# Strain Energies in Hydrocarbons from Heats of Combustion. I. 4,5- and 2,7-Dimethylphenanthrenes, 1,12- and 5,8-Benzo(c)phenanthrenes and 1',9- and 3',6-Benzanthracenes[1a]

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Heat of combustion measurements have established the strain energies due to methyl interferences as 12.6 ± 1.5 kcal./mole for 4,5- (compared to 2,7-) dimethylphenanthrenes; as 11.0 ± 1.6 kcal./mole for 1,12- (compared to 5,8-) dimethylbenzo(c)phenanthrenes; and as 15.0 ± 0.7 kcal./mole for 1',9- (compared to 3',6-) dimethyl-1,2-benzanthracenes. The structural implications are discussed.

Interest in the synthesis of certain compounds containing methyl groups in close proximity to each other arose in connection with the problem of chemical carcinogenesis. The compounds 4,5-dimethylchrysene (I) and 1',9-dimethyl-1,2-benzanthracene (II) were desired for testing as they represented structures bearing a similarity to the potent carcinogen, 3,4-benzpyrene (III).
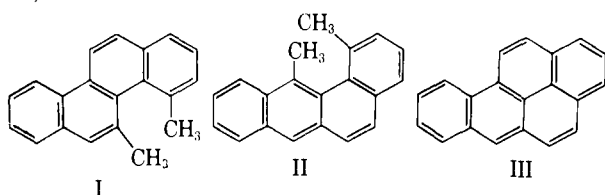
The syntheses of I and II have been accomplished.[2a,b] During the course of this work other features of interest with regard to compounds of this type arose. The discovery of optical activity due to warping of the normally planar aromatic system by intramolecular overcrowding was made[3] and this led eventually to the synthesis and resolution of 1,12-dimethylbenzo(c)-phenanthrene-5-acetic acid[3] (IV) and of hexahelicene[4] (V).

IV, $[\alpha]_D$ ca. $\pm360°$ V, $[\alpha]_D$ ca. $\pm3600°$
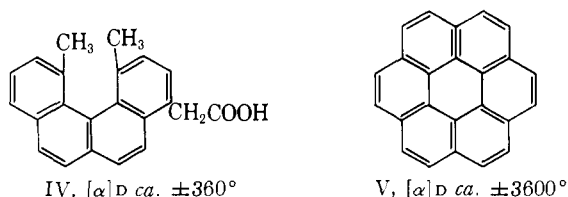
Another question which arose during this work was that of the magnitude of the strain introduced into molecules such as I, II, and other analogs. In order to determine the strains involved, a joint program was agreed upon in which the strained hydrocarbons and unstrained isomers were to be synthesized at Ohio State University and combustion studies would be carried out at the University of Wisconsin. The differences in heats of combustion would then give a measure of the intramolecular strain involved, along with any crystal lattice energy effects due to the non-planarity of the strained molecules. Heats of fusion for hindered hydrocarbons, for example, are known to be higher than for the isomeric, non-hindered molecules.[5]

In this paper, heat of combustion data for three isomeric pairs will be described and discussed as if the heats of sublimation of these pairs are identical, i.e., VI = VII, VIII = IX, etc. Experimental measurements to check this assumption are in progress.

2,7- and 4,5-Dimethylphenanthrenes.—The difference in heats of combustion obtained in this case

VI   VII
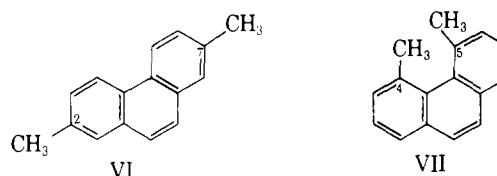
$(12.6 \pm 1.5$ kcal./mole) might be called the standard value for steric strain due to intramolecular overcrowding because these two compounds are the simplest isomers which can be written in which the pertinent feature is accommodated. The experimental combustion data are presented in Table I.

