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## New Materials Design

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**Abstract.** In this paper we report our recent results on the design of materials with controlled properties by the application of computational chemistry methods, new algorithms and scalable software.

### 1 Introduction

Developments of new materials (such as new high energy density materials; POSS (polyhedral oligomeric silsesquioxanes) that are highly resistant to extreme environments and are therefore desirable coatings for rocket engines; nonlinear optical materials; and liquid crystals) are important in many applications of interest to the Air Force. However, the design of large and complex material systems with controlled properties is challenging. Therefore, the calculations we describe in this paper would not have been possible without scalable quantum chemistry codes such as GAMESS (General Atomic and Molecular Electronic Structure System), developed under the auspices of a DoD CHSSI (Computational High Performance Scalable Software Initiative) grant, Gaussian, and molecular dynamics codes, as well as the availability of the DoD Computation Centers through our computational challenge project.

### 2 Results and Discussion

#### 2.1 High-Energy Density Materials (HEDM)

##### 2.1.1 Synthesis of new polynitrogen compounds.

The identification, development, and formulation of new energetic materials for advanced rocket propulsion applications is an area of long standing interest to the Air Force. The performance limits of currently used propellants have been reached, so new energetic compounds are required to significantly improve the ability of the warfighter to access and control space.

Polynitrogen species such as the recently discovered  $N_5^+$  cation are of interest as potential energetic ingredients in new propellant formulations. The recent successful synthesis of  $N_5^+$  in macroscopic quantities has prompted the search for additional polynitrogen compounds. Computational chemistry plays a central role in determining the stabilities, potential synthetic pathways, and key spectroscopic "fingerprints" of new polynitrogen species.

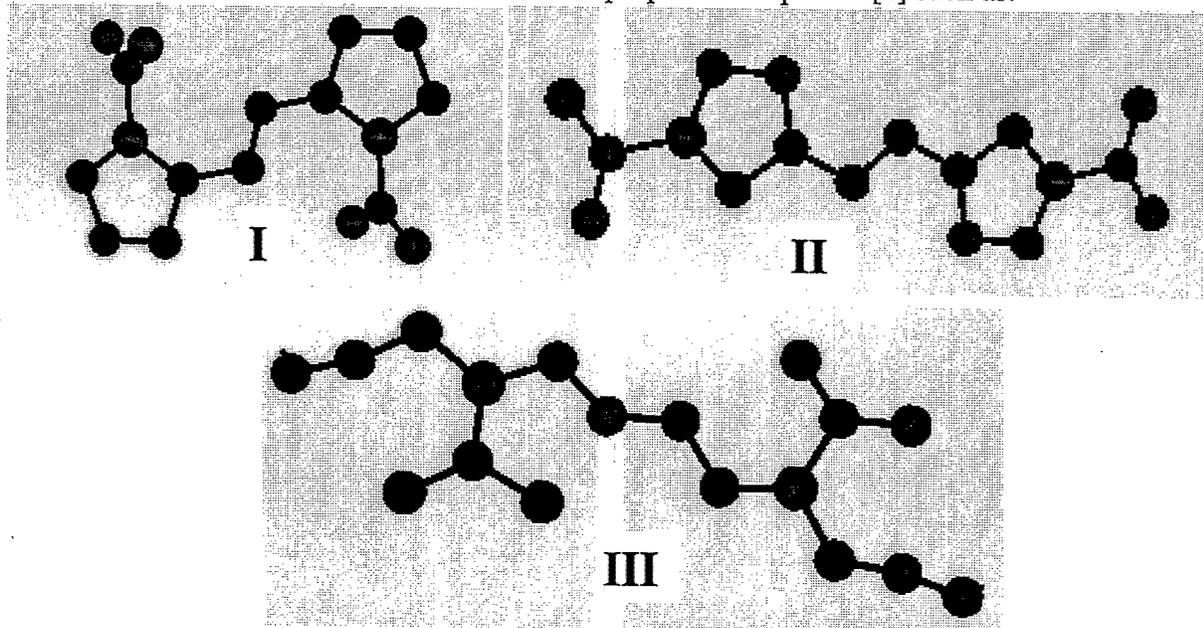
The structures, stabilities, vibrational frequencies, and infrared intensities of several potential synthetic precursors to new polynitrogen species have been computed using ab initio electronic structure theory, at the second order perturbation theory level (MP2, also known as MBPT(2)), using the 6-31G(d) valence double-zeta polarized basis set. Shown in the figure below is the predicted structure of tris(para-nitrophenyl)methyldiazonium cation, which is a possible precursor to new polynitrogen compounds such as pentazole, a 5-membered nitrogen ring system. The calculated structure (see Figure 1) shows that this cation is unstable with respect to dissociation of  $N_2$ . A similar result is found for an analogue of the trityldiazonium cation (Figure 1) in which the central carbon atom is replaced with silicon. Therefore, these calculations predict that these cations are not viable polynitrogen precursors.

