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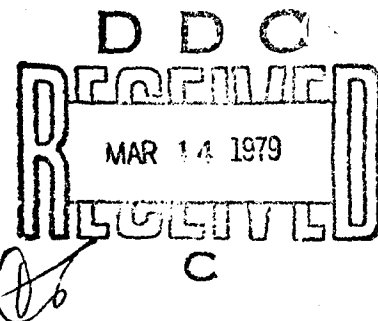
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1 October 1977 - 30 September 1978

LEVEL

THERMODYNAMICS OF ORGANIC COMPOUNDS

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

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ENTHALPY OF COMBUSTION	2,2'-BIINDANYL	DIALKYLINDANS
ENTHALPY OF FORMATION	2,2'-BITETRALIN	DIALKYLNAPHTHALENES
VAPOR PRESSURE	RAMJET FUELS	
HEAT CAPACITY	RJ-4-I	
2-ETHYL-6-METHYLNAPHTHALENE	JP-9	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Both basic and applied research continued on the thermodynamic properties of currently used high energy fuels and of possible constituents of high energy fuels of the future. Enthalpies of combustion were measured for two ramjet fuels currently in use, and differential scanning calorimetry evaluated heat capacities of four such fuels. Enthalpies of combustion were measured for two pure organic compounds having the energetic cyclobutane ring in their molecular structure, and the study of compounds that may have higher combustion energies because of steric interaction of adjacent alkyl groups was continued with vapor pressure study on dialkylnaphthalene.

FINAL TECHNICAL SUMMARY REPORT

THERMODYNAMICS OF ORGANIC COMPOUNDS

* * * * * * * * * * *

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Project Director: W. D. Good   Report* prepared by: N. K. Smith
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                                                       S. Lee-Bechtold
                                                       A. G. Osborn
                                                       W. D. Good

* Synthesis and purification of research samples were provided by
Professor E. J. Eisenbraun, Oklahoma State University, where the
samples were produced by purchase agreement for the above project.

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FOREWORD

The objectives of this research program are formulated within the
framework of an integrated and interrelated program of basic and
applied research in chemical thermodynamics and thermochemistry.
Knowledge of variation of thermodynamic and physical properties of
materials with molecular structure is used to select substances for
study that may be useful as high energy fuels or that may be useful
in the synthesis of high energy fuels. These materials are synthe-
sized, and the thermodynamic properties are evaluated. Ram-jet fuels
already in use are subjected to careful thermodynamic evaluation.

ABSTRACT

Both basic and applied research have continued on the thermodynamic properties of currently used high energy fuels and of possible constituents of high energy fuels of the future.

Enthalpies of combustion were measured for two ram-jet fuels currently in use, and differential scanning calorimetry evaluated heat capacities of four such fuels.

Enthalpies of combustion were measured for two pure organic compounds having the energetic cyclobutane ring in their molecular structure, and the study of compounds that may have higher combustion energies because of steric interaction of adjacent alkyl groups was continued with vapor-pressure study on a dialkylnaphthalene.

Results of parts of the research were reported both orally and in special reports and journal articles.

1. NOMENCLATURE

This annual report will describe research on the thermodynamic prop-
erties of several organic compounds with rather complex molecular
structure. In an effort to facilitate understanding, the molecular
structure and nomenclature of these compounds are given in Table 1.

TABLE 1. Nomenclature of Compounds

1.
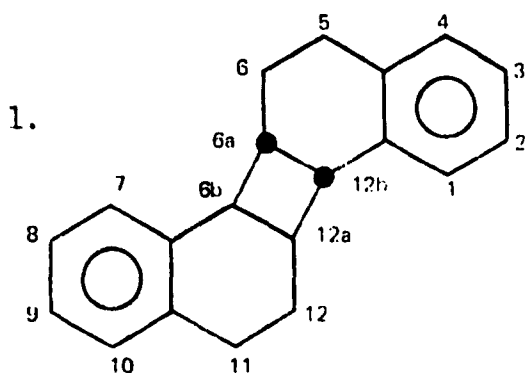
$5,6,6a\beta,6b\alpha,11,12,12a\,\alpha,12b\beta$-
Octahydrocyclobuta[1,2-a:3,4-a′]-
dinaphthalene

(or)

$5,6,6a,6b,11,12,12a,12b$-Octa-
hydrodibenzo[a,g]biphenylene

2.
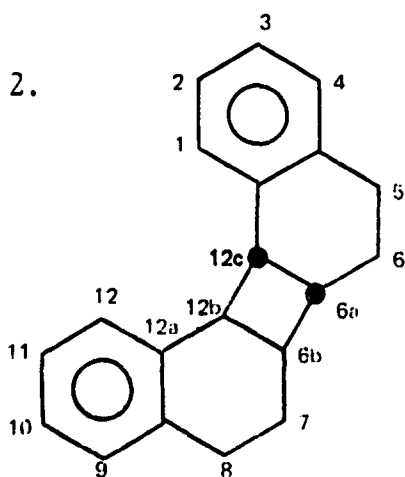
$5,6,6a\beta,6b\alpha,7,8,12b\alpha,12c\beta$-
Octahydrocyclobuta[1,2-a:4,3-a′]-
dinaphthalene

