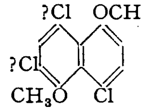
490. *The Stereochemistry of Some Aromatic Ethers.*

By K. B. EVERARD and L. E. SUTTON.

The electric dipole moments of 1 : 5- and 1 : 4-dimethoxynaphthalene are shown to be 0·67 and 2·09 D., respectively. The difference between these and that of the analogous quinol dimethyl ether (1·73 D.) is believed to be due to (i) the fixation of the methoxy-groups in the plane of the rings by resonance involving the use of a π-orbital between these groups and the rings, and (ii) the steric inhibition by the *peri*-hydrogen atoms of one of the two coplanar configurations which each methoxy-group can assume.

The moments of 4 : 8-dichloro- and -dibromo-1 : 5-dimethoxynaphthalene are found to be 0·95 and 0·93 D., *i.e.*, greater than that of the parent ether. It is suggested that the *peri*-substituents force one another out of the plane of the rings, giving rise to three different configurations, two of which are not centrosymmetrical (and hence may possess a dipole moment) : these two configurations should be optically antimeric. The application of this hypothesis to explain some other anomalous moments is explored.

BY chlorinating 1 : 5-dimethoxynaphthalene, Thomson (*J. Org. Chem.*, 1948, **13**, 371) obtained the compound 4 : *x*-dichloro-1 : 5-dimethoxynaphthalene (I) in which he believed *x* to be either 6 or 8. He suggested that, in order to settle this orientation, the electric dipole moment of this compound should be compared with that of 1 : 5-dimethoxynaphthalene. If *x* were 8 the two moments should be the same, by symmetry, whereas the isomer should be distinguishable by a higher moment (*ca.* 2·6 D.).



(I.)

The dipole moments of the two compounds were measured in benzene solution at 25°. The values obtained threw unexpected light on the stereochemistry of naphthalene derivatives, and suggested that the measurement of additional compounds would provide fruitful results. Those which have been examined are : 1 : 4-dimethoxynaphthalene, 4 : 8-dibromo-1 : 5-dimethoxynaphthalene, quinol dimethyl ether, anisole, 1-methoxynaphthalene, and 2 : 5-dichloroquinol dimethyl ether.

EXPERIMENTAL.

(Temperatures are uncorrected.)

Preparation and Purification of Materials.—" AnalaR " Benzene was purified by freezing out thrice, drying (P_2O_5), and distilling it over phosphoric oxide in a stream of dry air under which it was stored until required.

Samples of 1 : 4- and 1 : 5-dimethoxynaphthalene and the dichloro- and dibromo-derivatives of the latter were supplied by Dr. R. H. Thomson. Their m. p.s were given respectively as 88°, 181°, 159°, and 189°. In every case the m. p. range was less than 1°.

Quinol dimethyl ether was prepared by Vermeulen's method (*Rec. Trav. chim.*, 1906, **25**, 28), thrice recrystallised from aqueous ethanol, and finally sublimed in a vacuum; m. p. 55·6—56·0° (Vermeulen gives 55—56°).

A specimen of anisole was kindly provided by Mr. J. W. Bayles, who had purified it by successive treatment with potassium hydroxide and phosphoric oxide, followed by two distillations at 152·5—153°. It was distilled a third time before use; b. p. 153°.

1-Methoxynaphthalene was prepared by Gattermann's method (*Annalen*, 1888, **244**, 72). It was distilled twice under atmospheric pressure [b. p. 265—265·5° : 269°/753·1 mm. (corr.), Nasini and Bernheimer, *Gazzetta*, 1885, **15**, 79; 265—266°, Marchetti, *ibid.*, 1879, **9**, 545; 258°, Staedel, *Annalen*, 1883, **217**, 42] and once under reduced pressure, at 133°/11 mm. (Found : C, 83·80; H, 6·37. Calc. for $C_{11}H_{10}O$: C, 83·6; H, 6·3%).

2 : 5-Dichloroquinol dimethyl ether was made by methylating the quinol. The latter, which had been made by Hammick, Hampson, and Jenkins (*J.*, 1938, 1263), was purified by recrystallisation from water and benzene and sublimation in a vacuum (m. p. 167—168°). 7 G. of this were heated under reflux with 7 ml. of methyl sulphate and 16 ml. of 5N-sodium hydroxide for 5 minutes. The brown solid which formed on cooling was triturated with 2N-sodium hydroxide to remove phenolic material, twice recrystallised from ethanol, and sublimed in a vacuum. The 3·4 g. of pure white crystals thereby obtained melted at 131—131·5° (126° Habermann, *Ber.*, 1878, **11**, 1034; Ciamician and Silber, *Gazzetta*, 1892, **22**, 59, give 131° for x,x-dichloroquinol dimethyl ether; constitution proved by Kohn and Gurewitsch, *Sitz. Akad. Wiss. Wien*, 1939, **139**, 405).