TABLE I

HEATS OF COMBUSTION

Run	m (air), g.	ΔR, ohm (a)	$-\Delta E_{tot}$, cal.	ΔE_{fuse}, cal.	ΔE_{jgn}, cal.	$-\Delta E_c$, cal. g.$^{-1}$	Deviation, cal. g.$^{-1}$
			2,7-Dimethylphenanthrene				
1	0.99869	0.1191771	9651.03	4.19	0.90	9658.59	0.22
2	0.98597	.1176574	9527.96	4.00	0.75	9658.73	0.36
3	1.00010	.1192073	9653.48	4.58	1.00	9646.93	-11.44^a
4	0.62058	.0741599	5998.57	5.51	0.78	9655.93	$- 2.44$
5	0.61768	.0738438	5973.00	5.51	0.57	9660.22	1.86
						Av. 9658.37	± 0.89

$\Delta E_c = -1990.67 \pm 0.40$ kcal./mole $\Delta H_c^0 = -1991.72 \pm 0.40$ kcal./mole

$\Delta E_c^0 = -1989.65 \pm 0.40$ kcal./mole $\Delta H_{f,298}^0 = 8.69 \pm 0.56$ kcal./mole

Run	m (air), g.	ΔR, ohm	$-\Delta E_{tot}$, cal.	ΔE_{fuse}, cal.	ΔE_{jgn}, cal.	$-\Delta E_c$, cal. g.$^{-1}$	Deviation, cal. g.$^{-1}$
			(b) 4,5-Dimethylphenanthrene				
1	0.99091	0.1189649	9633.85	4.04	0.90	9717.24	$- 2.07$
2	.99396	.1193101	9661.80	4.42	.75	9715.31	$- 4.00$
3	.99545	.1193801	9667.47	4.97	.82	9705.84	-13.47
4	.63339	.0762522	6167.81	4.66	.67	9729.38	10.07
5	.64411	.0774960	6268.42	5.39	.57	9722.66	3.35
6	.63938	.0769290	6224.19	5.26	.68	9725.43	6.13
						Av. 9719.31	± 3.42

$\Delta E_c = -2003.23 \pm 1.40$ kcal./mole $\Delta H_c^0 = -2004.28 \pm 1.40$ kcal./mole

$\Delta E_c^0 = -2002.21 \pm 1.40$ kcal./mole $\Delta H_{f,298}^0 = + 21.25 \pm 1.40$ kcal./mole

^{a} Discarded.

5,8- and 1,12-Dimethylbenzo(c)phenanthrenes.—The difference in heats of combustion of these com-

VIII   IX

(1) (a) Abstracted, in part, from the thesis presented to the University of Wisconsin by Margaret A. Frisch in partial fulfillment of the requirements for the Ph.D. degree, August, 1962; (b) University of Wisconsin; (c) The Ohio State University.

(2) (a) M. S. Newman, J. Am. Chem. Soc., 62, 2295 (1940); (b) M. S. Newman, W. C. Sagar and M. V. George, ibid., 82, 2376 (1960); see also J. Cason and D. D. Phillips, J. Org. Chem., 17, 298 (1952).
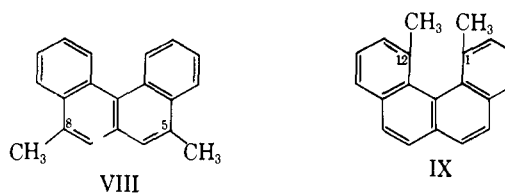
(3) This development is reviewed by M. S. Newman and R. M. Wise, J. Am. Chem. Soc., 78, 450 (1956).

(4) M. S. Newman and D. Lednicer, ibid., 78, 4765 (1956).

(5) D. D. Tunnicliff, Shell Development Co., Houston, Texas, as cited in "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 10.

pounds is less than the standard value (11.0 ± 1.6 kcal./mole); experimental data are summarized in Table II.