Although this is a negative result in the sense that it indicates that these cations are not stable precursors, it is nonetheless a highly useful result in that it saves significant time and effort by eliminating from consideration for subsequent attempts at synthesis compounds which are not likely to be stable. Ongoing/future work in this area includes other substituted silyldiazonium derivatives  $[R_3Si-N_2]^+$  ( $R=Me, F, Cl, CF_3$ ) and additional classes of promising polynitrogen precursors such as  $Fe(N_5)_2$ .

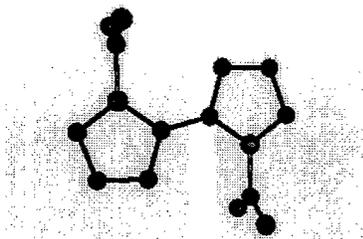
Recently, the first new all-nitrogen compound in nearly a century,  $N_5^+$ [2], was synthesized. The counterion for this species was  $AsF_6^-$ , the result being a rather unstable solid. In order to understand the potential energy surface for this species, we performed MP2 calculations[3] on the various stationary points. The first step in this process was to separate the two ions by a large distance and optimize the geometry. The result was an ion pair  $[N_5^+][AsF_6^-]$  complex that is, not surprisingly, 98 kcal/mol below the separated ions. What was somewhat surprising is that this complex is 47 kcal/mol below the neutral species that is formed when one  $F^-$  ion is transferred to  $N_5^+$  to form neutral  $AsF_5 + FN_5$ . The former is a well-known species, but the latter has not previously been reported.  $FN_5$  has several isomers, whose relative energies and the barriers separating them were determined using large basis set CCSD(T) calculations. The lowest lying isomers were found to have small energy barriers ( $< 10$  kcal/mol) separating them from the much more stable decomposition products  $FN_3 + N_2$ . The exothermicity of this decomposition is more than 50 kcal/mol, so the products  $AsF_5 + FN_3 + N_2$  are slightly lower in energy than the original ion pair  $[N_5^+][AsF_6^-]$ . Since  $FN_3$  is itself an energetic species with a relatively small barrier to further decomposition, it is therefore not surprising that the original species made by Christe et al. is unstable. In order to study this system further, we have employed the dynamic reaction path (DRP) method in GAMESS to analyze the effect of putting photons into vibrational modes that might lead to decomposition. Interestingly, this molecule appears to be very RRKM-like, since the energy dumped into specific modes rapidly gets distributed to many other, apparently strongly coupled, modes. So, one must put much more energy into these modes than the barrier height in order to induce dissociation.

