Free Radicals in Amine Solutions of Elemental Sulfur

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Electron spin resonance has shown that free radicals were formed whenever elemental sulfur was dissolved in an amine to give a colored solution. At room temperature a single line was observed with a g-value of 2.030. On the basis of this g-value and the structure of the resonance at $-196°$ the radicals have been identified as radicals in which the free spins are localized on sulfur atoms. Catalysis of the addition of sulfur to triphenyl-phosphine by amines which gave radicals with sulfur was observed. The origin of the radicals is suggested to be the homolytic scission of long sulfur chains of polythiobisamines and amine polysulfides.

Introduction

We report here the results of an investigation of free radicals which were found to be present in certain amine solutions of elemental sulfur. A previous electron spin resonance (e.s.r.) investigation of radicals in liquid sulfur[1] has established that radicals in which the unpaired electrons are located on sulfur atoms give a resonance with a g-value outside the narrow range found for radicals containing C, H, O, and N atoms. Recent work also has shown that radicals in colored sulfur deposits condensed at $-196°$ from heated sulfur vapor gave resonances with a distinctive shape.[2] Similar structured resonances were observed from radicals trapped after high energy irradiation of solids whose molecules contained sulfur.[3,4] The structure has been interpreted in terms of a sulfur radical in which the density of the unpaired electron spin is mainly concentrated around the sulfur atom.[5] E.s.r., therefore, can be a means of identifying and studying sulfur radicals and was used as such in this investigation. The catalytic effect of systems containing radicals on the addition of sulfur to triphenylphosphine also was studied.

The formation of colored solutions of elemental sulfur in certain amines is well known and some products of the reactions which occur have been investigated.[6] These are generally N,N'-polythiobisamines which must be formed by the scission of S–S bonds in order to open the S_8 rings. The interaction of sulfur and amines is important in a number of chemical reactions,[7,8] particularly the catalysis of reactions of sulfur by amines.

Experimental

Materials[9]

Piperidine.—For conductivity and e.s.r. studies, commercially available piperidine was redistilled through a 1.5 m. column and the heart cut, b.p. 105–106°, was used.

Sulfur.—Flowers of sulfur were recrystallized once from a benzene–acetone mixture, m.p. 112–113°.

Triphenylphosphine was recrystallized from ethanol, m.p. 80–81°. Solutions were prepared by weighing, and were checked for degree of oxidation before each determination.

Reagent grade **benzene** and spectral grade **cyclohexane** which had been chromatographed through alumina were used.

Kinetic Study.—The procedure developed by Bartlett and Meguerian[10] was followed. The molar concentration of sulfur varied from 3.79×10^{-3} to 3.92×10^{-3}, that of triphenylphosphine, from 2.16×10^{-3} to 10.69×10^{-3}. Iodine in aqueous KI solution was substituted for the solution in 95% ethanol used by Bartlett.

Preparation of Triphenylphosphine Sulfide.—A solution of 0.1 g. (0.003 gram-atom) of sulfur in 5 cc. of ethylenediamine was added to 0.45 g. (0.0017 mole) of triphenylphosphine in 2 cc. of benzene. After 3 minutes, the mixture was poured onto 75 cc. of water, and the product was filtered; yield of crude material, m.p. 152–156°, was quantitative. Recrystallization from ethanol gave 0.4 g. (80%) of needles, m.p. 158–161°, lit. 157°, 158°, 161°.[11]

Electron Spin Resonance Measurements.—Electron spin resonance measurements were made with a Varian V4502 spectrometer operating at X band frequency and using a modulation frequency of 100 kc. Measurements on the frozen solutions at $-196°$ were made with a quartz dewar which fitted into the cavity. Temperatures between -196 and $+100°$ were achieved by a flow of nitrogen gas through a regulated heat exchanger and around the sample. Measurements of radical concentrations were made by comparing the resonances from the amine solution of sulfur with the resonances from solutions of α,α-diphenyl-β-picryl hydrazyl (d.p.p.h.). The standard solutions were estimated spectrophotometrically. Comparative measurements of spin concentration were made as a function of temperature. In these measurements, the strength of the resonance was determined by multiplying the peak to peak height of the derivative signal by the square of the line width. Corrections were applied for changes in instrument sensitivity when the sample was changed or the temperature was varied. The correction factor was determined from measurements of the resonance of a piece of solid d.p.p.h. or synthetic ruby included in the cavity along with the sample. Measurements of g-values were made with reference to the known g-value of d.p.p.h.