(or)

$5,6,6a,6b,7,8,12b,12c$-Octa-
hydrodibenzo[a,i]biphenylene

TABLE 1. Nomenclature of Compounds--Continued

3.
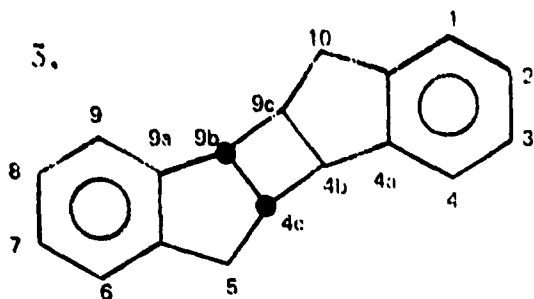
$4b\alpha,4c\beta,5,9b\beta,9c\alpha,10$-Hexahydrocyclobuta[1,2-a:3,4-a']-diindene

(or)

anti,trans-Truxane

4.
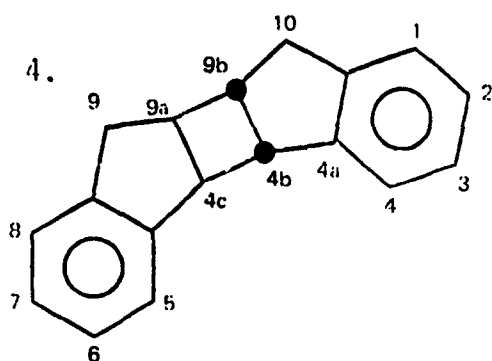
$4b\beta,4c\alpha,9,9a\alpha,9b\beta,10$-Hexahydrocyclobuta[1,2-a:4,3-a']-diindene

(or)

syn,trans-Truxane

5.
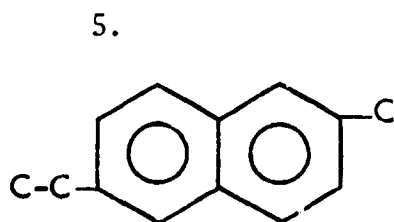
2-Ethyl-6-methylnaphthalene

TABLE 1.   Nomenclature of Compounds--Continued

6.

2,2'-Biindanyl

7.
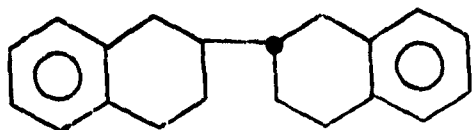
2,2'-Bitetralin

8.
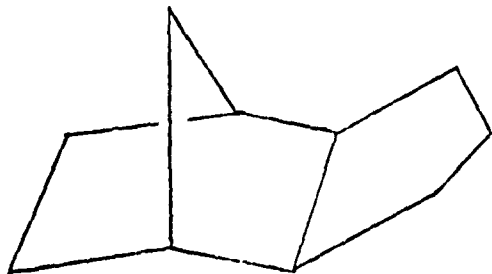
exo-Tetrahydrodicyclopentadiene

9.

C   C

exo-Tetrahydrodi(methyl-
    cyclopentadiene)

3
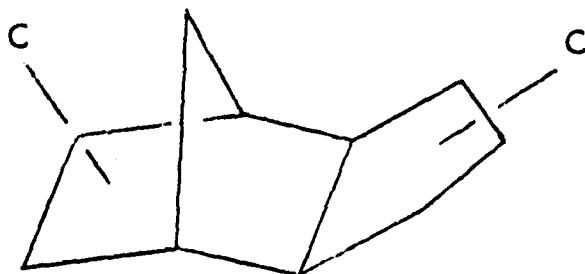
TABLE 1.   Nomenclature of Compounds--Continued

10.
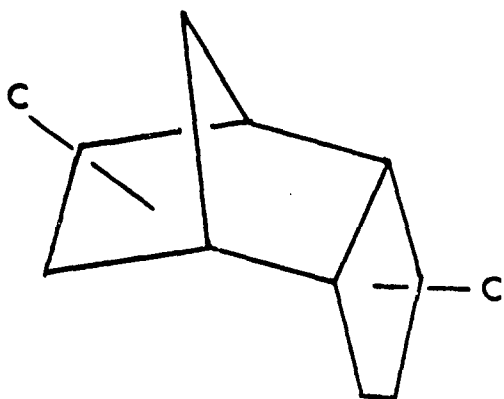
endo-Tetrahydrodi(methylcyclo-
    pentadiene)

11.

