

4. Further Studies on the Stereochemistry of Aromatic Ethers.

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The electric dipole moments of five arylene dimethyl diethers (IV)—(VIII) have been measured, and compared with those previously found for others of the series [(I)—(III)] (*J.*, 1949, 2312). Views put forward in the latter paper are thereby supported. There is a tendency for all the methoxy-groups to lie coplanar with the aromatic rings, but this is overridden in (VI), (VII), and (VIII) by steric interference, so that the substituents in these three compounds lie in planes almost orthogonal to those of the rings. The moment of hexamethoxybenzene has also been measured, but the stereochemistry is too complicated for the value (2.05) to be unambiguously interpreted.

RECENTLY (*J.*, 1949, 2312) we reported that the electric dipole moments of 1:5- and 1:4-dimethoxynaphthalene (I, 0.67 D.; II, 2.09 D.) were not the same as that of quinol dimethyl ether (III, 1.73 D.). The moment of the last compound is usually ascribed to the free rotation of the angular methoxy-groups about the $C_{\text{aryl}}\text{-O}$ bonds; the same result would, however, follow if these groups were constrained to lie in the plane of the ring, but were free to assume the *cis*- or the *trans*-configuration in equal degree. It was suggested that in all three compounds the increase in the $C_{\text{aryl}}\text{-O}$ bond order brought about by resonance imposes this constraint. In the case of the naphthalene derivatives the configurations with the methoxy-groups lying *cis* to the *peri*-hydrogen atoms are believed to be extremely improbable, because of the steric interference between these atoms and the methyl groups.

If this hypothesis is correct, we should predict that 1:5-dimethoxyanthracene (V) would have a small moment like that of (I). 9:10-Dimethoxyanthracene (VI), however, because it has *peri*-hydrogen atoms on both sides of each methoxy-group, could not assume a planar configuration at all, and would have to exist with the planes of its methoxy-groups roughly orthogonal to the anthracene ring plane; these could take up *cis*- and *trans*-configurations (with respect to each other) equally, so the compound should have much the same moment as quinol dimethyl ether (III). Further confirmation would come from the moments of 9:10-dimethoxy-1:2-benz- and 9:10-dimethoxy-1:2-5:6-dibenz-anthracene (VII and VIII), which from the preceding argument should also be close to that of (III).

We must next consider how coplanar the "coplanar" configurations are. As has previously been remarked (Everard and Sutton, *loc. cit.*), the actual moments of (I) and (II) are respectively not as small or as large as would be required if the compounds were perfectly flat ($\mu_{\text{I}} = 0$; $\mu_{\text{II}} = 2.45$); so we may consider the possibilities: (a) that the equilibrium positions of the methoxy-groups are coplanar, but the weakness of the π -bonding permits considerable oscillation; (b) that owing to the steric interference between the methyl groups and the β -hydrogen atoms, there are equilibrium positions on each side of the ring plane (see Fig. 1 of previous paper; in the caption thereto the words *cis* and *trans* should be interchanged); or (c) that the π -bonding is strong enough to compel the groups to be coplanar with the ring, but the *cis*- are less probable than the *trans*-configurations because the repulsion between the methyl groups and the *peri*-hydrogen atoms is greater than that between the methyl groups and the β -hydrogen atoms.

Some elimination of these alternatives should be possible from the new measurements: thus if (c) were correct, we should expect the moment of (VIII) to be markedly less than that of (VI) or of (VII) because, even if the *peri*-hydrogen atoms were not able to block the planar positions, the additional benzene rings certainly would.

By the kindness of Professor J. W. Cook, F.R.S., who lent us specimens of (V), (VII), and (VIII), we have been able to complete measurements on this series.

The importance of the major hypothesis in application to benzene derivatives has been further investigated by measuring the moment of 2:5-dibromoquinol dimethyl ether. Hexamethoxybenzene was examined in an attempt to discover how the methoxy-groups in it are disposed.

DISCUSSION.