Results

An e.s.r. signal was detected whenever elemental sulfur dissolved in an amine to give a colored solution. The most frequently observed colors were orange and red although green and brown solutions also were formed. In surveying a number of amines, order of magnitude estimates were made of radical concentrations and the results are shown in Table I. At room temperature the g-value for all resonances was (2.030 $\pm$ 0.001). Line widths were between 35 and 45 gauss except for the ethylenediamine solution which had a line width of 75 gauss. The lines were Lorentzian in shape.

TABLE I

E.S.R. SIGNALS FROM SOLUTIONS OF SULFUR IN VARIOUS AMINES

No signal (estimated $<10^{-6}$ free spins/mole)	Weak signal ($\sim 10^{-5}$ free spins/mole)	Strong signal ($\geqslant 10^{-4}$ free spins/mole)
$(C_2H_5)_2NH$	$n\text{-}C_4H_9NH_2$	$H_2NCH_2CH_2NH_2$
$(C_2H_5)_3N$	$n\text{-}C_7H_{15}NH_2$	$HN(C_2H_4NH_2)_2$
$C_6H_5NH_2$	$HOCH_2CH_2NH_2$	$NH(C_3H_6NH_2)_2$
$C_4H_5N(CH_3)_2$	O⟨ ⟩NH	$(-CH_2NHC_2H_4NH_2)_2$
$(HOCH_2CH_2)_3N$		$(CH_3)_2NC(=NH)N(CH_3)_2$
C_5H_5N		⟨ ⟩NH

Absolute determinations were made of the radical concentration in piperidine solutions of sulfur from 0.3 to 3 M. The number of unpaired spins/ml. is plotted as a function of sulfur concentration in Fig. 1. The results show that there is one unpaired spin for every

(1) D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **78**, 3279 (1956).

(2) H. E. Radford and F. O. Rice, *J. Chem. Phys.*, **33**, 774 (1960).

(3) H. Shields and W. Gordy, *J. Phys. Chem.*, **62**, 789 (1958).

(4) T. Henriksen, *J. Chem. Phys.*, **36**, 1258 (1962).

(5) Y. Kurita and W. Gordy, *ibid.*, **34**, 282 (1961).

(6) T. G. Levi, *Gazz. chim. ital.*, **60**, 975 (1930); **61**, 286 (1931).

(7) "Neuere Methode der Präparativen Org. Chem.," Band III, Verlag Chemie, Weinheim, 1961, p. 1.

(8) C. G. Moore and R. W. Saville, *J. Chem. Soc.*, 2082 (1954).

(9) All purified materials were stored under nitrogen.

(10) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956); P. D. Bartlett, E. F. Cox and R. E. Davis, *ibid.*, **83**, 103 (1961).

(11) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 117.
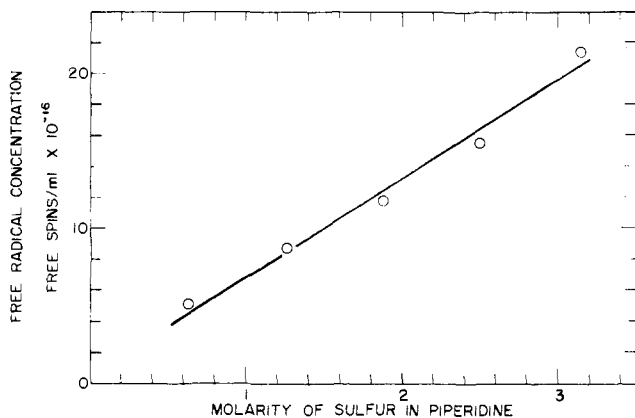
Fig. 1.—The concentration of free radicals in piperidine solutions of elemental sulfur as a function of sulfur concentration.
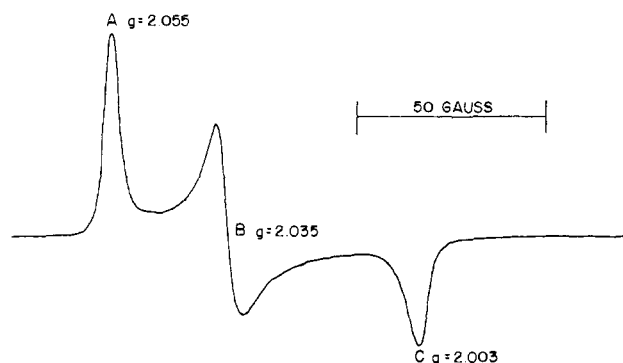

