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BARTLESVILLE ENERGY RESEARCH CENTER OKLA
THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS AND THERMODYNAMIC--ETC(U)
1976 D R DOUSLIN, D W SCOTT, W D GOOD

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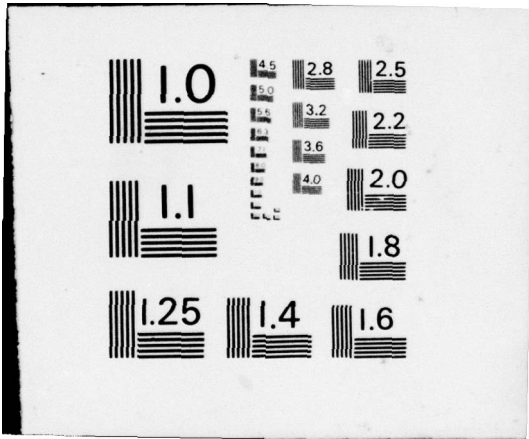
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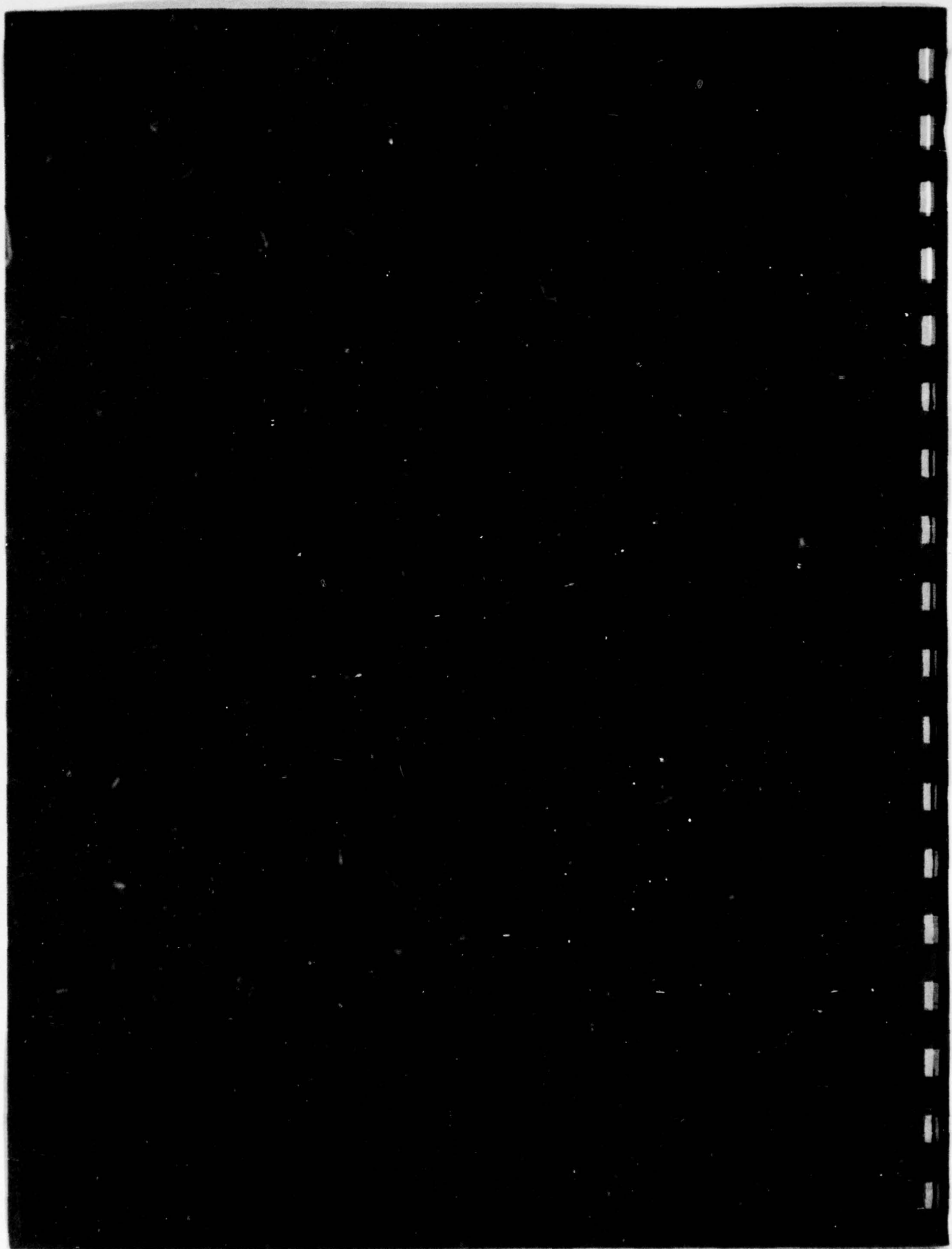