## 2.1.2 High nitrogen-containing components

A recent major focus centers around a series of proposed compounds[1] such as:



Using a combination of isodesmic reactions and the G2 model, the heat of formation for **I** is predicted to be 456.8 kcal/mol. It is important to consider the stability of such high-energy species to various reactions, before asserting their viability as fuels. One possible reaction of **I** is the loss of molecular nitrogen to form the smaller species shown below:



Using our highly scalable second order perturbation theory code with a large basis set, we have found that this decomposition process is exothermic by 60 kcal/mol. It may be that the barrier for decomposition is large, in which case the species may still be viable. Dr. Jeff Bottaro (SRI) suggested that **I** may be unstable, because it could open at either or both ends to an azide. He suggested instead that we consider an isomer of **I**, in which the CNO<sub>2</sub> group on the left in the figure is shifted one position to the left, and the CNO<sub>2</sub> group on the right is shifted one position to the right, giving **II** (shown above), since this structure is less likely to open to an azide or a diazide. We therefore initiated MP2 geometry optimizations for both **II** and the diazide **III**. We find that **II** is indeed lower in energy than **I**, by about 15 kcal/mol, but that the diazide **III**, in which both ends of **I** are opened, is much higher in energy than either **I** or **II**. So, it appears that **II** should be studied further as a possible HEDM, but that **I** may still be viable as well. We are now investigating feasible decomposition products of both **I** and **II**, as well as the heat of formation of **II**.

## 2.2 POSS Compounds

There is great interest in POSS compounds because of their resistance to extreme environments and the ease with which they are synthesized. Since almost nothing is known experimentally about the mechanism by which they are formed, we have embarked on a long term project to determine the possible competing mechanisms as a function of catalyst, solvent, and substituents (e.g., in [4]). The synthesis begins with hydrolysis of  $\text{RSiX}_3$  to  $\text{RSi(OH)}_3$ , followed by condensation to the siloxane  $\text{RSi(OH)}_2\text{-O-Si(OH)}_2\text{R}$ . Subsequent condensations lead to the 3D cage compounds. We have shown that the initial hydrolysis and condensation steps all have very high-energy barriers in the gas phase, but are being reduced to nearly zero by the presence of one water molecule added to represent the solvent. Thus, all steps leading to the initial disiloxanes and to the ring compounds  $\text{D}_3$  and  $\text{D}_4$  occur with net energy requirements of less than 10 kcal/mol. In this paper we describe current efforts to (a) determine substituent effects on these barriers, (b) determine the effects of adding additional water molecules, and (c) to compare the properties of the 3D POSS compounds with their Ti analogs. The substituents studied include  $\text{R}=\text{H}$ , methyl, t-butyl and phenyl, and  $\text{X}=\text{Cl}$ ,  $\text{OCH}_3$ . There is experimental interest in synthesizing incompletely condensed POSS. Because the reaction is very fast, it always goes to completion. The interest in substituent effects lies in attempting to slow down the reaction, possibly using bulky R groups. There is industrial interest in the possibility that Ti POSS may be another class of materials with desirable properties. Hammes-Schiffer et al.[5] have been developing methodologies for the simulation of hydrogen transfer reactions, and most recently a new molecular orbital method for the simultaneous calculation of electronic and hydrogen vibrational wavefunctions, now incorporated into GAMESS. This method may be used to obtain minimum energy reaction paths and direct dynamics trajectories of hydrogen transfer reactions, with the advantage that nuclear quantum effects such as zero point energy and hydrogen tunneling are incorporated during the generation of the reaction paths and trajectories, rather than subsequently included as corrections. This approach will be combined with a mixed quantum/classical surface hopping method to study the quantum dynamics of hydrogen transfer reactions with an *ab initio* potential energy surface obtained "on the fly," and used to investigate hydrogen transfer reactions in the hydrolysis and condensation steps required for the synthesis of POSS, in order to determine the influence of different trihalosilane reactants on the rates and yields of these steps and aid in the efficient synthesis of POSS.

