

852. Molecular Polarisability. The Conformations of 1,4- and 1,5-Dimethoxynaphthalene and 9-Methoxy- and 9,10-Dimethoxy-anthracene as Solutes in Benzene.

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Molar Kerr constants for the compounds in the title are recorded. High and low positive values for 1,4- and 1,5-dimethoxynaphthalene, respectively, are reconcilable with conformations (I) and (II), in which the C-O-Me triangles may be variously rotated about their C-O bonds by angles probably not exceeding $\pm 30^\circ$. A large negative ${}_mK$ for 9,10-dimethoxyanthracene indicates the presence of the *cis*-orthogonal isomer (III), as deduced from dipole-moment data by Everard and Sutton. For 9-methoxyanthracene the calculated and observed ${}_mK$ values are equal if the methoxyl is out-of-plane by $\pm 30^\circ$.

WITH a knowledge of the anisotropic polarisabilities of the C-O bond¹ and of the naphthalene² or anthracene³ molecule it seemed likely that information on the apparent conformations adopted by the compounds in the title as solutes in benzene could be obtained by measuring their molar Kerr constants⁴ in this medium.

EXPERIMENTAL

Solutes.—1,4-Dimethoxynaphthalene had m. p. 87—88° (from ethanol) (lit.,⁵ 86—87.5°); 1,5-dimethoxynaphthalene had m. p. 183—184° (from ethanol), as in ref. 6; 9,10-dimethoxyanthracene, purified and stored as noted by Everard and Sutton,^{7a} had m. p. 202° (lit.,⁸ 202°); 9-methoxyanthracene had m. p. 97—98° (from ethanol), as in ref. 9. Preparative details were as given in refs. 5, 6, 8, and 9, respectively.

TABLE I.

Incremental values of Kerr constants for solutions in benzene at 25°.

<i>Solute: 1,4-Dimethoxynaphthalene</i>						<i>Solute: 1,5-Dimethoxynaphthalene</i>							
$10^5 w_2 \dots$	323	541	739	1021	1242	1419	$10^5 w_2 \dots$	432	758	921	1145	1326	1540
$10^{10} \Delta B$	29	49	64	90	112	124	$10^{10} \Delta B$	4	8	9	11	13	16
whence $\Sigma \Delta B / \Sigma w_2 = 8.85_s \times 10^{-7}$.						whence $\Sigma \Delta B / \Sigma w_2 = 0.99_s \times 10^{-7}$.							
<i>Solute: 9-Methoxyanthracene</i>						<i>Solute: 9,10-Dimethoxyanthracene</i>							
$10^5 w_2 \dots$	821	1459	2732	3150		$10^5 w_2 \dots$	474	689	941	1125	1391	1511	
$10^4 \Delta n \dots$	—	28	53	61		$-10^{10} \Delta B \dots$	22	28	39	45	59	63	
$10^4 \Delta n^2 \dots$	—	84	159	183		whence $\Sigma \Delta B / \Sigma w_2 = -4.18 \times 10^{-7}$.							
$10^{10} \Delta B \dots$	7	13	24	31									
whence $\Sigma \Delta n / \Sigma w_2 = 0.193$; $\Sigma \Delta n^2 / \Sigma w_2 = 0.580$;													
$\Sigma \Delta B / \Sigma w_2 = 0.92 \times 10^{-7}$.													

Observations and Results.—Table I records, as ΔB or Δn , the differences between the Kerr constants or refractive indices of solutions and solvent (for benzene at 25° and with D-light, $B = 0.410 \times 10^{-7}$, and $n = 1.4973$); concentrations are expressed as weight-fractions, w_2 , of solute. By combination of these data with dielectric polarisation and other information from

¹ Le Fèvre, Sundaram, and Pierens, *J.*, 1963, 479.

² Le Fèvre and Le Fèvre, *J.*, 1955, 1641.

³ Le Fèvre and Sundaram, preceding paper.

⁴ Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261; "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., 1960, Vol. I, p. 2459.

⁵ Baker and Carlson, *J. Amer. Chem. Soc.*, 1942, **64**, 2657, 2662.

⁶ Naylor and Gardner, *J. Amer. Chem. Soc.*, 1931, **53**, 4109.

⁷ Everard and Sutton, (a) *J.*, 1951, 16; (b) *J.*, 1949, 2312.