Physical Measurements.—Electric dipole moments were computed from measurements of dielectric constant, specific volume, and refractive index of benzene solutions by the procedure described by

Halverstadt and Kumler (*J. Amer. Chem. Soc.*, 1942, **64**, 2988), in which ε_1, v_1, and n_1 are obtained by extrapolation to $\omega_2 = 0$. The symbols have the same significance as in Halverstadt and Kumler's paper.

Dielectric constants were measured at 25° with a heterodyne capacity meter designed by R. A. W. Hill and L. E. Sutton (description to be published) in conjunction with a condenser similar to that described by Jenkins and Sutton (*J.*, 1935, 609).

Specific volumes were measured at 25° with a 10-ml. Sprengel–Ostwald pyknometer.

Refractive indices relative to that of benzene were measured with a Jamin interferometer of Kuhn and Wheatley's design (*J. Sci. Instr.*, 1945, **22**, 110). It was later found, however, that the error associated with such instruments (Weissberger, " Physical Methods of Organic Chemistry," Interscience, 1945, p. 728) when the substances examined have large dispersions, was giving spurious values in all cases other than anisole and quinol dimethyl ether. Accordingly, all the dimethoxynaphthalenes and 2 : 5-dichloroquinol dimethyl ether were re-examined with a Pulfrich refractometer, and the values reported are those so obtained for them. The molar refraction of 1-methoxynaphthalene was calculated from Nasini and Bernheimer's data (*loc. cit.*).

The dielectric constant of pure dry benzene used to calibrate the condenser was taken as 2·2727 at 25° (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, **123**, *A*, 664), and its refractive index as 1·50144 (20°, for interferometer) or 1·49794 (25°, Pulfrich refractometer).

All dipole moments are given in Debye units.

Refractive Index Data.

Compound.	ω_2.	Δn_D^{25}.
1 : 4-Dimethoxynaphthalene	0·01410	0·00127
1 : 5-Dimethoxynaphthalene	0·01251	0·00123
4 : (8)-Dichloro-1 : 5-dimethoxynaphthalene	0·03551	0·00373
4 : 8-Dibromo-1 : 5-dimethoxynaphthalene	0·01905	0·00183
2 : 5-Dichloroquinol dimethyl ether	0·01740	0·00079

1 : 4-*Dimethoxynaphthalene.*

ω_2.	ε_{12}.	v_{12}.	Δn.	ω_2.	ε_{12}.	v_{12}.	Δn.
0·002202	2·2792	1·1445	—	0·010206	2·3014	1·1422	—
0·004793	2·2865	1·1439	—	0·012484	2·3079	1·1417	—
0·008085	2·2955	1·1430	—				

$$\varepsilon_{12} = 2{\cdot}2731 + 2{\cdot}782\,\omega_2;\ v_{12} = 1{\cdot}1452 - 0{\cdot}283\,\omega_2;\ {}_{\mathrm{T}}P_2 = 146{\cdot}8 \text{ c.c.};$$
$$ {}_{\mathrm{E}}P_2 = 57{\cdot}2 \text{ c.c.};\ \mu = 2{\cdot}09 \pm 0{\cdot}02.$$

1 : 5-*Dimethoxynaphthalene.*

0·003913	2·2745	1·1441	—	0·008666	2·2767	1·1426	—
0·005801	2·2757	1·1433	—	0·011158	2·2785	1·1422	—

$$\varepsilon_{12} = 2{\cdot}2724 + 0{\cdot}534\,\omega_2;\ v_{12} = 1{\cdot}1450 - 0{\cdot}253\,\omega_2;\ {}_{\mathrm{T}}P_2 = 68{\cdot}9 \text{ c.c.};$$
$$ {}_{\mathrm{E}}P_2 = 59{\cdot}8 \text{ c.c.};\ \mu = 0{\cdot}67 \pm 0{\cdot}1.$$

This supersedes the result quoted by Thomson (*loc. cit.*).