## 2.3 Nonlinear Absorbing Materials

In order to predict the nonlinear absorption of organic and organometallic dyes, including a number of free-base porphyrins, phthalocyanines, and their metal complexes, representing a broad range of  $\pi$ -conjugated systems (cf. Figure 2), we systematically examine time-dependent density functional theory (TDDFT) using Becke's three-parameter hybrid functional (B3LYP) results. We found that the B3LYP functional provides good approximations to experimental  $\text{S}_0\text{-T}_1$  and  $\text{T}_1\text{-T}_n$  excitation energies and oscillator strengths (cf. Figures 3 & 4). The average error for triplet-triplet excitation energies obtained by TD-B3LYP is comparable to those predicted by highly correlated *ab initio* methods for ground state spectra. The basis set effect on excitation energy calculations was found to be small, and the standard double- $\zeta$  basis sets appears to be adequate for predicting/interpreting electronic spectra of large  $\pi$ -conjugated molecules. The computed  $\text{S}_0\text{-T}_1$  (zero-point corrected) energies have an average error of 0.14 eV to experiment

for 47 organic and organometallic chromophores, while the average error for 6 experimental gas-phase values is slightly (0.08 eV) higher. Therefore, the average error of 0.11 eV for 86 experimental  $T_1-T_n$  energies is likely larger when compared to gas-phase data.

## 2.4 Liquid Crystals

Recent work is in progress for studying a liquid crystalline droplet to model the behavior of a liquid crystal in the bulk, with the details reported elsewhere.[6] Indeed, atomic level simulations are proven important in understanding the structure-property relations of materials. Due to the size of the LC droplet, very large-scale classical MD simulations of such systems are required, that may, become computationally prohibitive. The fast multipole method (FMM)[7], which uses a multiscale hierarchy of partitions of the volume and a divide-and-conquer strategy to compute the power series, allows all the forces to be computed to any specified accuracy in  $O(N)$  operations. FMM3D (an implementation and improvement to FMM in 3-D), which contains a variety of schemes for computing multipole translations, has been implemented into the MD program that is being developed in our group.[8]

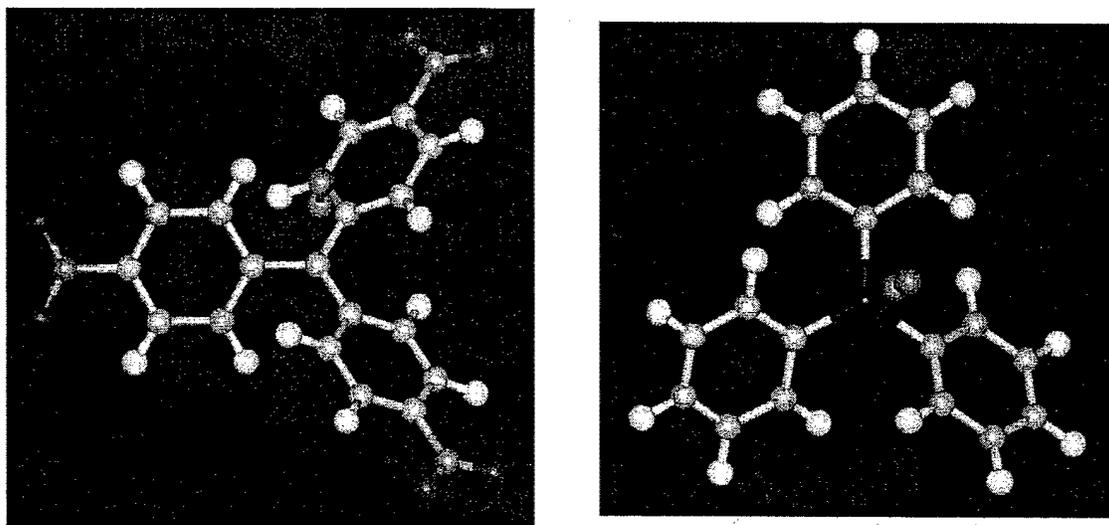


Figure 1. MP2/6-31G(d) optimized structures of triphenylsilyldiazonium  $[\text{SiC}_{18}\text{H}_{15}\text{N}_2]^+$  and tris(para-nitrophenyl)methylidiazonium  $[\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_6]^+$  cations