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19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 18 AFOSR TR-76-1075	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS AND THERMODYNAMIC PROPERTIES OF FLUIDS.		5. TYPE OF REPORT & PERIOD COVERED FINAL 1 July 1975 - 30 June 1976
7. AUTHOR(s) DONALD R. DOUSLIN, ↓ ANN G. OSBORN DONALD W. SCOTT WILLIAM D. GOOD		6. PERFORMING ORG. REPORT NUMBER
8. CONTRACT OR GRANT NUMBER(s) AFOSR-ISSA-76-0002		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 681308 9750-01 61102F
9. PERFORMING ORGANIZATION NAME AND ADDRESS BARTLESVILLE ENERGY RESEARCH CENTER ✓ ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION BARTLESVILLE, OKLAHOMA 74003		11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332		12. REPORT DATE 1976
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 17
9 Final technical summary rept. 1 Jul 75 - 30 Jun 76		15. SECURITY CLASS. (of this report) UNCLASSIFIED
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited 16 AF-9750 17 975001		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) THERMAL PROPERTIES BIPHENYLENE ENTHALPY OF COMBUSTION TRIPHENYLENE ENTHALPY OF FORMATION DODECAHYDROTRIPHENYLENE VAPOR PRESSURE VAPOR HEAT CAPACITY ENTHALPY OF VAPORIZATION & SUBLIMATION (cont)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The search for molecular hydrocarbon structures that contain higher energies than usual hydrocarbon jet fuel liquids was centered on compounds that contain strained bridging bonds between ring systems. Enthalpies of combustion and formation, vapor pressures, enthalpies of sublimation and vaporization, and chemical thermodynamic properties were determined.		

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SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Key Words (cont)

5,6,6a,6b,7,8,12b,12c-OCTAHYDRODIBENZO a,i -BIPHENYLENE
1,2'-DINAPHTHYLMETHANE
1',2',3',4'-TETRAHYDRO-1,2'-BINAPHTHYLMETHANE
1,3-EPOXYPROPANE

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FINAL TECHNICAL SUMMARY REPORT

THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS

AND

THERMODYNAMIC PROPERTIES OF FLUIDS

* * * * *

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

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Project Director: D. R. Douslin

Report* prepared by: D. W. Scott
W. D. Good
A. G. Osborn
D. R. Douslin

* 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

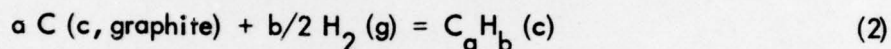
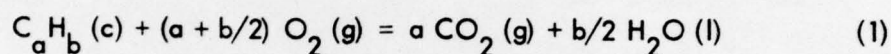
The objectives of the program are formulated within the framework of an integrated and interrelated program of experimental and theoretical research in chemical thermodynamics and thermochemistry. Emphasis is placed on areas of unclassified work that complement, wherever possible, developments in the studies of organic derivatives of the lighter elements as they relate to the thermochemical technology of possible new high energy fuels.

ABSTRACT

The search for molecular hydrocarbon structures that contain higher energies than usual hydrocarbon jet fuel liquids was centered on compounds that contain strained bridging bonds between ring systems. Enthalpies of combustion and formation, vapor pressures, enthalpies of sublimation and vaporization, and chemical thermodynamic properties were determined.

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

Enthalpies of combustion were measured for six compounds that have bridging bonds between both aromatic and saturated ring systems. 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, all for the crystalline state, and the derived value of $\Delta H_f^\circ(g)$ (298.15 K) for biphenylene only, are given in Table I. Values of ΔE_c° and ΔH_c° refer to the idealized combustion reaction (1). Values of ΔH_f° refer to reaction (2).



All uncertainties are the "uncertainty interval" equal to twice the final overall standard deviation of the mean.