Fig. 2.—Derivative of the electron spin resonance absorption spectrum of a 3 M tetramethylguanidine solution of elemental sulfur measured with a microwave frequency of 9.14 kMc./sec. at $-196°$.

10^4 sulfur atoms. Associated with the production of radicals is the formation of ions which were detected in conductivity measurements on piperidine solutions of sulfur.[12]

In air the piperidine solutions decolorized slowly depositing a white crystalline solid which could not be isolated in a pure state. The solid broke down with evolution of hydrogen sulfide on drying and deposited sulfur on attempted recrystallization from water, acetone and other solvents. This material did not give an e.s.r. signal. Infrared analysis showed the presence of S–O bonds and it is suggested that the material was $(C_5H_{10}NH_2^+)_2S_2O_4^-$. Analysis of the crude material gave C, 41.3; H, 8.2; N, 10.1; S, 21.0. Calculated for $C_{10}H_{24}N_2S_2O_4$: C, 40.0; H, 8.0; N, 9.35; S, 21.3.

In sealed tubes under nitrogen the white solid material did not deposit from piperidine solutions but, over a period of days, the solution separated into two layers; a lower dark red oily layer which gave an enhanced e.s.r. signal and an upper light orange layer which gave a very weak e.s.r. signal. A similar separation into two layers was caused by passing hydrogen sulfide into a freshly prepared solution of sulfur in piperidine. The radical concentration was maintained in the lower layer over a period of several months. The only system studied in which the radicals observed initially were not stable was sulfur in ethylenediamine in which radicals could not be detected after 24 hours. When hydrogen sulfide was passed through a suspension of sulfur in triethylamine an orange solid was formed which gave a weak resonance extending over 100 gauss.

(12) (a) We are indebted to Dr. C. A. Streuli for these measurements. (b) R. E. Davis and H. Nakshbendi report that ion formation is general in solutions of sulfur in primary and secondary amines, J. Am. Chem. Soc., 84, 2085 (1962).
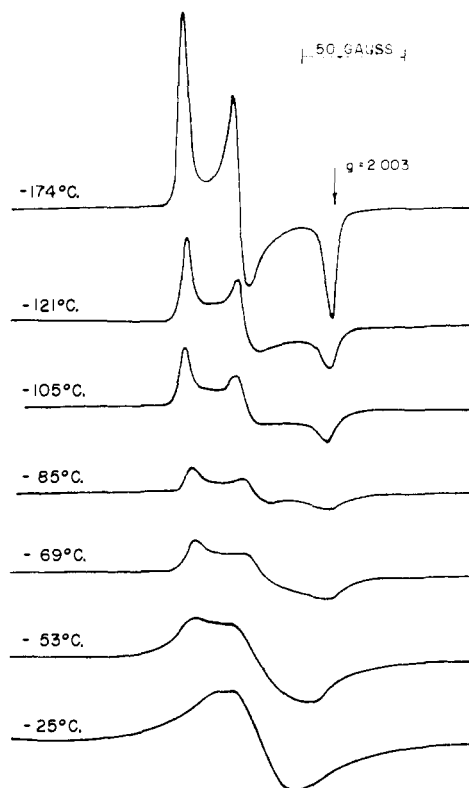

Fig. 3.—The effect of temperature on the derivative of the electron spin resonance absorption spectrum at 9.14 kMc./sec. of a tetramethylguanidine solution of elemental sulfur. The instrument sensitivity was approximately constant except for the spectrum at $-25°$ when dielectric losses in the cavity had reduced the sensitivity by a factor of two.