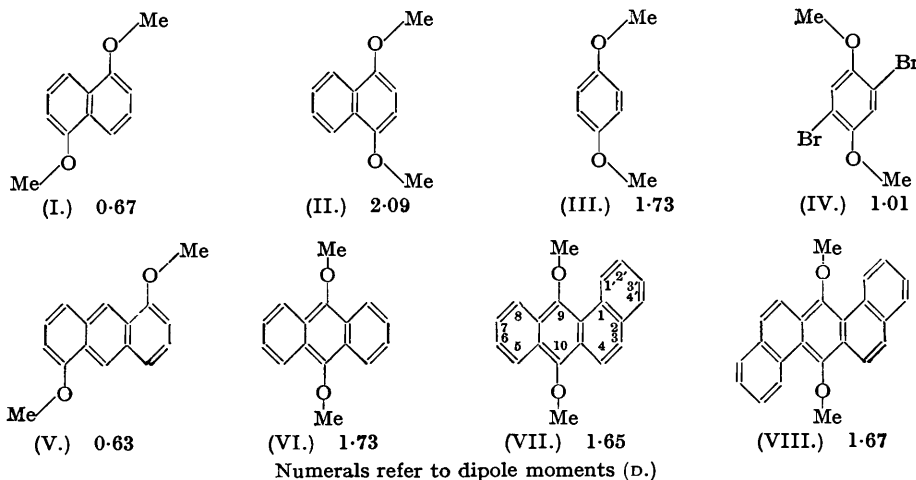
From the results for (V)—(VIII) collected in Table IV and repeated beneath the formulæ, it is clear that all the essential predictions from our major hypothesis are verified. We therefore conclude that there is π -bonding between the methoxy-groups and the aromatic rings strong enough to produce approximate fixation in the plane of the rings, unless a *peri*-hydrogen atom gets in the way. In this case, the methoxy-group is either restricted to one planar orientation

or, if there are two *peri*-hydrogen atoms, it projects roughly orthogonally from the plane of the ring.

Jones has examined the ultra-violet absorption spectra of 10-methoxy- and of 9-methoxy-10-methyl-1:2-benzanthracene, and has also concluded that the methoxy-groups project orthogonally (*J. Amer. Chem. Soc.*, 1945, **67**, 2127). In addition, Badger and Lynn (*J.*, 1950, 1726) have just postulated this to explain the anomalous rate of addition of osmium tetroxide to (VII).

The fact that (IV) has a moment so much less than that of (III) indicates either a marked restriction of rotation of the methoxy-groups by the bromine atoms, or a combination of π -bonding and obstruction of a planar position.

It is now necessary to consider how much more detailed information about the stereochemistry of these compounds can be extracted from the results.



First, the mathematical treatment of the moment of a compound with two rotating polar groups must be extended. This is done in an appendix following this section.

If now we suppose that there is free rotation within limits (*i.e.*, half-amplitude = $\theta = \theta' = \theta''$; see appendix) of the two methoxy-groups in 1:5-dimethoxynaphthalene, 1:5-dimethoxyanthracene, and 2:5-dibromoquinol dimethyl ether, estimate θ from scale models,* and then calculate the moments expected for these molecules by equation (6) in the appendix [taking μ as 1.22, from the moment of (III) and equation (8)], we find for each compound that $\theta \approx 110^\circ$ (relative to *trans* planar positions) and $\mu_{\text{total}} \approx 1.5$. This value of μ_{total} is much too high. The corresponding value, 1.9, for 1:4-dimethoxynaphthalene is too low. Such calculations confirm our hypothesis that these moments are due to somewhat imperfect planar fixation by π -bonding (*cf.* previous paper; the interpenetration of the van der Waals zones is *ca.* 0.1 Å. between the methyl group and an *o*- or β -hydrogen atom, but *ca.* 0.9 Å. with an *o*-bromine atom and *ca.* 1.1 Å. with a *peri*-hydrogen atom).

The half-amplitudes of free oscillation, $\pm\theta$, necessary to give the observed moments are 63° for 2:5-dichloro- and 2:5-dibromo-quinol dimethyl ether, 40° for 1:5-dimethoxynaphthalene †, 37° for 1:5-dimethoxyanthracene, and 83° for 1:4-dimethoxynaphthalene †. A possible explanation of these differences, *viz.*, that π -bonding is loosened when there are two methoxy-groups on the same benzene ring, was put forward in the previous paper.

Scale models show that, whatever the orientation of the 9-methoxy-group in (VII) and (VIII), it touches the 8- and 1'-hydrogen atom. There is least overlap, *ca.* 0.2 Å., of the methyl group with each such hydrogen atom when the plane containing the methoxy-group is inclined

* Wooster models have been used (Wooster, McGowan, and Moore, *J. Sci. Instr.*, 1949, **26**, 140).

