly flat.

(3) The σ bridge must be saturated (not conjugated). It must be long enough to prevent extensive ground-state mixing of the donor molecular orbitals with the acceptor molecular orbitals (> 3 carbon-like atoms), yet short enough (< 9 carbon-like atoms) or rigid enough to prevent the curling of the D end over the A end of the molecule. Molecular modeling shows that 5 or 6 carbon atoms seems to be the optimal length. The σ bridge must be flat enough to provide good lateral LB film packing.

(4) The D- σ -A molecule must pack well in monolayers. For this, one end must be hydrophobic, the other hydrophilic. There should be no overlap of D- σ -A over A- σ -D (which would cancel dipole moments and destroy the directionality of the device **6**). The lateral π - π attractive interactions, and maybe a mixed-valence ground state, as exists in the quasi-one-dimensional salt TTF TCNQ, may reduce the cost of ionization of D- σ -A to D⁺- σ -A⁻ from 4 eV to maybe 1 or 2 eV.

(5) The I_D and A_A values must match as closely as possible the work functions of the metal layers M and N (see Table 1). As can be seen, the match is far from perfect., even for the best donors and acceptors known to date.

Table 1. Ionization potentials I_D for the donors D, electron affinities A_A for the acceptors A, and work functions ϕ for the metals M, N

I_D (eV)	A_A (eV)		ϕ (eV)	
TMPD	6.25 [37]	DDQ	3.13 [39]	Al 3.74 [41]
TTF	6.83 [18]	TCNQ	2.8 [19]	Au 4.58 [41]
pyrene	7.41 [38]	Chloranil	2.76 [40]	Pt 5.29 [41]

(6) The bridge-building organic reaction **14** leading to D- σ -A must be more likely, or more efficient, than the competing reaction of charge transfer (CT) salt formation **15**:



(7) The Franck-Condon reorganization of the molecular geometry of D to D⁺ and of A to A⁻ [42] must be small, or fast, so that the overall ET within D- σ -A does not become slow [42-44]. Under the right conditions, ET through the molecule could be faster than 1 ns [43-46].

(8) The monolayers must be close-packed and defect-free for at least a few μm in the lateral direction (to prevent electrical shorting of metal layer M to metal layer N). It is known that over hydrophobic, oxide-free metals (Pt, Au, Ag) cadmium arachidate films have larger defects (probably at domain boundaries) [47], and have maybe a disordered, fan-like structure [48]. Over hydrophilic, oxide-covered metals (Al, Sn) or glass or quartz, the defects seem smaller, allowing for a percolative current j across the film and through disclinations [49] (the voltage dependence of j is $\log j = aV^{1/4}$ [50] and not $\log j = bV^{1/2}$ [51]). One way of achieving freedom from defects on the scale of a few microns would be to use a thin interdigitated layer M, where the film perfection is sampled on several small disks of radius 3 μm radius (these disks would be connected to macroscopic electrodes).

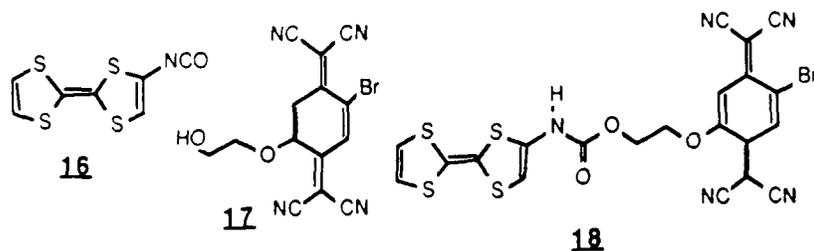
(9) At the M to N distance of, typically, 2 nm, the directed TB tunneling must be much more likely than the undirected TS tunneling. So far, in inelastic electron tunneling spectroscopy (IETS) [52] for random films of insulators placed between superconducting Pb and normal Al electrodes at 4.2 K, the ratio $\text{TB}/(\text{TB}+\text{TS})$ is only 0.01. For the organic rectifier to succeed, this ratio (for compact monolayers) must be much closer to 1.0.

(10) The process of laying down the second metal layer N atop M | D- σ -A as a sputtered or evaporated film, and also the exothermicity of the TB tunneling in the device 6, must both avoid heating the monolayer above 100°C. Similarly, high voltages that may cause dielectric breakdown must be avoided.

RESULTS

Coupling reactions

In 1976 Hertler prepared carbamate, or urethane, polymers of TTF with TCNQ if one reacts the 2,2'-bisisocyanate of TTF with a 2,5-dihydroxyethoxyTCNQ; the resulting insoluble black polymer was semiconducting, not metallic [53]. However, the utility of Hertler's contribution was to show that carbamates of strong donors with strong acceptors could be prepared, and that reaction 14 was preferred over reaction 15 for carbamates. Baghdadchi prepared the monoisocyanate of TTF, 16, and coupled it with 2-bromo-hydroxyethoxyTCNQ, 17 [4-6, 54] to yield the carbamate 18 of TTF with TCNQ. However, two forms were found, of which one seemed zwitterionic, the other neutral (as evidenced by the infrared CN stretching frequencies). Neither product could be isolated in acceptable purity.



Esters of TTF with TCNQ 17 were also prepared, using the 2-acyl chloride of TTF, but, again, two products were obtained [6]. The neutral form of the TTF carbamate with TCNQ did form LB monolayers, but with the wrong geometry (probably with the molecule lying almost flat on the water subphase, rather than normal to it).

Since that time, most of our efforts have been concentrated on the carbamate coupling, although one may conceive of other possible coupling reactions.