TABLE II
HEATS OF COMBUSTION

Run	m (air), g.	ΔR, ohm	$-\Delta E_{tot}$, cal.	ΔE_{fuse}, cal.	ΔE_{ign}, cal.	$-\Delta E_c$, cal. g.$^{-1}$	Deviation, cal. g.$^{-1}$
(a)	5,8-Dimethylbenzophenanthrene						
1	0.97562	0.1155416	9356.62	7.14	0.90	9582.20	7.93[a]
2	.99752	.1176384	9526.42	4.23	.90	9544.97	−29.30[a]
3	1.00226	.1196299	9687.70	4.23	.75	9660.88	86.62[a]
4	1.00351	.1191500	9648.83	4.54	.80	9609.77	35.50[a]
5	0.61781	.0732431	5924.42	5.82	.59	9579.00	4.73
6	.61613	.0729371	5899.66	4.50	.55	9567.16	−7.11
7	.61712	.0731097	5915.18	4.87	.94	9575.73	1.46
8	.64930	.0769178	6223.28	5.12	1.00	9575.17	0.91

Av. 9574.26 ± 2.51

$\Delta E_c = -2452.35 \pm 1.28$ kcal./mole $\Delta H_c^0 = -2453.41 \pm 1.28$ kcal./mole

$\Delta E_c^0 = -2451.04 \pm 1.28$ kcal./mole $\Delta H_{f}^{0},_{298} = +25.86 \pm 1.28$ kcal./mole

Run	m (air), g.	ΔR, ohm	$-\Delta E_{tot}$, cal.	ΔE_{fuse}, cal.	ΔE_{ign}, cal.	$-\Delta E_c$, cal. g.$^{-1}$	Deviation, cal. g.$^{-1}$
(b)	1,12-Dimethylbenzophenanthrene						
1	0.99722	0.1184608	9593.02	4.58	0.85	9614.32	−3.07
2	.99522	.1182664	9577.28	4.00	.80	9618.46	1.06
3	.99749	.1185804	9602.71	4.69	.90	9621.26	3.87
4	.58833	.0700598	5666.93	4.77	2.61	9619.69	2.29
5	.57023	.0678639	5489.31	5.01	2.54	9613.25	−4.14

Av. 9617.40 ± 1.55

$\Delta E_c = -2463.40 \pm 0.80$ kcal./mole $\Delta H_c^0 = -2464.46 \pm 0.80$ kcal./mole

$\Delta E_c^0 = -2462.09 \pm 0.80$ kcal./mole $\Delta H_{f}^{0},_{298} = +36.91 \pm 0.92$ kcal./mole

[a] Discarded.

At first glance this result is surprising, since on inspection of the formulas, the degree of hindrance seems greater than that in the preceding case. However, the argument might be advanced that even in the parent aromatic hydrocarbon, benzo(c)phenanthrene, there is considerable loss of resonance energy due to the noncoplanarity caused by hindrance at the 1- and 12-positions. In support of this argument two facts may be adduced: (1) The experimentally determined resonance energy for benzo(c)phenanthrene (127.7 kcal./mole) is the smallest of any of the five tetracyclic hydrocarbons of formula $C_{18}H_{12}$: triphenylene, 135.8; chrysene, 134.4; 1,2-benzanthracene, 130.4; and naphthacene, 129.6.[6] (2) X-Ray crystallographic studies show that benzo(c)phenanthrene is not a planar molecule.[7] Since there is already a certain amount of strain in VIII, the introduction of the 1,12-methyl groups in IX does

X   XI
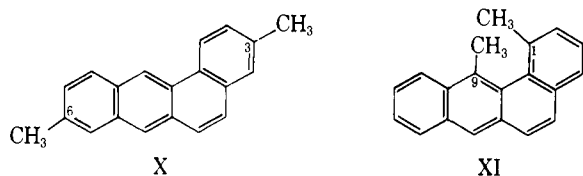
not produce as much strain as the introduction of two methyl groups in the 4,5-positions of phenanthrene does in the phenanthrene series.

3',6- and 1',9-Dimethyl-1,2-benzanthracenes.— The difference in heats of combustion of these com-

(6) A. Magnus and F. Becker, *Erdol u. Kohle*, **4**, 115 (1951).