These have conventional van der Waals radii. It has been assumed that the $\text{C}-\hat{\text{O}}-\text{Me}$ angle is 120° , and that methyl groups in contact with unbonded atoms are rotated about the $\text{C}-\text{Me}$ bonds so as always to present the minimum van der Waals "radius" towards the interfering atom. If the van der Waals zone of a methyl group were taken as the volume it sweeps out when it rotates, the interpenetration in a coplanar anisole molecule would be ~ 1 Å.

† The values given in the previous paper are erroneous.

towards the 8-hydrogen atom at an angle of about 80° to the plane of the rings. This disposition would make the moment of (VIII) somewhat less than that of (VI) [equation (6)]: for *trans*-molecule $\psi' - \psi'' = \pi$; for *cis*, $\psi' - \psi'' > 0$, while that of (VII) would remain the same as that of (VI) [see equation (8)]. The value calculated for (VIII), on this basis, is 1.71.

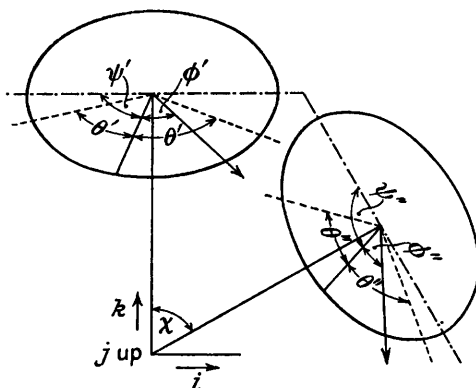
A further complication is the possibility that the oxygen atoms of the methoxy-groups in (VIII) would be forced out of the plane of the anthracene ring (cf. the case of 4:8-dichloro-1:5-dimethoxynaphthalene discussed in the previous paper). It is only possible to estimate the extent of this deflection very crudely; but if it is sufficient to relieve half the van der Waals overlap between the oxygen atoms and the "benz" groups, then the $C_{\text{aryl}}\text{-O}$ bonds are deflected through about 10° , and the methoxy-groups can then oscillate freely with a half-amplitude of about 20° about the equilibrium positions described above. These angles are approximately doubled if the deflection is sufficient to avoid any overlap at all. It is important to note that if a methoxyl-oxygen atom is deflected upwards, its methyl group must also be above the plane of the rings. An attempt has been made to estimate the moments of (VII) and (VIII), by supposing that the $C_{\text{aryl}}\text{-O}$ bond of each trapped methoxy-group is deflected 10° out of the anthracene plane, and by using equation (5) with what seem the best values for the several parameters. The moments so obtained for (VII) and (VIII) are 1.65 and 1.53 respectively.

It is only possible to conclude that such deflection may take place, but that these compounds provide no definite proof that it does.

The molecule of hexamethoxybenzene is too complex for rigorous treatment, but the moments to be expected for some possible dispositions of the methoxy-groups can be calculated. If each group rotated independently and freely, the moment would be $\sqrt{6}\mu = 3.0$ (see Zahn, *Physikal. Z.*, 1932, 33, 400, for the relevant equation). This value would also apply to a molecule in which each group had an equal probability of being up or down, in planes orthogonal to the ring. If the π -bonding were so strong as to require the methoxy-groups to lie coplanar with the ring, which would result in 0.5-A. overlaps of van der Waals zones in a swastika-shaped molecule (much more in others), the moment would be zero. Such simple pictures of the molecule are shown not to correspond to reality by the observed dipole moment, 2.05, which agrees with neither estimate. Perhaps the unmethylated compound, hexahydroxybenzene, would have a considerably smaller moment, owing to the substitution of repulsive forces by the attractive ones of hydrogen-bonding in the coplanar configuration. The dipole moment of this substance has not been measured.

APPENDIX.

In order to facilitate discussion of the experimental results, a general equation has been derived expressing the root mean square moment of non-rigid molecules such as quinol dimethyl ether and its derivatives.