Acceptors

Most of the work has been done with Hertler's TCNQ alcohol 17 (BHTCNQ), whose crystal structure was recently determined (Fig. 1) [13]. From cyclic voltammetric studies we estimate that the electron affinity of 17 is 2.9 ± 0.2 eV [13]. The inefficient synthesis of 17 has caused us to seek better, or more accessible acceptors. The anthraquinone analog 19 has been prepared in excellent yield [9], but the molecule is severely bent, and 19 is a weak two-electron acceptor, rather than a strong one-electron acceptor. The synthesis of 20 has been accomplished [55], and the crystal structure of its methyl ester, 21, has been determined [14] (Fig. 2).

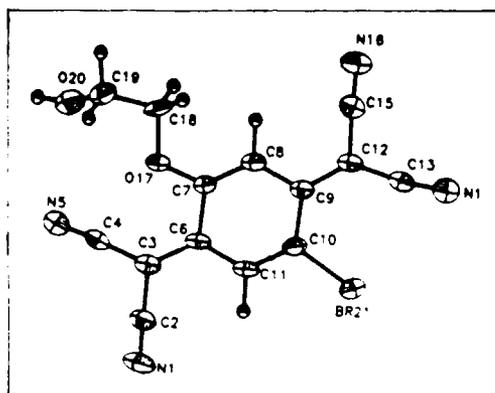
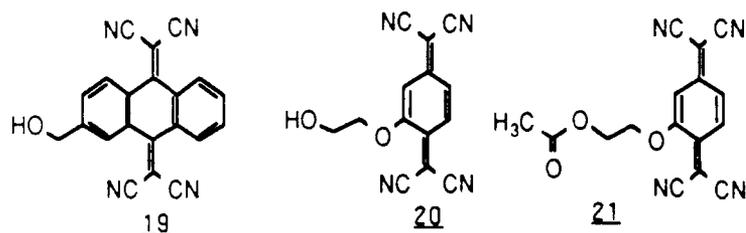


Fig. 1. ORTEP plot of BHTCNQ, 17 (monoclinic, space group $P2_1/n$, $a = 9.258$ Å, $b = 13.618$ Å, $c = 10.947$ Å, $\beta = 92.14^\circ$, $Z = 4$, $R = 3.9\%$ [13])

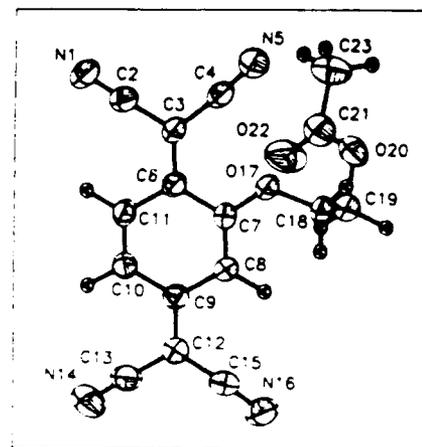


Fig. 2. ORTEP plot of AETCNQ, 21 (triclinic, space group $P1\bar{bar}$, $a = 7.165$ Å, $b = 9.058$ Å, $c = 13.244$ Å, $\alpha = 70.06^\circ$, $\beta = 87.14^\circ$, $\gamma = 68.22^\circ$, $Z = 2$, $R = 3.4\%$ [14]).

Donors

After the early work on TTF isocyanate (a strong donor) [4-6], our attention turned to the isocyanate of pyrene, 22 (a medium donor), and to substituents of phenyl isocyanate (a weak donor); adding a dodecyloxy group made weak donor 24; adding the dimethylamino group made the medium donor DMAP-NCO, 25. The crystal structure of its methyl carbamate, DMAPCMe, 26, was determined (Fig. 3) [11]; its calculated (AM1) ionization potential (7.17 eV) and its cyclic voltammetry showed that 26 is a donor weaker than TMPD or TTF but stronger than pyrene [12]. There is extensive hydrogen bonding in the crystal of DMAPCMe [11], in solution

[12], and also in solution of its electrochemically generated radical anion [12]. We have also prepared the bis-dodecyl and the bis-hexyl derivatives of 25.

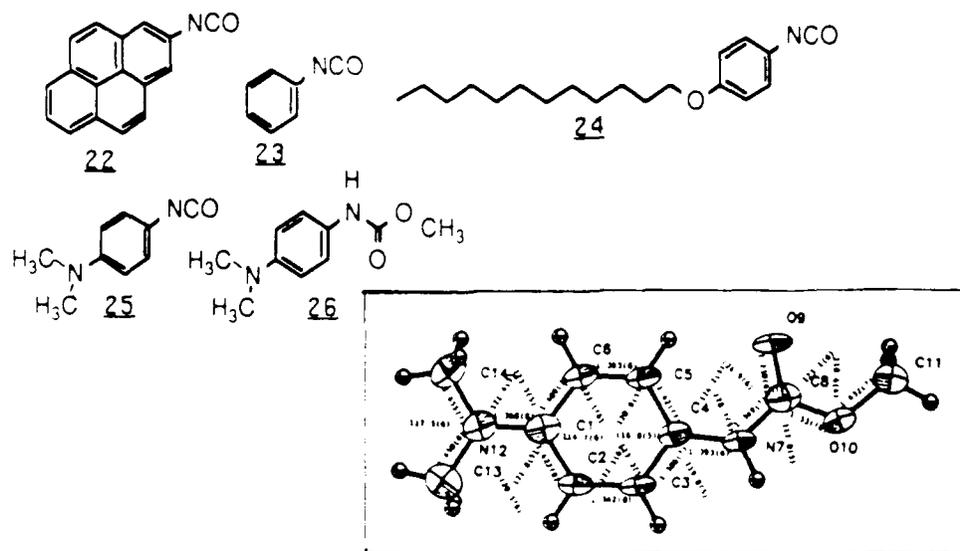


Fig. 3. ORTEP plot of DMAPCMe, 26 (orthorhombic, space group $Pbca$, $a = 13.926 \text{ \AA}$, $b = 9.999 \text{ \AA}$, $c = 14.845 \text{ \AA}$, $Z = 8$, $R = 5.9\%$ [11])

