73. *Diamagnetic Anisotropy of Conjugated Compounds.*

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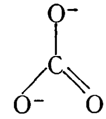
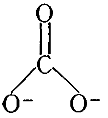
In order to extend quantitative knowledge of crystal susceptibilities to different types of conjugated compounds, data are given for metal-free phthalocyanine, oxalic acid dihydrate, stilbene, tolan, and *trans*-azobenzene. These have been correlated with the available *X*-ray data for the molecular direction cosines in order to obtain the principal susceptibilities of the molecules. The anisotropy of the oxalate group is about twice that of the carbonate radical and about one-sixth of that of benzene. Stilbene and tolan possess, not only the expected anisotropy normal to the molecular plane, which may be explained in terms of molecular orbitals, but also a considerable anisotropy *in* that plane, which is not yet explained. It is shown that large diamagnetic anisotropy is associated with the existence of bond resonance (mesomerism), plane arrangement of atoms in the molecule and tendency to equalisation of bond distances, not only in closed rings (as predicted by theory) but also in open systems.

Recent studies, both experimental and theoretical (Krishnan, Guha, and Banerjee, *Phil. Trans.*, 1933, **231**, 235; Krishnan and Banerjee, *ibid.*, 1935, **234**, 265; Pauling, *J. Chem. Physics*, 1936, **4**, 673; Lonsdale, *Proc. Roy. Soc.*, 1937, *A*, **159**, 149; London, *J. Physique*, 1937, **8**, 397), of the diamagnetic anisotropy of various aromatic molecules have shown that the degree of conjugation of the molecular framework is closely connected with the magnitude of the anisotropy. Systems containing large or numerous conjugated rings have a large diamagnetic susceptibility perpendicular to the plane of the ring, whereas normal aliphatic molecules have small anisotropies. Octahydrochrysene is found to have the same anisotropy as naphthalene (Lonsdale, *loc. cit.*), indicating that the *cyclo*hexane ring is nearly isotropic. The presence of conjugation, or resonance, even without a closed ring structure, is accompanied by high anisotropy; *e.g.*, the carbonate radical CO_3^{--}, which is known to have trigonal symmetry (Ewald and Hermann, "Strukturbericht," 1931, p. 317; Pauling, Brockway, and Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2706; Sidgwick, "The Organic Chemistry of Nitrogen," 1937, Introduction, p. xvii) and must therefore be a combination of the systems (I), (II), and (III), has an anisotropy of

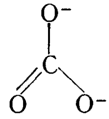
(I.)



(II.)



(III.)



4·0 → 5·0 × 10^{-6} (Krishnan, Guha, and Banerjee, *loc. cit.*), and so has NO_3^-, whereas that of the sulphate and the selenate group, which have a tetrahedral structure, is only about 0·75 × 10^{-6}. Such conjugated systems are also plane, or tend to be plane even when opposed by considerable distorting forces (Clews and Lonsdale, *Proc. Roy. Soc.*, 1937, *A*, **161**, 493; Lonsdale, *Z. Krist.*, 1936, **95**, 471).

The existence of large anisotropy in a diamagnetic crystal is therefore presumptive evidence of (i) molecular conjugation, (ii) the arrangement of atoms (or the tendency of atoms to arrange themselves) in sheets normal to the direction of greatest numerical diamagnetic susceptibility.

Most of the studies hitherto carried out have concerned derivatives of benzene and cyanuric rings. The author has now measured the principal susceptibilities of metal-free phthalocyanine, oxalic acid dihydrate, stilbene, tolan, and *trans*-azobenzene, all of which have been (or are being) subjected to a complete *X*-ray analysis.

Experimental.

