

851. Molecular Polarisability. The Molar Kerr Constants, Polarizations, etc., of Ten Polynuclear Hydrocarbons as Solutes in Benzene.

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Values, from experiment, of the semi-axes of the polarisability ellipsoids of benzene, triphenylene, and coronene, suggest that $10^{23}b_3 = 0.413 + 0.0548n$, where n is the number of carbon-carbon links in the molecule. This empirical equation is used, in conjunction with molar Kerr constants and refractivities, to estimate b_1 , b_2 , and b_3 for eight other polynuclear hydrocarbons. Results appear credible but at present cannot be checked by direct measurement.

LEAST unsuccessful of the attempts to correlate carcinogenic activity with molecular features seem to be those involving the sizes^{1,2} or shapes^{2,3} of the carcinogens and details of the electron distributions^{4,5} therein. The anisotropy of polarisability of a molecule depends considerably on the same factors;^{6a} information—to date absent from the literature—on this property for cancer-producing substances might therefore be of interest. As a background to subsequent work the ten polynuclear hydrocarbons listed in Tables 1 and 2 have been examined. Several of them are parent structures of active carcinogens. Moreover, through their non-polarities, they present difficulties similar to those previously encountered with naphthalene;^{6b} ways of overcoming these require consideration.

¹ Barry, Cook, Haslewood, Hewett, Hieger, and Kennaway, *Proc. Roy. Soc.*, 1935, *B*, **117**, 318.

² Bergmann, *Cancer Res.*, 1942, **2**, 660.

³ Lettré, *Z. physiol. Chem.*, 1944, **280**, 28.

⁴ Pullman, *Ann. Chim.*, 1947, **2**, 5; *Bull. Assoc. franç. Cancer*, 1947, **34**, 245; *Compt. rend.*, 1947, **224**, 120; **225**, 738.

⁵ Pullman and Pullman, *Experientia*, 1946, **2**, 364; *Rev. Sci.*, 1946, **84**, 145.

⁶ Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (b) *J.*, 1955, 1641; (c) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., 1960, Vol. I, p. 2459; (d) *J.*, 1954, 1577.

TABLE I.

Increments of refractive indexes, densities, Kerr and dielectric constants observed with solutions in benzene at 25°.

Solute: Anthracene										
$10^5 w_2$	191	222	319	320	409	654	856	897	994	1244
$10^4 \Delta n$	4	5	7	—	9	12	17	19	20	24
$10^4 \Delta n^2$	12	16	20	—	26	35	50	57	59	72
$10^5 \Delta d$	38	—	—	—	77	122	155	—	179	237
$10^4 \Delta \epsilon$	10	11	20	18	26	40	50	52	64	78
$10^{11} \Delta B$	104	—	—	—	220	-366	477	—	540	651

whence $\sum \Delta n / \sum w_2 = 0.202$; $\sum \Delta n^2 / \sum w_2 = 0.600$; $\sum \Delta d / \sum w_2 = 0.1859$; $\sum \Delta \epsilon / \sum w_2 = 0.604$;
 $\sum \Delta B / \sum w_2 = 5.42 \times 10^{-7}$.

Solute: Phenanthrene					Solute: Naphthalene				
$10^5 w_2$	995	1611	2554	3256	$10^6 w_2$	120	156	194	203
$10^4 \Delta n$	16	26	42	53	$10^5 \Delta n$	2	4	5	6
$10^4 \Delta n^2$	48	78	126	159	$10^5 \Delta n^2$	6	12	15	18
$10^5 \Delta d$	199	324	522	663	$10^5 \Delta d$	2	4	5	6
$10^4 \Delta \epsilon$	50	81	127	164	$10^5 \Delta \epsilon$	—	10	12	19
$10^{10} \Delta B$	21	38	57	71	$10^{11} \Delta B$	12	14	18	20

whence $\sum \Delta n / \sum w_2 = 0.163$; $\sum \Delta n^2 / \sum w_2 = 0.488$;
 $\sum \Delta d / \sum w_2 = 0.2029$; $\sum \Delta \epsilon / \sum w_2 = 0.5014$;
 $\sum \Delta B / \sum w_2 = 2.22 \times 10^{-7}$.

whence $\sum \Delta n / \sum w_2 = 0.252$; $\sum \Delta n^2 / \sum w_2 = 0.756$;
 $\sum \Delta d / \sum w_2 = 0.2526$; $\sum \Delta \epsilon / \sum w_2 = 0.741$;
 $\sum \Delta B / \sum w_2 = 9.51 \times 10^{-7}$.