Crystal structures of Donor-sigma Acceptor Molecules

To test the proposition that the σ bridge allows for an extended structure of

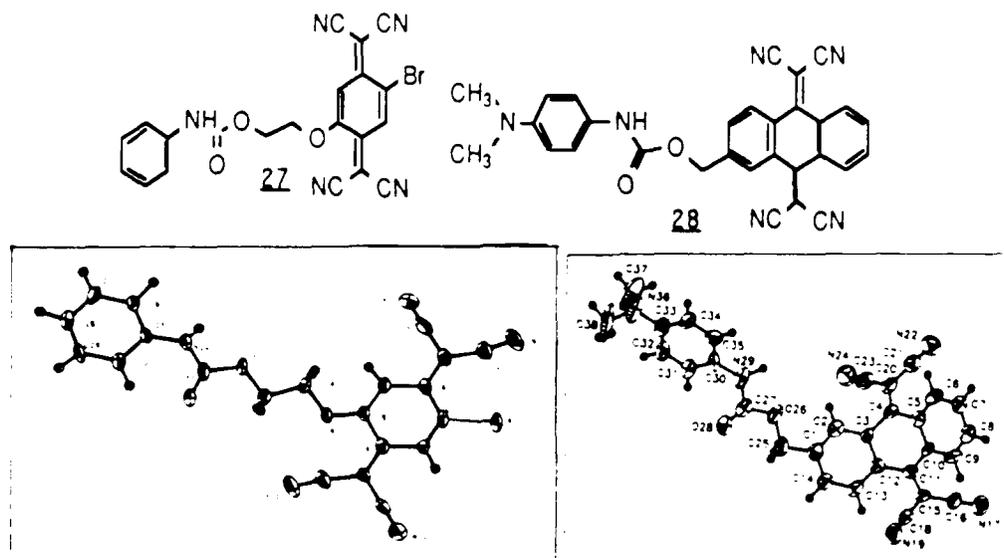


Fig. 4. ORTEP plot of Phenyl-C-BHTCNQ, 27 (monoclinic, space group $P2_1/n$, $a = 8.310 \text{ \AA}$, $b = 9.278 \text{ \AA}$, $c = 25.383 \text{ \AA}$, $\beta = 96.15^\circ$, $Z = 4$, $R = 7.9\%$ [11])

Fig. 5. ORTEP plot of DMAP-C-HMTCNQ, 28 (triclinic, $P1\bar{1}a$, $a = 8.748 \text{ \AA}$, $b = 10.989 \text{ \AA}$, $c = 13.541 \text{ \AA}$, $\alpha = 90.67^\circ$, $\beta = 99.15^\circ$, $\gamma = 98.62^\circ$, $Z = 2$, $R = 12.7\%$ [15])

the D- σ -A adducts, crystal structures have been determined for phenyl-C-BHTCNQ, **27** (Fig. 4) [11] and for DMAP-C-HMTCAQ, **28** (Fig. 5) [15]. In both cases the molecules do not form LB films, but the crystal structure reveals an extended conformation; the crystals belong to the centrosymmetric space group P1 bar; the molecules pack in the crystal so that D- σ -A packs nearly over A- σ -D.

Pockels-Langmuir and Langmuir-Blodgett Films

It was found that only certain D- σ -A molecules **29-33** form monolayers at the air-water interface; the data are given in Table 2, and the relevant pressure-area isotherms (and molecular structures) are shown in Figs. 6-10.

The collapse pressure Π_c is defined to be the differential surface tension, which, if exceeded, leads to the collapse of the film, and to the irreversible "riding of ice floes over each other". The area per molecule can be defined in several ways; the area at the collapse point is A_c , and is the smallest; the area per molecule at zero pressure, A_0 , is the point in the Π -A isotherm obtained when the steepest part of the curve is extrapolated linearly to zero pressure; A_m is defined as the mid-point between A_c and A_0 . Of all these points, A_c gives what probably is the best estimate of the lateral dimensions of the molecule in a well-packed film.

The shape of the Π -A isotherm is indicative of the fluidity or rigidity within the film. For cadmium arachidate, the slope is almost vertical, because the film is almost crystalline in its two-dimensional packing. For the molecules described in Figs. 6-10, the slope indicates a more fluid-like environment, in which the molecules probably do not pack as rigidly as they would in a crystal. Of the molecules given above, only Py-C-BHTCNQ lacks an alkyl "greasy chain"; DDOP-C-BHTCNQ, BDDAP-C-BHTCNQ and BDDAP-C-HMTCAQ all have dodecyl groups that help provide a hydrophobic region in the molecule (if the dodecyl groups are replaced by methyl groups, no monolayers are formed). Since, however, the presence of long alkyl chains may retard the TB ET, it was important to find a shorter alkyl chain which would help in providing monolayer formation. Thus we are pleased with the recent result that the bis-hexyl chain in **33** was "sufficient" to provide good PL monolayers. Work on similar molecules is continuing.