(a)
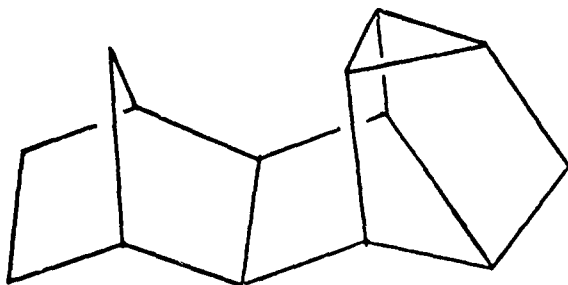
Hydrogenated dimers of
    norbornadiene ($C_{14}H_{18}$)

(b)

4
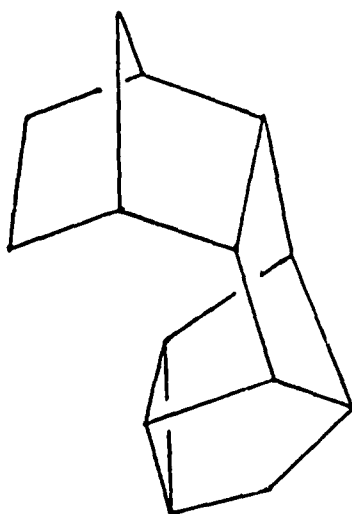
2. ENTHALPIES OF COMBUSTION OF PURE COMPOUNDS

Measurements of the enthalpies of combustion of four compounds with complex molecular structures centered about a cyclobutane ring (compounds 1,2,3, and 4 of Nomenclature Section) were reported in the last annual report. This report describes study of the enthalpies of combustion of two compounds that are closely related to those molecules. 2,2'-Biindanyl and 2,2'-bitetralin, (compounds 6 and 7, Nomeclature Section) were synthesized and purified in the laboratories of Professor E. J. Eisenbraun at Oklahoma State University.

Precision oxygen-bomb combustion calorimetry of 2,2'-biindanyl and 2,2'-bitetralin gave values of their enthalpies of combustion and formation. For 2,2'-biindanyl the combustion and formation reactions are (1) and (2), respectively.

$$C_{18}H_{18}(c) + 45/2\ O_2(g) = 18\ CO_2(g) + 9\ H_2O(l) \qquad (1)$$

$$18\ C(c, graphite) + 9\ H_2(g) = C_{18}H_{18}(c) \qquad (2)$$
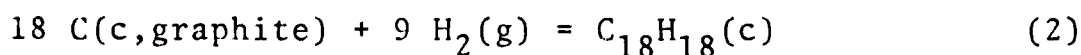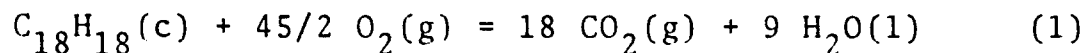
For 2,2'-bitetralin the combustion and formation reactions are (3) and (4), respectively.

$$C_{20}H_{22}(c) + 51/2\ O_2(g) = 20\ CO_2(g) + 11\ H_2O(l) \qquad (3)$$

$$20\ C(c, graphite) + 11\ H_2(g) = C_{20}H_{22}(c) \qquad (4)$$
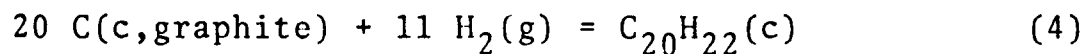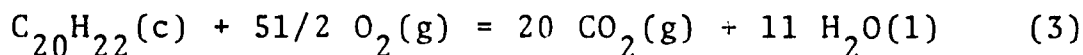
Summaries of individual combustion experiments with 2,2'-biindanyl and 2,2'-bitetralin are given in Tables 2 and 3, respectively. Values of $\Delta Ec°/m$ for 2,2'-biindanyl and 2,2'-bitetralin refer to equations (1) and (3), respectively. Values of $\Delta Ec°$, the standard molar energy of the idealized constant-volume combustion reaction, $\Delta Hc°$, the standard molar enthalpy of combustion and $\Delta Hf°$, the standard molar enthalpy of formation, for both compounds are given in Table 4. Values of $\Delta Ec°$ and $\Delta Hc°$ refer to equations (1) and (3). Values of $\Delta Hf°$ refer to equations (2) and (4). Uncertainties expressed in Table 2 are the "uncertainty interval" equal to twice the final overall standard deviation of the mean.