Metal-free Phthalocyanine, $C_{32}H_{18}N_8$.—Preliminary measurements of the magnetic anisotropy of this substance gave $(\chi_2 - \chi_1)_{\text{mol.}} = -372 \pm 18$, $(\chi_3 - \chi_1)_{\text{mol.}} = -397 \pm 40$ (the factor 10^{-6} is omitted in this and all succeeding data). The best single crystals were used for the measurements of anisotropy, and since they were rather fragile, they did not survive that part of the investigation. Those that remained weighed less than 0·1 mg., and therefore a modification of Krishnan's "suspension method" (Krishnan and Banerjee, *Current Sci.*, 1935, **3**, 548) was used for the measurement of absolute susceptibility. The crystal density was 1·445 g./c.c. at 20°; two solutions of this density were made up, one of strontium bromide (more diamagnetic), the other of this salt together with nickel chloride (less diamagnetic than the estimated value of the minimum crystal susceptibility). In a suitable mixture of these two, the crystals merely orientated themselves without any tendency to move laterally when the magnetic field was imposed. The crystals and solution were contained in a thin-walled glass tube, which could be suitably closed to prevent evaporation, and then suspended from one arm of a sensitive balance. By arranging that the lower part of the tube should be in a uniform field of about 8000 gauss, and the upper part in a negligible field, while the gradient was as large as possible over a region of 3 mm. at the edge of the pole-pieces, the behaviour of the crystals within this gradient could be observed and the susceptibility of the surrounding liquid measured almost simultaneously by the Gouy method. Distilled water was used as a standard, and this was checked by measurement of the susceptibilities of water-free methyl and ethyl alcohols. On the assumption that $\chi_{H_2O} = -0{\cdot}720$ and $\kappa_{air} = +0{\cdot}029$ at 20°, the method gave $\chi_{MeOH} = -0{\cdot}677 \pm 0{\cdot}004$, and $\chi_{EtOH} = -0{\cdot}733 \pm 0{\cdot}004$, at 21°, as compared with Cabrera and Fahlenbrach's values (*Z. Physik*, 1933, **85**, 568), $\chi_{MeOH} = -0{\cdot}6743 \pm 0{\cdot}0036$ at 19·8°, and $\chi_{EtOH} = -0{\cdot}7324 \pm 0{\cdot}0024$ at 20°. Since the temperature dependence of χ in these cases is negligible, the agreement was very satisfactory.

Owing to the very small size and lath-like shape of the phthalocyanine crystals, together with their high density, the method was not capable of giving very accurate results. The solutions were rather viscous, and convection currents set up by changes of temperature had to be avoided. The possible error with the most intense gradient available was estimated at about ± 5%, taking the mean of several separate determinations. The measurement of absolute susceptibility was made along χ_1, which is inclined at 47·5° to the *c* axis in the obtuse angle β; $\chi_1 = -166 \pm 8$, hence $\chi_2 = -538 \pm 26$, normal to χ_1 in (010), and $\chi_3 = -563 \pm 48$, along [010].

Oxalic Acid Dihydrate.—Most of the measurements were made on a large fine crystal weighing 24·63 mg., *d* 1·615 g./c.c. at 20°. The absolute susceptibility was measured by the Rabi–Krishnan method (Krishnan, Guha, and Banerjee, *loc. cit.*), but since oxalic acid reacts with most salts, a mixture of water and glycerol, both previously saturated with oxalic acid, was used. This gave $\chi_1 = -53{\cdot}1 \pm 0{\cdot}5$. Measurements of anisotropy, using *s*-triphenylbenzene ($\chi_c - \chi_a = -173$) as a standard, gave $\chi_2 - \chi_1 = -1{\cdot}91$, $\chi_3 - \chi_1 = -7{\cdot}05$, $\chi_3 - \chi_2 = -5{\cdot}14$. Hence $\chi_1 = -53{\cdot}1 \pm 0{\cdot}5$, $\chi_2 = -55{\cdot}01$, normal to χ_1 in (010), $\chi_3 = -60{\cdot}15$, along [010]; χ_1 makes an angle of 0·6° with the *c* axis in the obtuse angle β.