Langmuir-Blodgett films and tests on rectification

Efforts were made to find rectification behavior in sandwiches of molecules **18** [4,5], **29** [7], and **31** [7]. For **18**, sandwiches Pt|**18**|Hg and SnO|**18**|Hg were electrical shorts [4,5]. This was not surprising, since the large molecular A_c for **18** indicated that it was "sitting" with the longest axis almost parallel to the water subphase, and therefore almost parallel to the Pt of SnO substrate; if this is true, then the film thickness, probably only 6 Å, was so small that TS tunneling, or tunneling through defects could not be avoided. For **29** and **31**, electrical shorts were observed in similar sandwiches [7]. However, in the same laboratory, sandwiches Al|**12**|Hg using monolayers of cadmium arachidate were not insulating [7], even though they had been prepared previously as high-resistance sandwiches in other laboratories [51]. Therefore it can be stated that a proper test of rectification of **29** or **31** had not been made.

Important structural information is provided by Fourier Transform Infrared (FTIR) spectroscopy [32,56-60]. Figs. 11-13 were obtained on a Nicolet 60SXR spectrometer, operated at 4 cm^{-1} resolution, using grazing angle specular reflectance and a Brewster angle polarizer. In all cases the samples were transferred as LB films onto aluminium-coated glass slides. The molecule studied was BDDAP-C-HMTCAQ, **32**; in Figs. 11,12 a single monolayer is present, yet one can resolve the aliphatic CH stretch bands at 2951, 2910, and 2849 cm^{-1} and the CN stretch at 2221 cm^{-1} . In Fig. 13 the LB films consists of 16 monolayers.

Table 2. Molecular areas and collapse pressures for PL monolayers

Molecule	No.	T K	Π_c mN/m	A_c \AA^2	A_m \AA^2	A_c \AA^2	Ref.
TTF-C-BHTCNQ	18	292	12.7	134±50	--	--	[5]
DDOP-C-BHTCNQ	29	292	20.2	50	55	60	[5,16]
BDDAP-C-BHTCNQ	30	293	47.3	57	69	82	[16]
		303	45.9	54	70	82	
Py-C-BHTCNQ	31	283	28.2	53	60	66	[16]
BDDAP-C-HMTCAQ	32	293	22.3	58	71	83	[16]
BHAP-C-HMTCAQ	33	293	35.8	42	47	53	

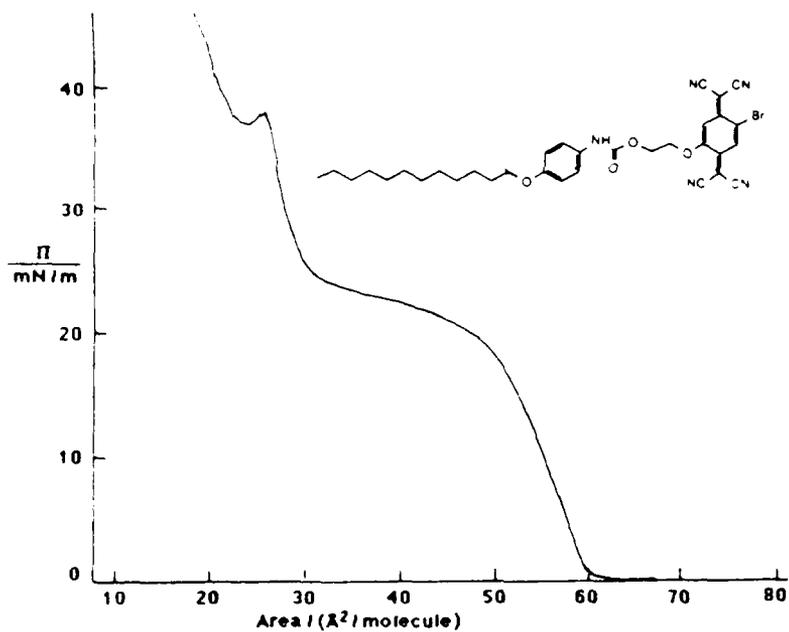


Fig. 6. Pressure-area isotherm for DDOP-C-BHTCNQ, 29 [5,16].

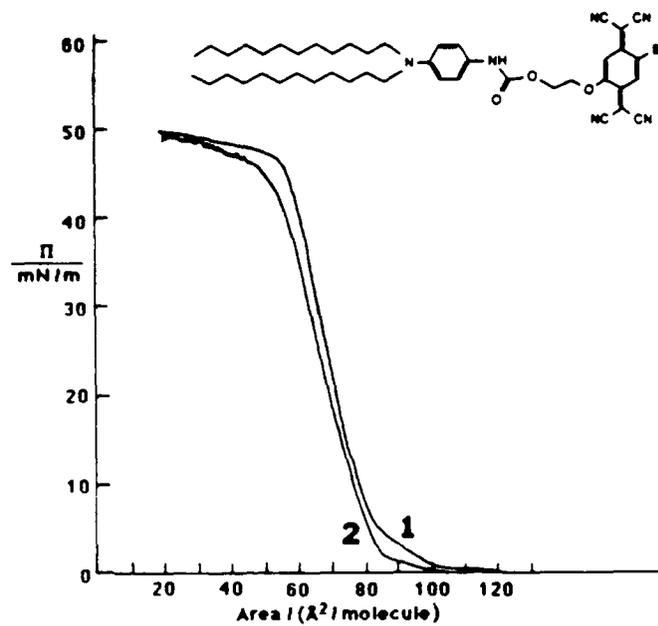


Fig. 7. Pressure-area isotherm for BDDAP-C-BHTCNQ, 30, at 293 K (curve 1) and at 303 K (curve 2) [16].