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TABLE 2. Summary of Calorimetric Experiments for 2,2'-Biindanyl at 298.15 K[a]

(cal$_{th}$ = 4.184 J)

Experiment number	1	2	4	7	8	9	10	11
m'(compound)/g	0.801402	0.812955	0.813036	0.805969	0.813628	0.811789	0.812979	0.811761
m''(auxiliary substance)/g	-	-	-	-	-	-	-	-
m'''(fuse)/g	0.001736	0.001804	0.001715	0.001764	0.001793	0.001846	0.001490	0.001627
n^i(H$_2$O)/mol	0.05555	0.05555	0.05555	0.05555	0.05535	0.05535	0.05535	0.05555
Δt_c/K = $(t_f - t_i + \Delta t_{corr})$/K	1.974050	2.001946	2.001845	1.984294	2.001611	1.998491	2.000821	1.997801
ε(calor)$(-\Delta t_c)$/cal$_{th}$	-7910.06	-8021.84	-8021.45	-7951.11	-8020.56	-8008.00	-8017.33	-8005.23
ε(cont)$(-\Delta t_c)$/cal$_{th}$[b]	-8.73	-8.85	-8.79	-9.01	-10.06	-10.04	-10.06	-9.97
ΔE_{ign}/cal$_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE_{dec}(HNO$_3$)/cal$_{th}$	-	-	-	-	-	-	-	-
ΔE(corr to std states)/cal$_{th}$[c]	4.18	4.25	4.25	4.21	4.25	4.25	4.25	4.24
$(-m''(\Delta Ec°/M)$(auxiliary substance))/cal$_{th}$	-	-	-	-	-	-	-	-
$(-m'''(\Delta Ec°/M)$(fuse))/cal$_{th}$	7.03	7.31	6.95	7.14	7.26	7.48	6.03	6.52
$(m(\Delta Ec°/M)$(compound))/cal$_{th}$	-7907.40	-8018.95	-8018.84	-7949.49	-8018.87	-8006.15	-8016.95	-8004.13
$((\Delta Ec°/M)$(compound))/cal$_{th}$ g^{-1}	-9866.96	-9863.95	-9862.83	-9863.27	-9862.97	-9862.54	-9861.28	-9862.28
$((\Delta Ec°/M)$(compound))/cal$_{th}$ g^{-1}	-9862.97 ± 0.71 (mean and standard deviation of the mean)							

a   The symbols and abbreviations of this table are those of W. N. Hubbard et al, Experimental Thermochemistry, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: New York. 1956.

b ε^i(cont)$(t_i - 298.15$ K) + ε^f(cont)(298.15 K $- t_f + \Delta t_{corr}$). (footnote a).

c   Item 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

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TABLE 3. Summary of Calorimetric Experiments for 2,2'-Bitetralin at 298.15 K[a]

(cal$_{th}$ = 4.184 J)

Experiment number	1	2	3	4	6	7	8	9
m'(compound)/g	0.810175	0.805517	0.804840	0.805757	0.805703	0.805926	0.804550	0.804922
m''(auxiliary substance)/g	-	-	-	-	-	-	-	-
m'''(fuse)/g	0.001779	0.001654	0.001967	0.001895	0.001778	0.001851	0.001787	0.001655
n^i(H$_2$O)/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
Δt_c/K = (t$_f$ - t$_i$ + Δt_{corr})/K	2.018286	2.006373	2.005104	2.006620	2.006618	2.002092	2.003565	2.004635
ε(calor)(-Δt_c)/cal$_{th}$	-8087.31	-8059.53	-8054.45	-8040.57	-8040.56	-8022.45	-8027.57	-8032.62
ε(cont)(-Δt_c)/cal$_{th}$ [b]	-8.99	-8.80	-8.80	-8.85	-8.83	-8.79	-8.81	-8.82
ΔE_{ign}/cal$_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE_{dec}(HNO$_3$)/cal$_{th}$								
$\Delta E_{(corr\ to\ std\ states)}$/cal$_{th}$ [c]	4.10	4.07	4.66	4.07	4.07	4.06	4.06	4.06
{-m''(ΔEc°/M)(auxiliary substance)}/cal$_{th}$								
{-m'''(ΔEc°/M)(fuse)}/cal$_{th}$	7.21	6.70	7.97	7.68	7.20	7.50	7.21	6.70
{m'(ΔEc°/M)(compound)}/cal$_{th}$	-8084.81	-8037.43	-8051.08	-8037.45	-8037.94	-8019.48	-8024.85	-8030.50
{(ΔEc°/M)(compound)}/cal$_{th}$ g^{-1}	-9979.09	-9977.98	-9978.45	-9975.33	-9976.51	-9975.40	-9974.35	-9975.88
{(ΔEc°/M)(compound)}/cal$_{th}$ g^{-1}	-9976.60 ± 0.60 (mean and standard deviation of the mean)							

[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, Experimental Thermochemistry, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: New York. 1956.

[b] ε^i(cont)(t$_i$ - 298.15 K) + ε^f(cont)(298.15 K - t$_f$ + Δt_{corr}). (footnote a).