Stilbene, Azobenzene, and Tolan.—These compounds form fine large monoclinic crystals, which are isomorphous both in habit and in structure (Robertson, Prasad, and Woodward, *Proc. Roy. Soc.*, 1936, *A*, **154**, 187). Stilbene and azobenzene are insoluble in water, but tolan proved to be slightly soluble in hot water. The absolute susceptibilities and anisotropies were measured on a number of different crystals, and consistent results were obtained, which were estimated to be correct to within 0·5%. Mean results are given in the following table, the measurement of absolute susceptibility having been made in each case on the numerically least of the three principal values (italicised).

	d.	$(\chi_2 - \chi_1)$.	$(\chi_2 - \chi_3)$.	$(\chi_3 - \chi_1)$.	χ_1.	χ_2.	χ_3.	ψ.
Stilbene	1·161	−46·9	−48·0	+1·4	−99·9	−146·8	*−98·8*	−66·0°
Tolan	1·133	−50·9	−49·0	−1·4	*−98·5*	−149·4	−99·9	−62·5
Azobenzene.........	1·225	−49·3	−54·4	+5·2	−88·1	−137·4	*−83·0*	−65·6

In each case χ_1 lies very close to the *a* crystallographic axis. The results for stilbene and azobenzene differ from those first reported by Krishnan, Guha, and Banerjee (*loc. cit.*), but are in agreement with later measurements (privately communicated by Professor Krishnan in reply to an enquiry).

DISCUSSION OF RESULTS.

Molecule Susceptibilities.—*Metal-free phthalocyanine.* Robertson has carried out a complete Fourier analysis of the structure of this compound, and gives the direction cosines of a molecule relative to the *a*, *b*, *c'* (normal to *a* and *b*) axes, as

$$\left.\begin{array}{llllll} \cos\alpha_L & 0{\cdot}3532 & \cos\beta_L & 0{\cdot}0395 & \cos\gamma_L & 0{\cdot}9347 \\ \cos\alpha_M & 0{\cdot}6615 & \cos\beta_M & 0{\cdot}6960 & \cos\gamma_M & -0{\cdot}2794 \\ \cos\alpha_N & -0{\cdot}6617 & \cos\beta_N & 0{\cdot}7169 & \cos\gamma_N & 0{\cdot}2197 \end{array}\right\} \quad . \quad . \quad (1)$$

L and M being specified directions *in* the plane of the molecule, and N normal to that plane. Relative to the χ_1, χ_2, χ_3 axes the direction cosines of L, M, N are

$$\left.\begin{array}{llllll}\cos\theta_{L1} & 0{\cdot}9951 & \cos\theta_{L2} & -0{\cdot}0906 & \cos\theta_{L3} & 0{\cdot}0395 \\ \cos\theta_{M1} & -0{\cdot}0924 & \cos\theta_{M2} & -0{\cdot}7121 & \cos\theta_{M3} & 0{\cdot}6960 \\ \cos\theta_{N1} & 0{\cdot}0349 & \cos\theta_{N2} & 0{\cdot}6963 & \cos\theta_{N3} & 0{\cdot}7169\end{array}\right\} \quad . \quad . \quad (2)$$

This shows that the χ_1 axis is only about 5° away from the L direction in the molecule; it follows therefore that the susceptibility along L (κ_L) must be very nearly equal to χ_1 ($= -166$). By assuming $\kappa_L = \kappa_M$ and using the formulæ $\chi_1 = \kappa_L + \Delta\kappa . \cos^2\theta_{N1}$, $\chi_2 = \kappa_L + \Delta\kappa . \cos^2\theta_{N2}$, etc., $\kappa_2 = -166$, $\Delta\kappa = \chi_1 + \chi_2 + \chi_3 - 3\kappa_L = -769$, we obtain the following estimate of the orientation of N, the normal to the molecular plane, relative to the χ_1, χ_2, χ_3 axes :

$$\cos\theta_{N1} = 0 \qquad \cos\theta_{N2} = 0{\cdot}6956 \qquad \cos\theta_{N3} = 0{\cdot}7185$$