Carbon dioxide recoveries from the combustion products of all six compounds were essentially quantitative, an excellent evidence of the purity of the compounds.

Two of the compounds had been studied previously, but a new study appeared worthwhile either because of relatively high uncertainties or of disagreement in earlier values. A comparison of results is given in Table II. The value of Bedford *et al.*⁽¹⁾ for biphenylene does not agree with the more precise value of this research. The value of Magnus *et al.*⁽²⁾ for triphenylene almost agrees with the value of the present research. No explanation can be offered for the disagreement with the value of Westrum and Wong.⁽³⁾

¹ Bedford, A. F., J. G. Carey, I. T. Millar, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.* 3895 (1962).

² Magnus, A., H. Hartmann, and F. Becker, *Z. Phys. Chem.*, 197, 75 (1951).

³ Westrum, E. F., and S. Wong, *Thermodynamics Symposium*, Paper II 10, Heidelberg, 1967.

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

Compound	Empirical Formula	ΔE_c° kcal mol ⁻¹	ΔH_c° kcal mol ⁻¹	ΔH_f° kcal mol ⁻¹
Biphenylene	C ₁₂ H ₈	-1480.38±0.22	-1481.56±0.22	+79.68±0.26 ^a
Triphenylene	C ₁₈ H ₁₂	-2137.33±0.29	-2139.11±0.29	+36.28±0.35
Dodecahydro- triphenylene	C ₁₈ H ₂₄	-2462.81±0.32	-2466.37±0.32	-46.34±0.40
5,6,6a,6b,7,8,12b,12c- Octahydrodibenzo[<i>a</i> , <i>i</i>]- biphenylene	C ₂₀ H ₂₀	-2580.37±0.36	-2583.33±0.36	+19.15±0.43
1,2'-Dinaphthylmethane	C ₂₁ H ₁₆	-2557.96±0.40	2560.33±0.40	+38.73±0.46
1',2',3',4'-Tetrahydro- ^b 1,2'-dinaphthylmethane	C ₂₁ H ₂₀	-2665.82±0.36	-2668.78±0.36	+10.55±0.44

^a $\Delta H_f^\circ(g)$ (298.15 K) = 79.68 ± 0.26 + 20.8 ± 0.2 = 100.48 ± 0.46 kcal mol⁻¹.

^b Alternate nomenclature, 2-(1-naphthylmethyl)-1,2,3,4-tetrahydronaphthalene.

TABLE II. Comparison of Results. Molar Enthalpies
of Combustion in Crystalline State

Compound	$\Delta H_c^\circ (298.15)$ kcal mol ⁻¹	Reference
Biphenylene	-1486.3 ± 1.4	Reference 1
	-1481.56 ± 0.22	This Research
Triphenylene	-2138.01 ± 0.52	Reference 2
	-2136.53 ± 0.11	Reference 3
	-2139.11 ± 0.29	This Research

II. VAPOR PRESSURE AND ENTHALPIES OF VAPORIZATION AND SUBLIMATION OF BIPHENYLENE

The inclined-piston method^(4, 5) was used to determine vapor pressures in solid and liquid phases of biphenylene, Table III. From the intersection of vapor pressure curves, an approximate melting temperature, 110.9°C, was determined which, although imprecise according to calorimetric standards, is much better than the range 109.5 - 111°C reported in the literature. By use of the Clapeyron equation and the vapor pressure derivative, $d \ln p/d(1/T)$, determined by graphical differentiation of the data in Table III, the enthalpies of vaporization and sublimation, Table III, were determined over a center section of the temperature range covered by the vapor pressure measurements on each phase. Also, an approximate value for the enthalpy of fusion, 5120 cal mol⁻¹, was obtained as the difference in the enthalpies of sublimation and vaporization extrapolated to the melting temperature.