[c] Item 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 4. Derived Molar Values for Condensed State at 298.15 K

(cal$_{th}$ = 4.184 J)

Substance	State	ΔEc° kcal$_{th}$ mol^{-1}	ΔHc° kcal$_{th}$ mol^{-1}	ΔHf° kcal$_{th}$ mol^{-1}
2,2'-Biindanyl	Crystalline	-2311.33 ± 0.52	-2314.00 ± 0.52	6.24 ± 0.56
2,2'-Bitetralin	Crystalline	-2617.84 ± 0.55	-2621.10 ± 0.55	-11.38 ± 0.60

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3. HEAT CAPACITIES OF PURE COMPOUNDS

Values of the heat capacity at 298.15 K are needed in combustion calorimetry to convert the energy of the actual bomb process to that of the isothermal process at 298.15 K. Values were measured by differential scanning calorimetry for compounds 1, 2, 3, 4, 6 and 7 of Table 2. These values are listed in Table 5.

TABLE 5.   HEAT CAPACITIES OF PURE COMPOUNDS AT 298.15 K

COMPOUND	$\dfrac{C_p}{\mathrm{cal_{th}\ g^{-1}}}$
1	0.29_7
2	0.30_6
3	0.26_0
4	0.28_3
6	0.33_9
7	0.34_6

4. ENTHALPIES OF COMBUSTION OF RAM-JET FUELS

Precise measurements of the enthalpies of combustion of two ram-jet fuels were completed. RJ-4-I is a mixture of isomers of exo-tetrahydro(dimethylcylopentadiene), compound 9 of Nomenclature Section. JP-9 is a mixture of 65-70 percent exo-tetrahydrodicyclopentadiene (compound 8 of Nomenclature Section), 20-25 percent RJ-5 (compounds 11(a) and 11(b) of the Nomenclature Section), and 10-12 percent methylcyclohexane. Since these fuels are mixtures, the molar values of enthalpy of combustion and enthalpy of formation are not meaningful, and only energies and enthalpies of combustion on a weight basis are reported.

Summaries of the individual combustion experiments with RJ-4-I are reported in Table 6, and similar summaries for JP-9 are given in Table 7. Values of $\Delta Ec°/m$ for RJ-4-I refer to equation 5. Values of $\Delta Ec°/m$ for

$$C_{10}H_{16}(l) + 14\ O_2(g) = 10\ CO_2(g) + 8\ H_2O(l) \tag{5}$$

JP-9 refer to equation 6.

$$C_{10.529}H_{16.202}(l) + 14.579\ O_2(g) = 10.529\ CO_2(g) \tag{6}$$

$$+ 8.101\ H_2O(l)\ .$$
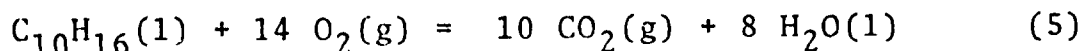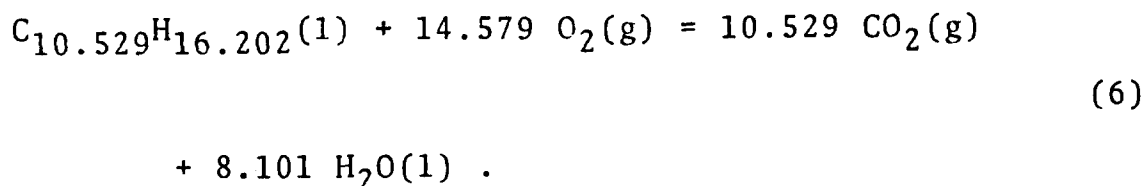
The values of $\Delta Ec°/m$ in Tables 6 and 7 are the energy of the idealized constant-volume bomb reaction at 25° C with all reactants and products in their standard states. If these values are converted to those for the constant pressure reaction at 25° C, the so-called "gross heats" of combustion, or enthalpies of combustion, of RJ-4-I and JP-9 become -(10781.95 ± 0.57) cal g^{-1} and -(10686.16 ± 0.78) cal g^{-1}, respectively. If these values are converted to those of the combustion reaction yielding gaseous CO_2 and gaseous H_2O, the values of the "net" heat of combustion are -(10141.7 ± 2.2) and -(10089.5 ± 2.4) cal g^{-1} for RJ-4-I and JP-9, respectively.