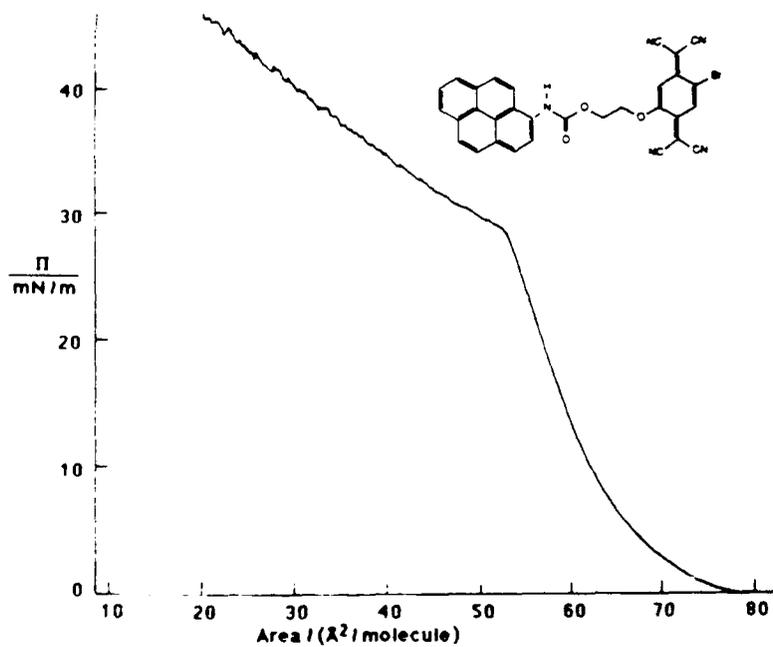


Fig. 8. Pressure-area isotherm for Py-C-BHTCNQ, 31 [16].

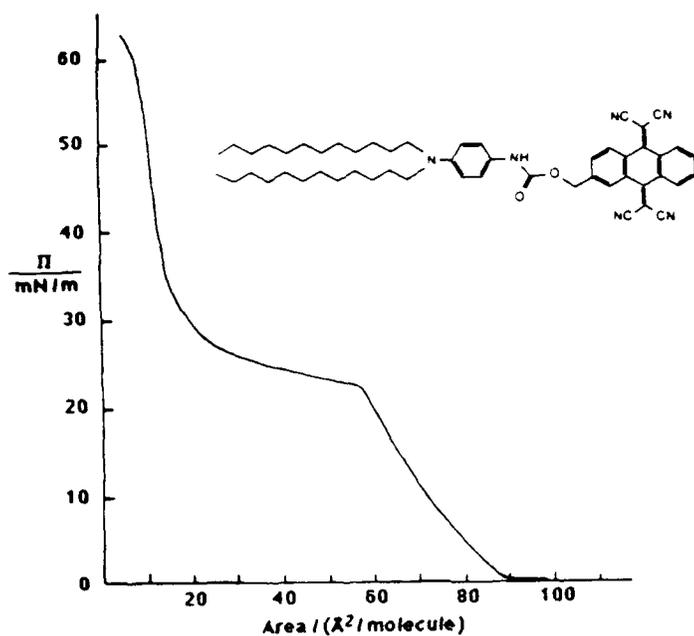


Fig. 9. Pressure-area isotherm for BDDAP-C-HMTCAQ, 32 [16].

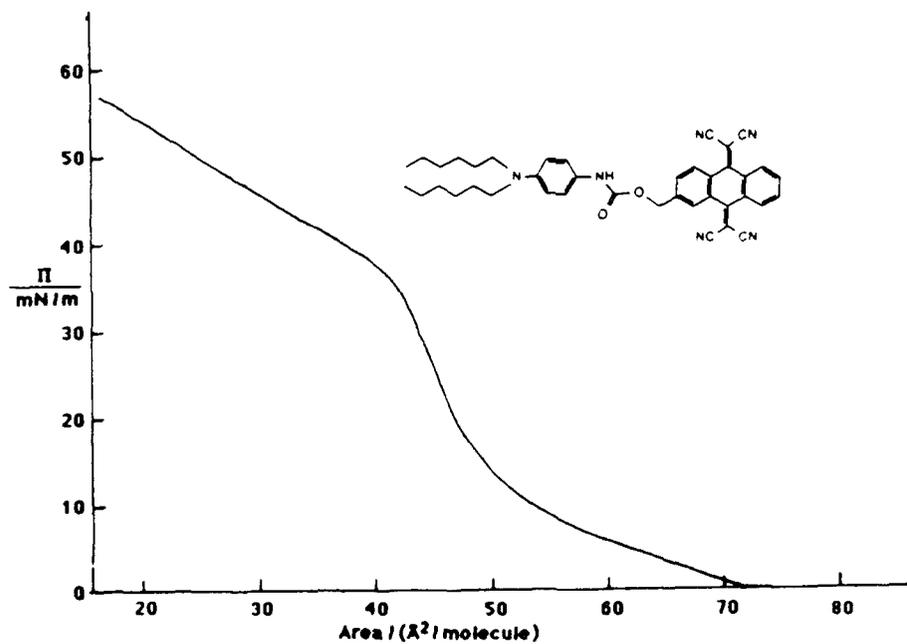


Fig. 10. Pressure-area isotherm for BHAP-C-HMTCAQ, 33 (this study).