These values are very close to those of Robertson, *viz.*,

$$\cos\theta_{N1} = 0{\cdot}0347 \qquad \cos\theta_{N2} = 0{\cdot}6963 \qquad \cos\theta_{N3} = 0{\cdot}7169$$

If, however, the reverse process is followed and the values of the molecule susceptibilities κ_L, κ_M, κ_N are calculated from the set of equations

$$\chi_1 = \kappa_L \cos^2\theta_{L1} + \kappa_M \cos^2\theta_{M1} + \kappa_N \cos^2\theta_{N1}, \text{ etc.}$$

we find $\kappa_L = -165$, $\kappa_M = -120$, $\kappa_N = -982$.

Alternatively, κ_L, κ_M, κ_N can be calculated directly (see Lonsdale and Krishnan, *loc. cit.*) from χ_1, χ_2, χ_3 and α_L, γ_L, α_M, and hence an independent estimate of ψ, the angle between χ_1 and the *c* crystal axis, can be obtained. Adopting this method, we find $\kappa_L = -166$, $\kappa_M = -104$, $\kappa_N = -997$, $\psi = +50{\cdot}2°$ (cf. observed value $+47{\cdot}5°$).

Robertson's analysis showed that the molecule is plane and nearly tetragonal, in which case it seems unlikely that κ_M should be so much less than κ_L. A little time, therefore, has been spent in investigating the dependence of the calculated values of κ_M upon the values of the molecular direction cosines.

The angle whose cosines are given above (2) are obtained from Robertson's values, given by a Fourier analysis of the structure (J., 1936, 1195) and the directly measured value of ψ.

If we assume that one of these, say θ_{L1}, is correct, and that $\kappa_L = \kappa_M = -166$, $\kappa_N = -935$, we can calculate a set of direction cosines which will give the observed values of χ_1, χ_2, χ_3. These direction cosines are as follows :

$$\left.\begin{array}{llllll}\cos\theta_{L1} & 0{\cdot}9951 & \cos\theta_{M1} & -0{\cdot}0985 & \cos\theta_{N1} & 0 \\ \cos\theta_{L2} & -0{\cdot}0709 & \cos\theta_{M2} & -0{\cdot}7150 & \cos\theta_{N2} & 0{\cdot}6956 \\ \cos\theta_{L3} & 0{\cdot}0684 & \cos\theta_{M3} & 0{\cdot}6922 & \cos\theta_{N3} & 0{\cdot}7185\end{array}\right\} \quad . \quad . \quad (3)$$

None of these values gives an angle differing from the former experimental result by more than 2°, and six of them differ by not more than a few minutes. It follows therefore that the values of κ_M and κ_N are closely dependent upon the accuracy of the molecular direction cosines, small variations in the cosines producing large variations in κ_M, κ_N, although κ_L is not much affected by small changes in these cosines. On the other hand, calculations of the orientation of the molecular plane from the measured values of χ_1, χ_2, χ_3 and estimated molecule susceptibilities κ_L, κ_M, κ_N, will be nearly correct, even if the assumption that $\kappa_L = \kappa_M$ is far from true.

The implications of the very large anisotropy of the phthalocyanine molecule have already been discussed (Lonsdale, *Proc. Roy. Soc.*, 1937, *A*, **159**, 149).

Oxalic acid dihydrate. The complete *X*-ray examination of this substance by Robertson and Woodward (J., 1936, 1817) showed that the molecule is plane and the C–C distance in the oxalate group is only 1·43 → 1·45 A. This indicates the presence of double-bond properties in this link, presumably due to the conjugation of double bonds in adjacent carboxyl groups. It seemed likely, therefore, that there might be a marked molecular anisotropy, which could be compared with that due to the carbonate CO_3^{--} group, in which there is a similar plane arrangement of atoms, with a shortening of the C–O link (Elliott, *J. Amer. Chem. Soc.*, 1937, **59**, 1380).