Consider two vectors of scalar magnitude μ formally able to rotate about axes which are inclined at an angle χ , and to which the vectors are severally orthogonal. Angles relating to these two vectors will be distinguished by one or by two primes. For convenience let us define reference positions measured by the angles ψ' and ψ'' between them and the plane containing the two axes of rotation; and let the limits of rotation about these positions be through angles $\pm\theta'$ and $\pm\theta''$. The instantaneous positions of the vectors relative to the above reference positions are designated ϕ' and ϕ'' ($|\phi'| \leq |\theta'|$). We take as our system of rectangular Cartesian co-ordinates

the directions represented by i , j , and k , i and k being in the plane containing the axes of rotation, and k parallel to the one with a single prime. The components of any additional, fixed moments which the molecule may have are represented by μ_i° , μ_j° , and μ_k° , and their vector sum is μ° .

Thus the total moment of the molecule, μ_t , is given by the four equations:

$$\mu_i = \mu_i^\circ + \mu [\cos(\psi' + \phi') + \cos(\psi'' + \phi'') \cos \chi] \quad . \quad . \quad . \quad (1)$$

$$\mu_j = \mu_j^\circ + \mu [\sin(\psi' + \phi') + \sin(\psi'' + \phi'')] \quad . \quad . \quad . \quad (2)$$

$$\mu_k = \mu_k^\circ + \mu \cos(\psi'' + \phi'') \sin \chi \quad . \quad . \quad . \quad (3)$$

$$\mu_t^2 = \mu_i^2 + \mu_j^2 + \mu_k^2 \quad . \quad . \quad . \quad (4)$$

The next step is to integrate μ_t^2 over the ranges $\phi' = \pm\theta'$, $\phi'' = \pm\theta''$, in order to find the mean value $\overline{\mu_t^2}$. The following result is obtained (the abbreviations s' and s'' are used for $\sin \theta'/\theta'$ and $\sin \theta''/\theta''$ respectively):

$$\begin{aligned} \overline{\mu_t^2} &= \left(\int_{-\theta'}^{+\theta'} \int_{-\theta''}^{+\theta''} \mu_t^2 d\phi' d\phi'' \right) / \left(\int_{-\theta'}^{+\theta'} \int_{-\theta''}^{+\theta''} d\phi' d\phi'' \right) \\ &= \mu^{\circ 2} + 2\mu\mu_i^\circ (s' \cos \psi' + s'' \cos \psi'' \cos \chi) + 2\mu\mu_j^\circ (s' \sin \psi' + s'' \sin \psi'') + \\ &\quad 2\mu\mu_k^\circ s'' \cos \psi'' \sin \chi + 2\mu^2 + 2\mu^2 s' s'' (\cos \psi' \cos \psi'' \cos \chi + \sin \psi' \sin \psi'') \quad . \quad (5) \end{aligned}$$

Certain special cases are useful: (1a) If $\mu^\circ = 0$, $\chi = 0$, and $\theta' = \theta''$,

$$\overline{\mu_t^2} = 2\mu^2 [1 + s^2 \cos(\psi' - \psi'')] \quad . \quad . \quad . \quad (6)$$

(1b) If $\theta = \pi$, then

$$\overline{\mu_t^2} = \mu^{\circ 2} + 2\mu^2 \quad . \quad . \quad . \quad (7)$$

(2) If there are equal numbers of each of two kinds of molecule, one kind with $\psi' = \psi_1'$ and $\psi'' = \psi_1''$, the other kind with $\psi' = \psi_2'$ and $\psi'' = \psi_2''$; and if $\mu^\circ = 0$ for each; and if $\psi_1' = \psi_2'$ and $\psi_1'' - \psi_2'' = \pi$ (corresponding to a mixture of *cis*- and *trans*-types), then:

$$\overline{\mu_t^2} = 2\mu^2 \quad . \quad . \quad . \quad (8)$$

This result does not depend on all values of ϕ between $\pm\theta$ being equally probable; it holds for any distribution function which is the same for both ϕ' and ϕ'' , as may be seen by multiplying each integrand for this particular case by a distribution function $f(\phi)$. The latter vanishes in the final expression for $\overline{\mu_t^2}$.

These results mean that a molecule such as quinol dimethyl ether would have the same moment whether (i) the methoxy-groups rotate freely [case (1b), with $\mu^\circ = 0$], (ii) they are fixed in equally probable *cis*- and *trans*-forms [case (2)], (iii) the groups in these *cis*- and *trans*-forms rotate freely within the limits $\pm\theta$ [case (2)], or (iv) the oscillation, not being free, is such that the probability of any angle of swing is some function of that angle, the same function applying to each group [case (2)].

