

It is relevant that amines which do not dissolve sulfur with the formation of colored products can be converted to colored amine polysulfide salts upon treatment with sulfur and hydrogen sulfide.⁶ These salts undoubtedly could function as radical precursors. For triethylamine the presence of radicals in the orange polysulfide has been demonstrated.

The question as to whether the radicals are an important factor in chemical reactivity or merely incidental cannot be answered at this time. The situa-

tion is much the same in the case of the observed catalysis with amines which form radicals directly since the reaction may occur by an ionic route with polysulfides or by a free radical path with their homolytic scission products.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

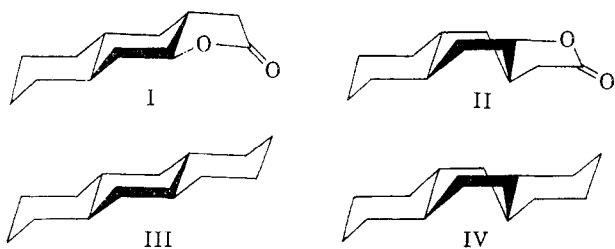
Further Studies on the Energy Difference between the Chair and Twist Forms of Cyclohexane

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Calorimetric and heat of vaporization measurements have been performed on *trans-syn-trans*- and *trans-anti-trans*-perhydroanthracene, III and IV. The energy of the twist isomer IV was thus shown to be greater than that of the all-chair form III by 5.39 ± 0.86 kcal./mole in the vapor phase at 25°. From this value it has been possible to calculate that the difference in energy of the chair and twist forms of cyclohexane is 4.79 ± 0.94 kcal./mole, which is in good agreement with the value previously obtained from another system.

In a previous communication from this laboratory,¹ combustion calorimetric and heat of vaporization measurements were reported for the pair of stereoisomeric lactones I and II, the configuration of which requires that the central ring assume the chair conformation in the former and the twist in the latter isomer. The energy of lactone II was thus shown to be greater than that of I by 4.1 ± 0.4 kcal./mole in the vapor phase at 25°. From this value it was calculated that the difference in energy between the chair and twist forms of cyclohexane is approximately 5.5 kcal./mole. This calculation involved correcting for non-cancelling energy effects of the terminal rings. An argument was advanced¹ to show that the homocyclic terminal ring resulted in a destabilization of the twist relative to the chair form by a maximum value of 0.3 kcal./mole. The effect of the lactone ring, on the other hand, was considered to result in a stabilization of the twist relative to the chair form by about 1.65 kcal./mole. In order to obviate the necessity of making this latter relatively large and somewhat uncertain correction, we have now carried out a similar study with the *trans-syn-trans*-(central ring chair)- and *trans-anti-trans*-(central ring twist)-perhydroanthracenes III and IV, which constitutes the subject of the present report.



Experimental

Preparation of Materials.—*trans-syn-trans*-Perhydroanthracene was prepared according to the method of Fries and Schilling² except that Raney nickel was used instead of a mixed nickel-cobalt-copper catalyst. A mixture of 100 g. (0.56 mole) of anthracene, 25 g. of Raney nickel and 250 ml. of acid-washed cyclohexane was treated with hydrogen under 2000 p.s.i. at 200°

for 19 hr. One hundred and three per cent of the theoretical amount of hydrogen was absorbed. The mixture was filtered, and the filtrate was concentrated to a residue which partially solidified. The solid was recrystallized from 350 ml. of methanol to give 11.7 g. of colorless plates, m.p. 88–90°. Two recrystallizations from absolute ethanol gave 8.9 g. of needles which reverted to plates on standing during the process (apparent polymorphism), m.p. 89.0–90.5°; and two further recrystallizations from methanol gave 6.2 g. of plates, m.p. 89.5–90.7°. The residue from the mother liquor of the last recrystallization showed this same melting point.

Anal. Calcd. for C₁₄H₂₄: C, 87.42; H, 12.58. Found: C, 87.4; H, 12.3.

The *trans-anti-trans* isomer (IV)^{3,4} was prepared⁵ in quantity and carefully purified as already described.³ The final specimen of substance IV melted at 48.5–49.7°. Analytical gas chromatography showed that the purified form of III was a single substance and indicated that that of IV was contaminated with 0.2% of the *cis-anti-cis* isomer. Because the heats of combustion of all of the perhydroanthracenes must be of the same order of magnitude, it is obvious that this small amount of impurity could not affect the measurements within the experimental error.

