Strain Energies in Hydrocarbons from Heats of Combustion. III. 3,4,5,6- and 2,4,5,7-Tetramethylphenanthrenes[1a]

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High-purity samples of 3,4,5,6- and 2,4,5,7-tetramethylphenanthrenes have been synthesized. Heats of combustion and vapor pressure measurements have established the buttressing effect of the methyl groups in the 3- and 6-positions on the 4- and 5-methyl groups as 3.6 ± 1 kcal./mole/CH_3 group. The buttressing effect of the fused ring in 1',9-dimethyl-1,2-benzanthracene is 3.0 ± 1 kcal./mole.

The reasons for the synthesis of strained polycyclic hydrocarbons and measurement of their strain energies by combustion experiments have been discussed previously.[2] In this paper,[2] the fact that the difference in energy of 4,5-dimethylphenanthrene (I) and 2,7-dimethylphenanthrene is 12.6 ± 1.5 kcal., whereas the difference between 1',9-dimethyl-1,2-benzanthracene (II) and 3',6-dimethyl-1,2-benzanthracene is 15.0 ± 0.7 kcal., was explained by invoking a buttressing effect, as indicated in the formula of II.


I   II
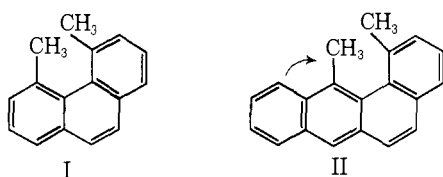
The present work was undertaken in order to get more information about the buttressing effect.[3] Herein are described the syntheses of 3,4,5,6-tetramethylphenanthrene (III) and 2,4,5,7-tetramethylphenanthrene (IV), as well as thermochemical measurements leading to a quantitative evaluation of the buttressing energy effect.

III   IV
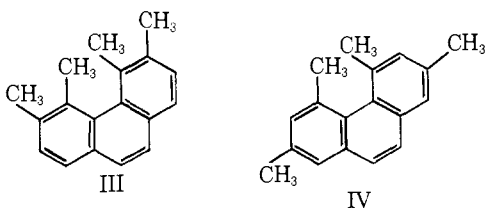
Synthetic Program

The synthetic route shown below was essentially that described for the synthesis of 4,5-dimethylphenan-

threne,[4] but in several steps improvements in preparation of intermediates have been accomplished.

Va, R_1 =CH_3; R_2= H   VIa, b
b, R_1 =H; R_2 =CH_3

VIIa, b   VIIIa, b

IXa, b   Xa, b XIa, b

XIIa, b
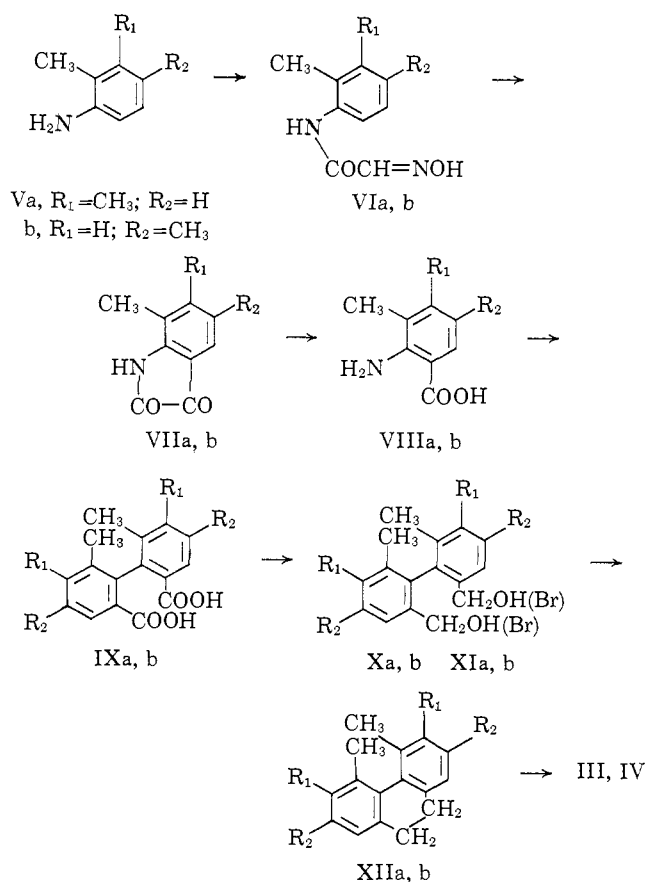
The general procedure described for the conversion of aniline to isatin[5] has been improved by effecting the conversions of 2,3-dimethylaniline (Va) and 2,4-dimethylaniline (Vb) to the corresponding isonitroso-anilides (VIa,b) at a temperature well below 100°. Also the cyclization of the isonitrosoanilides (VIa,b) to the isatins (VIIa,b) proceeds better in anhydrous hydrogen fluoride, a reagent previously not used for such reactions, than in sulfuric acid.[6] However, in the case of 2-chloroisonitrosoacetanilide no cyclization occurred in hydrogen fluoride.