⁸ Meyer, *Annalen*, 1911, **379**, 70.

⁹ Barnett, Cook, and Matthews, *J.*, 1923, **123**, 1994.

TABLE 2.

Molar Kerr constants at infinite dilution, apparent dipole moments, etc., of solutes in benzene at 25°.

Solute	$\alpha\epsilon_1$	β	∞P (c.c.)	R_D (obs.) (c.c.)	μ (D) *	γ	δ	$10^{12} \infty ({}_m K_2)$
1,4-Dimethoxynaphthalene	2.83 ₃ ^a	0.2416 ^a	146.8 ^a	57.2 ^a	2.09 ^a	0.060 ^d	21.6	298.3
1,5-Dimethoxynaphthalene	0.49 ₄ ^a	0.2485 ^a	68.9 ^a	59.8 ^a	0.67 ^a	0.065 ^d	2.43	41.0
9-Methoxyanthracene	1.36 ₅ ^b	0.2781 ^b	105.1 ^b	73.4	1.24 ₅	0.129	2.24 ₄	34.3
9,10-Dimethoxyanthracene	1.81 ₅ ^c	0.3111 ^c	141.1 ^c	79.8 ^c	1.73 ^c	0.103 ^e	-10.20	-189.0

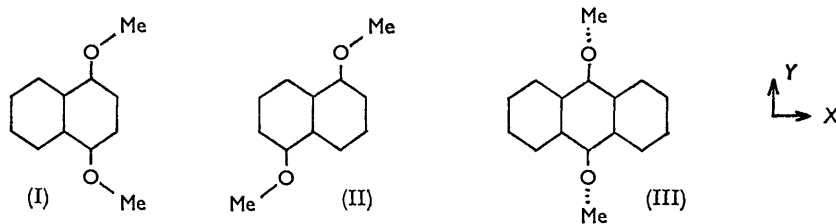
* Calculated by taking ${}_D P = R_D$.

^a From ref. 7b. ^b From ref. 10. ^c From ref. 7a. ^d Calc. from values of Δn in ref. 7b. ^e Calc. from values of Δn in ref. 10.

refs. 7 and 10, the results in Table 2 are obtained *via* the equations summarised in *J.*, 1962, 1494, and explained, together with their associated experimental techniques, in ref. 4.

DISCUSSION

Everard and Sutton⁷ explained the differing polarities of 1,4- and 1,5-dimethoxynaphthalene and 9,10-dimethoxyanthracene by the reasonable suggestion that in these cases conformations are mainly decided by resonance effects, which require the methoxyls to be in the ring-planes, and by steric interferences of *peri*-H-atoms with methyl groups, which prevent attainment of coplanarity in dimethoxyanthracene and permit it for only one of the three extremes foreseeable for each dimethoxynaphthalene. Formulæ (I)–(III)



were therefore written for equilibrium structures; in (III) the methoxyls were thought to be in the orthogonal plane and to lie equally *cis* and *trans* to one another (thus accounting for an observed dipole moment equal to that of quinol dimethyl ether).

Present measurements are reconcilable with such ideas. Qualitatively, high and low positive molar Kerr constants, respectively, are to be expected for flat conformations as (I) and (II), while the negative ${}_m K$ observed for 9,10-dimethoxyanthracene cannot be understood unless at least some non-planarity is assumed. Attempts to approach the matter quantitatively are summarised in Table 3, the calculations in which are based on the following data: C-C-C angles in naphthalene and anthracene 120°, C-O-C angles 110°; polarisability semi-axes for naphthalene,² $b_1 = 2.15$, $b_2 = 1.76$, $b_3 = 1.03$, for anthracene,³ $b_1 = 3.39$, $b_2 = 2.92$, $b_3 = 1.29$, and for the C-O bond,¹ $b_L = 0.089$, $b_T = 0.046$ (all polarisabilities are quoted in 10^{-23} c.c. units); $b_L^{OH} = b_T^{OH} = b_V^{OH} = 0.064$, and $\mu_{O-O} = 1.1$ D. The calculated moment of 9-methoxyanthracene is therefore 1.2₅ D and of flat *cis*-modifications of 1,4-dimethoxynaphthalene and 9,10-dimethoxyanthracene, 2.07 D (the higher value, 2.45 D, used in ref. 7a was computed as $\sqrt{2}\mu_{\text{quinol dimethyl ether}}$). The reference axes are located as indicated alongside (III), with X and Y in the Ar-plane, and Y parallel to the O...O line.