Combustion Experiments.—Prior to combustion the hydrocarbons were dried meticulously at high vacuum, then pressed into 0.580-g. pellets. (This size was chosen to be approximately equivalent to the heat of combustion of 1.000 g. of benzoic acid.) The samples were weighed on an Ainsworth micro-analytical balance to 0.01 mg. as was the 1.4 mg. cotton thread used as the fuse. A Parr double-valve Illium bomb of 0.334-l. capacity containing 1.00 g. of water was flushed three times with 10 atm. of oxygen, then charged to 30.0 atm. with oxygen at 25.0°. All of these procedures were followed in the calibration experiments with benzoic acid.

The calorimeter well was filled with water delivered by a 7.28-l. buret, the interior of which had been treated with "Desicote." The well was enclosed in a constant temperature bath maintained at 25° with a short period variation of ± 0.003 degree. The temperature rise in the calorimeter was followed by a 25-ohm platinum resistance thermometer in conjunction with a Rubicon Mueller bridge and a 2284-d Leeds and Northrup galvanometer. The sensitivity of 1.5 cm. for a 10⁻⁴-ohm unbalance was obtained with a thermometer current of 3.5 ma. The heat of combustion of the cotton thread was determined to be 3.88 cal./mg. The ignition energy was measured with a current integrating circuit similar to that described by Pilcher and Sutton.⁶ The calorimeter system will be described in more detail elsewhere.⁷

Three sets of calibration experiments of six determinations each were required due to changes in the calorimeter system. The energy equivalent of the calorimeter was evaluated using

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TABLE I
 HEAT OF COMBUSTION OF *trans-syn-trans*-PERHYDROANTHRACENE

Run	<i>m</i> (air), g.	ΔR , ohm	Calories			$-\Delta E_0$, cal. g. ⁻¹	Deviation, cal. g. ⁻¹	
			$-\Delta E_{tot}$	ΔE_{fuss}	$\Delta E_{ign.}$			
1	0.58017	0.0766529	6199.91	5.16	1.07	10675.64	-15.86 ^a	
2	.58019	.0767871	6210.77	3.69	0.62	10697.30	5.80	
3	.57953	.0767278	6205.97	5.59	0.67	10697.83	6.34	
4	.57891	.0766033	6197.84	5.24	0.83	10695.56	4.06	
5	.57870	.0765116	6190.42	5.51	0.83	10686.15	-5.34	
6	.58001	.0766735	6203.52	5.72	0.68	10684.49	-7.00	
7	.57743	.0764103	6182.26	5.28	1.10	10695.47	3.98	
8	.58144	.0769073	6222.43	5.57	0.75	10690.90	-0.60	
9	.58063	.0767511	6209.80	5.76	0.52	10684.11	-7.38	
10	.57970	.0766813	6204.15	5.35	0.85	10691.64	0.15	
						Av.	10691.49	±1.82

$$\Delta E_0 = -2054.56 \pm 0.70 \text{ kcal./mole}, \Delta H_0^0 = -2057.48 \pm 0.70 \text{ kcal./mole}$$

$$\Delta E_0^0 = -2053.92 \pm 0.70 \text{ kcal./mole}, \Delta H_0^0{}_{f,298.16} = -79.02 \pm 0.82 \text{ kcal./mole}$$

^a Discarded.

 TABLE II
 HEAT OF COMBUSTION OF *trans-anti-trans*-PERHYDROANTHRACENE

Run	<i>m</i> (air), g.	ΔR , ohm	Calories				$-\Delta E_0$, cal. g. ⁻¹	Deviation, cal. g. ⁻¹
			$-\Delta E_{tot}$	ΔE_{fuss}	$\Delta E_{ign.}$	Carbon		
1	0.57859	0.0768663	6219.12	5.80	0.65	-0.55	10738.55	0.63
2	.58152	.0772681	6251.63	5.98	0.97		10738.55	0.63
3	.58001	.0770872	6236.99	4.71	1.40	-0.16	10742.97	5.05
4	.57665	.0765615	6194.46	5.66	0.67		10731.16	-6.76
5	.58095	.0771948	6245.70	5.88	1.30		10738.47	0.55
6	.57635	.0765302	6191.92	5.20	0.67		10733.16	-4.46
7	.58097	.0772159	6247.40	5.59	1.12		10741.86	3.94
8	.58056	.0771286	6240.34	5.28	0.63		10738.65	0.73
						Av.	10737.92	±1.39

$$\Delta E_0 = -2063.46 \pm 0.54 \text{ kcal./mole}, \Delta H_0^0 = -2066.38 \pm 0.54 \text{ kcal./mole}$$

$$\Delta E_0^0 = -2062.82 \pm 0.54 \text{ kcal./mole}, \Delta H_0^0{}_{f,298.16} = -70.12 \pm 0.68 \text{ kcal./mole}$$

U.S. Bur. Stds. 39h benzoic acid under certified conditions. For series 1, the results gave a value of 80883.0 ± 7.2 cal./ohm; for series 2, 80908.2 ± 7.7 cal./ohm; and for series 3, 80922.1 ± 5.8 cal./ohm. The defined calorie, equal to exactly 4.184 abs. joules, was used.