Significant improvement in the oxidation of the isatins (VIIa,b) to the amino acids (VIIIa,b) was made by controlled addition of alkaline peroxide (see Experimental Section) to the isatin in sodium hydroxide–potassium chloride solution at 10–12°. Yields were essentially

(1) (a) Abstracted, in part, from the thesis presented to The Ohio State University by H. A. Karnes in partial fulfillment of the requirements for the Ph.D. degree, 1965; (b) The Ohio State University; (c) Rice University.

(2) M. A. Frisch, C. Barker, J. L. Margrave, and M. S. Newman, *J. Am. Chem. Soc.*, **85**, 2356 (1963).

(3) For a discussion of the buttressing effect, see F. H. Westheimer "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 552.

(4) G. Wittig and H. Zimmerman, *Ber.*, **86**, 629 (1953).

(5) C. S. Marvel and G. S. Hiers, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 327.

(6) Compare B. R. Baker, *et al.*, *J. Org. Chem.*, **17**, 149 (1952).

quantitative with several isatins but no amino acid was obtained when 4,7-dimethylisatin was the reactant. The syntheses of III and IV from VIIIa and VIIIb, respectively, proceeded essentially as described for similar syntheses.[4]

Experimental Section[7]

Synthesis of 3,4,5,6-Tetramethylphenanthrene (III). 2,3-Dimethylisonitrosoacetanilide (VIa). In a 2-gal. enameled pail equipped with stirrer and thermometer were placed 146 g. of chloral hydrate, 4 l. of water, a solution of 176 g. of hydroxylamine hydrochloride in 1 l. of water, 1136 g. of anhydrous sodium sulfate, and a solution of 96.8 g. of freshly distilled 2,3-dimethylaniline (Aldrich Chemical Co.) in 800 ml. of water containing 88 g. of concentrated hydrochloric acid. The resulting thick white mixture was heated to 53° during 1 hr. and heated to 60° during 1 hr. To this mixture, now light brown, was added 20 g. of hydroxylamine hydrochloride, and the temperature was held at 62–65° for 1 hr. After cooling to room temperature, the solid VIa was collected by filtration, washed with 2 l. of water, and dried at 70°. The entire filtrate and washings were treated with 36 g. of chloral hydrate and 360 g. of hydroxylamine hydrochloride at 80° for 1 hr. Cooling and filtration afforded an additional 19 g. of VIa, to make a total of 135.0 g. (88%), m.p. 122–126°. This material was carried on in the next step without further purification.