EXPERIMENTAL.

Preparation and Purification of Materials.—AnalaR benzene was purified as before.

2 : 5-Dibromoquinol dimethyl ether was prepared by methylating the quinol. The latter, which had been made by Hammick, Hampson, and Jenkins (*J.*, 1938, 1263), was purified by two recrystallisations from water and by sublimation in a vacuum. The white crystals melted at 189.5–191°. 6 G. of these were heated under reflux with methyl sulphate (4 ml.) and sodium hydroxide (1.8 g.) in water (9 ml.) for 10 minutes. After trituration with 2*N*-sodium hydroxide to remove phenolic material, the solid product was twice recrystallised from ethanol and sublimed at 9 mm. The white crystals (1.1 g.) melted at 144–144.5° (Kohn and Guttman, *Sitz. Akad. Wiss. Wien*, 1924, 133, 573, give 142°).

Specimens of 1 : 5-dimethoxyanthracene and 9 : 10-dimethoxy-1 : 2-benz- and 9 : 10-dimethoxy-1 : 2 : 5 : 6-dibenz-anthracene were provided by Professor J. W. Cook, F.R.S., and had m. p.s of 231–232°, 136–139°, and 232–235° respectively (cf. Cook and Pauson, *J.*, 1949, 2726; 232–232.5°; Badger, Cook, and Ongley, *J.*, 1950, 873; 137–138°, 234–235.5°).

9 : 10-Dimethoxyanthracene was made by Meyer's method with minor modifications (*Annalen*, 1911, 379, 70). After the methylation the product was trituated with 2*N*-sodium hydroxide, and recrystallised twice from ethanol and once from benzene, forming colourless plates with a strong blue fluorescence, m. p. 202° (cf. Meyer, 202°). After the last recrystallisation the substance was exposed only to dim red light until the dielectric constant measurements had been completed (it forms a photo-oxide).

A specimen of hexamethoxybenzene made in the Dyson Perrins Laboratory (see Robinson and Vasey, *J.*, 1941, 660; Baker, *ibid.*, p. 662) was recrystallised from water without change of m. p., 82°. The original material, which had been recrystallised from ligroin (b. p. 60–80°) was used.

Physical Measurements.—All measurements were carried out in benzene at 25°. Dielectric-constant measurements on 2 : 5-dibromoquinol dimethyl ether solutions were done with a condenser similar to the one described by Jenkins and Sutton (*J.*, 1935, 609); but since its volume is 50 ml. it cannot be used for scarce materials (only 0.05 g. of 9 : 10-dimethoxy-1 : 2-5 : 6-dibenzanthracene was available to us). Consequently, for the remaining compounds a modified Sayce–Briscoe type of condenser was used. It differs from that described by Le Fèvre ("Dipole Moments," Methuen, 1938, p. 32) in having, instead of leads to mercury cups, tubular brass connectors fitted with thumb-screws, and in having an earthed brass sleeve surrounding the lead to the inner plate. The advantage of the latter is that it obviates the need for keeping the water-surface in the thermostat either calm or at the same level. The condenser was silvered according to Sugden's recipe (*J.*, 1933, 770). Its volume is 6 ml. and its electrical capacity is 50 cm.

Solutions are made up in a small bottle with a standard neck and stopper. One limb of a 1-mm. bore Ω -shaped delivery tube is internally sealed to the top of the bottle and reaches right to the bottom; the other limb is internally sealed into a standard cone, which can be covered with a cap (this arrangement prevents wetting of the cone). The solute is weighed out from a microchemical balance into the dry, weighed bottle, and the dry solvent introduced through the Ω -tube from a reservoir by upward delivery given by pressure of dry air, under which the solvent is stored. The bottle is capped, stoppered, and weighed and, after dissolution has occurred, its contents are transferred to the condenser, which has a standard socket, by pressure of dry air. The same agency is later used to fill a 4-ml. Sprengel–Ostwald pycnometer directly from the condenser, and the remaining liquid is placed in one compartment of the refractometer cell. By this procedure the possibility of hygroscopic solvents being contaminated by atmospheric moisture is eliminated.

