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THERMODYNAMICS OF ORGANIC COMPOUNDS.(U)
SEP 77 W D GOOD, D W SCOTT, N K SMITH

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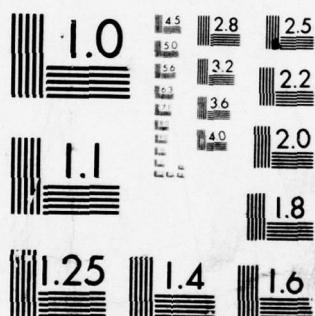
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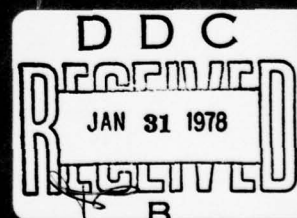
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Research continued on hydrocarbons with unusual strained bridging bonds that may contribute knowledge needed to tailor organic molecules having good energy/volume or energy/mass characteristics. Three compounds were studied containing the cyclo-butane bridge, a study commenced in FY 76. A study was begun on certain alkyl naphthalenes and indans in which high steric interaction energy should contribute to high enthalpy of combustion. Two ram-jet fuels were studied, fuels already in use.		

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FINAL TECHNICAL SUMMARY REPORT

THERMODYNAMICS OF ORGANIC COMPOUNDS

Bartlesville Energy Research Center
Energy Research and Development Administration
Bartlesville, Oklahoma

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DDC	Buff Section ☐
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Project Director: W. D. Good

Report* prepared by: N. K. Smith
D. W. Scott
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 the program are formulated within the framework of an integrated and interrelated program of experimental and theoretical research in chemical thermodynamics and thermochemistry. Emphasis is placed on areas of unclassified work that complement, wherever possible, developments in the studies of organic derivatives of the lighter elements as they relate to the thermochemical technology of possible new high energy fuels.

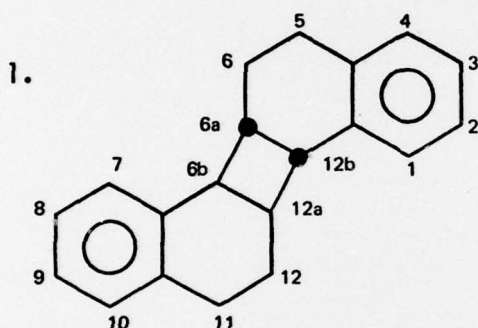
ABSTRACT

Research continued on hydrocarbons with unusual strained bridging bonds that may contribute knowledge needed to tailor organic molecules having good energy/volume or energy/mass characteristics. Three compounds were studied containing the "cyclo-buta" bridge, a study commenced in FY 76. A study was begun on certain alkylnaphthalenes and indans in which high steric interaction energy should contribute to high enthalpy of combustion. Two ram-jet fuels were studied, fuels already in use.

I. NOMENCLATURE OF COMPOUNDS

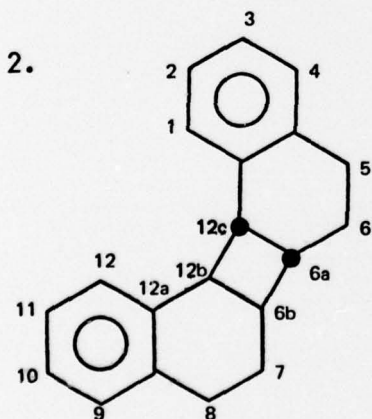
Research on the synthesis, purification and thermodynamic properties of several rather complex organic compounds will be described in this annual report. In an effort to facilitate understanding, the molecular structure and nomenclature for these compounds is given in Table I.

TABLE I. Nomenclature of Compounds *



5,6,6a β ,6b α ,11,12,12a α ,12b β -
Octahydrocyclobuta[1,2-a:3,4-a']-
dinaphthalene (or)

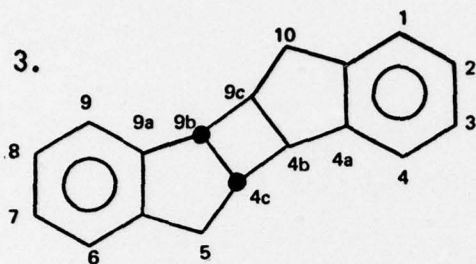
5,6,6a,6b,11,12,12a,12b-Octa-
hydrodibenzo[a,g]biphenylene