6,7-Dimethylisatin (VIIa). To 1.4 l. of anhydrous hydrogen fluoride in a 2-l. polyethylene bottle was added during 15–20 min., with external cooling, 116 g. of the above VIa in small portions. After standing until the acid had evaporated, 400 ml. of 4 N sulfuric acid was added. The resulting mixture was warmed and the solids were collected and washed with 500 ml. of water. The crude product was treated with 900 ml. of water containing 40 g. of sodium hydroxide. This mixture was heated to 80° and filtered through Hyflo Super-cel.[8] The solid VIIa, m.p. 255–258° (98.0 g., 93%), obtained on acidification with hydrochloric acid, washing, and drying, was orange in color.[9]

2-Amino-3,4-dimethylbenzoic Acid (VIIa). A solution prepared from 40.0 g. of VIIa, 10 g. of sodium hydroxide, 40 g. of potassium chloride, and 450 ml. of water was cooled to 10–12° and treated dropwise during 1 hr. with a cold solution of 44 g. of 30% hydrogen peroxide and 36 g. of sodium hydroxide in 400 ml. of water. After allowing the temperature to rise for 30 min. without external cooling (never over 25°), dropwise addition of 90 ml. of acetic acid caused precipitation of 36.0 g. (96%) of VIIIa, m.p. 180–184° (lit.[6] m.p. 184–186°), as an almost colorless solid. In a similar run, except that only 18 g. of sodium hydroxide

was used in the hydrogen peroxide solution, the yield fell to 83%.

5,5',6,6'-Tetramethyldiphenic Acid (IXa). A solution at 10° of 74.1 g. of pure VIIIa in 750 ml. of water containing 24 g. of sodium hydroxide and 31.8 g. of sodium nitrite was added in small portions to a stirred solution at 0–5° of 690 g. of 10% hydrochloric acid. On standing in the cold a colorless crystalline material separated. This was collected and dissolved in 300 ml. of cold water; the resulting solution was added to the above filtrate.

To a solution of 193 g. of hydrated cupric sulfate in 600 ml. of water was added 322 g. of concentrated ammonium hydroxide and the resulting solution was cooled to 10°. A solution at 10° prepared by adding 65 g. of hydroxylamine sulfate in 190 ml. of water and then 131 ml. of 6 N sodium hydroxide was added to the cuprammonium solution. To the resulting solution was added the above diazonium solution through an ice-cooled addition funnel having a tip curved upward and extending below the surface of the cuprammonium solution. Dow Silicone Antifoam B was added as necessary to prevent excess foaming. The addition required about 2 hr. and the temperature was held at 10–12°. The mixture was then heated to 90° during 45 min. and acidified with 600 ml. of concentrated hydrochloric acid. The crude product was filtered, washed with 1 l. of water, and dissolved in 300 ml. of 10% sodium hydroxide. After adding 15 g. of zinc dust and heating to 80°, the mixture was filtered and acidified to yield 63.0 g. (94%) of pale tan solid. Two recrystallizations from methanol afforded 37.0 g. (55%) of pure IXa, m.p. 253–255°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1. Found: C, 72.2; H, 6.0.

When crude VIIIa was used the yield of pure IX varied from 44 to 52%.

2,2'-Bis(hydroxymethyl)-5,5',6,6'-tetramethylbiphenyl (Xa). To a stirred mixture of 41 g. of lithium aluminum hydride in 3 l. of dry ether at reflux in a 5-l. flask was added 99.0 g. of XIa in portions through a Gouch rubber tube attached to an erlenmeyer flask. After 17 hr. at reflux the mixture was cooled to 0° and treated dropwise with 200 ml. of water. The resulting slurry was filtered (Hypo Super-cel) and the solids were extracted well with ether. Concentration and crystallization from benzene afforded 82.0 g. (90.5%) of colorless Xa, m.p. 135–137°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 80.1; H, 8.2.

2,2'-Bis(bromomethyl)-5,5',6,6'-tetramethylbiphenyl (XIa). To a solution of 27.9 g. of Xa and 2 ml. of pyridine in 900 ml. of dry benzene was added dropwise 67 g. of phosphorus tribromide. The mixture was held at 58–60° for 2 hr. and worked up as usual to yield 36.0 g. (90%) of colorless XIa, m.p. 111.5–113.0°, on crystallization from hexane. In other similar runs, yields of 83 to 85% of pure XIa were obtained.