E.s.r. investigations were also made at temperatures between -196 and $+100°$. At $-196°$ all solutions containing radicals gave a resonance with the structure seen in Fig. 2. The orange solid formed by passage of hydrogen sulfide into a suspension of sulfur in triethylamine also gave this structured resonance at $-196°$. The room temperature resonance of the orange solid appears to be derived from the low temperature resonance with considerable broadening of the peaks. The structured resonance at low temperatures has the shape expected for a polycrystalline radical with three principal g-values. Such systems have been treated theoretically by Kneubühl.[13] His analysis shows that measurements of field values at points A, B and C give the principal g-values for the radical, g_3, g_2, and g_1, respectively. Measurements at $-196°$ for sulfur in 3,3-diaminodipropylamine, tetramethylguanidine, ethylenediamine, heptylamine and piperidine gave these sets of principal g-values, which were identical within the range of experimental accuracy: $g_1 = 2.003 \pm 0.001$, $g_2 = 2.035 \pm 0.001$, $g_3 = 2.055 \pm 0.001$.

In a series of piperidine solutions from 0.3 to 3 M there was no difference in the shape or spread of the resonances at $-196°$. The amplitude of the resonance was proportional to sulfur concentration.

Spectra measured at temperatures between -196 and $+100°$ for sulfur in piperidine and in tetramethylguanidine showed that the structured resonance at $-196°$ decreased sharply in amplitude with increasing temperature. The peaks in the spectra became broader until all the peaks had merged to a single line at about $-30°$. Figure 3 shows a series of spectra at different temperatures for sulfur in tetramethylguanidine. Increasing the temperature from 0 to $+95°$ caused a reversible sixfold increase in radical concentration for both piperidine and tetramethylguanidine solutions.

(13) F. K. Kneubühl, J. Chem. Phys., 33, 1074 (1960).

The relationship between the presence of radicals in amine solutions of sulfur and the catalysis of sulfur reactions by amines was explored in a study of the reaction between triphenylphosphine and sulfur to form triphenylphosphine sulfide using a modification of the procedures of Bartlett, et al.[10] In agreement with their findings, no catalysis was observed with triethylamine. The radical producing amines gave accelerated rates as shown in Table II. Two sulfenamides are included in the table as examples of radical catalysts.[14] They cannot form ions of the type detected in amine solutions of sulfur and illustrate the catalytic effect of materials which produce free radicals.

TABLE II

RATE CONSTANTS FOR THE ADDITION OF SULFUR TO $(C_6H_5)_3P$ AT 30°

EDA = $NH_2CH_2CH_2NH_2$; TMG = $(CH_3)_2NC(:NH)N(CH_3)_2$

M = [structure]

C = [structure]
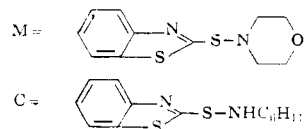
Solvent	Catalyst (0.05 mole %)	$k \times 10^3$	k/k_0
Cyclo-C_6H_{12}		0.059 ± 0.008^a	0.015
Cyclo-C_6H_{12}	EDA^d	0.309 ± 0.021	0.077
C_6H_6		4.0 ± 1.0^b	1
C_6H_6	Et_3N	4.1 ± 0.5^c	1.02
C_6H_6	$C_5H_{11}N$	10.8 ± 1.7	2.7
C_6H_6	TMG^e	11.1 ± 1.0	2.8
C_6H_6	H_2O	7.4 ± 1.0	1.85
C_6H_6	EDA	~300–370	>75
C_6H_6	M	15.1 ± 1.9	3.8
C_6H_6	C	17.3 ± 0.9	4.3

^{a} Bartlett's value: 0.058 at 25°. ^{b} Bartlett's value: 4.4 at 25°. ^{c} Bartlett's value: 4.4–4.6 at 25°. ^{d} EDA = NH_2CH_2-CH_2NH_2; ^{e} TMG = $(CH_3)_2NC(:NH)N(CH_3)_2$.