5,6,6a β ,6b α ,7,8,12b α ,12c β -
Octahydrocyclobuta[1,2-a:4,3-a']-
dinaphthalene (or)

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

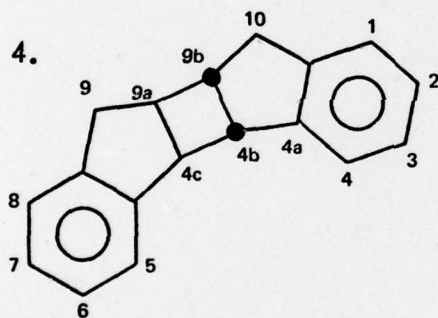
TABLE I. Nomenclature of Compounds *--Continued



4b α , 4c β , 5, 9b β , 9c α , 10-
Hexahydrocyclobuta[1,2-a:3,4-a']-
diindene

(or)

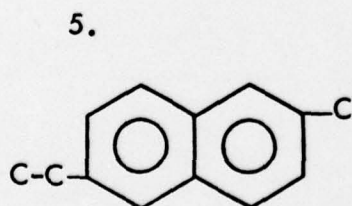
anti, trans-Truxane



4b β , 4c α , 9, 9a α , 9b β , 10-
Hexahydrocyclobuta[1,2-a:4,3-a']-
diindene

(or)

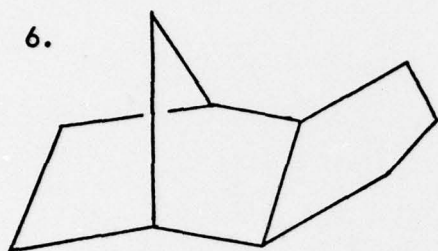
syn, trans-Truxane



2-Ethyl-6-methylnaphthalene

TABLE I. Nomenclature of Compounds *--Continued

6.

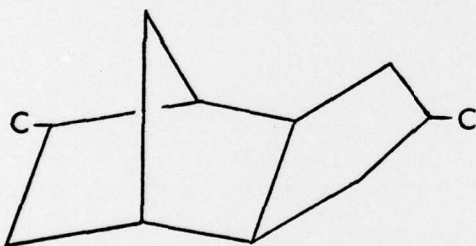


"exo-THDC"

(or)

exo-Tetrahydrodicyclopentadiene

7.



"RJ-4"

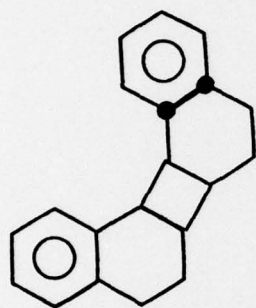
(or)

Tetrahydromethylcyclopentadiene
dimer

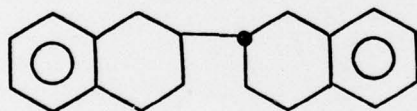
-
- * α indicates that hydrogen atom is below the plane of the paper.
 β indicates that hydrogen atom is above the plane of the paper.

II. ENTHALPIES OF COMBUSTION OF COMPOUNDS WITH BRIDGING BONDS BETWEEN RING SYSTEMS

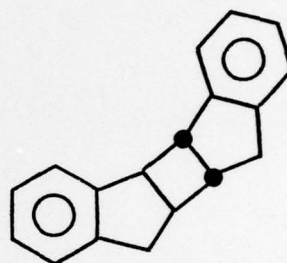
Research in the laboratories of Professor E. J. Eisenbraun at Oklahoma State University¹ showed that hydrocarbons (1) and (2) are selectively cleaved to hydrocarbons (3) and (4) by treatment with lithium or sodium in ether-ammonia (Birch reduction).