Refractive indices of all compounds were measured for Na_D light with a Pulfrich refractometer (Hilger, London), and those of the anthracene derivatives also at the other wave-lengths shown in Table I. Refraction values derived from these measurements are not very accurate for three reasons: first, the intensities of the 6438, 4800, and 4358 Å. lines are rather low, especially with the use of a divided cell; secondly, the solutes absorbed some of the light; and thirdly, the Δn values were relatively small, because all the solutions used were dilute. The first difficulty was alleviated by placing a cylindrical lens (a tube of water) of the same focal length, f , as the cylindrical cell, in the path of the incident parallel beam at a distance of $2f$ from the cell. The light reaching the cell is hence divergent. On entering the cell it is, however, brought parallel again, and remains so when refracted downwards through the prism into the telescope; without the lens much of the light is lost.

Computation of Moments.—The notation used here is explained by Everard, Hill, and Sutton (*Trans. Faraday Soc.*, 1950, 46, 417). The experimental procedure described above justifies the use of the method advocated in the latter paper for computing α , rather than the one suggested by Halverstadt and Kumler (*J. Amer. Chem. Soc.*, 1942, 64, 2988). The dielectric constant of benzene at 25° was taken as 2.2727 (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, A, 123, 664; cf. values in a list given by Clay, Dekker, and Hemelrijk, *Physica*, 1943, 10, 768). The specific volume of each batch of benzene was measured, and is recorded in Table IV under the heading v_1 : v_1' and ϵ_1' are values obtained by the method of least squares from the v - ω and ϵ - ω graphs.

Molar refractions have been computed with the equation:

$$[R]/M_2 = [(n_1^2 - 1)/(n_1^2 + 2)] \cdot \beta + [6n_1 v_1 / (n_1^2 + 2)^2] \cdot \gamma + v_1 (n_1^2 - 1) / (n_1^2 + 2)$$

(Everard, Hill, and Sutton, *loc. cit.*), in which the coefficients of β and γ , and the constant term, have the values c_1 , c_2 , and c_3 respectively in Table I. These are based on a specific volume of 1.14515 ml./g. for benzene at 25°, and on the observed n_λ^2 values shown in Table I.

TABLE I.

(These figures refer to benzene at 25°.)

Line.	Cd_ν	Na_D	Hg_ν	Cd_ν	Cd_δ	Hg_δ
λ (Å.)	6,438	5,983	5,461	5,086	4,800	4,358
$10^{-30} \nu^2$ (sec. ⁻²)	2,167	2,586	3,012	3,472	3,898	4,728
n_λ^2	2.23225	2.24398	2.25612	2.26971	2.28282	2.30962
$10^5 c_1$	29,116	29,312	29,513	29,738	29,953	30,388
$10^5 c_2$	57,312	57,145	56,973	56,781	56,596	56,222
$10^5 c_3$	33,342	33,566	33,797	34,054	34,300	34,799

Molar dispersions, D , are expressed as $[R]_D - [R]_\infty$ (see Bauer and Fajans, *J. Amer. Chem. Soc.*, 1942, 64, 3023). $[R]_\infty$ is estimated by the reciprocal plotting method of Wulff (*Z. physikal. Chem.*, 1933, B, 21, 368), in which $1/[R]$ is plotted against the square of the frequency of the light (ν^2 : Table I). This is a linear plot if there are no absorption bands near the frequency region examined. Even so, the extrapolation can be hazardous, owing to the visible region being but a small part of the spectrum, and to the uncertainties in the individual $[R]$ values noted in the last section. The probable uncertainty in D is indicated in the column headed \pm in Table III.

It is common practice to take $[R]_D$ as a measure of the distortion polarisation of the solute molecules *i.e.*, ${}_A P + {}_B P$. Therefore, since ${}_B P = [R]_\infty$, D represents the allowance made for ${}_A P$. With substances