(7) F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3320 (1954). A private communication to M. S. Newman from Dr. Schmidt states that a more detailed and accurate study will soon be published.

pounds is greater than the standard value (15.0 ± 0.7 kcal./mole). The data are presented in Table III.

TABLE III
HEATS OF COMBUSTION

Run	m (air), g.	ΔR, ohm	$-\Delta E_{tot}$, cal.	ΔE_{fuse}, cal.	ΔE_{ign}, cal.	$-\Delta E_c$, cal. g.$^{-1}$	Deviation, cal. g.$^{-1}$
(a)	3',6-Dimethylbenzanthracene						
1	0.63276	0.0747392	6045.29	4.50	0.67	9545.67	
3	.64407	.0760531	6151.56	5.08	.90	9541.78	
4	.62677	.0739596	5982.23	5.01	.65	9535.51	
5	.64720	.0765141	6188.85	5.01	1.00	9553.22	
					Av.	9544.05[a]	−0.69
6	0.63577	0.0750626	6074.22	6.05	0.73	9544.43	−0.31
7	0.64420	0.0760660	6155.42	6.40	0.67	9545.75	1.01
					Av.	9544.74 ± 0.52	

$\Delta E_c = -2444.69 \pm 0.48$ kcal./mole $\Delta H_c^0 = -2445.75 \pm 0.48$ kcal./mole

$\Delta E_c^0 = -2443.38 \pm 0.48$ kcal./mole $\Delta H_{f}^{0},_{298} = +18.20 \pm 0.67$ kcal./mole

Run	m (air), g.	ΔR, ohm	$-\Delta E_{tot}$, cal.	ΔE_{fuse}, cal.	ΔE_{ign}, cal.	$-\Delta E_c$, cal. g.$^{-1}$	Deviation, cal. g.$^{-1}$
(b)	1',9-Dimethylbenzanthracene						
1	0.64783	0.0770164	6229.48	4.73	3.34	9603.46	
2	.65065	.0773140	6253.55	4.69	0.72	9602.92	
3	.64990	.0771722	6242.08	4.66	.73	9596.38	
4	.65067	.0773611	6257.36	4.27	.80	9609.00	
					Av.	9602.94[a]	−0.46
5	0.64551	0.0766890	6205.83	6.17	0.60	9604.81	1.41
6	0.64668	0.0768176	6216.24	6.71	0.67	9602.46	−0.94
					Av.	9603.40 ± 0.72	

$\Delta E_c = -2459.69 \pm 0.48$ kcal./mole $\Delta H_c^0 = -2460.75 \pm 0.48$ kcal./mole

$\Delta E_c^0 = -2458.38 \pm 0.48$ kcal./mole $\Delta H_{f}^{0},_{298} = +33.20 \pm 0.67$ kcal./mole

[a] Weighted as one experiment.

This result is undoubtedly due to the buttressing effect[8] of the fused ring on the 9-methyl group. The buttressing effect of a fused ring should approximate that of a methyl group since the steric effect of an adjacent fused ring on a function is about the same as the effect of a methyl group located at the same position.[9] In a similar vein, a fused aromatic ring containing a methyl group ortho to the point of fusion should approximate the steric effect of an *ortho tert*-butyl group.[10] Viewed in this way the degree of strain in *o*-di-*tert*-butylbenzene should be comparable to that of 4,5-dimethylphenanthrene (VII). A recent combustion of the isomers, 1,2,4- and 1,3,5-tri-*tert*-butylbenzenes[11] has given 16.8 ± 1.7 kcal./mole for the energy difference.

Further studies on the strain involved in the buttressing effect are under way in this cooperative program.

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

(9) This similarity in effect was pointed out in the article by M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941). See also J. Packer, J. Vaughan and E. Wong, *ibid.*, **80**, 905 (1958), for further discussion of this effect.

(10) M. S. Newman and W. H. Powell, *J. Org. Chem.*, **26**, 812 (1961).

(11) U. Kruerke, C. Hoogzard and W. Hübel, *Ber.*, **94**, 2817 (1961).