Vapor Pressure Measurements.—The vapor pressure was determined by continuously weighing a sample contained in a graphite Knudsen cell with a magnesium oxide lid. The weighing at reduced pressure was performed with a magnetically controlled microbalance, previously described.⁸

The Knudsen cell was suspended inside a glass envelope contained in a low-temperature furnace. The orifice of the Knudsen cell lid, made of a single crystal of magnesium oxide, had an area of 1.66×10^{-3} cm.² and a Clausing factor equal to 0.79.⁹ The cross-sectional area of the graphite cell was 0.70880 cm.²

The heating furnace consisted of a 5-l. dewar flask containing a 15-watt bulb for runs above room temperature. Voltage input into the bulb was controlled by a variable transformer. For temperatures below room temperature, the light bulb attachment was removed, and a suitable cooling medium such as cold water, ice or Dry Ice, was used. Below the ice temperature the Dewar was partly filled with Dry Ice and was maintained at various distances from the Knudsen cell in order to obtain different temperatures. The temperature was measured by means of a chromel-alumel thermocouple inside the glass envelope.

The vapor pressures were calculated from the rate of weight loss of the sample at a given temperature. For increased accuracy, several readings were taken at each temperature, and the time-weighted average of all of the weight loss readings was calculated and reported as one pressure point. The heat of vaporization was obtained by making a least squares plot of $\log P$ vs. $1/T$. All of these calculations were made with a Fortran program on a Control Data 1604 digital computer.

Results

The results for the heats of combustion of the perhydroanthracene isomers are listed in Tables I and II. In only two runs was the presence of carbon detected, and this was corrected for by weighing the residue in the platinum crucible. The nitric acid in the bomb solution was negligible in both the calibration and perhydroanthracene combustions. The heats of formation ($\Delta H_0^0{}_{f,298.16}$) for the *trans-syn-trans* and the *trans-*

anti-trans isomers are -79.02 ± 0.82 and -70.12 ± 0.68 kcal./mole, respectively. These values were derived by using -68.3149 ± 0.0096 and 94.0517 ± 0.0108 kcal./mole for the $\Delta H_0^0{}_{f,298.16}$ of H₂O¹⁰ and CO₂,¹¹ respectively, which have been adjusted for the new atomic weight scale.¹² For the evaluation of the thermodynamic quantities on a per mole basis, we used a density of 1.08 g./cc. for the *vacuo* correction and a molecular weight of 192.347 which is also based on the new scale.

The energy difference between the solid *trans-syn-trans* and *trans-anti-trans* isomers is, thus, 8.90 ± 0.88 kcal./mole, with the twist form having the higher energy.

The vapor pressure experiments for the *trans-syn-trans* (chair form) and *trans-anti-trans* (twist form) perhydroanthracene are summarized in Tables III and IV, respectively. The heat of sublimation of the

 TABLE III
 VAPOR PRESSURE DATA FOR *trans-syn-trans*-PERHYDROANTHRACENE

Point no.	<i>T</i> (°K.)	<i>P</i> (atm.)
(a) Experiment no. 1		
1	293.4	3.90×10^{-6}
2	320.7	7.58×10^{-6}
3	312.0	3.63×10^{-6}
4	304.8	1.52×10^{-6}
5	296.5	6.03×10^{-6}
(b) Experiment no. 2		
1	297.1	6.45×10^{-6}
2	309.3	2.32×10^{-6}
3	310.2	2.22×10^{-6}
4	335.1	3.91×10^{-4}

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TABLE IV
VAPOR PRESSURE DATA FOR *trans-anti-trans*-
PERHYDROANTHRACENE

Point no.	<i>T</i> (°K.)	<i>P</i> (atm.)
1	274.5	1.16×10^{-6}
2	269.0	9.54×10^{-7}
3	282.8	4.82×10^{-6}
4	286.8	7.98×10^{-6}
5	289.2	9.43×10^{-6}
6	296.0	1.43×10^{-5}
7	299.8	2.18×10^{-5}
8	306.2	4.17×10^{-5}
9	312.6	8.61×10^{-5}

trans-syn-trans-perhydroanthracene is calculated to be 20.89 ± 0.57 kcal./mole. The heat of sublimation obtained for the *trans-anti-trans*-perhydroanthracene is 17.38 ± 0.79 kcal./mole. Hence, in the vapor phase the *trans-syn-trans* is energetically more stable than the *trans-anti-trans* isomer by 5.39 ± 0.86 kcal./mole.