4 : (8)-*Dichloro*-1 : 5-*dimethoxynaphthalene.*

0·004957	2·2766	1·1433	—	0·014769	2·2833	1·1387	—
0·009104	2·2795	1·1413	—	0·019221	2·2864	1·1369	—

$$\varepsilon_{12} = 2{\cdot}2732 + 0{\cdot}683\,\omega_2;\ v_{12} = 1{\cdot}1455 - 0{\cdot}451\,\omega_2;\ {}_{\mathrm{T}}P_2 = 86{\cdot}2 \text{ c.c.};$$
$$ {}_{\mathrm{E}}P_2 = 67{\cdot}8 \text{ c.c.};\ \mu = 0{\cdot}95 \pm 0{\cdot}05.$$

This supersedes the result quoted by Thomson (*loc. cit.*).

4 : 8-*Dibromo*-1 : 5-*dimethoxynaphthalene.*

0·004573	2·2758	1·1425	—	0·011087	2·2789	1·1385	—
0·007547	2·2775	1·1408	—	0·014162	2·2813	1·1367	—

$$\varepsilon_{12} = 2{\cdot}2732 + 0{\cdot}553\,\omega_2;\ v_{12} = 1{\cdot}1453 - 0{\cdot}609\,\omega_2;\ {}_{\mathrm{T}}P_2 = 91{\cdot}3 \text{ c.c.};$$
$$ {}_{\mathrm{E}}P_2 = 73{\cdot}4 \text{ c.c.};\ \mu = 0{\cdot}93 \pm 0{\cdot}03.$$

Quinol dimethyl ether.

0·005524	2·2862	1·1435	0·00011	0·016135	2·3113	1·1415	0·00038
0·010234	2·2971	1·1427	0·00022	0·020366	2·3221	1·1403	0·00047
0·013667	2·3055	1·1419	0·00031				

$$\varepsilon_{12} = 2{\cdot}2725 + 2{\cdot}418\,\omega_2;\ v_{12} = 1{\cdot}1447 - 0{\cdot}211\,\omega_2;\ \Delta n = -0{\cdot}00003 + 0{\cdot}025\,\omega_2;$$
$$ {}_{\mathrm{T}}P_2 = 101{\cdot}3 \text{ c.c.};\ {}_{\mathrm{E}}P_2 = 40{\cdot}0 \text{ c.c.};\ \mu = 1{\cdot}73 \pm 0{\cdot}01.$$

Other values : 1·67, 1·81, 1·73 (*Trans. Faraday Soc.*, 1934, **30**, Appendix), 1·70 (Mizushima, Morino, and Okazaki, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1938, **34**, 1147), and 1·73 (Meyer, *Z. physikal. Chem.*, 1930, *B*, **8**, 27).

Anisole.

ω_2.	ε_{12}.	v_{12}.	Δn.	ω_2.	ε_{12}.	v_{12}.	Δn.
0·002441	2·2769	1·1444	0·00006	0·014959	2·2976	1·1429	0·00026
0·006311	2·2833	1·1441	0·00012	0·019498	2·3056	1·1421	0·00036

$$\varepsilon_{12} = 2\cdot2727 + 1\cdot684\,\omega_2;\ v_{12} = 1\cdot1449 - 0\cdot136\,\omega_2;\ \Delta n = 0\cdot00001 + 0\cdot018\,\omega_2;$$
$${}_{\mathrm{T}}P_2 = 66\cdot8 \text{ c.c.};\ {}_{\mathrm{E}}P_2 = 33\cdot3 \text{ c.c.};\ \mu = 1\cdot28 \pm 0\cdot01.$$

Other values : 0·8 (Estermann, *Z. physikal. Chem.*, 1928, *B*, **1**, 134), 1·16, 1·23 (*Trans. Faraday Soc.*, 1934, **30**, Appendix), 1·22 (Phadke, Gokhale, Phalnikar, and Bhide, *J. Indian Chem. Soc.*, 1945, **22**, 235), 1·35 (Groves and Sugden, *J.*, 1937, 1782), and 1·54 (Böttcher, *Physica*, 1939, **6**, 59).