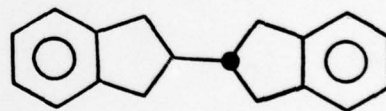
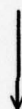
(1)



(3)

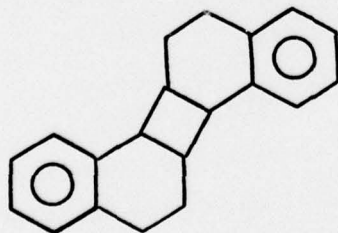


(2)

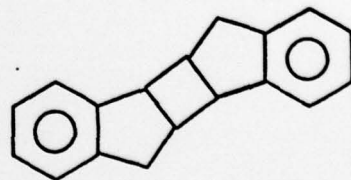


(4)

In contrast, hydrocarbons (5) and (6), isomers of (1) and (2), respectively,



(5)



(6)

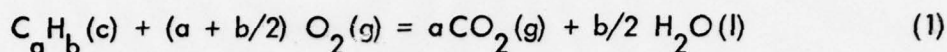
¹ P. H. Ruehle, T. K. Dobbs, L. L. Ansell, Dick van der Helm, and E. J. Eisenbraun, *J. Org. Chem.*, 42, 1098 (1977).

are totally inert to the lithium-ammonia cleavage reaction under comparable conditions. It has been shown by x-ray crystallographic analysis² of hydrocarbon (1) that the four-membered ring is planar and that it has an elongated bond (1.579 Å). It is this bond that is cleaved during the lithium-ammonia reduction. It was suggested¹ that relief of steric strain is involved in the reductive cleavage of (1). Measurement of the thermodynamic properties of these compounds commenced in FY 1976, and the value of the enthalpy of combustion of compound (2) was reported in FY 76. Measurement of the enthalpy of combustion of compounds (1), (3) and (4) has been completed in FY 77. Derived molar values of ΔE_c° , the standard energy of the idealized combustion reaction, ΔH_c° , the standard enthalpy of combustion, and ΔH_f° , the standard enthalpy of formation, of compounds 1, 2, 3 and 4 are given in Table II. All values are for the crystalline state at 298.15 K. Table II values of ΔE_c° and ΔH_c° refer to the idealized combustion reaction (1).

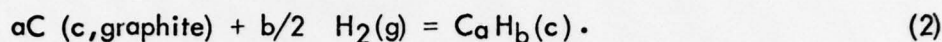
TABLE II. Derived Molar Values for Crystalline State at 298.15 K

Compound (State)	Empirical Formula	$\frac{-\Delta E_c^\circ}{\text{kcal mol}^{-1}}$	$\frac{-\Delta H_c^\circ}{\text{kcal mol}^{-1}}$	$\frac{-\Delta H_f^\circ}{\text{kcal mol}^{-1}}$
5,6,6a,6b,11,12,12a,12b- Octahydrodibenzo [<u>a</u> , <u>g</u>]- biphenylene	C ₂₀ H ₂₀	-2578.01±0.58	-2580.97±0.58	16.80±0.64
5,6,6a,6b,7,8,12b,12c- Octahydrodibenzo [<u>a</u> , <u>i</u>]- biphenylene	C ₂₀ H ₂₀	-2580.37±0.36	-2583.33±0.36	19.15±0.43
4b α ,4c β ,5,9b β ,9c α ,10- Hexahydrocyclobuta- [1,2-a: 3,4-a'] diindene	C ₁₈ H ₁₆	-2274.13±0.38	-2276.50±0.38	37.06±0.44
4b β ,4c α ,9,9a α ,9b β ,10- Hexahydrocyclobuta- [1,2-a: 4,3-a'] diindene	C ₁₈ H ₁₆	-2274.79±0.76	-2277.16±0.76	37.73±0.80

² J. E. Burke, Jr., D. van der Helm, T. K. Dobbs, L. L. Ansell, P. H. Ruehle, and E. J. Eisenbraun, *Acta Crystallogr.*, submitted.



Values of ΔH_f° refer to reaction (2)



The 1961 atomic weight scale was used ($C = 12.01115$, $H = 1.00797$) as was the defined thermochemical calorie equal to 4.184 joules. All uncertainties are the "uncertainty interval" equal to twice the final overall standard deviation of the mean.

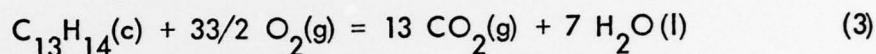
Comparison of the values of Table II shows that hydrocarbon (2) may have about 2 kilocalories more "strain" than hydrocarbon (1) and likewise that hydrocarbon (4) may be more strained by about 0.6 kilocalorie than hydrocarbon (3). It would be more informative if it were possible to compare these molecules in the ideal gaseous state, but values of the enthalpy of vaporization are not available.