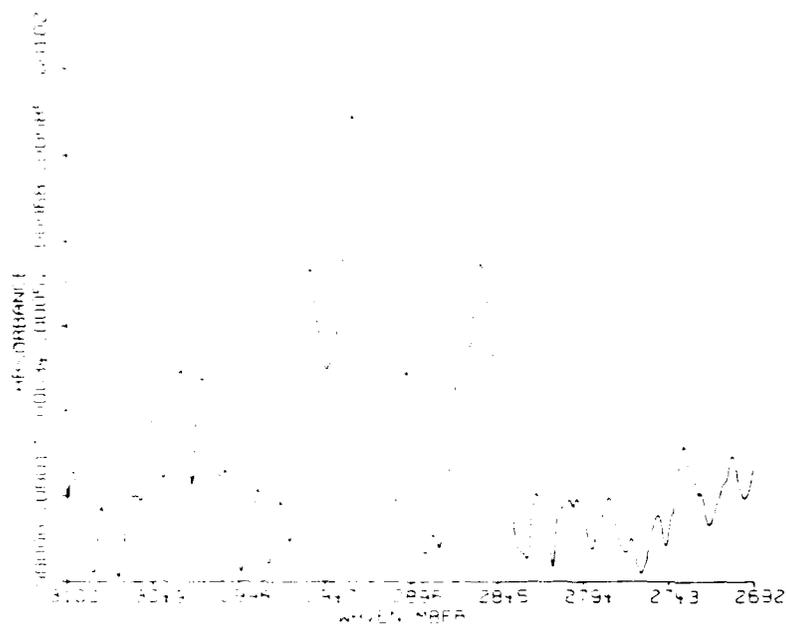


Fig.11. FTIR of single LB monolayer of BDDAP-C-HMTCAQ, **32**, on aluminum, showing aliphatic CH stretch bands.

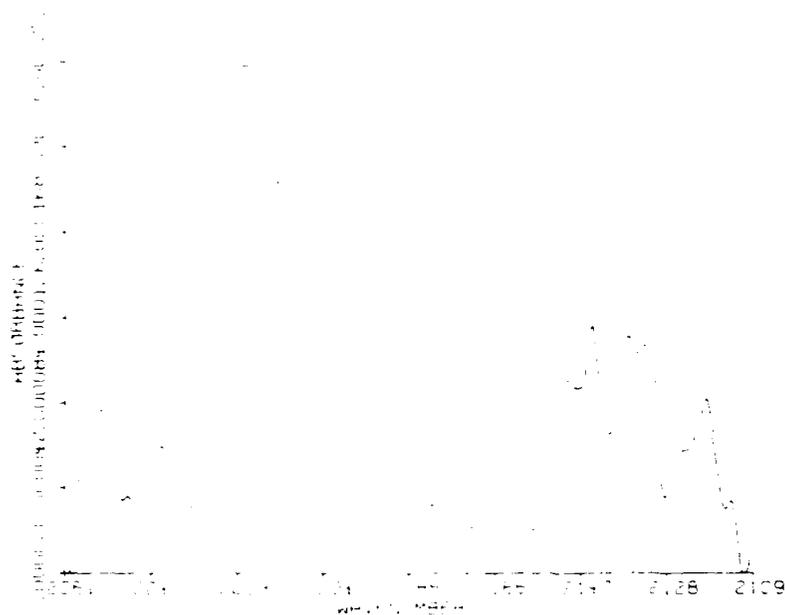


Fig.12. FTIR of single LB monolayer of BDDAP-C-HMTCAQ, **32**, on aluminum, showing CN stretch bands.

WORK OF OTHER GROUPS

Conceptually, our synthetic program is related to efforts by many groups to model the photosynthetic reaction center: linked D- σ -A systems (D = porphyrin, A = quinones) are under intense study in several laboratories [61-66].

It should be mentioned that Kuhn et al. [67] and later Sugi et al. [68] have prepared rectifiers based on seven or more monolayers of cadmium arachidate, three of them randomly doped (5:1) with an electron donor dye, one a pure cadmium arachidate layer, the other three doped (5:1) with an electron acceptor dye. However, the device does not work if there are fewer than seven monolayers.

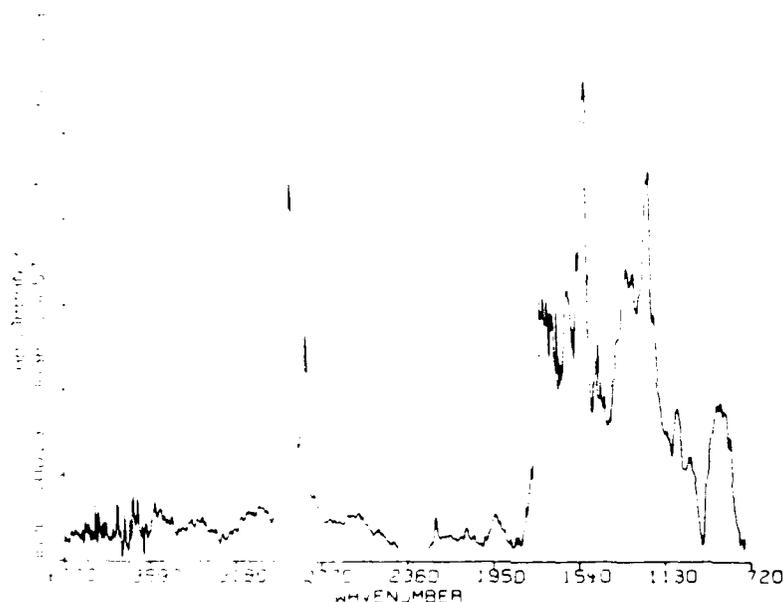
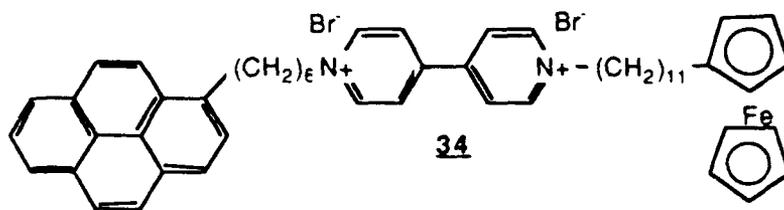


Fig. 13. FTIR of 16 LB monolayers of BDDAP-C-HMTCAQ, 32, on aluminum.