The derived values of the enthalpy of sublimation, which are linear with respect to temperature within experimental precision, were extrapolated to 298.15 K to obtain 20.8 ± 0.2 kcal mol⁻¹. This value is in marked disagreement with 30.8 kcal mol⁻¹, also obtained by extrapolation, as reported by Cass, Springall, and Quincey.⁽⁶⁾

From the derived enthalpy of sublimation for biphenylene, 20.8 ± 0.2 kcal mol⁻¹, described in the section on vapor pressure measurements, its standard enthalpy of formation in the gas state, $\Delta H_f^\circ(g)$, is 100.48 ± 0.46 kcal mol⁻¹, in serious disagreement with the value 115.2 ± 1.5 ⁽³⁾ kcal mol⁻¹ determined by Cass, Springall and Quincey and Bedford, Carey, Millar, Mortimer, and Springall as quoted by Cox and Pilcher.⁽⁷⁾ The major cause for the disagreement is in the widely different values for the enthalpy of sublimation.

⁴ Douslin, D. R., and A. G. Osborn, *J. Sci. Instr.*, **42**, 369 (1965).

⁵ Osborn, A. G., and D. R. Douslin, *J. Chem. Eng. Data*, **20**, 229 (1975).

⁶ Cass, R. C., H. D. Springall, and P. G. Quincey, *J. Chem. Soc.*, 1188 (1955).

⁷ Cox, J. D., and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.

TABLE III. Vapor Pressure and Enthalpies of Vaporization and Sublimation of Biphenylene

$t, ^\circ\text{C}$	$p, \text{ mm Hg}$	$\Delta H_v, \text{ cal}_{\text{th}} \text{ mol}^{-1}$
	SOLID	
65	0.132	
70	0.206	
75	0.312	20,133
80	0.470	20,095
85	0.703	20,019
90	1.038	19,980
95	1.507	19,840
100	2.167	
105	3.083	
109	4.062	
	LIQUID	
111	4.651	
115	5.679	14,337
120	7.158	14,059
125	8.957	13,948
130	11.141	13,790
135	13.766	

III. THERMODYNAMIC PROPERTIES OF 1,3-EPOXYPROPANE (TRIMETHYLENE OXIDE)

In the Annual Progress Report for the period July 1974 - June 1975, AFOSR-TR-75-1364, vapor pressures, enthalpy of vaporization, and revised standard entropy were reported as a continuation of the low-temperature properties in the condensed solid and liquid phases reported in the Annual Technical Summary 1973-74. Calculation of the chemical thermodynamic properties in the perfect gas state, which was completed under last year's contract but was not completed in time to appear in the Annual Progress Report for 1974-75, is reported here.

A revision of a table of the chemical thermodynamic properties of 1,3-epoxypropane (trimethylene oxide) was made on the basis of experimental values of the vapor heat capacity reported in Annual Progress Report 1974-75. A comparison of observed versus calculated vapor heat capacity are in Table IV, and the standard chemical thermodynamic properties based on a statistical mechanical treatment of the spectroscopic and experimental thermodynamic data are in Table V.

TABLE IV. Comparison of Observed and Calculated Vapor Heat Capacity for 1,3-Epoxypropane

T	C_p° (obs)	C_p° (calc)	C_p° (obs) - C_p° (calc)
K	$\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
298.15	14.63	14.61	0.02
323.15	15.94	15.92	0.02
348.15	17.26	17.26	0.00
373.15	18.61	18.61	0.00
398.15	19.92	19.94	-0.02
423.15	21.21	21.24	-0.03
448.15	22.48	22.50	-0.02
473.15	23.68	23.69	-0.01
498.15	24.84	24.84	0.00
523.15	25.97	25.95	0.02

TABLE V. Standard Chemical Thermodynamic Properties of 1,3-Epoxypropane in the Ideal Gas State

T K	$-\frac{\{G^\circ(T)-H^\circ(0)\}}{T}$ cal _{th} K ⁻¹ mol ⁻¹	$\frac{\{H^\circ(T)-H^\circ(0)\}}{T}$ cal _{th} K ⁻¹ mol ⁻¹	$H^\circ(T)-H^\circ(0)$ kcal _{th} mol ⁻¹	S° cal _{th} K ⁻¹ mol ⁻¹	C_p° cal _{th} K ⁻¹ mol ⁻¹	$\frac{\Delta H_f^\circ}{T}$ kcal _{th} mol ⁻¹	$\frac{\Delta G_f^\circ}{T}$ kcal _{th} mol ⁻¹	$\log_{10} K_f^\circ$
0	0	0	0	0	0	-14.44	-14.44	∞
200	50.64	9.24	1.848	59.88	10.48	-17.65	-7.46	8.16
273.15	53.61	9.93	2.711	63.54	13.36	-18.86	-3.55	2.84
298.15	54.49	10.27	3.061	64.76	14.61	-19.25	-2.12	1.56
300	54.56	10.29	3.087	64.85	14.71	-19.28	-2.02	1.47
400	57.75	12.06	4.825	69.81	20.04	-20.72	+3.96	-2.17
500	60.66	14.16	7.08	74.82	24.93	-21.88	10.27	-4.49
600	63.43	16.31	9.78	79.74	29.02	-22.79	16.79	-6.12
700	66.10	18.37	12.86	84.47	32.41	-23.48	23.45	-7.32
800	68.68	20.31	16.25	88.99	35.25	-23.99	30.19	-8.25
900	71.18	22.11	19.90	93.29	37.66	-24.34	36.66	-8.90
1000	73.60	23.77	23.77	97.37	39.70	-24.56	43.81	-9.57