Anal. Calcd. for $C_{18}H_{20}Br_2$: C, 54.6; H, 5.1. Found: C, 54.5; H, 4.9.

9,10-Dihydro-3,4,5,6-tetramethylphenanthrene (XIIa). A solution of 60.0 g. of XIa in 700 ml. of dry ether was added dropwise during 3.5 hr. to a solution at reflux of the phenyllithium prepared from 75 g. of bromoben-

(7) All melting points of intermediate compounds were taken on a Fisher-Johns melting point apparatus and are uncorrected. Melting points of final pure products were taken in a Hershberg-type melting point apparatus using N.B.S. calibrated short stem thermometers. All microanalyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The phrase "treated in the usual manner" means that the organic solvent layer of the product was washed successively with dilute acid and/or base, saturated sodium chloride solution, filtered through anhydrous magnesium sulfate, and concentrated under reduced pressure. Alcoa chromatographic alumina, activated by heating to 220° for 24 hr., was used for chromatography unless stated otherwise.
(8) An inert cellulose filter aid.
(9) German Patent 514,595; *Chem. Abstr.*, **25**, 2157 (1931), gives m.p. 252°.

zene and 7.2 g. of lithium in 300 ml. of ether. After 1.5 hr. at reflux the reaction mixture was worked up as usual to yield 29.6 g. (84%) of XIIa, b.p. 155–165° (1.7 mm.). This was 98% pure by g.l.c. On crystallization from 75 ml. of absolute alcohol 27.0 g. of colorless XIIa, m.p. 98.0–100.0°, was obtained.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.3; H, 8.4.

3,4,5,6-Tetramethylphenanthrene (III). In a 300-ml. steel bomb equipped with a glass liner was heated for 10 hr. at 300–305° a mixture of 5.0 g. of XIIa, 40 ml. of pure benzene, and 7.5 g. of 5% rhodium on alumina (air flushed out with nitrogen). The crude product was shown by g.l.c. to consist of 46% of XIIa, 51% of III, and 3% of an unknown substance. On chromatography over 450 g. of alumina, elution with hexane (6 l.) afforded 2.5 g. of XIIa (90% pure by g.l.c.) followed by 2.4 g. of III (>97% pure by g.l.c.) on elution with 5 l. of 5% benzene in hexane. On recrystallization from alcohol 2.1 g. of pure III, m.p. 70.0–71.2°, was obtained. This material was over 99% pure by g.l.c. and molecular weight determination.[10]

Anal. Calcd. for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 92.3; H, 8.0.

The 1,3,5-trinitrobenzene derivative, m.p. 104.5–106°, was prepared and crystallized from ethanol as orange crystals.

Anal. Calcd. for $C_{24}H_{21}N_3O_6$: N, 9.4. Found: N, 9.2.

In a dehydrogenation run in which the thermocouple control failed, the temperature rose above 310° by an unknown amount. On crystallization of the product a substance, m.p. 151.0–152.0°, was obtained in about 50% yield. Analysis and n.m.r. analysis indicated that demethanation to 3,5-dimethyl-4H-cyclopenta-[def]phenanthrene had occurred. A peak at γ 7.58 (6H) was obtained for the 3,5-methyl groups and a peak at γ 6.25 (2H) for the methylene hydrogens. A parent peak at 218 was obtained on mass spectrographic analysis.[10]

Anal. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.2; H, 6.4.