Solute: 1,2-Benzanthracene							Solute: Chrysene				
$10^5 w_2$...	33	68	99	170	240	320	$10^5 w_2$	96	162	284	351
$10^4 \Delta n$...	1	2	3	4	6	7	$10^4 \Delta n$	2	4	7	9
$10^4 \Delta n^2$...	3	6	9	12	18	21	$10^4 \Delta n^2$	6	12	21	27
$10^5 \Delta d$...	8	18	26	43	60	84	$10^5 \Delta d$	24	45	72	81
$10^4 \Delta \epsilon$...	—	5	7	13	18	24	$10^4 \Delta \epsilon$	7	12	20	26
$10^{10} \Delta B$...	3	6	9	14.4	21	28	$10^{10} \Delta B$	7	13	21	26

whence $\sum \Delta n / \sum w_2 = 0.247$; $\sum \Delta n^2 / \sum w_2 = 0.741$;
 $\sum \Delta d / \sum w_2 = 0.2567$; $\sum \Delta \epsilon / \sum w_2 = 0.744$;
 $\sum \Delta B / \sum w_2 = 8.79 \times 10^{-7}$.

whence $\sum \Delta n / \sum w_2 = 0.246$;
 $\sum \Delta n^2 / \sum w_2 = 0.739$; $\sum \Delta d / \sum w_2 = 0.2486$;
 $\sum \Delta \epsilon / \sum w_2 = 0.728$; $\sum \Delta B / \sum w_2 = 7.50 \times 10^{-7}$.

Solute: Pyrene							Solute: Triphenylene							
$10^5 w_2$...	810	1082	1304	1621	1833	2165	2431	2698	$10^5 w_2$...	121	206	303	434	541
$10^4 \Delta n$...	18	24	29	36	43	48	55	58	$10^4 \Delta n$...	3	4	6	9	12
$10^4 \Delta n^2$...	54	71	87	107	129	144	164	173	$10^4 \Delta n^2$...	9	12	18	27	36
$10^5 \Delta d$...	193	257	309	387	438	516	580	647	$10^5 \Delta d$...	32	50	76	109	130
$10^4 \Delta \epsilon$...	54	71	95	108	123	138	160	175	$10^4 \Delta \epsilon$...	8	14	18	31	35
$10^{10} \Delta B$...	34	45	54	66	76	89	100	121	$10^{11} \Delta B$...	78	134	209	273	347

whence $\sum \Delta n / \sum w_2 = 0.223$; $\sum \Delta n^2 / \sum w_2 = 0.666$;
 $\sum \Delta d / \sum w_2 = 0.2386$; $\sum \Delta \epsilon / \sum w_2 = 0.656$;
 $\sum \Delta B / \sum w_2 = 4.195 \times 10^{-7}$.

whence $\sum \Delta n / \sum w_2 = 0.212$;
 $\sum \Delta n^2 / \sum w_2 = 0.636$; $\sum \Delta d / \sum w_2 = 0.2474$;
 $\sum \Delta \epsilon / \sum w_2 = 0.661$;
 $\sum \Delta B / \sum w_2 = 6.486 \times 10^{-7}$.

Solute: Fluoranthrene							Solute: Coronene								
$10^5 w_2$	234	501	675	844	919	1132	$10^6 w_2$...	529	540	693	812	1028	1138		
$10^4 \Delta n$	5	12	15	18	21	26	$10^4 \Delta n$...	1	1	2	3	3	4		
$10^4 \Delta n^2$...	15	36	45	54	63	77	$10^4 \Delta n^2$...	3	3	6	9	9	12		
$10^5 \Delta d$	50	111	142	170	192	242	whence $\sum \Delta n / \sum w_2 = 0.295$; $\sum \Delta n^2 / \sum w_2 = 0.886$.								
$10^4 \Delta \epsilon$	15	30	49	56	62	69	$10^6 w_2$...	348	529	540	693	764	812	820	903
$10^{11} \Delta B$...	136	276	411	472	515	645	$10^5 \Delta d$...	10	15	15	20	21	23	23	25

whence $\sum \Delta n / \sum w_2 = 0.225$;
 $\sum \Delta n^2 / \sum w_2 = 0.674$; $\sum \Delta d / \sum w_2 = 0.2107$;
 $\sum \Delta \epsilon / \sum w_2 = 0.653$; $\sum \Delta B / \sum w_2 = 5.70 \times 10^{-7}$.

whence $\sum \Delta d / \sum w_2 = 0.2810$.
 $\sum \Delta \epsilon / \sum w_2 = 0.944$.