1-*Methoxynaphthalene.*

0·004638	2·2789	1·1439	—	0·015188	2·2936	1·1415	—
0·005636	2·2809	1·1434	—	0·017329	2·2969	—	—
0·014990	2·2934	1·1413	—				

$$\varepsilon_{12} = 2\cdot2727 + 1\cdot381\,w_2;\ v_{12} = 1\cdot1448 - 0\cdot228\,w_2;\ {}_{\mathrm{T}}P_2 = 84\cdot3 \text{ c.c.};$$
$${}_{\mathrm{E}}P_2 = 50\cdot9 \text{ c.c.};\ \mu = 1\cdot28 \pm 0\cdot03.$$

2 : 5-*Dichloroquinol dimethyl ether.*

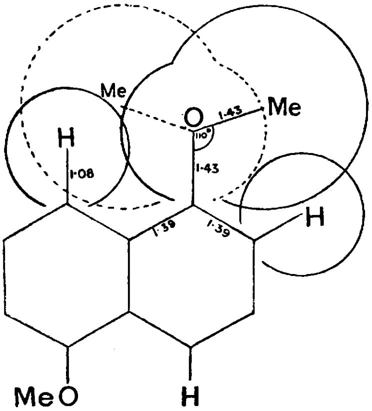
0·002634	2·2740	1·1440	—	0·008367	2·2779	1·1416	—
0·005489	2·2759	1·1427	—	0·010525	2·2793	1·1406	—

$$\varepsilon_{12} = 2\cdot2723 + 0\cdot675\,\omega_2;\ v_{12} = 1\cdot1451 - 0\cdot420\,\omega_2;\ {}_{\mathrm{T}}P_2 = 71\cdot0 \text{ c.c.};$$
$${}_{\mathrm{E}}P_2 = 49\cdot4 \text{ c.c.};\ \mu = 1\cdot03 \pm 0\cdot02.$$

DISCUSSION.

The dipole moment of 1 : 5-dimethoxynaphthalene is 0·67 : therefore if $x = 8$ the moment of 4 : x-dichloro-1 : 5-dimethoxynaphthalene should likewise be 0·67, since that of 1 : 5-dichloronaphthalene is zero (this and other dipole moments are taken from *Trans. Faraday Soc.*, 1934, **30**, Appendix). If, however, $x = 6$, then the moment of the compound should approximate to that of 1 : 7-dichloronaphthalene, *viz.*, 2·6. Other values of x would give, on the same basis, moments of 1·85 ($x = 2$), 2·4 (3), and 1·4 (7), but these are ruled out on organic chemical grounds (Thomson, *loc. cit.*). The measured value of the moment of the dichloro-compound is 0·95. The melting point shows the substance to be pure, and not a mixture. The moment therefore shows beyond reasonable doubt that the first-mentioned alternative ($x = 8$) is correct.

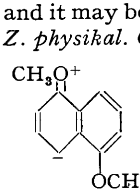
FIG. 1.



The full lines represent the methoxy-group in the cis-*position ; the dotted lines, in the* trans-*position. This and other scale diagrams are based on dimensions given in Pauling's " Nature of the Chemical Bond."*

There is, however, not only a considerable and unexpected discrepancy between the moments of the parent substance and its dichloro-derivative, but the absolute magnitudes of both occasion some surprise, in that they are not equal to that of the benzene analogue, quinol dimethyl ether (1·73). This last moment is usually regarded as arising from the free rotation of the methoxy-groups about the C_{aryl}–O bonds, giving all configurations from *cis* to *trans* with equal probability (though an equal mixture of these extreme configurations would possess the same dipole moment). It seems that in 1 : 5-dimethoxynaphthalene free rotation is much reduced and that the methoxy-groups are constrained to lie approximately *trans* to each other.

The steric effect of the hydrogen atoms situated *peri* to the substituents is sufficient only to prevent each methoxy-group from swinging to within about 60° of one of the coplanar positions; and it may be shown by integrating the moments of all the permitted configurations (cf. Williams, *Z. physikal. Chem.*, 1928, *A*, **138**, 75) that the theoretical moment of such a system is distinctly higher than that observed. However, one of the effects of resonance involving structures such as (II), with π-bonds between the oxygen and the ring, should be the restriction of rotation of the methoxy-groups about the C_{aryl}–O bonds. If such structures make an appreciable contribution to the hybrid, then the resonance effect and the steric effect are together able to account for the low moment observed. The former limits the possible configurations of each methoxy-group to two : the latter eliminates one of these, so that groups are constrained to lie *trans* to each other (Fig. 1).