Carbon dioxide was recovered from the combustion products of all four of these compounds having the "cyclobuta" bridge. While carbon dioxide recovery is not an absolute check on purity, quantitative carbon dioxide recovery is an excellent indication of the absence of all but isomeric impurity. Values of carbon dioxide recovery (mean value and standard deviation of the mean) were:

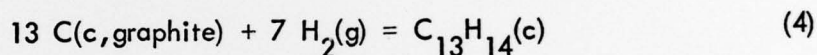
5,6,6a,6b,11,12,12a,12b- Octahydrodibenzo [<u>a</u> , <u>g</u>]- biphenylene	100.005 $\pm$ 0.004 percent
5,6,6a,6b,7,8,12b,12c- Octahydrodibenzo [<u>a</u> , <u>i</u>]- biphenylene	99.972 $\pm$ 0.006
4b α ,4c β ,5,9b β ,9c α ,10- Hexahydrocyclobuta- [1,2-a: 3,4a'] diindene	99.985 $\pm$ 0.002
4b β ,4c α ,9,9a α ,9b β ,10- Hexahydrocyclobuta- [1,2-a: 4,3-a'] diindene	99.994 $\pm$ 0.004

III. THERMODYNAMIC PROPERTIES OF ALKYLNAPHTHALENES AND INDANS

Earlier research of this laboratory has shown³ that the enthalpy of combustion of 1,8-dimethylnaphthalene is greater than that of 2,3-, 2,6-, and 2,7-dimethylnaphthalene by 7 or 8 kcal mol⁻¹. This finding is being pursued into the methyl-ethyl and methyl-isopropyl naphthalenes and indans. The first of these compounds, 2-ethyl-6-methylnaphthalene, has been synthesized and purified in the laboratories of Professor E. J. Eisenbraun at Oklahoma State University. The enthalpy of combustion has been measured, and the enthalpy of formation was derived. For combustion according to equation (3),



ΔEc° , the standard enthalpy of the idealized combustion reaction, is -1691.60 ± 0.36 kcal mol⁻¹, and ΔHc° , the standard enthalpy of combustion, is -1693.67 ± 0.36 kcal mol⁻¹. For formation according to reaction (4), ΔHf° ,



the standard enthalpy of formation, is -7.19 ± 0.38 kcal mol⁻¹. All thermodynamic values refer to 298.15 K, the defined calorie equal to 4.184 joules and the 1961 atomic weight scale. Carbon dioxide recovery in the combustion products of 2-ethyl-6-methylnaphthalene was 99.998 ± 0.003 percent (mean and standard deviation of the mean) of that expected.

Measurements of the vapor pressure of 2-ethyl-6-methylnaphthalene are in progress from which the value of the enthalpy of sublimation will be derived.

Synthesis and purification of 1-ethyl-8-methylnaphthalene, 1-isopropyl-8-methylnaphthalene and 2-isopropyl-6-methylnaphthalene are in progress.

³ Good, W. D. J. Chem. Thermodynamics, 1973, 5, 715-720.

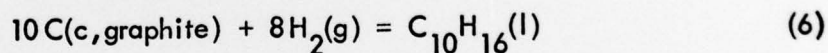
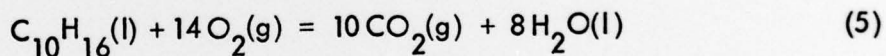
IV. ENTHALPIES OF COMBUSTION OF RAM-JET FUELS

In cooperation with researchers at Wright-Patterson Air Force Base and the Naval Weapons Center, precise measurements were made of the enthalpies of combustion of two ram-jet fuels currently in use, *exo*-tetrahydrodicyclopentadiene or "*exo*-THDC" and tetrahydromethylcyclopentadiene dimer or "RJ-4", compounds 6 and 7 of Table I. *exo*-THDC is a rather pure organic compound, but RJ-4 is a complex mixture of isomers, all of formula $C_{12}H_{20}$. Molar values of ΔE_c° , the standard energy of the idealized combustion reaction, ΔH_c° , the standard enthalpy of combustion, and ΔH_f° , the standard enthalpy of formation, are given in Table III.