Solute: Perylene					Solute: Coronene							
$10^5 w_2$	80	129	199	221	$10^6 w_2$...	529	540	693	764	812	820	1138
$10^4 \Delta n$	2	3	4	5	$10^4 \Delta \epsilon$...	5	6	5	7	8	8	11
$10^4 \Delta n^2$...	6	9	12	15	whence $\sum \Delta \epsilon / \sum w_2 = 0.944$.							
$10^5 \Delta d$	19	30	48	53	$10^6 w_2$...	264	439	703	914			
$10^4 \Delta \epsilon$	5	8	13	15	$10^{10} \Delta B$...	3	5	8	11			
$10^{10} \Delta B$...	4.5	8	12	14	whence $\sum \Delta B / \sum w_2 = 11.64 \times 10^{-7}$.							

whence $\sum \Delta n / \sum w_2 = 0.223$; $\sum \Delta n^2 / \sum w_2 = 0.668$;
 $\sum \Delta d / \sum w_2 = 0.2385$; $\sum \Delta \epsilon / \sum w_2 = 0.652$;
 $\sum \Delta B / \sum w_2 = 6.12 \times 10^{-7}$.

TABLE 2.

Total polarisations at infinite dilution, molar refractions, dipole moments, and molar Kerr constants calculated from Table 1.

Solute	$\alpha\epsilon_1$	β	γ	$\gamma'n_1^2$	δ	∞P_2 (c.c.)	∞R_D (c.c.)	$\infty (mK_2)$ $\times 10^{13}$
Anthracene	0.604	0.2126	0.135	0.573	13.22	68.0	67.3	183
Phenanthrene	0.501 ₄	0.2322	0.109	0.488	5.41 ₅	63.4 ₄	62.4 ₄	78.5
Naphthacene	0.741	0.2891	0.168	0.756	23.20	87.1	87.2	403
1,2-Benzanthracene	0.744	0.2938	0.165	0.741	21.44	86.9	86.3	373
Pyrene	0.656	0.2731	0.149	0.666	10.23	75.0	74.9	160
Chrysene	0.728	0.2845	0.164	0.739	18.30	86.9	86.9	319
Triphenylene	0.661	0.2831	0.142	0.636	15.82	84.2	82.5	277
Fluoranthrene	0.653	0.2411	0.150	0.674	13.90	77.1	77.4	217
Perylene	0.652	0.2730	0.149	0.668	14.93	93.5	93.6	288
Coronene	0.944	0.3216	0.197	0.886	28.40	122.6	118.9	650

EXPERIMENTAL

Solvent and Solutes.—Sodium-dried thiophen-free benzene was partially frozen, and the remelted solid stored over sodium wire. The solutes used had m. p.s as follow: anthracene (chromatographically pure), 216—217°; phenanthrene, 101—102°; naphthacene, 340—341°; 1,2-benzanthracene, 159—160°; pyrene, 149—150°; chrysene, 250—251°; triphenylene, 198—199°; fluoranthrene, 110—111°; perylene, 273—274°; and coronene, >400° (lit., 438—440°). The triphenylene was a gift from Professor G. M. Badger (University of Adelaide); apart from this the hydrocarbons were commercial specimens recrystallised from benzene. Purified samples of anthracene, fluoranthrene, perylene, and coronene were also presented by Dr. L. E. Lyons (University of Sydney).

Measurements and Results.—Apparatus and techniques have been those standard here.^{6a,c,7} Table 1 lists the changes of refractive index (Na light), density, dielectric constant, and Kerr constant caused by weight fractions w_2 of solute in benzene; when $w_2 = 0$ the properties named have values, respectively, at 25° as follow: $n_1 = 1.4973$, $d_1 = 0.87378$, $\epsilon_1 = 2.2725$, and $B_1 = 0.410 \times 10^{-7}$. Symbols are defined and methods of calculation explained in refs. 6a and c; they are briefly summarised in ref. 8.

DISCUSSION

Dipole Moments.—Despite the non-centrosymmetric structures of phenanthrene (I), 1,2-benzanthracene (II), and fluoranthrene (III), the closeness of the total polarisations and molecular refractions listed in Table 2 shows each solute to have a dipole moment experimentally undistinguishable from zero. Similar conclusions have previously been reached with anthracene,⁹ phenanthrene,¹⁰ naphthacene,¹¹ and triphenylene.¹² Wesson¹³ quotes the polarity of perylene as 1.3—2.1 D, but Bergmann, Fischer, and Pullman¹² report it as 0.45 ± 0.15 D. Our experience has been that the dielectric constants of solutions of several of these hydrocarbons rise on storage, presumably owing to oxidation, and thus lead to apparent moments up to ca. 1 D; the higher past results with perylene may have been so caused. Of course, from the molecular dimensions given in ref. 14 for anthracene, pyrene, perylene, and coronene, and in ref. 15 for chrysene, non-polarity is to be expected.