Recently Fujihira prepared a LB photodiode [68] using a single monolayer of molecule 34, which consists of a donor D (ferrocene), a sensitizer S (pyrene), and an acceptor A (viologen), deposited as an LB film onto a semitransparent gold electrode (with the viologen on the Au surface), and placed in a 0.1 molar potassium chloride solution, with a platinum counter electrode. The electron transfer is from solution to D, then to the ground state of S; upon irradiation of the film at 330 nm, the electron is pushed to the excited state of S, S*, which is above the LUMO of A, which finally gets the electron and transfers it to the Au layer. 2 nA of current at 0.0 V versus SCE was measured when light was on [69].



CONCLUSIONS

We have demonstrated that LB films of D-σ-A molecules can be synthesized; we are on our way to fabricating metal | organic | metal sandwiches which should give us a realistic test for the organic rectifier.

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REFERENCES

- [1] A. Aviram, M. J. Freiser, P. E. Seiden, and W. R. Young U.S. Patent US-3,953,874 (27 April 1976).
- [2] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277-283 (1974).
- [3] A. Aviram, P. E. Seiden, and M. A. Ratner, in "Molecular Electronic Devices", F. L. Carter, ed. (Dekker, New York, 1982) page 5.
- [4] R. M. Metzger and C. A. Panetta, J. Phys. (Les Ulis, Fr.) Colloque **44**, C3-1605 to C3-1611 (1983).
- [5] R. M. Metzger and C. A. Panetta, in "Molecular Electronic Devices, Vol. II", F. L. Carter, ed. (Dekker, New York, 1987) page 1.
- [6] C. A. Panetta, J. Baghdadchi, and R. M. Metzger, Mol. Cryst. Liq. Cryst. **107**, 103-113 (1984).
- [7] R. M. Metzger, C. A. Panetta, N. E. Heimer, A. M. Bhatti, E. Torres, G. F. Blackburn, S. K. Tripathy, and L. A. Samuelson, J. Molec. Electronics, **2**, 119-124 (1986).
- [8] R. M. Metzger, C. A. Panetta, Y. Miura, and E. Torres, Synth. Metals **18**, 797-802 (1987).
- [9] E. Torres, C. A. Panetta, and R. M. Metzger, J. Org. Chem. **52**, 2944-2945 (1987).
- [10] R. M. Metzger and C. A. Panetta, Proc. of the Eighth Winter Conference on Low-Temperature Physics, Cuernavaca, Mexico, January 1987, in press.
- [11] R. K. Laidlaw, Y. Miura, C. A. Panetta, and R. M. Metzger, Acta Cryst., submitted.
- [12] R. K. Laidlaw, Y. Miura, J. L. Grant, L. Cooray, M. Clark, L. D. Kispert, and R. M. Metzger, J. Chem. Phys., in press.
- [13] R. K. Laidlaw, J. Baghdadchi, C. A. Panetta, Y. Miura, E. Torres, and R. M. Metzger, Acta Cryst., submitted.
- [14] Y. Miura, R. K. Laidlaw, C. A. Panetta, and R. M. Metzger, Acta Cryst., submitted.
- [15] R. M. Metzger, R. K. Laidlaw, E. Torres, and C. A. Panetta, J. Cryst. Spectr. Res., submitted.