Robertson and Woodward give the direction values of the principal directions in the oxalate group (L, M in the plane of the group, N normal to that plane). These can be combined with χ_1, χ_2, χ_3, and ψ, to give κ_L, κ_M, κ_N as before :

$$\kappa_L = -53{\cdot}13,\ \kappa_M = -52{\cdot}73,\ \kappa_N = -62{\cdot}40.$$

In this case the anisotropy is relatively small and the susceptibilities do not vary much with small changes in the direction cosines. The anisotropy is large, however, compared with that usually expected for aliphatic molecules, and is about twice the value found for the CO_3^{--} group. Although the influence of the water molecules is not known, it seems probable that the anisotropy is mainly, if not entirely, due to the resonance in the oxalate group.

The diamagnetic oxalates studied by Krishnan and Banerjee (*Phil. Trans.*, 1936, *A*, **235**, 343) also showed an anisotropy more than five times as large as that of diamagnetic sulphates and selenates.

It is noteworthy that in the oxalate and the carbonate group there is no closed chain of conjugated bonds. The presence of a closed ring is therefore not essential to the existence of abnormal diamagnetism. One may predict a similar conjugation, with plane arrangement of atoms, tendency to equalisation of bond distances, and large anisotropy, in such compounds as maleic and fumaric acids, muconic acid, cinnamic acid, as well as in benzil, benzophenone, and in all the diphenylpolyenes, including stilbene, the discussion on which now follows.

Stilbene. Since χ_1 lies along the *a* crystal axis, it follows that χ_1, χ_2, χ_3 are coincident with *a*, *c'*, *b*; and since there are two independent pairs of centrosymmetrical molecules in the unit cell (Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568), we have

$$\left.\begin{aligned}\chi_1 &= \tfrac{1}{4}\,[\kappa_L\textstyle\sum\limits_4 \cos^2\alpha_L + \kappa_M\sum\limits_4 \cos^2\alpha_M + \kappa_N\sum\limits_4 \cos^2\alpha_N]\\ \chi_2 &= \tfrac{1}{4}\,[\kappa_L\textstyle\sum\limits_4 \cos^2\gamma_L + \kappa_M\sum\limits_4 \cos^2\gamma_M + \kappa_N\sum\limits_4 \cos^2\gamma_N]\\ \chi_3 &= \tfrac{1}{4}\,[\kappa_L\textstyle\sum\limits_4 \cos^2\beta_L + \kappa_M\sum\limits_4 \cos^2\beta_M + \kappa_N\sum\limits_4 \cos^2\beta_N]\end{aligned}\right\}\quad .\ .\ .\ .\ .\quad (4)$$

Robertson and Woodward have given the following data for the molecular direction cosines, relative to the *a*, *b*, *c* axes.

Molecules 1 and 3	$\cos\alpha_L$	$0{\cdot}8352$	$\cos\alpha_M$	$-0{\cdot}4190$	$\cos\alpha_N$	$-0{\cdot}3563$
	$\cos\beta_L$	$\pm 0{\cdot}1748$	$\cos\beta_M$	$\pm 0{\cdot}8187$	$\cos\beta_N$	$\mp 0{\cdot}5469$
	$\cos\gamma_L$	$0{\cdot}5219$	$\cos\gamma_M$	$0{\cdot}3939$	$\cos\gamma_N$	$0{\cdot}7567$
Molecules 2 and 4	$\cos\alpha'_L$	$0{\cdot}8533$	$\cos\alpha'_M$	$-0{\cdot}3076$	$\cos\alpha'_N$	$-0{\cdot}4212$
	$\cos\beta'_L$	$\mp 0{\cdot}0278$	$\cos\beta'_M$	$\pm 0{\cdot}8333$	$\cos\beta'_N$	$\pm 0{\cdot}5521$
	$\cos\gamma'_L$	$-0{\cdot}5208$	$\cos\gamma'_M$	$-0{\cdot}4595$	$\cos\gamma'_N$	$-0{\cdot}7194$