TABLE 6. Summary of Calorimetric Experiments for RJ-4-I at 298.15 K

$$(cal_{th} = 4.184 \text{ J})$$

Experiment number	1	2	3	4	5	6
m'(compound)/g	0.656454	0.657437	0.661629	0.664266	0.671437	0.690385
m''(auxiliary substance)/g	0.088773	0.084967	0.081998	0.078245	0.071440	0.052527
m'''(fuse)/g	0.001362	0.001247	0.001250	0.001410	0.001280	0.001070
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
Δt_c/K = $(t_f - t_i + \Delta t_{corr})$/K	2.006933	1.998944	2.002348	1.998786	1.999118	1.997937
$\mathcal{E}$(calor)$(-\Delta t_c)$/cal$_{th}$	-8041.84	-8009.81	-8023.45	-8009.18	-8010.51	-8005.78
$\mathcal{E}$(cont)$(-\Delta t_c)$/cal$_{th}$[b]	-10.29	-10.17	-10.19	-10.23	-10.23	-10.15
ΔE_{ign}/cal$_{th}$	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{dec}(HNO_3)$/cal$_{th}$	-	-	-	-	-	-
ΔE(corr) to std states/cal$_{th}$[c]	2.91	2.90	2.91	2.91	2.91	2.92
{-m''($Ec°/M$)(auxiliary substance)}/cal$_{th}$	976.89	935.01	902.33	861.04	786.15	578.03
{-m'''($\Delta Ec°/M$)(fuse)}/cal$_{th}$	5.52	5.05	5.06	5.71	5.18	4.33
{m'($\Delta Ec°/M$)(compound)}/cal$_{th}$	-7066.63	-7076.84	-7123.16	-7149.57	-7226.32	-7430.47
{($\Delta Ec°/M$)(compound)}/cal$_{th}$ g^{-1}	-10764.85	-10764.29	-10766.09	-10763.11	-10762.47	-10762.79
{($\Delta Ec°/M$)(compound)}/cal$_{th}$ g^{-1}	-10763.93 $\pm$ 0.57 (mean and standard deviation of the mean)					

a The symbols and abbreviations of this table are those of W. N. Hubbard et al, Experimental Thermochemistry, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: New York. 1956.

b $\mathcal{E}^i$(cont)$(t_i - 298.15 \text{ K}) + \mathcal{E}^f$(cont)$(298.15 \text{ K} - t_f + \Delta t_{corr})$. of Hubbard et al (footnote a).

c Item 81 to 85, 87 to 90, 93 and 94 of the computation form

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TABLE 7. Summary of Calorimetric Experiments for JP-9 at 298.15 K[a]

$$(cal_{th} = 4.184\ J)$$

Experiment number	1	2	3	4	5	6
m'(compound)/g	0.671018	0.670861	0.675054	0.684136	0.686320	0.696639
m''(auxiliary substance)/g	0.079766	0.077597	0.073573	0.065586	0.062454	0.053173
m'''(fuse)/g	0.001260	0.001230	0.001078	0.000907	0.001208	0.001296
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	2.005814	1.998772	1.998899	2.000508	1.998630	2.000358
$\varepsilon(calor)(-\Delta t_c)/cal_{th}$	-8037.34	-8009.12	-8009.63	-8016.08	-8008.55	-8015.48
$\varepsilon(cont)(-\Delta t_c)/cal_{th}$[b]	-10.18	-10.25	-10.15	-10.15	-10.20	-10.14
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{dec}(HNO_3)/cal_{th}$	-	-	-	-	-	-
$\Delta E_{(corr)\ to\ std\ states}/cal_{th}$[c]	3.10	3.08	3.09	3.10	3.10	3.11
$\{-m''(\Delta Ec^\circ/M)(auxiliary\ substance)\}/cal_{th}$	877.78	853.91	809.63	721.74	687.27	585.14
$\{-m'''(\Delta Ec^\circ/M)(fuse)\}/cal_{th}$	5.10	4.98	4.36	3.67	4.89	5.25
$\{m'(\Delta Ec^\circ/M)(compound)\}/cal_{th}$	-7161.36	-7157.22	-7202.52	-7297.54	-7323.31	-7431.94
$\{(\Delta Ec^\circ/M)(compound)\}/cal_{th}\ g^{-1}$	-10672.38	-10668.71	-10669.55	-10666.80	-10670.40	-10668.28
$\{(\Delta Ec^\circ/M)(compound)\}/cal_{th}\ g^{-1}$	-10669.35 $\pm$ 0.78 (mean and standard deviation of the mean)					

a
The symbols and abbreviations of this table are those of W. N. Hubbard et al, Experimental Thermochemistry, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: New York. 1956.

b
$\varepsilon^i(cont)(t_i - 298.15\ K) + \varepsilon^f(cont)(298.15\ K - t_f + \Delta t_{corr})$.