Synthesis of 2,4,5,7-Tetramethylphenanthrene. 2,4-Dimethylisonitrosoacetanilide (VIb). A reaction mixture as described for VIa, except that all amounts were on half-scale, was heated slowly to 80° during 3 hr. The resulting brown solid was collected, washed with 500 ml. of water, and dried to yield 39.0 g. (50.7%) of VIb, m.p. 158–169°. Treatment of the filtrate and washings to which 130 g. of potassium bicarbonate had been added with 72 g. of chloral hydrate and heating to 82° during 1.5 hr. produced an additional 13.0 g. of VIb, m.p. 152–159°, so that the total yield was 67.5%. On recrystallization of the crude material twice from benzene–ethanol (19:1) pure VIb, m.p. 173–175°, was obtained in colorless form with little loss. Evidently a polymorphic form was at hand as the reported[6] m.p. is 158–159°.

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.5; H, 6.1. Found: C, 62.7; H, 6.3.

(10) Mass spectrographic analysis by Dr. Mynard Hamming, Continental Oil Co., Ponca City, Okla., whom we thank, showed this material to be almost 100% pure. A small peak at 218 was present. This undoubtedly arose from a loss of methane by cyclization of one of the most hindered methyl groups. Such a cyclization product has been obtained by us in another run which was accidently over-heated.

5,7-Dimethylisatin (VIIb). By essentially the same treatment as described for VIa, VIb was cyclized to pure VIIb, m.p. 249–251° (lit.[6] m.p. 243°), in 89% yield.

2-Amino-3,5-dimethylbenzoic Acid (VIIIb). In reactions in which the scale was double that described for VIIa, except that the time used for addition of the alkaline peroxide solution was 3.5 hr., VIIb was converted in 96–98% yield into crude VIIIb, m.p. 192–194° after sintering at 178° (lit.[6] m.p. 188–189°, but in our experience the amino acid samples never had a sharp melting point). This crude acid was used directly in the next step.

4,4',6,6'-Tetramethyldiphenic Acid (IXb). The diazotization of VIIIb was carried out essentially as described for VIIIa to yield 172.0 g. (83%) of almost white IXb, pure enough for esterification. A pure sample of IXb, m.p. 275–282° dec., was obtained by crystallization from methanol.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1. Found: C, 72.3; H, 5.9.

Diethyl 4,4',6,6'-Tetramethyldiphenate. Esterification of IXb with ethanol by heating for 2 days with benzene and a small amount of sulfuric acid afforded the pure ester in 71% yield as a pale yellow oil, b.p. 185–195° (1 mm.). A colorless analytical sample, m.p. 70.5–71.5°, was obtained by recrystallization from ethanol.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.6; H, 7.4. Found: C, 74.6; H, 7.4.

2,2'-Bis(hydroxymethyl)-4,4',6,6'-tetramethylbiphenyl (Xb). A solution of 141.6 g. of the above ester in 1 l. of dry ether was added dropwise, at a rate to maintain reflux, to a suspension of 38 g. of lithium aluminum hydride in 1 l. of ether. After 16 hr. at reflux, the mixture at 0° was slowly treated with 152 ml. of water. This mixture was heated to reflux and then filtered. The aluminum salts were treated with 2 l. of dilute sulfuric acid and this mixture was extracted with ether. After treatment of the combined ether solutions as usual, crude Xb was obtained which, after recrystallization from benzene–ethanol (49:1), yielded 99.6 g. (93%) of colorless crystalline Xb, m.p. 172–175°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 80.2; H, 8.2.

The same diol was prepared in 88% yield by reduction of purified IXb directly.

2,2'-Bis(bromomethyl)-4,4',6,6'-tetramethylbiphenyl (XIb). As described above for Xa, 96.0 g. of Xb was converted into colorless XIb, m.p. 132.5–134.0°, in 89% yield. The crude product was purified by crystallization from petroleum ether, b.p. 65–70°.

Anal. Calcd. for $C_{18}H_{20}Br_2$: C, 54.6; H, 5.1. Found: C, 54.8; H, 5.2.