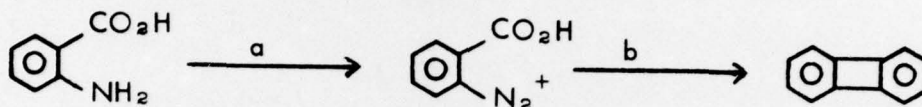
^a The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction:



IV. ACQUISITION OF RESEARCH SAMPLES

Research samples of the compounds listed in Table I were synthesized and purified at the 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.

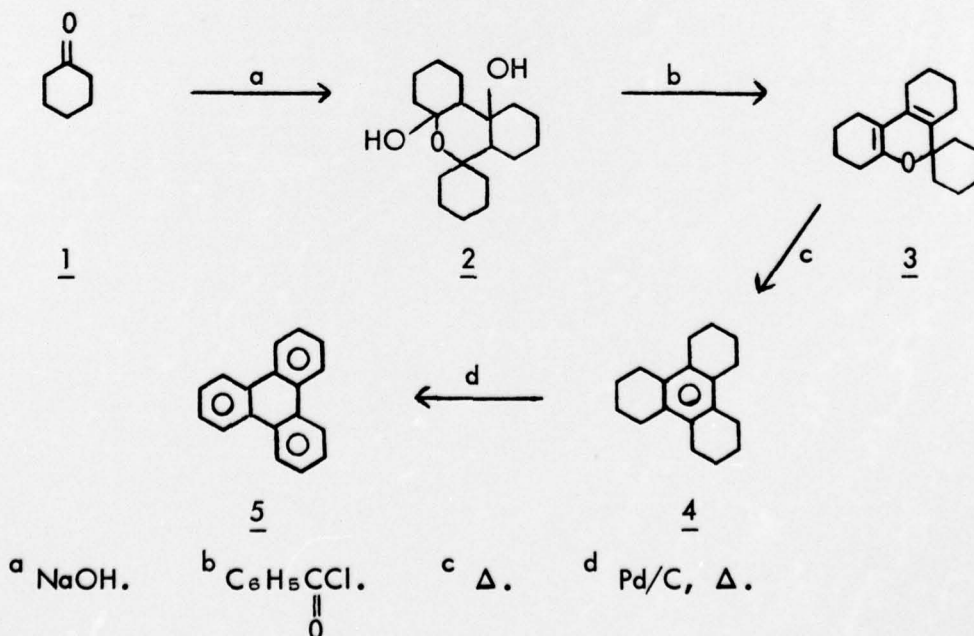
Biphenylene was obtained from the following reactions:



^a Isoamyl nitrite, $\text{CF}_3\text{CO}_2\text{H}$, tetrahydrofuran. ^b $\text{ClCH}_2\text{CH}_2\text{Cl}$, Δ .

The final sample in its purified state had a faint yellow color which was assumed to be natural since its nmr spectrum in carbon tetrachloride and its glc trace (8' x 0.25" of 6% UCW-98 on gas chrom G) indicated no impurity. Because the final solvent was hexane, the glc sample was dissolved in chlorobenzene. No residual hexane was found. The purification steps consisted of: extracting and concentrating by stripping the solvent; codistilling with ethylene glycol and subsequently crystallizing (no detectable impurity closely related to biphenylene at this point); picrate formation from ethanol; recrystallizing of picrate (red color) from ethanol (2X); regenerating of biphenylene from picrate using hexane and a Soxhlet extractor containing neutral alumina; recrystallizing from hexane; and, finally, Kugelrohr distillation (actually a sublimation).