having extensive conjugated systems (such as 9 : 10-dimethoxy-1 : 2-5 : 6-dibenzanthracene), dispersions ought to be measured, lest the ΔP allowance should be excessive (Everard, Hill, and Sutton, *loc. cit.*). All but one of the present anthracene derivatives have $[R]_D$ values agreeing within 1.5 c.c. with the values $\{[R]_D$ (calc.) in Table IV} calculated from those of anthracene (65.4 c.c.; Steiger, *Ber.*, 1923, 56, 998, and references therein), naphthalene (44.5), benzene (26.2), and anisole (33.0) (Landolt-Börnstein, "Tabellen"), so the ΔP allowance should not be more than usual in these cases; but as the value for 9 : 10-dimethoxy-1 : 2-5 : 6-dibenzanthracene shows an exaltation of 4.9 c.c. and the dispersion is large, the moment quoted for this compound may be too small by perhaps 0.05. However, in the absence of experimental ΔP data, no definite conclusions can be drawn, so all moments in Table IV are based on observed $[R]_D$ values therein. The latter are got from $\Delta n-\omega$ graphs, and they therefore differ slightly from those in Table III, which are obtained from single solutions. The column headed \pm in Table IV gives the observational uncertainty in μ , and takes no account of uncertainties in ΔP .

Results.—The experimental observations are given in Table II, where Roman numerals refer to the structural formulæ (p. 17), and to the names of the compounds printed against the same numerals below Table IV. The numerals in columns 1 and 2 of Table III, which gives the dispersion observations, correspond to those in Table II; values of Δn_D are omitted from Table III because they already appear in Table II.

TABLE II.

Com- pound.	Soln. no.	$10^6\omega$.	ϵ .	v .	$10^6\Delta n_D$.	Com- pound.	Soln. no.	$10^6\omega$.	ϵ .	v .	$10^6\Delta n_D$.
(IV)	1	2,858	2.2740	1.14321	—	(VII)	1	1,650	2.2755	1.14395	31
	2	4,701	2748	4206	—		2	9,265	2872	4140	168
	3	7,704	2762	4047	—		3	10,532	2893	4101	195
	4	9,169	2770	—	—	(VIII)	1	1,322	2745	4564	25
	5	9,624	2774	3910	—		2	5,015	2802	4437	106
	6	69,830	—	—	319		3	8,652	2860	4302	188
(V)	1	1,293	2736	4564	30	(IX)	1	1,818	2760	4410	—
	2	8,448	2782	4350	141		2	8,334	2872	4218	—
	3	8,829	2784	4341	142		3	10,995	2922	4140	4
(VI)	1	1,655	2757	4416	23						
	2	6,754	2850	4263	106						
	3	9,251	2896	4179	140						
	4	14,251	2984	4036	220						
	5	14,654	2993	4027	227						

TABLE III.

Com- pound.	Soln. no.	$10^6\Delta n_\lambda$.					$[R]_\lambda$.					D.	\pm .		
		λ :	6438.	5461.	5086.	4800.	4358.	6438.	5893.	5461.	5086.			4800.	4358.
(V)	3		142	153	160	182	—	80.4	80.9	82.8	84.2	88.0	—	9.2	2
(VI)	4		213	235	249	270	—	78.6	79.6	81.4	83.1	85.4	—	8.7	1
(VII)	3		193	206	223	235	272	98.7	99.2	101.3	104.3	106.6	113.1	11.9	2
(VIII)	3		183	200	214	—	—	118.9	120.5	123.6	127.0	—	—	15.1	2

TABLE IV.

Com- pound.	ϵ_1' .	$10^3\alpha$.	v_1 .	v_1' .	$-10^3\beta$.	$10^3\gamma$.	τP_2 .	$[R]_D$ (obs.).	$[R]_D$ (calc.).	μ .	\pm .
(IV)	2.2725	498	—	1.14491	594	46	76.2	55.5	55.4	1.01	0.05
(V)	2.2727	645	1.14609	1.14606	302	159	88.8	80.6	79.1	0.63	0.03
(VI)	2.2727	1820	1.14474	1.14470	306	156	141.1	79.8	79.1	1.73	0.01
(VII)	2.2728	1563	1.14450	1.14450	333	183	154.6	98.9	97.4	1.65	0.01
(VIII)	2.2726	1543	1.14609	1.14611	354	219	178.0	120.7	115.8	1.67	0.02
(IX)	2.2727	1760	1.14474	1.14470	301	4	150.4	64.5	67.3	2.05	0.01

(IV) 2 : 5-Dibromoquinol dimethyl ether. (V) 1 : 5-Dimethoxyanthracene. (VI) 9 : 10-Dimethoxyanthracene. (VII) 9 : 10-Dimethoxy-1 : 2-benzanthracene. (VIII) 9 : 10-Dimethoxy-1 : 2-5 : 6-dibenzanthracene. (IX) Hexamethoxybenzene.

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