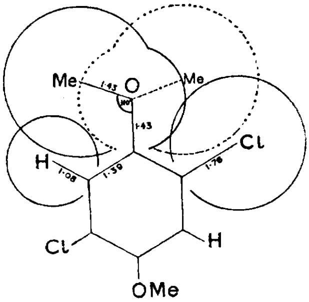
(II.)

This explanation was tested by measuring the dipole moment of 1 : 4-dimethoxynaphthalene. If it is correct, the moment of the compound should be up to $\sqrt{2}$ times that of quinol dimethyl ether, because the methoxy-groups would be constrained to lie *cis* to each other. However, the result is low—2·09 instead of the theoretical 2·45.

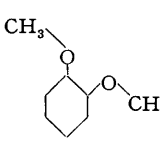
These facts indicate either that the groups cannot quite lie in the coplanar configurations, or that they are not rigidly fixed therein. The interference of the methyl groups with the β-hydrogen atoms, though much less than that with the *peri*-atoms, may prevent the methoxy-groups being completely coplanar, and cause them to be somewhat displaced upward or downward. Molecules in which each group is displaced one way would be polar, while those with the groups displaced in opposite directions would be non-polar. The two forms could be interchanged by thermal bombardment. On the other hand, the apparent polarity could be due to a torsional vibration about the C_{aryl}–O bonds, or, in other words, to an atom (or vibration) polarisation (see, *e.g.*, Sutton, *Ann. Reports*, 1940, **37**, 57).

If we assume that the methoxy-group moment is the same in naphthalene and in benzene ethers [the moments of 1-methoxynaphthalene and of anisole are equal (1·28)], then on the latter hypothesis we should have to suppose that the average amplitude of swing is approximately 32° for each group in 1 : 5-dimethoxynaphthalene and is 62° in 1 : 4-dimethoxynaphthalene, while on the former hypothesis these same deflections would exist but would be permanent. On both, therefore, we should have to suppose that the tendency for the methoxy-groups to lie coplanar is less when there are two of them on one benzene ring than when there is only one. It may be, therefore, that when two methoxy-groups are on the *same* ring they reduce each other's π-bonding (see below).

FIG. 2.



A similar fixation of angular groups in the plane of an aromatic ring by a resonance mechanism has been postulated by Pauling (" Nature of the Chemical Bond," 2nd edn., Cornell, 1940, pp. 320 *et seq.*) to explain why the infra-red absorption spectra of *o*-chloro-, -bromo-, and -iodo-phenol contain two well-resolved peaks characteristic of O–H vibrations. Evidence of this fixation has also been obtained from dipole-moment studies by Anzilotti and Curran (*J. Amer. Chem. Soc.*, 1943, **65**, 607), who observed that the moments of *o*-chloro-, -bromo-, and -fluoro-anisole and of *o*-chlorophenetole in benzene solution (2·50, 2·47, 2·31, and 2·54) agree closely with the values (obtained from bond-moment data) for the *trans*-configurations of these molecules (2·50, 2·45, 2·37, and 2·50), but not with those for the *cis*- (0·47, 0·43, 0·35, and 0·47) or with those calculated on the basis of free rotation (1·82, 1·78, 1·71, and 1·82). These authors gave an explanation of their results similar to ours. On the other hand, both Mizushima, Morino, and Okazaki (*loc. cit.*) and Curran (*J. Amer. Chem. Soc.*, 1945, **67**, 1835) observe that the moment of veratrole does not agree with the value calculated for the *trans-trans*-configuration (III). The former authors find values in benzene of 1·32 at 40°, 1·24 at 25°, and 1·18 at 10°, and Curran finds 1·23 at 25° in dioxan. The calculated value for the *trans-trans*-configuration is about 0·6, and for the *cis-trans*-, 2·2 (cf. Curran, *loc. cit.*). In both papers it is postulated that resonance between the methoxy-groups and the ring is much reduced (relative to *o*-chloroanisole, etc.), but Curran tentatively offers also the alternative explanation that there is an appreciable number of *cis-trans*-molecules, in which, he points out, the distance from the carbon atom of one methoxy-group to the oxygen atom of the other is 1·7 A., corresponding to a strong hydrogen bond. Furthermore, Oesper, Smyth, and Kharasch (*J. Amer. Chem. Soc.*, 1942, **64**, 937) have found the dipole moment of 2 : 5-di-*tert.*-butylquinol dimethyl ether to be 1·47 ± 0·13 (recalculation by the method advocated by Halverstadt and Kumler, *loc. cit.*, gives 1·23 ± 0·02), though the *tert.*-butyl groups are quite large enough to eliminate one of the two coplanar configurations of each methoxy-group. These authors were indeed searching for just the effect which we think we have observed in 1 : 5-dimethoxynaphthalene; and because they did not find it they concluded that the π-bonding was too weak to hold the methoxy-groups coplanar. The chlorine atoms in 2 : 5-dichloroquinol dimethyl ether are also large enough to elimate one configuration (Fig. 2), but we observe that this compound is polar too (μ = 1·03).