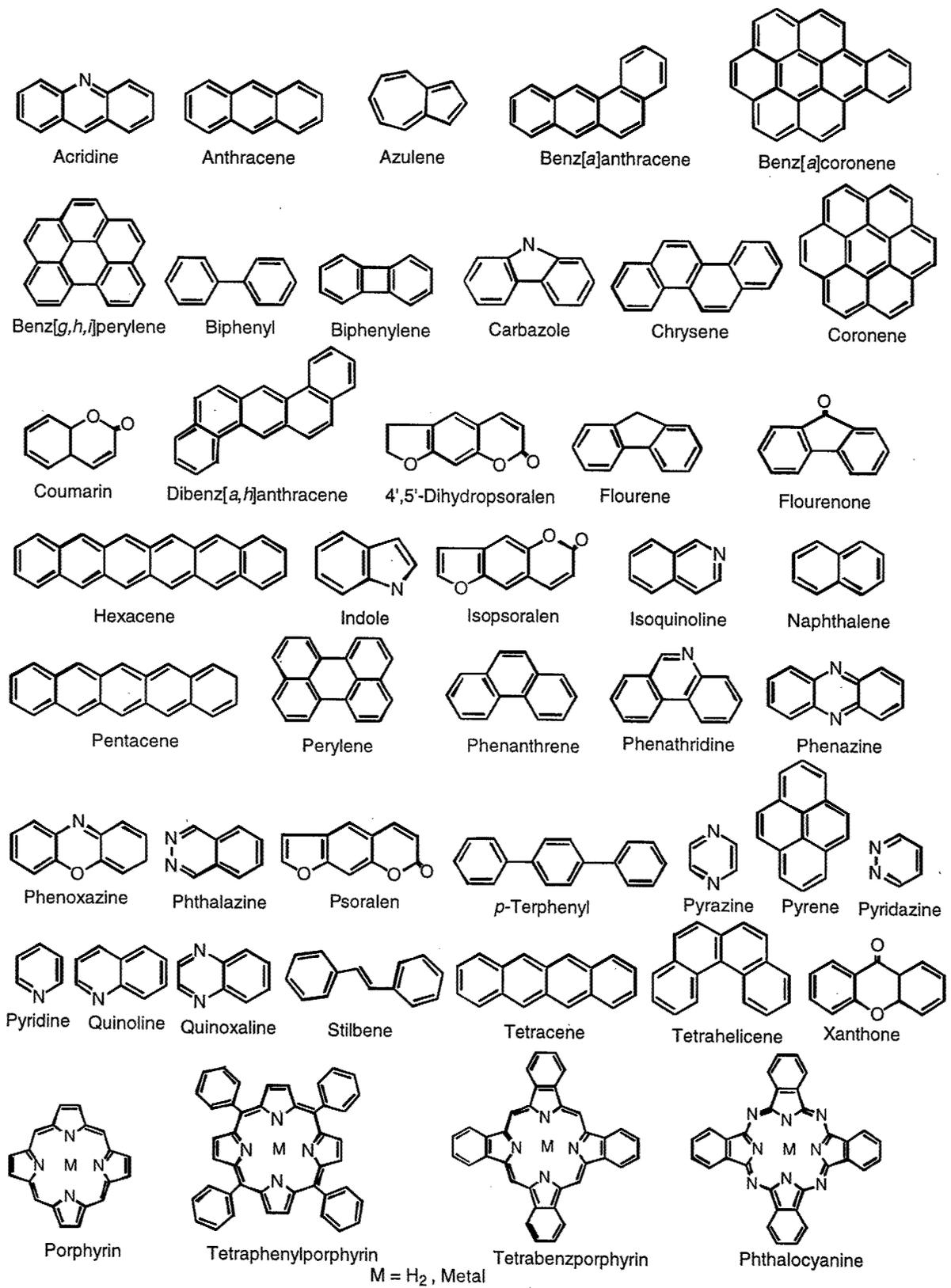


Figure 2.  $\pi$ -conjugated systems

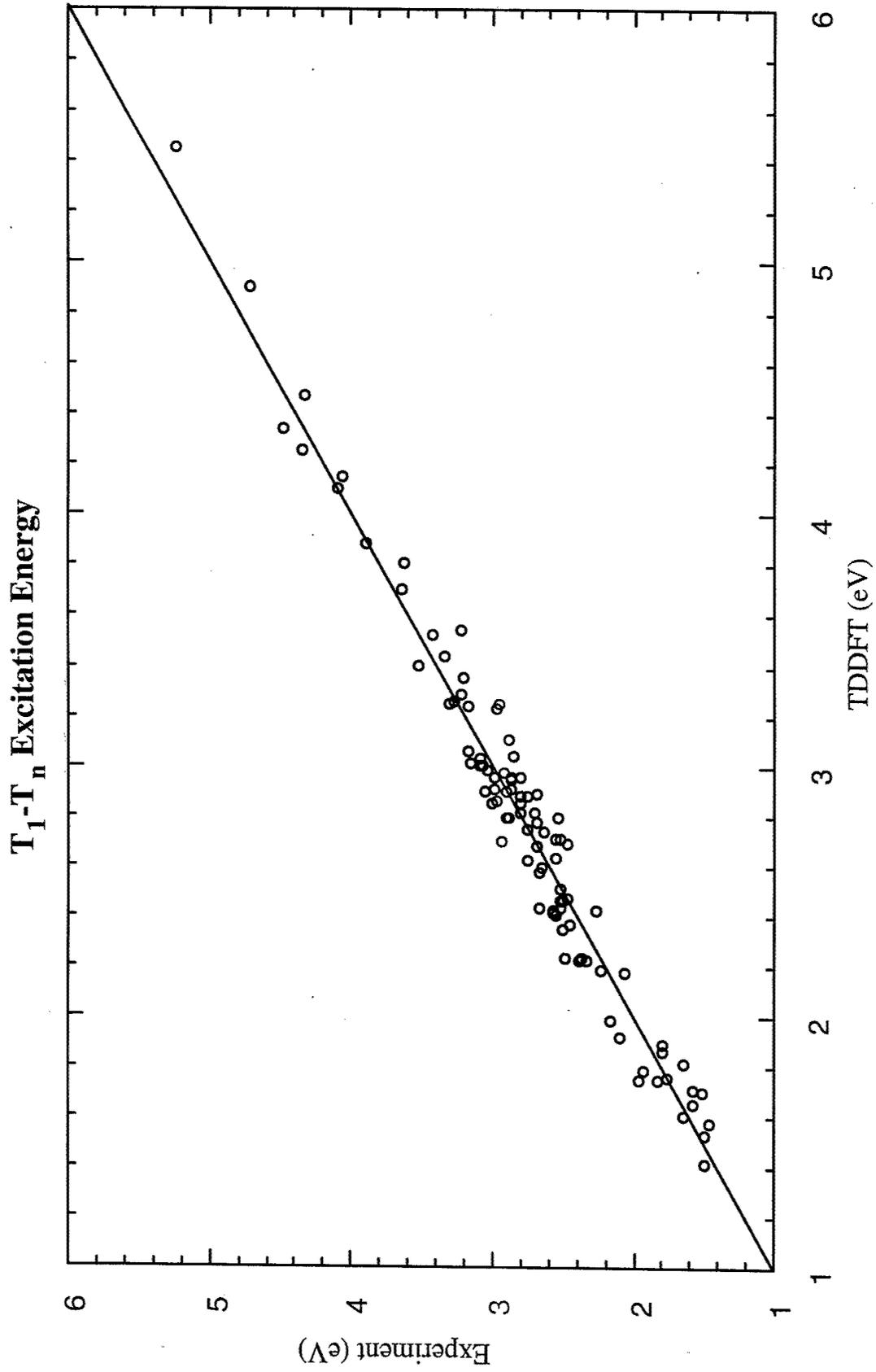