⁷ Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. 2; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

⁸ Le Fèvre and Sundaram, *J.*, 1962, 1494.

⁹ Campbell, Le Fèvre, Le Fèvre, and Turner, *J.*, 1938, 404.

¹⁰ Briegleb, *Z. phys. Chem.*, 1932, B, **16**, 276.

¹¹ Lumbroso, *Compt. rend.*, 1947, **225**, 1003.

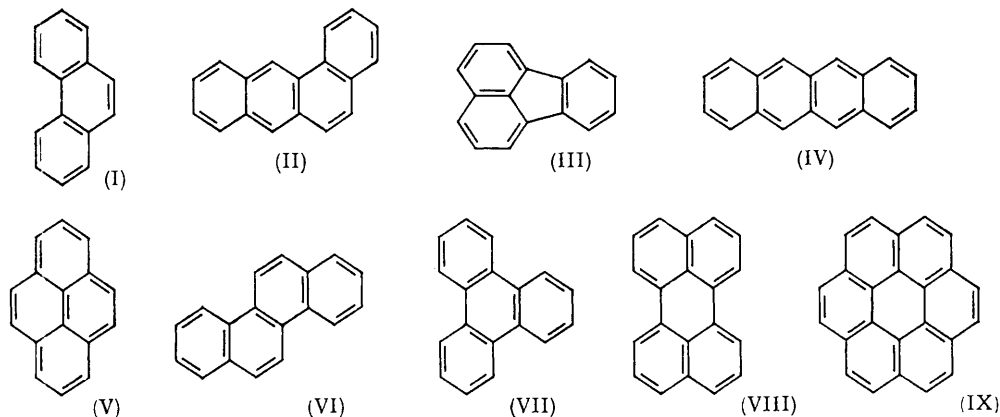
¹² Bergmann, Fischer, and Pullman, *J. Chim. phys.*, 1951, **48**, 356.

¹³ Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

¹⁴ Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11, 1958.

¹⁵ Burns and Iball, *Proc. Roy. Soc.*, 1960, A, **257**, 491.

Molar Kerr Constants.—To the values in Table 2 we add the ${}_mK$'s already recorded for benzene ^{6d} and naphthalene ^{6b} ($7.2_4 \times 10^{-12}$ and 48.1×10^{-12} , respectively). Being non-polar, all these hydrocarbons must have zero θ_2 terms in the expansion ${}_mK =$



$2\pi N(\theta_1 + \theta_2)/9$ (cf. p. 286 of ref. 6a), so that the observed molar Kerr constants can directly provide estimates of the quantity

$$Q = (b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2,$$

where b_1 , b_2 , and b_3 are the semi-axes of the molecular polarisability ellipsoid; Q is thus a measure of the anisotropy in each case. Alternatively, with $S = b_1 + b_2 + b_3$ from ${}_mP = 0.95R_D$, the anisotropy may be expressed by the quotient Q/S^2 (cf. Le Fèvre and Rao ¹⁶). Values of Q and S are in Table 3. By either criterion the rapid increase

TABLE 3.

Anisotropies of polynuclear hydrocarbons.

	$10^{16}Q$	$10^{23}S$	$10^8Q/S^2$		$10^{16}Q$	$10^{23}S$	$10^8Q/S^2$
Benzene	0.29	2.976	33	Pyrene	6.40	8.461	89
Naphthalene	1.92	4.970	78	Chrysene	12.8	9.817	133
Anthracene	7.32	7.602 ₅	127	Triphenylene ...	11.1	9.320	128
Phenanthrene	3.14	7.053 ₅	63	Fluoranthrene ..	8.68	8.743	113 ₅
Naphthacene	16.1	9.850 ₅	166	Perylene	11.5	10.57	103
1,2-Benzanthracene ...	14.9	9.749	157	Coronene	26.0	13.43	144

of anisotropy resulting from an additional ring is noticeable in the linear sequence, benzene, naphthalene, anthracene, and naphthacene, Q/S^2 changing by 0.04—0.05 per extra ring. Angular attachment appears to lower the anisotropy, *e.g.*, among the four isomers $C_{18}H_{12}$ from naphthacene (IV), through 1,2-benzanthracene (II), and chrysene (VI), to triphenylene (VII), or from anthracene to phenanthrene. However, no regular relations with numbers of rings or bonds can be discerned.