On a preparative scale it was found that triphenylphosphine sulfide was formed quantitatively within three minutes of mixing a solution of triphenylphosphine in benzene with sulfur in ethylenediamine at room temperature.

Discussion

There is strong evidence in the measurements above that the radicals detected in amine solutions of sulfur are radicals in which the unpaired electrons are located in the orbitals of sulfur atoms. The g-value of 2.03 is outside the range of g-values (2.002–2.008) reported for radicals containing only elements of the first row of the periodic table. High g-values have been reported for other sulfur radicals in liquid sulfur (g = 2.024),[1] sulfur in oleum (g = 2.032),[15] and ultramarine (g = 2.028).[16] The shift to higher g-values for radicals containing sulfur has been ascribed[1,2] to spin orbit interaction which increases for second row elements of the periodic table.

The low temperature resonance provides further evidence for radicals containing sulfur. Many polycrystalline solids whose molecules contain sulfur give an e.s.r. signal, after high energy irradiation, remarkably similar to that found for amine solutions of sulfur at −196°.[3,4] The principal g-values found for frozen amine solutions of sulfur (2.003, 2.035, 2.055) can be compared with the principal g-values of the stable radicals trapped in irradiated cystine (2.003, 2.029,

2.052) which have been identified as radicals of the type $>C$—$S\cdot$ by Kurita and Gordy.[5] They have shown that the principal g-values observed are in good accord with a model in which the unpaired electron is in a π orbital, the principal component of which is a 3p orbital of sulfur. The explanation of the low temperature resonance in terms of a radical with three principal g-values could equally well be applied to the e.s.r. spectrum from colored sulfur at −196° without postulating two radical species as suggested by Radford and Rice.[2] The different set of principal g-values (2.00, 2.025, 2.039) could then be ascribed to the changes in bonding which are expected to alter the spread of g-values.[5]

The transition from the structured resonance in the frozen material to a single line resonance in the liquid state is as expected from the theory of Kneubühl,[13] who showed that a radical with three principal g-values g_1, g_2, and g_3 should give a single line spectrum with a g-value approaching $(g_1 + g_2 + g_3)/3$ with increasing freedom of rotation. The observed room temperature g-value of 2.030 is in good agreement with the value of 2.031 for the average of the principal g-values. It is apparent that the e.s.r. signals from amine solutions of sulfur can be accounted for by the formation of one type of radical in which the unpaired electron is localized in the orbitals of one or more sulfur atoms.
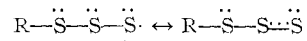
We suggest that the radicals in amine solutions of sulfur are the result of homolytic scission of S–S bonds in N,N′-polythiobisamines which are formed by stepwise nucleophilic attack on S_8 rings by the amine in a reaction similar to that suggested by Levi.[6]

$$2RR'NH + S_x \longrightarrow (RR'N)_2S_{x-1} + H_2S$$
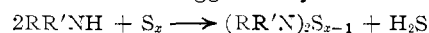
N,N′-polythiobisamines of the above form are responsible for the initial color of the solutions. The hydrogen sulfide may then react further with the formation of amine polysulfides.

$$2RR'NH + H_2S + S_x \longrightarrow (RR'NH_2)_2^+S_{x+1}^=$$
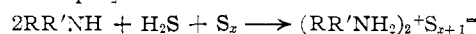
The dark red oil deposited by piperidine solutions of sulfur is such a salt formed with hydrogen sulfide evolved in initial stages of the reaction. The deposition of the red oil on treatment with hydrogen sulfide is also explained by this reaction. It is known that the S–S bond in long sulfur chains is much weaker than in S_8 rings[17] (<35 kcal./mole and 64 kcal./mole, respectively). Gee, et al., have suggested that radicals of the type RS_x are partly stabilized by a resonance structure containing a "three electron bond"

$$R—\overset{..}{\underset{..}{S}}—\overset{..}{\underset{..}{S}}—\overset{..}{\underset{..}{S}}\cdot \leftrightarrow R—\overset{..}{\underset{..}{S}}—\overset{..}{\underset{..}{S}}\vdots\overset{..}{\underset{..}{S}}$$

We have no information about the length of the sulfur chain in the radicals except that the di- and trisulfides of piperidine form no detectable radicals in piperidine solution. The reversible increase in radical concentration on heating is in accord with the suggested mechanism.