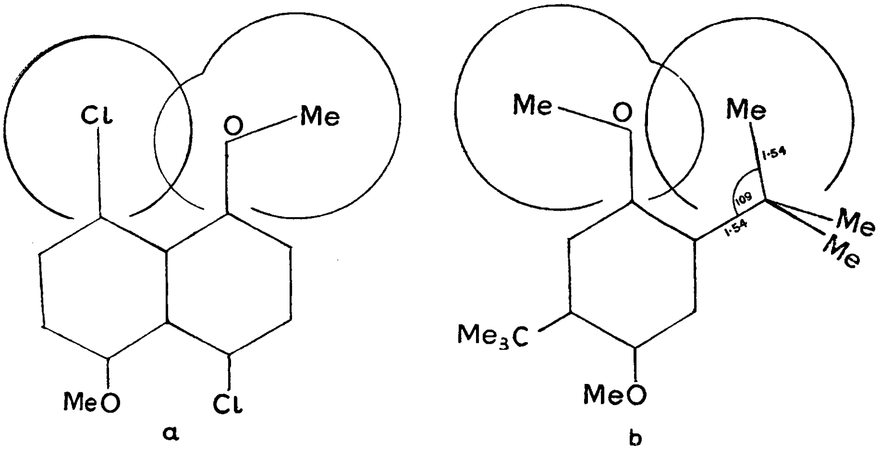
(III.)

All these indications of less perfect fixation can be correlated with the presence of two methoxy-groups in one and the same ring; and they can therefore be explained on the hypothesis that there is then a reduction of the π-bonding of each methoxy-group to the ring.

Clearly, however, no such hypothesis applies to 1 : 5-dimethoxynaphthalene. Also, in view of the observations on *o*-chloroanisole and similar compounds there is no reason to think that the additional polarity of 4 : 8-dichloro-1 : 5-dimethoxynaphthalene can be explained on such a basis. For this latter, a different explanation seems necessary.

A large atom polarisation has often been postulated to account for anomalous dipole moments, but on this occasion it is unlikely to be the true explanation. The differences between the total and the electron polarisations of the two symmetrical dichloronaphthalenes, 1 : 5 and 2 : 6, are each less than 1 c.c. Williams and Fogelberg, in obviously careful work (*J. Amer. Chem. Soc.*, 1931, **53**, 2096), found ${}_{\mathrm{T}}P - {}_{\mathrm{E}}P$ for the 2 : 6-isomer to be 0·1 c.c., whilst Weissberger and Sängewald found 0·8 c.c. (*Z. physikal. Chem.*, 1933, *B*, **20**, 145). Weissberger, Sängewald, and Hampson found ${}_{\mathrm{E}}P$ for the 1 : 5-isomer to *exceed* ${}_{\mathrm{T}}P$ by 5·7 c.c. (*loc. cit.*), but Weissberger and Hampson, in a painstaking repetition of their earlier work, found −0·2 c.c. for the 1 : 5- and 0·5 c.c. for the 2 : 6-compound. Nakata (*Ber.*, 1931, **64**, 2059; *Bull. Chem. Soc. Japan*, 1935, **10**, 318) reports 7·68 c.c. for the 2 : 6-isomer, but as he only makes measurements on two solutions and fails to extrapolate his polarisations to infinite dilution, his work is least acceptable of all. Consequently, it is reasonable to suppose that the contribution to the atom polarisation made by the chlorine atoms in 4 : 8-dichloro-1 : 5-dimethoxynaphthalene is negligible. The contribution of the methoxy-groups should not be larger than the polarisation of 1 : 5-dimethoxynaphthalene (9·1 c.c.). The following hypothesis is therefore put forward to account for the anomaly.

FIG. 3.