Semi-axes of Polarisability Ellipsoids.—As ref. 6b explains, with non-polar structures three differing semi-axes cannot be evaluated by the methods applicable to polar molecules. However, among the twelve hydrocarbons under consideration three should, by symmetry, have polarisability ellipsoids of revolution, so that only two unknowns ($b_1 = b_2$, and b_3) require to be found; from earlier ^{6d} measurements on benzene and the data in Table 2 the following can be deduced:

	$b_1 = b_2$	b_3
Benzene	1.12	0.73 ₆
Triphenylene	3.89	1.54
Coronene	5.68	2.07

¹⁶ Le Fèvre and Rao, *J.*, 1956, 3644.

Of the three polarisabilities (longitudinal, b_L^{CO} , transverse, b_T^{CO} , and vertical, b_V^{CO}) of the $C_{ar}-C_{ar}$ bonds in these planar hydrocarbons, the b_V^{CO} 's alone might be scalarly additive in the molecular b_3 's. In fact, we find that the b_3 's just quoted, together with the b_3 reported previously^{6b} for naphthalene, are covered by $b_3 = 0.413 + 0.0548n$, where n is the number of carbon-carbon links in the molecule:

	Benzene	Naphthalene	Triphenylene	Coronene
n	6	11	21	30
b_3 , calc.	0.74	1.02	1.56	2.06
b_3 , obs.	0.74	1.03	1.54	2.07

Applications of this empirical equation to the remaining hydrocarbons, and the results of using the b_3 's so calculated to reduce three unknown semi-axes to two, are given in Table 4.

The parentheses indicate cases where, in the last stage of evaluating b_1 and b_2 *via* a quadratic in either b_1 or b_2 , a small negative difference appears under the square-root sign. This trouble would be avoided were Q larger or S smaller than shown in Table 3, or were b_3 greater than in Table 4. We suspect, but without proof, that underestimation of b_3

TABLE 4.
Predicted semi-axes.

Hydrocarbon	n	b_3 (calc.)	b_1	b_2	Hydrocarbon	n	b_3 (calc.)	b_1	b_2
Anthracene	16	1.29	3.39	2.92	Pyrene	19	1.45	(3.5)	(3.5)
Naphthalene	21	1.56	4.82	3.47	Fluoranthrene	19	1.45	(3.6 ₅)	(3.6 ₅)
1,2-Benzanthracene	21	1.56	4.68	3.51	Chrysene	21	1.56	(4.1)	(4.1)
Phenanthrene	16	1.29	(2.9)	(2.9)	Perylene	24	1.73	(4.4)	(4.4)

is mainly responsible, since the least values of b_3 (calc.) which permit satisfactory solutions are for phenanthrene, pyrene, chrysene, fluoranthrene, and perylene, respectively, 1.51, 1.63, 1.59, 1.52₅, and 1.92; with these b_3 's the corresponding other axes become 2.8 for phenanthrene, 3.4 for pyrene, 3.6 for fluoranthrene, and 4.3 for perylene; the estimate of 4.1 for chrysene is unaffected.

Inspection of formulæ (I), (III) (V), (VI), and (VIII) suggests that for these structures the ratios of b_1 to b_2 might be nearly 1:1; rough calculations likewise indicate this. Le Fèvre,¹⁷ from a $C_{ar}-C_{ar}$ separation of 1.4 Å, has given b_L^{CO} as 0.22; from the b_3 's of benzene,^{6a} naphthalene,^{6b} triphenylene, and coronene (after allowance for the C-H polarisabilities, and division by the number of $C_{ar}-C_{ar}$ links), b_V^{CO} appears as 0.04–0.05. Noting that for the C=C bond b_T/b_V is almost unity, and is exactly so for the C-C bond, we may assume that in their hybrids the same applies. With $b_L^{CO} = 0.22$, $b_T^{CO} = 0.05$, and all CCC angles regarded as 120°, quotients b_1/b_2 emerge as phenanthrene 1.06, pyrene 1.05, fluoranthrene 1.02₅, chrysene 1.07, perylene 1.00, and the corresponding totals $b_1 + b_2$ (in order) as 5.61, 6.41, 6.42, 7.21, 8.02. These totals are smaller than those from Table 4 by approximately the amounts by which the sums $b_1 + b_2 + b_3$, if computed *via* 0.32 per $C_{ar}-C_{ar}$ and 0.19 per C-H bond, fall short of the S values in Table 3. Such deficiencies need not be wholly due to the crudities of the calculations; varying exaltations of polarisability in the $b_1 \times b_2$ planes of these hydrocarbons must be expected, but at present their contributions to the S 's cannot be predicted quantitatively.

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¹⁷ Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.