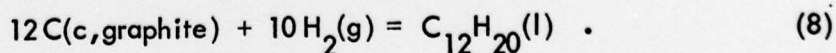
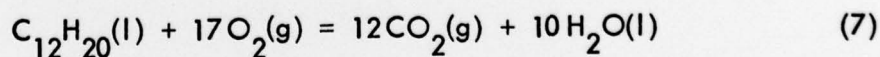
TABLE III. Derived Molar Values for Liquid State at 298.15 K

Compound	Formula	ΔE_c° kcal mol ⁻¹	ΔH_c° kcal mol ⁻¹	ΔH_f° kcal mol ⁻¹
<i>exo</i> -Tetrahydrodicyclopentadiene (<i>exo</i> -THDC)	$C_{10}H_{16}$	-1455.27 ± 0.32	-1457.64 ± 0.32	-29.39 ± 0.36
Tetrahydromethylcyclopentadiene dimer (RJ-4)	$C_{12}H_{20}$	-1770.32 ± 0.38	-1773.28 ± 0.38	-38.48 ± 0.40

The idealized combustion and formation reactions for *exo*-tetrahydrodicyclopentadiene, *exo*-THDC, are (5) and (6), respectively. The idealized combustion and formation



reactions for tetrahydromethylcyclopentadiene dimer, RJ-4, are (7) and (8), respectively.

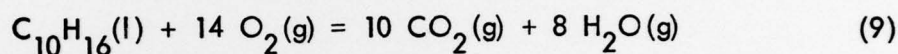


All values refer to 298.15 K, the defined calorie equal to 4.184 joules and the 1961 atomic weight scale.

Carbon dioxide in the combustion products of exo-THDC was $99.99_1 \pm 0.00_4$ percent of that expected from the empirical formula, and carbon dioxide recovery from RJ-4 was $99.98_3 \pm 0.00_6$ percent of that expected.

It should be noted that the values in Table III are for the enthalpy of combustion to gaseous carbon dioxide and liquid water, the so-called "gross" heat of combustion. For combustion to gaseous carbon dioxide and gaseous water, the combustion reactions become (9) and (10) for exo-THDC and RJ-4, respectively.