9,10-Dihydro-2,4,5,7-tetramethylphenanthrene (XIIb). A solution of 93.0 g. of XIb in 700 ml. of ether was added dropwise during 4 hr. to the phenyllithium prepared from 125 g. of bromobenzene and 12 g. of lithium wire in 1.4 l. of ether. After work-up as usual the crude product was vacuum distilled. The fraction, b.p. 160–175° (1 mm.), weighed 44.0 g. and on two recrystallizations from ethanol yielded 41.4 g. (76.2%) of colorless XIIb, m.p. 85–87°, which was 99% pure by g.l.c. analysis.

Table I. Heat of Combustion of 2,4,5,7-Tetramethylphenanthrene

Run	m (vacuum), g.	ΔE_{tot}, cal.	$\Delta E_{fuse.\ ign}$, cal.	$-$Washburn correction, cal.	$-\Delta E_c°/M$, cal. g.$^{-1}$	Dev., cal. g.$^{-1}$
1	0.49764	4905.88	4.86	1.41	9845.69	-4.34
2	0.49984	4931.59	3.89	1.66	9855.23	5.20
3	0.50178	4951.10	4.66	1.64	9854.88	4.85
4	0.49939	4921.79	4.08	1.56	9844.31	-5.72
5	0.49999	4918.88	4.86	1.55	9825.14	-24.89^a
					Av. 9850.03	±2.92

$$\Delta E_c° = -2308.32 \pm 0.68 \text{ kcal./mole} \qquad \Delta H_c° = -2311.58 \text{ kcal./mole}$$
$$\Delta H_f°_{298}(s) = 3.81 \pm 0.84 \text{ kcal./mole}$$

^{a} Discarded.

Table II. Heat of Combustion of 3,4,5,6-Tetramethylphenanthrene

Run	m (vacuum), g.	$-\Delta E_{tot}$, cal.	$\Delta E_{fuse.\ ign}$, cal.	ΔE_{carbon}, cal.	$-$Washburn correction, cal.	$\Delta E°/M$, cal. g.$^{-1}$	Dev., cal. g.$^{-1}$
1	0.50054	4940.86	4.86	0.39	1.67	9857.03	-4.01
2	0.50684	5002.52	4.86	0.78	1.69	9855.56	-5.48
3	0.50559	4992.53	5.25	0.39	1.66	9860.22	-0.82
4	0.50244	4962.19	4.27	0.00	1.68	9864.34	3.30
5	0.50109	4950.34	3.88	0.00	1.68	9868.05	7.01
						Av. 9861.04	±2.31

$$\Delta E_c° = -2310.90 \pm 0.54 \text{ kcal./mole} \qquad \Delta H_c° = -2314.16 \text{ kcal./mole}$$
$$\Delta H_f°_{298}(s) = 6.39 \pm 0.73 \text{ kcal./mole}$$

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.8; H, 8.3.

2,4,5,7-Tetramethylphenanthrene (IV). A mixture of 5.9 g. of XIIb, 9.0 g. of 5% rhodium on alumina, and 45 ml. of pure benzene was heated in a glass-lined steel bomb at 302–306° for 10 hr. On chromatography over 450 g. of alumina as in the case of III, fractions rich in IV were obtained. From these, by crystallization from hexane, was obtained 1.4 g. (23.6%) of pure IV, m.p. 111.0–113.0°, shown to be greater than 99% pure by g.l.c. and by mass spectrographic analysis.[10]

Anal. Calcd. for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 92.4; H, 7.7.

The 1,3,5-trinitrobenzene derivative, gold needles, m.p. 146.5–148°, was prepared and recrystallized from ethanol.

Anal. Calcd. for $C_{24}H_{21}N_3O_6$: N, 9.4. Found: N, 9.3.

In other runs small amounts of a yellow hydrocarbon were isolated by virtue of the slight solubility in hexane. This compound[11] was undoubtedly the known 2,7-dimethylpyrene as it melted at 240.0–241.0° and gave an n.m.r. spectrum consistent with this structure.