Triphenylene 5 were prepared according to the scheme below.



Dodecahydrotriphenylene 4, 15 g, and 10% palladium on charcoal, 1.5 g, were heated in a round-bottomed flask immersed in a fused sodium nitrite-sodium nitrate bath. Hydrogen gas started bubbling out (attached bubble tube) when the temperature reached 300°C. The flask was heated at this temperature for 2 hours until no more hydrogen evolved. The flask was cooled and the hard residue was dissolved in benzene and the suspended Pd/C catalyst was removed by filtering through Dicalite. Evaporation of the solvent gave a quantitative yield of triphenylene 5, mp 195 - 197°C [Buess and Lawson⁽⁸⁾ 199°C]; mass spectrum, m/e (rel intensity) 229 $[(M + 1)^+$, 818], 228 (M^+ , 3878), 227 (435), 114 (443), 113 (496), and 112 (214); pmr ($CDCl_3$) δ 7.54-7.74 (multiplet protons on C-1, C-4, C-5, C-8, C-9, C-12), 8.54-8.74 (multiplet protons on C-2, C-3, C-6, C-7, C-10, C-11). The course of the reaction could be followed by glc which showed the starting material giving rise to three other peaks and one of the peaks remaining at the end of the reaction. Attempts to stop the reaction after the formation of a partly aromatized product were unsuccessful, since the reaction always yielded a mixture of products, the ratio varying with time.

The crude 5 obtained by dehydrogenation of 4 was almost free of starting material and any of the partly dehydrogenated products. The following techniques were used to further purify 5 in the order given:

1. Soxhlet extraction through alumina.
2. Recrystallization from benzene-isohexane.
3. Picrate formation and recrystallization followed by decomposition of the picrate.
4. Sublimation.

Loss of material was encountered only in the second and third steps. After recrystallizing the picrate, it was decomposed by extracting it through basic alumina in a Soxhlet column. The final sublimation step removed all the trapped solvent in the crystals and yielded a highly pure sample of triphenylene. Carbon dioxide recoveries from combustion calorimetry experiments, described in section I of this report, showed 5 to be 99.999% pure.

Preparation and Purification of Dodecahydrotriphenylene 4

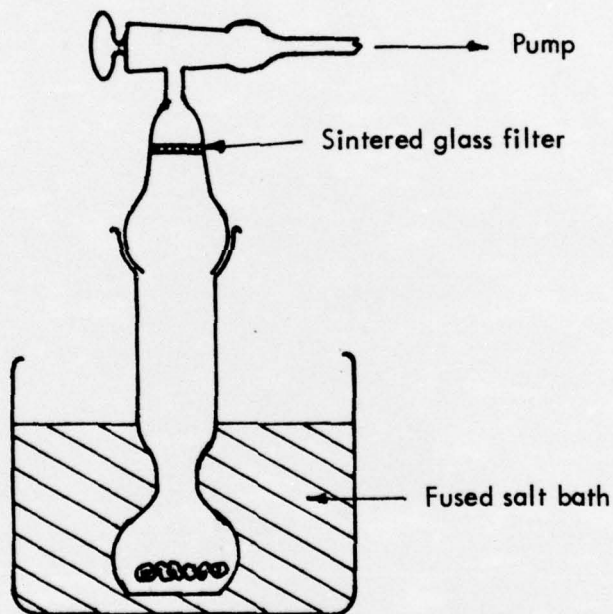
A 44-g sample of 3 (prepared using benzoyl chloride in pyridine) was heated in a fused salt bath at 350°C under nitrogen for 90 min. Water was eliminated. The flask was cooled, the solidified mass was then washed with small amounts of methanol in order to remove unreacted material. The residue, weighing 39 g (89% yield) was passed through alumina and 36.5 g (89% yield) of a white crystalline dodecahydrotriphenylene 4; mp 228-230°C [Svetozarskii et al.⁽⁹⁾, 232°C]; mass spectrum,

⁸ Buess, C. M., and D. D. Lawson, Chem. Rev., **60**, 313 (1960).