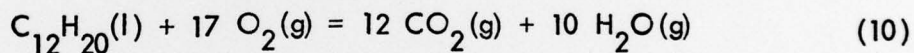
exo-THDC



$$\Delta \text{Hc}^\circ (298.15) = -1373.48 \pm 0.32 \text{ kcal mol}^{-1}$$

$$= -18134 \text{ Btu lb}^{-1}$$

RJ-4



$$\Delta \text{Hc}^\circ (298.15) = -1668.08 \pm 0.38 \text{ kcal mol}^{-1}$$

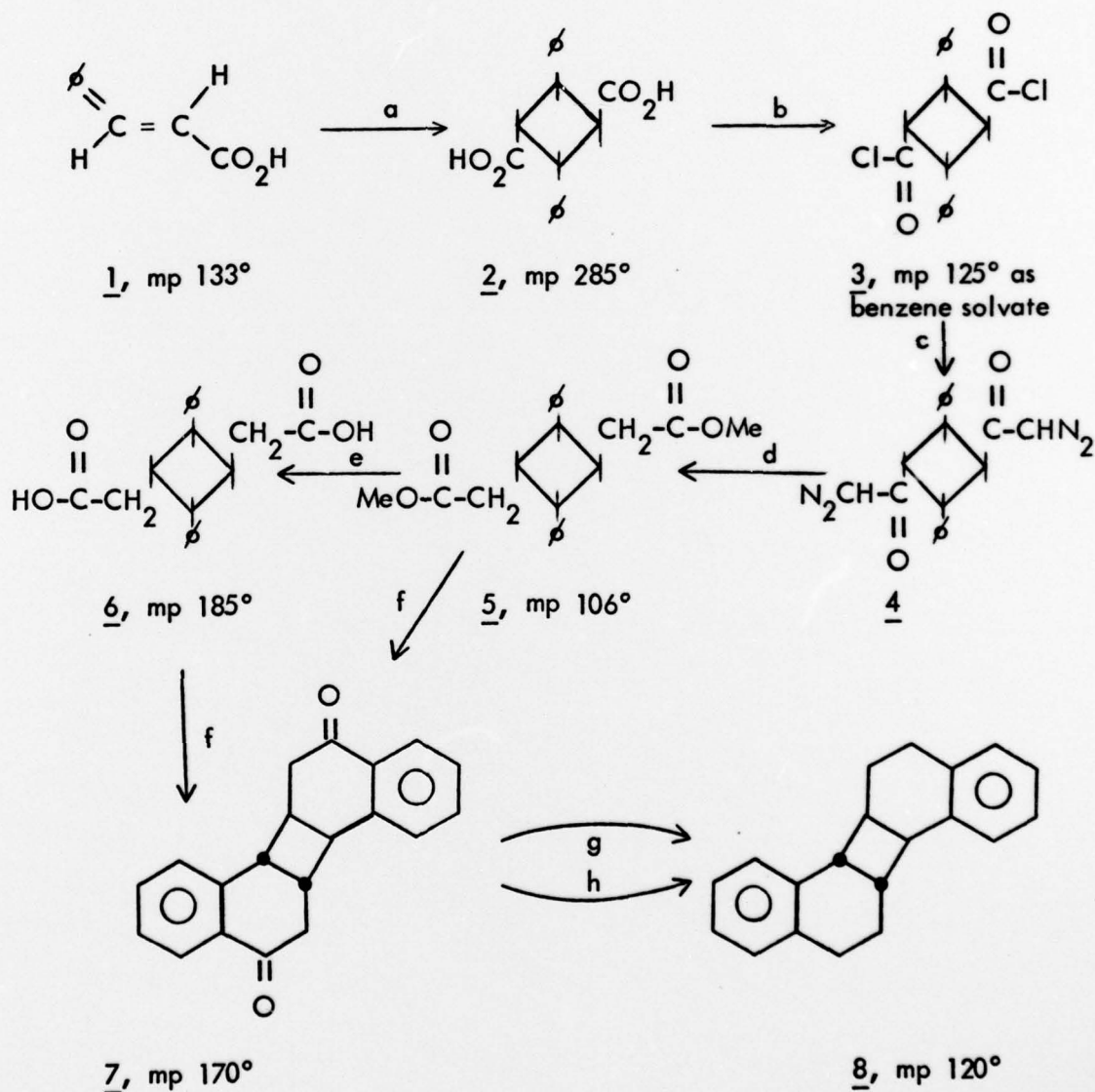
$$= -18264 \text{ Btu lb}^{-1}$$

These values are the so-called "net" heat of combustion.

V. ACQUISITION OF RESEARCH SAMPLES

Research samples of the pure compounds listed in Table I were synthesized and purified at Oklahoma State University under purchase agreement with Professor E. J. Eisenbraun. 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.

5,6,6a,6b,11,12,12a,12b-Octahydrodibenzo [a,g] biphenylene was prepared by the following synthesis route:



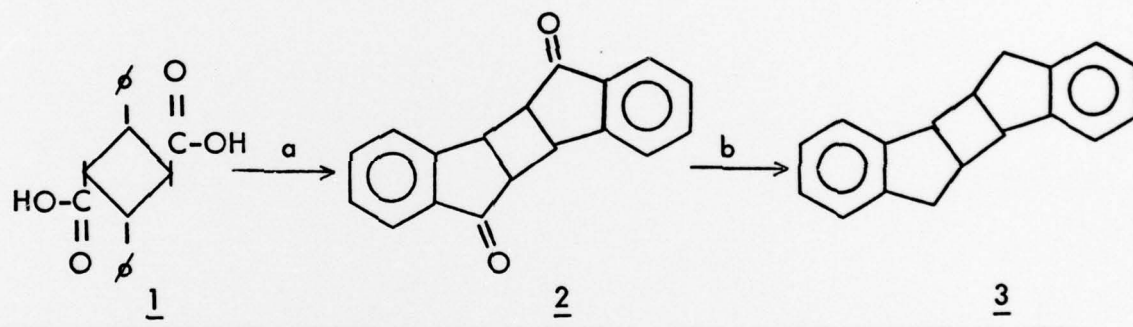
^ah ν . ^bSOCl₂. ^cCH₂N₂. ^dCO₂Ag, Et₃N, CH₃OH. ^eOH⁻, H₃O⁺. ^fPPA, Δ .