Figure 3. Computed  $T_1$ - $T_n$  compared to experimental results

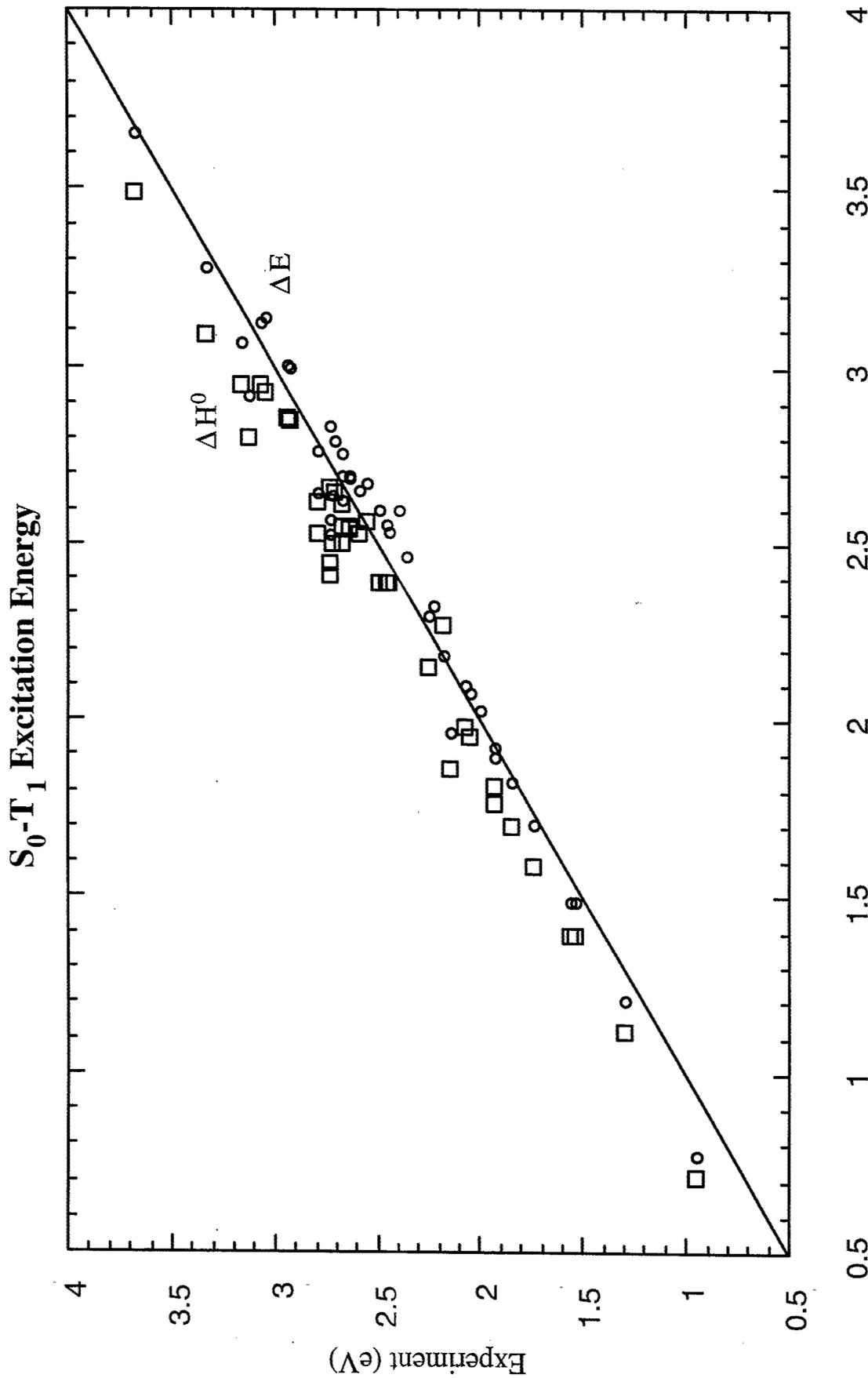


Figure 4. Computed  $S_0-T_1$  compared to experimental results

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