⁹ Svetozarskii, S. V., E. W. Zil'berman, and G. A. Razuvaev, Zhur. Obshchei Khim., **29**, 1454 (1959).

m/e (rel intensity) 240 (M^+ , 1641), 212 (538), 211 (401), 199 (497), 198 (572), and 183 (430); pmr ($CDCl_3$) δ 1.60-1.96 (broad singlet, all nonbenzylic protons) and δ 2.38-2.74 (broad singlet, all benzylic protons).

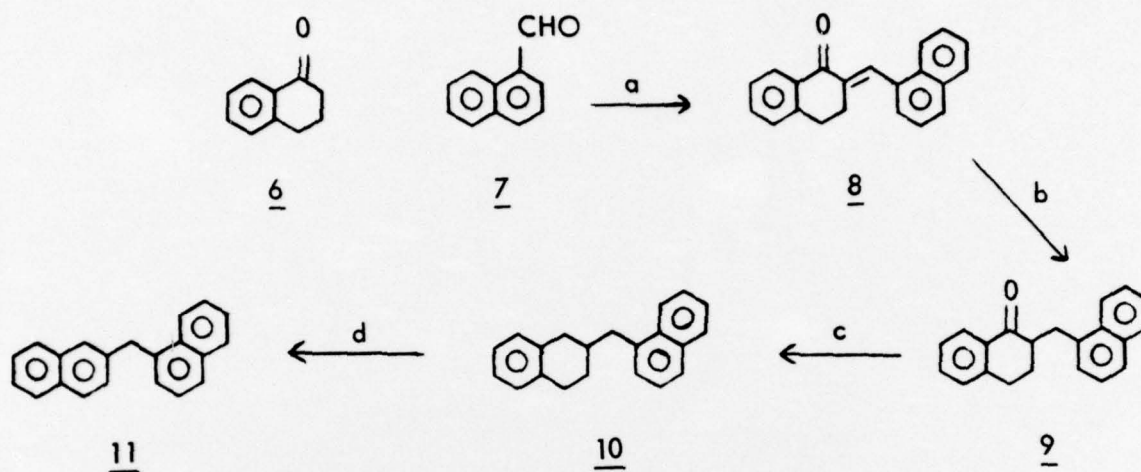
Crude dodecahydrotriphenylene 4 was passed through alumina in a Soxhlet column using isohexane as the refluxing solvent. Following this, the material was recrystallized three times from benzene-isohexane mixture. This procedure removed traces of oily impurities resulting from the pyrolysis. Some amount of solvent was retained in the crystals, even after extensive pumping. The compound was found to be devoid of detectable impurities (by glc) at this stage. A final sublimation procedure was adopted in order to remove the solvent and to improve the purity of the compound. A special apparatus shown below was constructed for this purpose.



The sublimed compound condensed on the stem above the level of the fused salt. When the major portion of the compound had sublimed, the material was scraped out and sealed in oven-baked, previously weighed vials.

Carbon dioxide recoveries from combustion calorimetry experiments, described in section I of this report, showed 4 to be 99.987%.

1',2',3',4'-Tetrahydro-1,2'-dinaphthylmethane 10 and 1,2'-dinaphthylmethane 11 were prepared by the following synthesis route:



^a OH^- , $\text{C}_2\text{H}_5\text{OH}$. ^b Pd/C , H_2 , $\text{C}_2\text{H}_5\text{OH}$. ^c NH_2NH_2 , OH^- , glycol, Δ .
^d Pd/C , Δ .

A sample of 9, 60 g, 0.21 mol; hydrazine hydrate, 40 ml; KOH, 28 g, 0.5 mol; and diethylene glycol, 800 ml, were added to a 1.2-l stainless steel reaction vessel⁽¹⁰⁾, and this reaction mixture was slowly heated to 250°. This temperature was maintained until 256 ml of distillate was obtained (2.5 hr). The cooled reaction mixture was added to 2 l of deionized water, and this solution was then extracted with benzene, 2 x 1 l. The aqueous layer was acidified with conc. HCl and was again extracted with benzene, 1 l. The benzene extracts were combined and washed with 10% HCl, 500 ml. A dark brown solid appeared which was removed by filtering. Rotary-evaporation gave additional brown solid which was eluted through a column of neutral alumina, 5.0 cm x 90 cm, with petroleum ether to give 39 g, 0.14 mol, 68%, of colorless, crystalline 10, mp 102-104°; mass spectrum, 70 eV, m/e (rel intensity) 272 (M⁺, 42), 142 (100), 141 (55), 131 (82), 115 (35), and 91 (24); pmr (CDCl_3) δ 8.10-7.91 (m, 1, ArH), 7.88-7.61 (m, 2, ArH), 7.53-7.20 (m, 4, ArH), 7.12-6.88 (m, 4, ArH), 3.06 (d, 2, ArCH_2 , $J=7$ cps), 2.93-2.36 (m, 4, ArCH_2), and 2.34-1.22 (m, 3, $\text{ArCH}_2\text{CHCH}_2$).