The presence of radicals as demonstrated in this study must be considered in connection with the catalysis of a broad variety of sulfur reactions by amines. The reaction of triphenylphosphine with sulfur is a relatively straightforward example about which much information is available. Bartlett, et al.,[10] have demonstrated that an ionic mechanism operates for this reaction in the absence of catalysts. They also found that triethylamine (which did not give a radical with sulfur) was not a catalyst alone, but functioned as such in the presence of hydrogen sulfide.

(14) B. A. Dogadkin, M. S. Fel'dshtein and E. N. Belyaeva, J. Polymer Sci., 53, 225 (1961); M. S. Fel'dshtein, I. G. Chernomorskaya, E. N. Gur'yanova and I. I. Eitington, Zhur. Priklad. Khim., 34, 2073 (1961).

(15) D. J. E. Ingram and M. C. R. Symons, J. Chem. Soc., 2437 (1957).

(16) D. M. Gardner and G. K. Fraenkel, J. Am. Chem. Soc., 77, 6399 (1955).

(17) F. Fairbrother, G. Gee and G. T. Merrall, J. Polymer Sci., 16, 459 (1955).

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 triethyl-amine 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 homo-lytic scission products.

Acknowledgment.—We wish to thank Miss Mildred M. Maguire for her assistance with the e.s.r. measure-ments. We are indebted to Dr. N. I. Adams of the Perkin-Elmer Corporation for supplying a synthetic ruby standard.


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 meas-urements 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 advanced[1] 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.
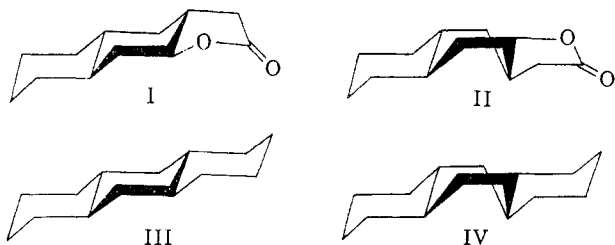
Experimental

Preparation of Materials.—*trans-syn-trans*-Perhydroanthra-cene was prepared according to the method of Fries and Schilling[2] 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 meth-anol to give 11.7 g. of colorless plates, m.p. 88–90°. Two re-crystallizations from absolute ethanol gave 8.9 g. of needles which reverted to plates on standing during the process (apparent poly-morphism), 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 $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.4; H, 12.3.

The *trans-anti-trans* isomer (IV)[3,4] was prepared[5] in quantity and carefully purified as already described.[3] The final specimen of substance IV melted at 48.5–49.7°. Analytical gas chroma-tography showed that the purified form of III was a single sub-stance 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 hydro-carbons 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 main-tained 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 un-balance 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

(1) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).

(2) K. Fries and K. Schilling, *Chem. Ber.*, **65**, 1494 (1932). The assign-ment of configuration was made by J. W. Cook, N. A. McGinnis and S. Mitchell, *J. Chem. Soc.*, 286 (1944).

(3) R. L. Clarke, *J. Am. Chem. Soc.*, **83**, 965 (1961).

(4) R. K. Hill, J. G. Martin and W. H. Stouch, *ibid.*, **83**, 4006 (1961).

(5) Work carried out at the Sterling-Winthrop Research Institute.

(6) G. Pilcher and L. E. Sutton, *Phil. Trans. Roy. Soc., London*, **A248**, 23 (1955).

(7) M. A. Frisch, Ph.D. Dissertation, University of Wisconsin, 1962.