Heats of Combustion

A new bomb calorimeter of conventional design has been put into operation at the Rice University. The ignition and temperature measuring systems have been described.[12] Benzoic acid calibrations established the precision and accuracy to be better than ±0.03%. The experimental combustion data are presented in Tables I and II. The sample mass was based on direct weighing with correction for buoyancy. Tests[13] showed that combustion was complete, with less than 0.01%

CO in the residual bomb gases. Corrections to standard states were made by the method of Hubbard, *et al.*[14] The heats of formation are based on a molecular weight of 234.346, and -94.054 and -68.317 kcal./mole for the heats of formation of carbon dioxide and liquid water, respectively. All energies are expressed in terms of the defined calorie equal to 4.1840 absolute joules.

Discussion of Results

The first paper in this series presented strain energies calculated directly from heats of combustion of crystals and though the heats of sublimation of these compounds are now available, it is of interest to calculate "solid" strain energies even though they may include variations characteristic of crystal effects. The heats of formation of the solid phases of 2,4,5,7- (III) and 3,4,5,6-tetramethylphenanthrene (IV) are shown in Table III; the difference, 2.6 kcal./mole is the additional strain energy in IV. The 4- and 5-methyl groups in both these compounds are intramolecularly overcrowded, but in III part of the resulting strain is relieved by bending of the methyl–ring bonds. This is partially prevented in IV by the 3- and 6-methyl groups. A portion of the strain energy can be attributed to the "normal" interaction of isolated *ortho* methyl groups which has been estimated to be $\sim$0.6 kcal./methyl group.[15,16] Consequently the solid buttressing effect is $\sim$0.7 kcal. per pair of methyl groups.

The heats of sublimation of III and IV, 2,7- (I) and 4,5-dimethylphenanthrene (II) and 3',6- (VI) and 1',9-dimethyl-1,2-benzanthracene (VII) have been obtained[17] by the Knudsen effusion method with, except

(11) F. Runge and A. Meckelburg, *Ber.*, 86, 373 (1953), give m.p. 238.5° for 2,7-dimethylpyrene.
(12) B. D. Kybett, G. K. Johnson, C. K. Barker, and J. L. Margrave, *J. Phys. Chem.*, 69, 3603 (1965).
(13) L. W. Winkler, *Z. anal. Chem.*, 102, 99 (1935).
(14) W. N. Hubbard, D. W. Scott, and G. Waddington, "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience Publishers, Inc., New York, N. Y., 1956.
(15) J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949).
(16) H. J. Bernstein, *Trans. Faraday Soc.*, 58, 2285 (1962).
(17) M. L. Fyster, B. D. Kybett, and J. L. Margrave, unpublished data.

Table III. Strain Energies in Aromatic Hydrocarbons

	$\Delta H_f°(s)$, kcal./mole	Strain energy, solid, kcal./mole	ΔH, sublimation, kcal./mole	$\Delta H_f°(vap)$, kcal./mole	Strain energy, vapor, kcal./mole
I 2,7-Dimethylphenanthrene	8.7 ± 0.6^a⎫	12.6 ± 1.5	25.5 ± 0.2	34.2 ± 0.6⎫	12.1 ± 1.5
II 4,5-Dimethylphenanthrene	21.3 ± 1.4^a⎰		25.0 ± 0.3	46.3 ± 1.4⎰	
III 2,4,5,7-Tetramethylphenanthrene	3.8 ± 0.8⎱	2.6 ± 1.1	27.3 ± 0.4	31.1 ± 0.9⎫	7.2 ± 1.4
IV 3,4,5,6-Tetramethylphenanthrene	6.4 ± 0.7⎰		31.9 ± 0.9	38.3 ± 1.1⎰	
V Phenanthrene	$27.5 \pm 0.6^{b,c}$		20.7 ± 0.5^d	48.2 ± 0.8	
VI 3′,6-Dimethyl-1,2-benzanthracene	18.2 ± 0.7^a⎫	15.0 ± 0.7	26.9 ± 0.4	45.1 ± 0.8⎫	15.0 ± 1.1
VII 1′,9-Dimethyl-1,2-benzanthracene	33.2 ± 0.7^a⎰		26.9 ± 0.8	60.1 ± 1.1⎰	
VIII 1,2-Benzanthracene	40.6 ± 0.6^e		25.0 ± 0.5^e	65.6 ± 0.8	