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}$: C, 92.60; H, 7.40. Found: C, 92.54; H, 7.30.

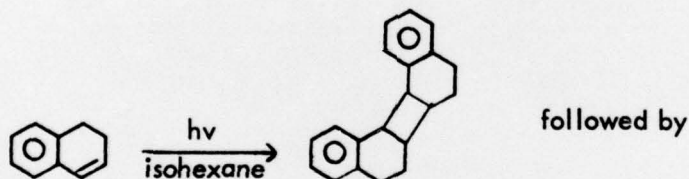
¹⁰ Eisenbraun, E. J., and H. Hall, Chem. Ind. (London), 1535 (1970).

Further Purification of 1',2',3',4'-Tetrahydro-1,2'-dinaphthylmethane 10.

An ethereal solution, 450 ml, of 10, 25.3 g, was added to 400 ml of a toluene-ether (1:5) solution of trinitrobenzene, TNB. The dark yellow solution was cooled to -14° , the resultant solid collected, the mother liquor concentrated and cooled to -14° , and a second yellow solid collected. The TNB complexes were cleaved by isohexane continuous extraction⁽¹¹⁾ through columns of Merck Activity⁽¹²⁾ basic alumina, 4 cm x 16 cm. Hydrocarbon from both cleavages were combined, 19.6 g, and continuously eluted⁽¹¹⁾ through Merck activity 1 basic alumina, 4 cm x 12 cm, with isohexane followed by crystallization from this solvent. Distillation (Kugelrohr) of the resultant solid gave 16.5 g of 10 which showed no impurity by glc.⁽¹³⁾ (15.8 g of the sample was sent to the ERDA station in Bartlesville.)

Purification of 1,2'-Dinaphthylmethane 11. Benzene solvent was removed and the concentrate recrystallized from isooctane.⁽¹⁴⁾ The resultant solid, 200 g, was continuously extracted⁽¹¹⁾ through two successive 6 cm x 5 cm basic alumina columns (Merck activity 1) with isohexane eluant. This purified sample, 170 g, mp $96-97^{\circ}$, was melted into a glass zone-refining ingot, sealed, and then passed for 279 cycles in a Princeton Ultrazone melting apparatus operating with alternate heaters, 5 zones.

5,6,6a,6b,7,8,12b,12c-Octahydrodibenzo[a,i]biphenylene was prepared by ultra-violet radiation of 1,2-dihydronaphthalene



purification consisting of the following steps: recrystallizing from ethanol four times; dissolving in petroleum ether and flushing through alumina (a layer of basic alumina above a layer of neutral alumina contained in a Soxhlet extraction apparatus; and, finally, crystallizing from the above solution followed by filtering and evacuating for 48 hrs at 56°C .

- ¹¹ Cowan, K. D., and E. J. Eisenbraun, Chem. Ind. (London), **46** (1975).
¹² Buu-Hoi and P. Cagniant, Rev. Sci., **71**, 30 (1943); [C.A., **39**, 4861 (1945)].
¹³ Analysis was done on a $1/4'' \times 6'$ glass column packed with 3.5% nematic liquid crystals (N,N'-bis(p-methoxybenzylidene)- α , α' -b-p-toluidine) on a 80-100 mesh AW DMCS-treated Chromosorb G using a Hewlett-Packard 5750B instrument operating at 220° with dual-flame ionization units.
¹⁴ Phillips Isooctane, bp $100-6^{\circ}$.

V. PUBLICATIONS

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

Accepted for publication by J. Chem. Thermodynamics

Thermodynamic Properties of Cyclopropylamine, Cyclopentylamine, and Methylene-cyclobutane

First draft completed and internal editorial review in progress