Implications of Table 3 are that none of the four solutes adopts a conformation which is either completely planar or has its methoxyl groups held completely orthogonally. Leybold models demonstrate (as did the scale drawings of Everard and Sutton⁷) that, although flat forms are impossible in certain cases, a limited amount of rotation (or

¹⁰ Angyal and Le Fèvre, *J.*, 1950, 562.

vibration) of the C-O-Me triangles might occur about the C-O bonds. Thus, with 1,5-dimethoxynaphthalene, a slight non-planarity would produce a non-zero μ_3 and bring ${}_{\text{m}}K$ calc. near to that observed (*e.g.*, with $\mu_3 = 0.37$ D, ${}_{\text{m}}K$ calc. is 40.9×10^{-12}); such a value for μ is possible within the accuracy of present measurement). For 9-methoxyanthracene we include details of a conformation (A) in which the C-O-Me is 30° out-of-plane and for which the ${}_{\text{m}}K$ calc. is close to the found value; for comparison the corresponding angle in anisole has been given¹¹ as *ca.* 18° . The positive ${}_{\text{m}}K$ determined for

TABLE 3.
Calculations of polarisability semi-axes, moment components, and molar Kerr constants.

Principal semi-axes	Direction cosines with X Y Z			Moment components (D)	$10^{12} {}_{\text{m}}K$ (calc.)	Principal semi-axes	Direction cosines with X Y Z			Moment components (D)	$10^{12} {}_{\text{m}}K$ (calc.)
<i>9-Methoxyanthracene</i> , planar											
b_1 3.65 ₂	<i>ca.</i> 1	<i>ca.</i> 0	0	μ_1 1.21	+407	b_1 3.91 ₀	1	0	0	μ_1 2.07	+821
b_2 3.19 ₀	<i>ca.</i> 0	<i>ca.</i> 1	0	μ_2 0.30		b_2 3.45 ₉	0	1	0	μ_2 0	
b_3 1.51 ₀	0	0	1	μ_3 0		b_3 1.73 ₀	0	0	1	μ_3 0	
orthogonal											
b_1 3.61 ₄	1	0	0	μ_1 0	-115	b_1 3.91 ₂	0.9978	0.0663	0	μ_1 0	+199
b_2 3.19 ₁	0	<i>ca.</i> 1	<i>ca.</i> 0	μ_2 0.30		b_2 3.45 ₇	-0.0663	0.9978	0	μ_2 0	
b_3 1.54 ₈	0	<i>ca.</i> 0	<i>ca.</i> 1	μ_3 1.21		b_3 1.73 ₀	0	0	1	μ_3 0	
form A											
b_1 3.63 ₉	0.9998	0.0094	0.0174	μ_1 0.63	+33.1	b_1 3.83 ₄	1	0	0	μ_1 0	-696
b_2 3.19 ₁	-0.0062	0.9990	0.0435	μ_2 0.34		b_2 3.45 ₉	0	1	0	μ_2 0	
b_3 1.52 ₈	-0.0200	-0.0429	0.9989	μ_3 1.02		b_3 1.80 ₆	0	0	1	μ_3 2.07	
<i>1,4-Dimethoxynaphthalene</i> , planar, <i>cis</i>											
b_1 2.66 ₆	1	0	0	μ_1 2.07	+427	b_1 3.83 ₄	1	0	0	μ_1 0	+175
b_2 2.29 ₈	0	1	0	μ_2 0		b_2 3.46 ₀	0	0.9997	0.0227	μ_2 0	
b_3 1.47 ₀	0	0	1	μ_3 0		b_3 1.80 ₅	0	-0.0227	0.9997	μ_3 0	
planar, <i>trans</i>											
b_1 2.66 ₈	0.9974	0.0715	0	μ_1 0	+56.3	b_1 3.843	0.9999	0	0.0140	μ_1 0.74	-520
b_2 2.29 ₄	-0.0715	0.9974	0	μ_2 0		b_2 3.459	0	1	0	μ_2 0	
b_3 1.47 ₀	0	0	1	μ_3 0		b_3 1.797	-0.0140	0	0.9999	μ_3 1.94	
orthogonal, <i>cis</i>											
b_1 2.59 ₀	1	0	0	μ_1 0	-381	b_1 3.844	0.9999	0.0033	0.0139	μ_1 0	+178
b_2 2.29 ₈	0	1	0	μ_2 0		b_2 3.459	-0.0042	0.9999	0.0029	μ_2 0	
b_3 1.54 ₈	0	0	1	μ_3 2.07		b_3 1.796	-0.0138	-0.0035	0.9999	μ_3 0	
orthogonal, <i>trans</i>											
b_1 2.59 ₀	1	0	0	μ_1 0	+43.7	b_1 3.845	0.9974	0.0715	0	μ_1 0	-601
b_2 2.29 ₈	0	0.9968	0.0802	μ_2 0		b_2 3.457	-0.0715	0.9974	0	μ_2 0	
b_3 1.54 ₄	0	-0.0802	0.9968	μ_3 0		b_3 1.797	0	0	1	μ_3 1.95	
form B											
b_1 2.64 ₈	0.9999	0	0.0140	μ_1 1.81	+216	b_1 3.843	1	0	0	μ_1 0.71	+245
b_2 2.29 ₆	0	1	0	μ_2 0		b_2 3.460	0	0.9997	0.0244	μ_2 0	
b_3 1.48	-0.0140	0	0.9999	μ_3 1.01		b_3 1.796	0	-0.0244	0.9997	μ_3 0	
<i>1,5-Dimethoxynaphthalene</i> , planar, <i>trans</i>											
b_1 2.66 ₈	0.9974	0.0715	0	μ_1 0	+56.3	b_1 3.843	1	0	0	μ_1 0	
b_2 2.29 ₄	-0.0715	0.9974	0	μ_2 0		b_2 3.459	0	1	0	μ_2 0	
b_3 1.47 ₀	0	0	1	μ_3 0		b_3 1.796	0	0	1	μ_3 0	