Conclusion.—From the data reported above, the difference in energy of the chair and twist forms of cyclohexane is calculated to be approximately 4.79 ± 0.94 kcal./mole which is obtained simply by subtracting 0.6 kcal./mole from the experimentally observed difference in energy between hydrocarbons III and IV. The 0.6 kcal./mole value represents the sum of two 0.3 kcal./mole increments due to the two non-cancelling interactions of the terminal rings which exert a destabilizing effect on the twist form (see above). This new value for cyclohexane is in good agreement with the previous one of about 5.5 kcal./mole¹ and indicates that the estimation of the non-cancelling energy effect of the five-membered lactone ring was approximately correct.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Microwave Absorption and Molecular Structure in Liquids. L. The Dielectric Relaxation of Several Substituted Naphthalenes and 4-Acetyl-*o*-terphenyl^{1,2}

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The dielectric constants and losses at wave lengths of 1.25, 3.22, 10.0 cm. and 575 m. have been measured for 1-fluoronaphthalene, 1-acetonaphthone, 2-acetonaphthone and 4-acetyl-*o*-terphenyl in benzene solutions at temperatures from 20 to 60° and for 1-acetonaphthone at 25 and 50 cm. also. Refractive indices were determined for the sodium D-line at only one temperature. The data obtained for 2-acetonaphthone and 4-acetyl-*o*-terphenyl in benzene have been analyzed in terms of two relaxation times, the value of the relaxation time corresponding to the high frequency dispersion region being consistent with the intramolecular mechanism of acetyl group rotation. Rotation of the acetyl group in 1-acetonaphthone is prevented by steric hindrance, but large atomic polarization indicates libration of the group. The heat of activation for rotational relaxation of the acetyl group is indistinguishable from the value of the resonance energy given by thermal data as the contribution of the group.

In dielectric investigations of substituted naphthalenes, it may be useful to have available the dielectric relaxation time of a molecule which shows a minimum difference in size and shape from the unsubstituted naphthalene molecule. For this reason, 1-fluoronaphthalene has been measured. The possibility of rotation of the strongly polar acetyl group in a molecule and the possible effects of steric hindrance and resonance energy are investigated in the present paper by determining the dielectric relaxation times of 1-acetonaphthone, 2-acetonaphthone, and 4-acetyl-*o*-terphenyl.

Experimental Methods

Apparatus.—The dielectric constants and losses of these molecules were measured in benzene solution by methods which have been previously described.⁴⁻⁶

Purification of Materials.—1-Fluoronaphthalene, 1-acetonaphthone, 2-acetonaphthone and 4-acetyl-*o*-terphenyl were obtained from the Eastman Kodak Company. 1-Fluoronaphthalene was fractionally distilled in a 91-cm. column utilizing a cold finger. The fraction collected had boiling points of 83.0°–83.2° (10 mm.), 80.8° (8 mm.), and 79° (7.5 mm.).

1-Acetonaphthone was fractionally distilled. The fractions collected had boiling points of 146.6° (50 mm.), 146.2° (4.5 mm.) and 146.0° (4.8 mm.).

2-Acetonaphthone was recrystallized from 60–70° benzene twice and was then vacuum dried in a desiccator containing anhydrous calcium chloride. The observed melting point was 55.8–56.1°. 4-Acetyl-*o*-terphenyl was used without further purification.

Benzene (Allied Chemical Corp.) was dried over "Drierite" (W. A. Hammond Drierite Company) for several weeks and then was used without further purification.

Experimental Results

Slopes a_0 , a' , a_D and a'' were obtained by plotting the static dielectric constants ϵ_0 , the high-frequency dielectric constants ϵ' , the refractive indices for the sodium D line, and the losses ϵ'' of the solutions against the concentrations of the polar solutes. Cole-Cole⁷ plots of a'' vs. a' were made in order to determine the distribution parameter α and the most probable relaxation time τ_0 .⁸

The experimental values for a_0 , a' and a'' obtained for these compounds are listed after each compound in Table I. The concentration range of the three solutions measured for each substance is given as mole fractions in parentheses. The values obtained for α , a_D , a_∞ and τ_0 , the "most probable relaxation time," are listed in Table II.

Discussion of Results

The relaxation time 12.6×10^{-12} sec. for 1-fluoronaphthalene at 20° in Table II and previously determined values in benzene solution, 15.8×10^{-12} for 1-chloronaphthalene⁹ and 18.0×10^{-12} for 1-bromo-

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(2) This paper represents part of the work submitted by F. K. Fong to the Graduate School of Princeton University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) Sayre Fellow, 1959–1960.

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