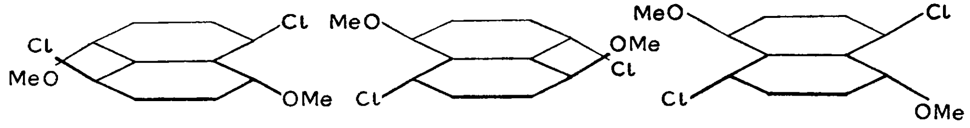


A scale diagram of the molecule shows that there is considerable interference between the oxygen atoms and the neighbouring chlorine atoms (Fig. 3*a*). The resulting strain can be relieved by movement of the substituents in two directions—one in the plane of the ring and one at right angles to it. A purely in-plane movement would not account for the moment observed, but an out-of-plane movement would give rise to an unsymmetrical (4*a* or 4*b*) as well as a symmetrical configuration (4*c*), and the former would possess a dipole moment.

It is not possible to form an exact estimate of the moment on the basis of this hypothesis, because of uncertainties in the atomic dimensions, particularly van der Waals radii, and in bond moments. Furthermore, nothing is known of the force field of the molecule, so it is impossible to say definitely (*a*) which bonds bend, by how much, and in what direction, and (*b*) what are the probabilities of each configuration, for if there is any kind of interaction between the groups at opposite ends of the naphthalene ring system, these probabilities need not be equal.

Nevertheless, a rough estimate has been made on the basis of the assumptions listed below and illustrated by Fig. 5. These are : (1) that the covalent and van der Waals radii have the values ascribed by Pauling (*op. cit.*, pp. 164, 189) ; (2) that the C–Cl bond moment effective in bending movements is −1·4 ; and that the corresponding component of the C–O–CH_3 group along the C–O direction is $+0{\cdot}2$; * (3) that the C–Cl and C–O bonds are equally deflected through an angle θ in a plane at right angles to that (plane A) containing the naphthalene rings before they are distorted; (4) that the methoxy-groups lie in planes B, B′ inclined at angles θ to plane A; (5) that the α, β, and central carbon atoms lie in four planes D, D′, D″, D‴ inclined at angles $\frac{1}{2}\theta$ to plane A; (6) that each configuration 4*a* and 4*b* is half as probable as 4*c*, so that the moment of the mixture is $1/\sqrt{2}$ times that of 4*a* (or 4*b*).

FIG. 4.

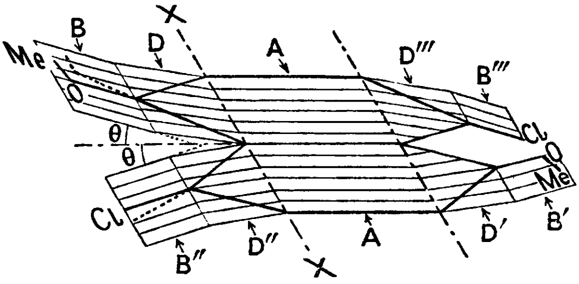


4*a*. 4*b*. 4*c*.

θ is calculated to be 33°, giving a polarisation of 29·4 c.c. According to a simple theorem, this can be added to the polarisation for the non-planarity of the methoxy-groups to give a total of 38·5 c.c. and a moment of 1·37 (observed, 0·95).

In the above treatment it has been assumed that the deflection is purely at right angles to plane A; and that no deflection occurs along the direction X–X. This is almost certainly an over-simplification. If we allow for deflection in the direction X–X by supposing that the force constants of the C–O and C–Cl bonds for deflection (*a*) in plane A, and (*b*) in the plane at right angles to it, are equal, another assumption is added to those already given, *viz.*, (3*a*) that the C–Cl and C–O bonds, having been deflected as defined in (3), are now deflected outwards through an angle $\frac{1}{2}\theta$ in planes B, B′, B″, B‴. (The final positions of the groups are shown dotted on the left-hand side of Fig. 5.)

FIG. 5.



When this case is worked out, θ is found to be altered to 18°, and the theoretical moment to 1·0.

As indicated previously, assumption (6) may be an over-simplification too, for it appears from a spring-valency model that 4*a* and 4*b* are more stable than 4*c*, which would tend to make the observed moment greater than those calculated above: if the substance were completely in the polar configuration the theoretical limits would be 1·8 [assumption (3) alone] and 1·3 [assumptions (3) and (3*a*)]. On the whole, therefore, this hypothesis is more than adequate to account for the observed moment.