^gPd/C, H₂, HOAc, Δ . ^hNH₂NH₂, OH⁻, glycol, Δ .

A 17.6 g sample of hydrocarbon 8, mp 119-120°, obtained from the previous reaction sequence and a subsequent Soxhlet extraction using acidic (1078) and basic (1076) Merck alumina with purified isohexane (Phillips Petroleum Co.), was recrystallized from acetone to give 15.5 g of 8 as a first crop. This fraction was distilled using a Kugelrohr apparatus at 200° (0.2 mm) to give 8, mp 120-121°.

5,6,6a,6b,7,8,12b,12c-Octahydrodibenzo [a,i] biphenylene synthesis was described in the report for fiscal year 1976.

4 α ,4 β ,5,9 β ,9 α ,10-Hexahydrocyclobuta [1,2-a:3,4-a'] diindene was prepared by the following synthesis route:



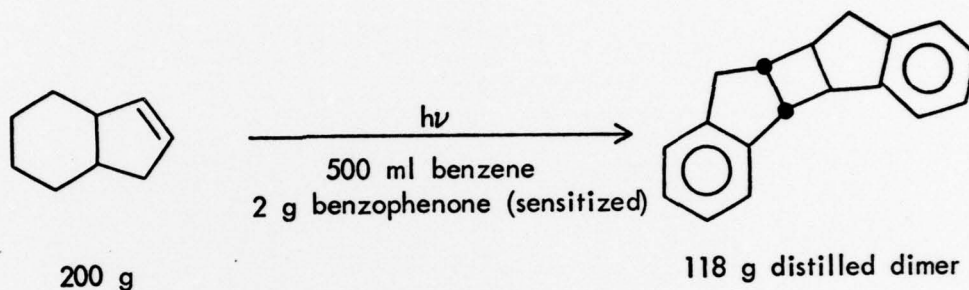
^aHF. ^b $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, diethylene glycol, Δ .

A 100 g (0.34 mol) sample of α -truxillic acid 1, mp 284-285° C, was cyclized by treating with liquid HF to yield 70 g (0.27 mol) of α -truxone 2 in 80% yield. This was purified to 2, mp 298-299° C, by Soxhlet extraction through basic alumina with toluene.

α -Truxone 2 (70 g, 0.27 mol) was then deoxygenated through the Wolff-Kischner process ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, KOH, Δ) to give 35 g (0.15 mol) of the diindene 3 in 56% yield. This hydrocarbon was partially purified by recrystallization from acetone, and the final purification of 35.5 g consisted of chromatography on 200 g of Merck basic alumina (no. 1976) using purified hexanes (Phillips Petroleum Co. isohexanes) in a Soxhlet apparatus. The eluate was concentrated and 3 was allowed to crystallize. The above process was repeated using the first crop of crystals with the modification that the alumina column was made up from 100 g acidic (no. 1078) and 100 g basic (no. 1076) Merck alumina.

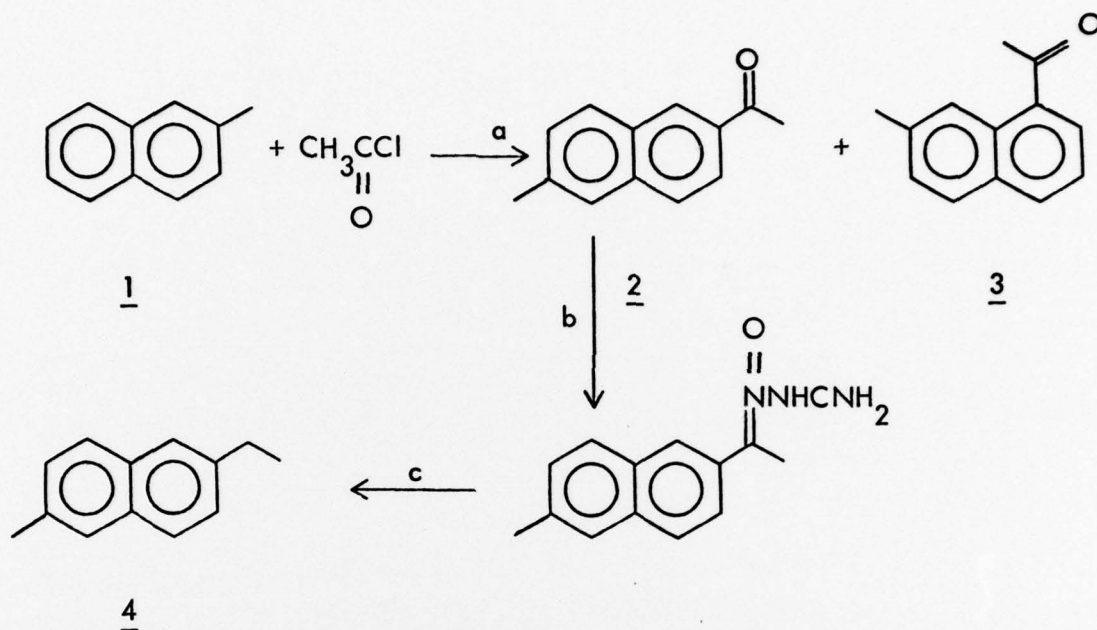
The first crystals from the second treatment were recrystallized from acetone and then distilled using a Kugelrohr distillation apparatus at about 190° C (0.2 mm) to give purified 3, mp 142-143°.