c   Item 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

5. HEAT CAPACITIES OF RAM-JET FUELS

Heat capacities were measured for four ram-jet fuels by means of the differential scanning calorimeter. The following equations were fitted to the experimental data:

exo-THDC (275-365 K)

$$C_s = 0.04606_1 + 0.001237_1 \; T(cal \; g^{-1} \; K^{-1}) \tag{7}$$

Root mean square deviation (RMSD) = 0.0015_3 cal g^{-1} K^{-1}

RJ-4 (275-330 K)

$$C_s = 0.1377_2 + 0.001021_7 \; T(cal \; g^{-1} \; K^{-1}) \tag{8}$$

RMSD = 0.0018_4 cal g^{-1} K^{-1}

RJ-4-I (260-360 K)

$$C_s = 0.1412_6 + 0.001006_6 \; T(cal \; g^{-1} \; K^{-1}) \tag{9}$$

RMSD = 0.0030_8 cal g^{-1} K^{-1}

JP-9 (260-360 K)

$$C_s = 0.09299_8 + 0.001006_0 \; T(cal \; g^{-1} \; K^{-1}) \tag{10}$$

RMSD = 0.0041_0 cal g^{-1} K^{-1}

6. THERMODYNAMIC PROPERTIES OF ALKYLNAPHTHALENES AND INDANS

As part of a continuing study of alkylnaphthalenes and indans in which high steric energies may contribute to higher values of enthalpy of combustion, the vapor pressure of 2-ethyl-6-methylnaphthalene in the liquid state was determined by inclined-piston-gauge manometry with the results listed in the first two columns of Table 8. The data were represented with the equation:

$$\ln \underline{P}_R = \underline{A} + \underline{B}/\underline{T}_R - 3.013 \ln \underline{T}_R + 5.512 \underline{T}_R - 3.294 \ T_R{}^2$$

$$+ \underline{C}(-62.646 \ln \underline{T}_R + 77.392 \underline{T}_R - 19.424 \ \underline{T}_R{}^2) \qquad (11)$$

$$+ 0.176 \ \underline{P}_R \exp\{(1.65 + 0.8 \ \underline{C}/\underline{T}_R - 0.9 \ \underline{C}\} \ .$$

The constants obtained are:

$$\underline{A} = -11.72143 \pm 0.93$$

$$\underline{B} = -18.47791 \pm 0.36$$

$$\underline{C} = 0.4679775 \pm 0.021$$

with

$$\underline{P}_R/kPa = \frac{P/kPa}{\pi_c/kPa} \qquad\qquad \underline{T}_R = \frac{T/K}{\Theta_c/K}$$

$$\Theta_c/K = 769.5 \quad \text{and} \quad \pi_c/kPa = 2203.0.$$

The calculated values of vapor pressure are compared with the observed ones in the third and fourth columns of Table 8, and the weighting factors are listed in the final column.

The enthalpy of vaporization at selected temperatures was calculated by use of the Clapeyron equation and estimated values of the second virial coefficient and molal volume of liquid. The results are in Table 9.

TABLE 8. Vapor pressure of 2-ethyl-6-methylnaphthalene

T/K	p(obs)	p(calc)	p(obs) − p(calc)	σ
			kPa	
337.816	0.0283	0.0283	0.0000	0.00027
343.15	0.0403	0.0406	−0.0003	0.00027
348.15	0.0559	0.0562	−0.0003	0.00028
353.15	0.0769	0.0771	−0.0002	0.00029
358.15	0.1045	0.1045	0.0000	0.00029
363.15	0.1407	0.1402	0.0005	0.00030
368.15	0.1865	0.1864	0.0001	0.00031
373.15	0.2458	0.2454	0.0004	0.00032
378.15	0.3200	0.3203	−0.0003	0.00034
383.15	0.4144	0.4144	0.0000	0.00037
388.15	0.5317	0.5320	−0.0003	0.00039
393.15	0.6778	0.6775	0.0003	0.00043
398.15	0.8563	0.8564	−0.0001	0.00047
403.15	1.0743	1.0750	−0.0007	0.00052
408.15	1.3406	1.3400	0.0006	0.00057

TABLE 9. Enthalpy of vaporization of 2-ethyl-6-methylnaphthalene

| T/K	$\Delta_L^G H/\text{kJ mol}^{-1}$
298.15	68.94 ± 0.54
300.	68.77 ± 0.52
325.	66.54 ± 0.36
350.	64.46 ± 0.21
375.	62.49 ± 0.08
400.	60.60 ± 0.09
425.	58.77 ± 0.20
450.	56.98 ± 0.33

7. ACQUISITION OF RESEARCH SAMPLES

Research samples of 2,2'-biindanyl and 2,2'-bitetralin (compounds 6 and 7 of Nomenclature Section) were synthesized and purified at Oklahoma State University under purchase agreement with Professor E. J. Eisenbraun. Brief descriptions of their synthesis and purification follow. Full accounts of the synthesis routes used will appear in the chemical literature under Professor Eisenbraun's authorship; inquiries concerning the preparation of these materials may be addressed directly to him.