Substituting in (4), we obtain the equations

$$\begin{aligned}-\ \ 99{\cdot}9 &= 0{\cdot}7127\kappa_L + 0{\cdot}1348\kappa_M + 0{\cdot}1525\kappa_N\\ -146{\cdot}8 &= 0{\cdot}2717\kappa_L + 0{\cdot}1828\kappa_M + 0{\cdot}5455\kappa_N\\ -\ \ 98{\cdot}8 &= 0{\cdot}0156\kappa_L + 0{\cdot}6824\kappa_M + 0{\cdot}3020\kappa_N\end{aligned}$$

whence $\kappa_L = -85{\cdot}8,\ \kappa_M = -50{\cdot}1,\ \kappa_N = -209{\cdot}6.$

This result is somewhat unexpected, showing as it does a big anisotropy in the plane of the molecule. Nor is it possible, as it was with phthalocyanine, to remove the difference between κ_L and κ_M by a relatively small adjustment of the direction cosines. For if $\kappa_L = \kappa_M$, the first and the last equation reduce to

$$\begin{aligned}-99{\cdot}9 &= \kappa_L + 0{\cdot}1525\,(\kappa_N - \kappa_L)\\ -98{\cdot}8 &= \kappa_L + 0{\cdot}3020\,(\kappa_N - \kappa_L)\end{aligned}$$

No reasonable values of κ_L, κ_N will satisfy these equations; the difference between κ_L and κ_M is, in fact, implied by the difference between $\bar{\alpha}_N$ and $\bar{\beta}_N$, χ_1 and χ_3 being nearly equal. A difference of approximately 2° in each of $\bar{\alpha}_N$, $\bar{\beta}_N$ (in order to make them more nearly equal) corresponds to values of $\overline{\alpha_N^2} = 0{\cdot}1790$, $\overline{\beta_N^2} = 0{\cdot}2755$, and gives $\kappa_L = -79$, $\kappa_M = -55$, $\kappa_N = -211$. The equality of κ_L, κ_M would therefore involve a highly improbable degree of inaccuracy both in the magnetic measurements and in the *X*-ray results. The cause of this large anisotropy in the plane of the molecule is obscure; it is worth noting, however, that in every case of a condensed or polyphenyl compound so far examined the susceptibility along the " length " of the molecule is greater than that along the " width " (Lonsdale and Krishnan, *loc. cit.*).

The values $\kappa_L = -86$, $\kappa_M = -50$, $\kappa_N = -210$ lead to an anisotropy $-124 < \Delta\kappa < -160$ (numerically). This is numerically greater than the value $-118{\cdot}6$ found for diphenyl, as might have been expected, for the chain between the phenyl groups is conjugated and will itself contribute to the anisotropy. Robertson and Woodward have found the values 1·33 A., 1·45 A. for the lengths of the "double" and "single" bonds respectively, indicating a degree of resonance about equivalent to that of the C–C bond in the oxalate group.

Tolan. A similar calculation for tolan, unpublished *X*-ray data being used for the direction cosines, very kindly given to me by Dr. Robertson and Miss Woodward, leads to molecule susceptibilities $\kappa_L = -81{\cdot}5$ (along length of molecule), $\kappa_M = -67{\cdot}8$ (normal to L, in plane of molecule), $\kappa_N = -198{\cdot}5$ (normal to plane of molecule). Here again the anisotropy *in* the plane of the molecule, though not as large as that of stilbene, is too large to be explained away by experimental inaccuracy. The anisotropy normal to the molecular plane, $-117 < \Delta\kappa < -131$, is of the same order as that of diphenyl.

trans-*Azobenzene.* The data for the molecular direction cosines of azobenzene are not yet available, although an *X*-ray analysis is in progress. The substitution of nitrogen for carbon atoms in the interphenyl chain has resulted in an all-round lowering of susceptibilities by about twelve units.

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