4b β , 4c α , 9, 9a α , 9b β , 10-Hexahydrocyclobuta[1, 2a:4, 3-a']diindene was prepared by the following reaction scheme:



1. Chromatography with isohexane (Soxhlet) on 200 g neutral alumina and crystallization from isohexane gave two crops of crystals -- 85 g.
2. Chromatography through 100 g acidic plus 100 g basic alumina with isohexane gave 61 g of white crystals free of isomeric impurities and a second crop of less pure material which was not used.
3. 61 g crop was recrystallized from MeOH, and only first crop was used.
4. Sample recrystallized from purified cyclohexane, two crops -- 35 g.
5. Sample sublimed at 0.2 mm and ca 150° C.
 No impurities by GC on UC W-98 or Carbowax 20M (which separates isomers).
 No residual indene or impurities by LC (C₁₈ methanol-H₂) gradient on UV detector).

2-Ethyl-6-methylnaphthalene 4 was synthesized as shown in the reaction scheme. Acetylation of 2-methylnaphthalene and separation of isomers through crystallization yielded 6-methyl-2-acetonaphthone 2. In addition to 7-methyl-1-acetonaphthone, three other minor peaks were observed in the gas chromatogram of the crude product.



^a AlCl_3 , $\text{CH}_3\text{CH}_2\text{NO}_2$. ^b $\text{NH}_2\text{NHCNH}_2 \cdot \text{HCl}$, $\text{CH}_3\text{CO}_2\text{Na}$. ^c KOH , diethylene glycol, Δ .

The ketone 2 was converted to the semicarbazone derivative, mp 236–237° dec. (lit. 237°), which was purified by leaching with hot 95% ethyl alcohol and then directly subjected to reduction in presence of NaOH in refluxing diethylene glycol. This reduction resulted in 2-ethyl-6-methylnaphthalene 4, which was purified as described below.

The crude 4 from the hydrazine reduction was collected in two fractions as a distillate during the reaction. The first cut was free of impurity peaks in the GC (6% UC W-98 on Chrom G at 180°). The second cut showed two minor impurity peaks. This cut was not used.

A picrate of 4 was prepared from cut 1. Recrystallization from 95% ethanol yielded a picrate of 4, mp 107.5–108.5° (lit. 109°) which was cleaved with hexane using a basic alumina column. The hexane solvent was removed and hydrocarbon 4 was recrystallized from methanol, filtered, and finally distilled using the Kugelrohr apparatus. This procedure yielded 4, mp 42.5–43.5° (lit. 44–45°), which was free of impurities by GC analysis.

VI. PUBLICATIONS

The Enthalpies of Formation of Selected Naphthalenes, Diphenylmethanes, and Bicyclic Hydrocarbons by W. D. Good and S. H. Lee

J. Chem. Thermodynamics, 1976, 8, 643-650.

The Enthalpies of Formation of Some Bridged-Ring Polynuclear Aromatic Hydrocarbons by W. D. Good

Accepted for publication by J. Chem. Thermodynamics.

Thermodynamic Properties of Cyclopropylamine, Cyclopentylamine, and Methylene cyclobutane

Internal editorial review in progress.