Lithium-ammonia Conversion of 5,6,6a,6b,7,8,12b,12c-Octahydrodibenzo[a,i]-biphenylene (1) to 1,1',2,2',3,3',4,4'-Octahydro-2,2'-binaphthyl (2)

A 25-g sample of the photodimer 1, was dissolved in 50-ml of anhydrous ether contained in a 1-liter round-bottomed flask. Anhydrous ammonia (500 ml) was condensed in the flask through use of a Dry Ice condenser. Li (14.4 g) as small pieces was added over 1 hour. Near the end of the addition period, the solution acquired a permanent blue color.

The reaction was quenched with solid ammonium chloride and the liquid ammonia was allowed to evaporate. About 500 ml of water was added with stirring and the resulting slurry was extracted with ether (3 x 150 ml). The extracts were combined, dried ($MgSO_4$), filtered and concentrated to give 23.4 g of 2, mp 83-85°.

The product was recrystallized from isohexane, ethanol, and from acetone. It was next chromatographed from 20 g of basic alumina contained in a Soxhlet apparatus using isohexane as eluant. The isohexane was evaporated and the product was distilled (Kugelrohr apparatus) at 140° (0.01 mm) to give 12.7 g of 2, mp 84-85°. The stereochemistry of 2 has been defined.[1]
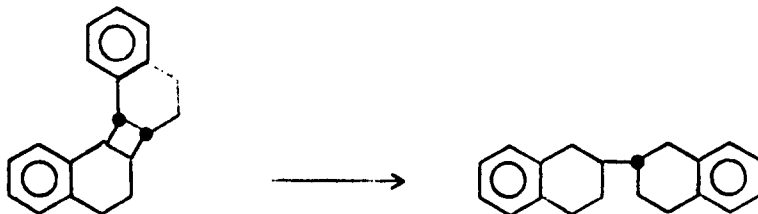
Reference

1. P. H. Ruehle, T. K. Dobbs, L. L. Ansell, Dick van der Helm, and E. J. Eisenbraun, J. Org. Chem., 42, 1098 (1977).

1   2
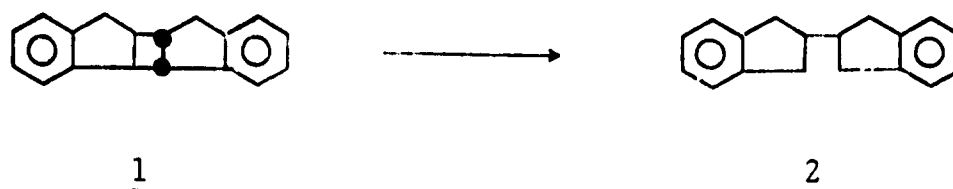
Lithium-Ammonia Reductive Cleavage of 4bβ,4cα,9,9aα,9bβ, 10-Hexahydrocyclobuta[1,2-a:4,3-a']diindene (1) to 2,2'-Biindanyl (2)

The indene photodimer 1, mp 110°, (PHR II-58c) was prepared[1] and purified[2] as previously described. A 20-g sample of 1 was reduced with Li in ammonia containing ether as cosolvent. The excess lithium was destroyed with 1,2-dibromoethane and 19.5 g of 2 was obtained. Light chromatography[3] and gas chromatography[4] studies showed the cleavage was complete.

The following steps were used to purify the product 2.

1. Recrystallization from acetone.

2. Chromatography using a Soxhlet apparatus containing a layer of 100 g of basic alumina (Merck activity I) and a layer of 100 g of acidic alumina (Merck activity I) with purified n-hexane as eluant. The eluant (~500 ml) was allowed to cool and the crystallized 2 was collected by filtration. Only the first crop of crystals were used in the subsequent steps.

3. Step 2 was repeated.

4. Recrystallization from anhydrous methanol to give 13.5 g, mp 165.5-166.5°C in 67% yield, (PHR II-67a).

5. Sublimation at 150° (0.02 mm) (PHR II-67B). The sample was bottled in an Argon atmosphere.

References and Notes

1. (a) P. H. Ruehle, T. K. Dobbs, L. L. Ansell, Dick
    van der Helm, and E. J. Eisenbraun, J. Org. Chem.,
    42, 1098 (1977).

2. Acetone was used for recrystallization of 1.

3. -Porasil column using purified isooctane as eluant.
    A uv detector was used.

4. A 0.25 in. x 6 ft. column containing 1% OV-17 on 80-100
    mesh Chromosorb G (AW amd DMCS treated at 180°C was
    used.

Synthesis in Progress

Several diakylindans and dialkylnaphthalenes are in the
process of synthesis and purification in Professor
Eisenbraun's laboratories.

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8. PUBLICATIONS AND PRESENTATIONS

Enthalpies of Combustion of
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Fuels, by W. D. Good

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