Tests of the Deflection Hypothesis.—If the above hypothesis is correct, we should expect that in 4 : 8-dibromo-1 : 5-dimethoxynaphthalene the bromine atoms would cause a larger out-of-

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* These values are obtained by taking the σ-bond moment and half of the π-electron moment, *i.e.*, of that arising from conjugation of the group with the ring system. It would be inappropriate to take the whole of the latter into account because, although its positive pole is on the Cl or O atom, its negative pole is somewhere in the middle of the ring system, so it is not deflected so much as the σ-bond moment.

Furthermore, the appropriate σ-bond moment is that of the C–Cl or C–O–CH_3 grouping itself, and not the algebraic difference between this and the C–H bond moment (taken as 0·4, C–H^+: cf. Bell, Thompson, and Vago, *Proc. Roy. Soc.*, 1948, **192**, *A*, 498). Accordingly, the correct σ-bond value for C–Cl is taken as $-2{\cdot}0 + 0{\cdot}4 = -1{\cdot}6$; and to this is added 0·2, being about half of the π-bond moment, giving $-1{\cdot}4$ as the net value of the moment which bends. The corresponding value for the methoxy-group is obtained from the moments of aliphatic ethers, anisole, *p*-chloroanisole, and chlorobenzene, and it is $+0{\cdot}2$, with the negative pole toward the ring.

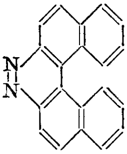
plane deflection than in the dichloro-compound, so the apparent moment should be larger. The observed moment are actually indistinguishable.*

It might appear that this hypothesis could explain the anomalous moment of 2 : 5-di-*tert.*-butylquinol dimethyl ether already mentioned (p. 2315), for the " radius " of the *tert.*-butyl groups is such as to give roughly as much overlap with the methoxy-oxygens as that of the chlorine atoms with the oxygens in the naphthalene compound (Fig. 3). If we suppose that the swinging of the methoxy-groups in the dibutyl ether contributes as much to the polarisation as does that in the 2 : 5-dichloro-compound, where there is practically no overlap (Fig. 2), and assess the polarity due to out-of-plane deflection as before, we obtain a maximum moment of 1·24 (observed, 1·23).

Bastiansen and Hassel have recently obtained electron-diffraction evidence for out-of-plane deflection of no less than 18° in *o*-dichlorobenzene and similar compounds (*Acta Chem. Scand.*, 1947, **1**, 489).

In order to have a further, unambiguous proof of this hypothesis, it is very desirable to take a compound such as 2 : 5-dichloro-(or dibromo-)-*p*-di-*tert.*-butylbenzene, where the complications caused by angular substituents should be absent. This is being attempted.

A completely different test was suggested by the nature of the distortion. It will be seen that the configurations 4*a* and 4*b* are not superimposable : they are mirror-images. Hence they are optically antimeric, and 4*c* is the corresponding internally compensated configuration. More generally, a suitable choice of X should enable a compound *peri*-di-X-naphthalene to be resolved, if the substituents are deflected out of the plane of the rings.



(IV.)

Difficulties were foreseen in preparing a suitable naphthalene derivative, but it was thought that these would be more easily surmountable in the phenanthrene system, in which there is even greater interference, in the 4- and the 5-positions. A still more favourable case appeared to be 3 : 4 : 5 : 6-dibenzphenanthrene, or the more easily prepared analogue, dinaphthopyridazine (IV), where the centre of one of the interfering hydrogen atoms in a scale diagram of the molecule is to be found in the bond joining the other hydrogen atom to the ring. It is difficult to see how such a compound, once resolved, could racemise.

After work had been started—it is being continued—on this problem, a preliminary communication came to light, in which Newman and Hussey (*J. Amer. Chem. Soc.*, 1947, **69**, 978; see also *idem, ibid.*, p. 3023, and Newman and Wheatley, *ibid.*, 1948, **70**, 1913) described the partial resolution of 4 : 5 : 8-trimethylphenanthrene-1-acetic acid, which owes its optical activity to an out-of-plane movement of the type we have postulated. The first suggestion of this source of optical isomerism seems to have been made by Porter (*J.*, 1938, 368) in connexion with some organometallic complexes. If the out-of-plane deflection is favoured in the naphthalene system as it is in the phenanthrene system, then the anomalous dipole moment of 4 : 8-dichloro-(or dibromo-)1 : 5-dimethoxynaphthalene is explained.

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