- [16] R. M. Metzger, R. R. Schumaker, M. P. Cava, R. K. Laidlaw, C. A. Panetta, and E. Torres, Langmuir, in press.
- [17] R. Hoffman, Acc. Chem. Res. **4**, 1-9 (1971).
- [18] R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferrans, J. Electron Spectrosc. **2**, 207-210 (1973).
- [19] R. N. Compton and C. D. Cooper, J. Chem. Phys. **66**, 4325-4329 (1977).
- [20] Z. G. Soos, Chem. Phys. Lett. **63**, 179-183 (1979).
- [21] F. Herman and I. P. Batra, Phys. Rev. Lett. **33**, 94-97 (1974).
- [22] See e.g. G. L. Gaines, Jr. "Insoluble Monolayers at Liquid - Gas Interfaces" (Interscience, New York, 1966).
- [23] K. B. Blodgett, J. Am. Chem. Soc. **57**, 1007-1022 (1935).
- [24] K. B. Blodgett and I. Langmuir, Phys. Rev. **51**, 964-982 (1937).
- [25] H. Kuhn, D. Moebius, and H. Buecher in "Techniques of Chemistry, Vol. I - Physical Methods of Chemistry - Part V - Determination of Thermodynamic and Surface Properties" A. Weissberger and B. W. Rossiter, eds. (Wiley - Interscience, New York, 1972) pages 577 - 702.
- [26] H. Kuhn, Pure Appl. Chem. **51**, 341-352 (1979).
- [27] H. Kuhn, Pure Appl. Chem. **53**, 2105-2122 (1981).
- [28] See e. g. Thin Solid Films **68** (1980), **99** (1983), **132-134** (1985).
- [29] W. C. Bigelow, D. L. Pickett, and W. A. Zisman, J. Colloid Sci. **1**, 513-538 (1946).
- [30] L. Netzer, R. Iscovici, and J. Sagiv, Thin Solid Films **99**, 235-241 (1983).
- [31] L. Netzer, R. Iscovici, and J. Sagiv, Thin Solid Films **100**, 67-76 (1983).
- [32] J. Gun, R. Iscovici, and J. Sagiv, J. Colloid Interf. Sci. **101**, 201-213 (1984).
- [33] R. W. Murray, Acc. Chem. Res. **13**, 135-141 (1980).
- [34] R. Maoz and J. Sagiv, Thin Solid Films **132**, 135-151 (1985).
- [35] R. G. Nuzzo, F. A. Fusco, and D. A. Allara, J. Am. Chem. Soc. **109**, 2358-2368 (1987).
- [36] G. Wegner, Z. Naturforschung **24b**, 829 (1969).
- [37] M. Batley and L. E. Lyons, Mol. Cryst. **3**, 357-374 (1968).
- [38] E. Clar, J. M. Robertson, R. Schloegl, and W. Schmidt, J. Am. Chem. Soc. **103**, 1320-1328 (1981).
- [39] E. C. M. Chen and W. E. Wentworth, J. Chem. Phys. **63**, 3183-3191 (1975).
- [40] C. D. Cooper, W. F. Frey, and R. N. Compton, J. Chem. Phys. **69**, 2367-2374 (1978).
- [41] D. R. Gray, Ed., "American Institute of Physics Handbook, II Edition" (McGraw-Hill, New York, 1963) pages 9-147 to 9-149.
- [42] R. A. Marcus, Disc. Faraday Soc. **29**, 21-31 (1960).
- [43] L. T. Calcaterra, G. L. Closs, and J. R. Miller, J. Am. Chem. Soc. **105**, 670-671 (1983).
- [44] J. R. Miller, L. T. Calcaterra, and G. L. Closs, J. Am. Chem. Soc. **106**, 3047-3049 (1984).
- [45] N. S. Hush, M. N. Paddon-Row, E. Cotsaris, H. Oevering, J. W. Verhoeven, and M. Heppener, Chem. Phys. Lett. **117**, 8-11 (1985).
- [46] P. L. Dutton, R. C. Prince, D. M. Tiede, K. M. Petty, K. J. Kaufmann, K. J. Netzel, and P. M. Rentzepis, Brookhaven Symp. Biol. **28**, 213-237 (1977).
- [47] I. R. Peterson and G. J. Russell, Thin Solid Films **134**, 143-152 (1985).
- [48] S. Garoff, H. W. Deckman, J. H. Dunsmuir, M. S. Alvarez, and J. M. Bloch, J. Phys. (Les Ulis, Fr.) **47**, 701-709 (1986).
- [49] I. R. Peterson, J. Mol. Electronics, submitted.
- [50] G. G. Roberts, P. S. Vincett, and W. A. Barlow, J. Phys. C **11**, 2077-2085 (1978).
- [51] B. Mann and H. Kuhn, J. Appl. Phys. **42**, 4398-4405 (1971).
- [52] P. K. Hansma, Ed. "Tunneling Spectroscopy: Capabilities, Applications, and New Techniques" (Plenum, New York, 1982).
- [53] W. R. Hertler, J. Org. Chem. **41**, 1412-1416 (1976).
- [54] J. Baghdadchi, Ph. D. dissertation, Univ. of Mississippi, Dec. 1982.
- [55] Y. Miura, C. A. Panetta, and R. M. Metzger, J. Org. Chem., in press.
- [56] N. E. Schlotter, M. D. Porter, T. B. Bright, and D. L. Allara, Chem. Phys. Letters **132**, 93-98 (1986).
- [57] W. G. Golden, D. D. Saperstein, M. W. Severson, and J. Overend, J. Phys. Chem. **88**, 574-579 (1984).

- [58] J. F. Rabolt, M. Junch, and J. D. Swalen, Applied Spectrosc. **39**, 269-272 (1985).
- [59] J. F. Rabolt, F. C. Burns, N. E. Schlotter, and J. D. Swalen, J. Chem. Phys. **78**, 946-952 (1983).
- [60] J. D. Swalen and J. F. Rabolt, in "Fourier Transform Infrared Spectroscopy, Vol. 4 (Academic, 1985) pages 283-314.
- [61] J. Lindsay, D. Mauzerall, and H. Linschitz, J. Am. Chem. Soc. **105**, 6528-6529 (1983).
- [62] A. R. McIntosh, J. R. Bolton, J. S. Connolly, K. L. Marsh, D. R. Cook, T.-F. Ho, and A. C. Weedon, J. Phys. Chem. **90**, 5640-5646 (1986).
- [63] A. D. Joran, B. A. Leland, G. G. Geller, J. J. Hopfield, and P. B. Dervan, J. Am. Chem. Soc. **106**, 6090-6092 (1984).
- [64] S. Nishitani, N. Kurata, Y. Sakata, S. Misumi, A. Karen, T. Okada, and N. Mataga, J. Am. Chem. Soc. **105**, 7771-7772 (1983).
- [65] T. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddell, W. R. Lehman, G. A. Nemweth, and A. L. Moore, Nature **307**, 630-632 (1984).
- [66] C. Krieger, J. Weiser, and H. A. Staab, Tetrahedron Lett. **26**, 60550-6058 (1985).
- [67] E. E. Polymeropoulos, D. Moebius, and H. Kuhn, Thin Solid Films, **68**, 173-190 (1980).
- [68] M. Sugi, K. Sakai, M. Saito, Y. Kawabata, and S. Iizima, Thin Solid Films **132**, 69-76 (1985).
- [69] M. Fujihira, K. Nishiyama, and H. Yamada, Thin Solid Films **132**, 77-82 (1985).