1,4-dimethoxynaphthalene, although large, is less than the calculated value for the planar *cis*-structure. By supposing that the C-O-Me triangles are oppositely rotated out of the planar *cis*-positions, or that the planar *cis*-form is admixed with the orthogonal *trans*-form, the calculated ${}_{\text{m}}K$ values and those observed can be brought together, but then the μ calc. becomes incorrect. We note that if the plane containing both *cis*-methoxyl groups is rotated, about the O...O line, above or below the XY plane in (I), numerically satisfactory values of ${}_{\text{m}}K$ can be achieved and a $\mu_{\text{resultant}}$ of 2.07 D can be retained. The conformation listed as B in Table 3 has this plane rotated by 30° ; other calculations (not

¹¹ Aroney, Le Fèvre, and Chang, *J.*, 1960, 3173.

reproduced) show that for every 10° of such rotation in the $\pm 30^\circ$ range the ${}_mK$ calc. changes by *ca.* 70×10^{-12} ; accordingly, the mean ${}_mK$ expected if the solute were a mixture of all forms with planes between $\pm 30^\circ$ would be $+286 \times 10^{-12}$, which approaches the measured value of $+298 \times 10^{-12}$.

For 9,10-dimethoxyanthracene as a 1 : 1 mixture of orthogonal *cis*- and *trans*-forms, a molar Kerr constant of -261×10^{-12} and a dipole moment of 1.46 D are deducible from Table 3. Since rigidity in such isomers is unlikely, computations have also been made for structures generated from these extremes by rotating the C-O-Me triangles about their C-O bonds. The four examples quoted (C-F in Table 3) involve 20° rotations, forms C and E being from the *cis*- and D and F from the *trans*-orthogonal precursor; analogous calculations for rotations of 30° give ${}_mK$ values of -311 , $+181$, -481 , and $+325$ (all $\times 10^{-12}$) for the structures corresponding to C, D, E, and F. Leybold models suggest that sterically unhindered oscillations of the methoxyls about their orthogonal dispositions are possible within limits of roughly $\pm 30^\circ$, so that molar Kerr constants and moments of the *cis*- and *trans*-species could credibly be about -600×10^{-12} , 2 D, $+200 \times 10^{-12}$, and 0.7 D, respectively; a 1 : 1 mixture (as diagnosed by Everard and Sutton) should therefore exhibit an observed moment of *ca.* 1.5 D and an ${}_mK$ of *ca.* -200×10^{-12} .

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