[a] Reference 2. [b] H. Skinner, private communication. [c] A. Magnus, H. Hartmann, and F. Becker, *Z. physik. Chem.* (Leipzig), **197**, 75 (1951). [d] R. S. Bradley and T. G. Cleasby, *J. Chem. Soc.*, 1690 (1953). [e] J. D. Kelley and F. O. Rice, *J. Phys. Chem.*, **68**, 3794 (1964).

for V, the same material as used for the combustion experiments. These are shown in Table III together with data for the parent compounds.

The differences between the heats of formation of I and phenanthrene (V) are 18.8 kcal./mole in the solid and 14.0 kcal./mole in the vapor and are similar to the corresponding differences between II and III, 17.5 and 15.2 kcal./mole, respectively. This indicates that the addition of the 2,7-dimethyl groups does not appreciably affect the stability of the molecule, even though the increment in the vapor phase is slightly smaller than the usual 15.7 kcal./mole.

In the vapor, from the data on I and II, one derives a strain energy of 12.1 ± 1.5 kcal./mole for the 4,5-methyl group interaction. This must be considered as a lower limit, since phenanthrene itself is nonplanar owing to interference between the 4,5-hydrogens, but the magnitude of this effect is not known. By comparison, the data for compounds III and IV, which contain the same 4,5-methyl group interaction, but with CH_3 buttressing groups in the 3,6-positions instead of H atoms, show a difference in the stabilities of 7.2 ± 1.4 kcal./mole. These CH_3 groups are causing 7.2 kcal./mole more distortion than do H atoms in the 3,6-positions and thus exerting a buttressing effect, making compound IV less stable. Since ΔH_f[3,6-dimethyl-

phenanthrene(s)] ≈ 11.9 ± 1.0 kcal./mole, one would have predicted ΔH_f[3,4,5,6-tetramethylphenanthrene(s)] ≈ −6 kcal./mole based on the 18-kcal./mole increment established from the I–V and II–III data, but this becomes ~+6 kcal./mole when allowance is made for the 4,5-strain energy.

The differences in the heats of formation of 1,2-benzanthracene and 3′,6-dimethyl-1,2-benzanthracene are 22.4 and 20.5 kcal./mole in the solid and vapor phases, respectively, which are larger than those in the phenanthrenes. The lattice energies of 3′,6- and 1′,9-dimethyl-1,2-benzanthracenes are identical, and the difference in their heats of formation is 15.0 kcal./mole. This is larger by 3.0 kcal./mole than that between the dimethylphenanthrenes, and the deviation is of the same sign as the change observed on substituting 3,6-methyl groups for 3,6-H atoms on the phenanthrenes. One concludes that the fused ring sterically approximates a methyl group located at the same position.[18]

(18) M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941).

Gaseous Products from Interactions of Recoil Carbon-11 Atoms with Liquid Hydrocarbons[1a]

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The chemical behavior of recoil carbon-11 in different types of C_5–C_7 hydrocarbons has been investigated by determining the radiochemical yields of gaseous products containing ^{11}C, in order to clarify the mechanism for the formation of these products. Initial studies showed that iodine scavenger lowers the yields of all of these products except acetylene, while increased radiation dose increases the yields of products other than acet-

ylene. Individual and relative yields of the two-carbon products are shown to be highly dependent on the structure of the target molecules. The results are discussed in terms of the decomposition modes available to the activated complexes assumed to result from insertion-type reactions of three primary species: ^{11}C, ^{11}CH, and $^{11}CH_2$. Reactions of recoil ^{11}C atoms with mixtures of benzene and methylcyclopentane were studied. The yields of these products are approximately linear functions of the molar concentrations of the two components.