

Investigations on Magne-Crystallic Action. III. Further Studies on Organic Crystals

K. S. Krishnan and S. Banerjee

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IX—Investigations on Magne-Crystallic Action

III—Further Studies on Organic Crystals

By Professor K. S. KRISHNAN and S. BANERJEE

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I—INTRODUCTION

In Part I* of this paper a convenient method of measuring the principal magnetic susceptibilities of single crystals was described, and several organic crystals, among others, were studied by this method. The results were discussed particularly in relation to the structure of the molecules and their orientations in the crystal lattice, and it was shown how a correlation of the principal magnetic susceptibilities of the crystal with those for the individual molecules (obtained from measurements on magnetic double-refraction in the liquid state, or from considerations of molecular structure) gives us useful information regarding the orientations of the molecules in the crystal lattice. Indeed, in favourable cases the molecular orientations may thus be determined much more easily, and some of the parameters defining the orientations also more accurately, than by X-ray methods of analysis. Conversely, where the molecular orientations in the crystal lattice are already known from X-ray studies, a knowledge of the principal magnetic susceptibilities of the crystal enables us to

* 'Phil. Trans.,' A, vol. 231, p. 235 (1933).

obtain the magnetic constants of the individual molecules, which are of interest. For example, it is thus found that as one proceeds from benzene to naphthalene and from naphthalene to anthracene, the numerical increase in susceptibility that occurs, is directed predominantly along the normal to the plane of the benzene rings.

In this paper is described another simple method of measuring magnetic anisotropies of crystals, which is as convenient as the oscillational method described in Part I, and which can, moreover, be adopted for measurements with even such small crystals as weigh a fraction of a milligram. Using this method it has been possible to extend the magnetic measurements to a number of organic crystals, specially chosen for their structural or other interest. Many of the crystals extensively studied by X-ray methods by Dr. ROBERTSON, Mrs. LONSDALE, Miss PICKETT, and others, have naturally been included in our list. These magnetic studies are described in Section II of the present Part. In Sections III to VII the results of the magnetic measurements are discussed, especially with a view to co-ordinating them with the X-ray data on the structure of the crystals and with their optical and other properties. The principal magnetic susceptibilities of individual molecules are calculated for a number of substances, and are discussed in relation to chemical and other evidence regarding molecular structure. Of these five Sections, Section III deals with benzene derivatives, Section IV with diphenyl and triphenyl compounds, Section V with naphthalene derivatives and Section VI with polynuclear compounds. Section VII contains some remarks on the optical properties of these crystals.

II—EXPERIMENTAL

Susceptibility measurements on crystals involve, in general,

- (1) the determination of the directions of the principal magnetic axes ;
- (2) the measurement of the differences between the principal susceptibilities, viz., $\chi_1 - \chi_2$ and $\chi_1 - \chi_3$;
- (3) the measurement of the absolute susceptibility along any one convenient direction in the crystal.

1—*The Magnetic Axes*

The determination of the axial directions usually presents no difficulty. In the trigonal, tetragonal, orthorhombic, and hexagonal systems the magnetic axes are naturally defined by considerations of crystal symmetry. For the monoclinic crystal the “*b*” axis must be one of the magnetic axes, and the other two must lie in the (010) plane. By suspending the crystal with its “*b*” axis vertical, in a uniform magnetic field, and determining the orientation of any vertical natural face (*h*0*l*) of the crystal, in the field, the directions of the two magnetic axes in the (010) plane are known. One method of determining the orientation of the face in the field has been described in Part I ; a second method was also adopted in the present measurements and will be described in sub-section 4.

With triclinic crystals the determination of the axial directions is naturally more complicated. Hexamethyl benzene was the only triclinic crystal studied here, and the method of measurement adopted for this crystal will be clear from the data given in Table I below.

2—*Measurement of Magnetic Anisotropy*

Knowing the directions of the three principal magnetic axes, if we measure the magnetic anisotropy $\Delta\chi$ for any two planes in the crystal, then $\chi_1 - \chi_2$ and $\chi_1 - \chi_3$ are known. One method of measuring $\Delta\chi$ that is adopted in the present paper, is the same as was described in Part I. The crystal is suspended at the end of a calibrated quartz fibre, in a uniform magnetic field. The upper end of the fibre is fixed to the centre of a torsion-head which can be rotated about the axis of suspension of the fibre by any known angle. When the field is put on, the crystal will naturally tend to turn round so as to bring the direction of maximum susceptibility in the horizontal plane, along the field. The torsion-head is suitably rotated so that the torsion is nothing in the equilibrium orientation of the crystal. The crystal is now made to execute torsional oscillations of small amplitude about this orientation. Let T be the period of these oscillations and let T' be the period of similar oscillations outside the field. Then the difference between the maximum and the minimum gram molecular susceptibilities of the crystal in the plane of oscillation is given by the relation

$$\Delta\chi = A \frac{T'^2 - T^2}{T^2}, \quad \dots \dots \dots (1)$$

where

$$A = \frac{Mc}{mH^2}; \quad \dots \dots \dots (2)$$

c is the torsional constant of the fibre, H is the field, m is the mass of the crystal, and M is the gram molecular weight. Thus $\Delta\chi$ is readily determined.

3—*Second Method for Measuring Magnetic Anisotropy*

In the present paper a second method has also been used for the measurement of $\Delta\chi$, which is as convenient as the oscillational method, and for crystals of small mass, say a fraction of a milligram,* also more accurate. In the above experimental arrangement, the crystal is allowed to set as before in the equilibrium orientation in the magnetic field under zero torsion of the fibre. If the torsion-head is slowly rotated from this position by an angle α , the crystal will also rotate in the same direction by a smaller angle ϕ . We shall suppose that the torsion of the fibre is chosen to be so small that ϕ will be much smaller than α . The relation between α and ϕ is evidently

$$c(\alpha - \phi) = \frac{1}{2} \frac{m}{M} H^2 \Delta\chi \sin 2\phi. \quad \dots \dots \dots (3)$$

* For a number of substances, *e.g.*, phenanthrene, quaterphenyl, crystals of only this mass could be obtained.

If the rotation of the torsion-head is continued very slowly, there will come a stage when ϕ just reaches the value $\pi/4$. Let α_c be the corresponding value of α . For this position, plainly

$$c \left(\alpha_c - \frac{\pi}{4} \right) = \frac{1}{2} \frac{m}{M} H^2 \Delta\chi, \quad \dots \dots \dots (4)$$

i.e.,

$$\Delta\chi = A \left(2\alpha_c - \frac{\pi}{2} \right), \quad \dots \dots \dots (5)$$

where A is the same constant as before (see (2)). Hence a knowledge of α_c enables us to calculate $\Delta\chi$.

The determination of α_c is simple and is based on the following property. If from the above position the torsion-head is rotated further by a small angle so as to make α just exceed α_c , ϕ would exceed $\pi/4$, and the restoring couple due to the field, which is proportional to $\sin 2\phi$, would tend to diminish, and the torsional couple of the fibre would be more than sufficient to compensate the restoring couple due to the field. Hence, the crystal would turn round over a large angle, indeed over $3\pi/4$ if the torsion of the fibre is sufficiently small. Thus, in practice, α_c would be the critical angle of rotation of the torsion-head, from its original position, which is just sufficient to start the crystal to turn round, and can, therefore, be measured accurately.

If after the above rotation the crystal is allowed to come to rest and the torsion-head is further rotated in the same direction as before, when α reaches a value $\alpha_c + \pi$, the crystal rotation ϕ would reach a value $5\pi/4$, which would again correspond to a maximum value of the couple due to the field, and the slightest further rotation of the torsion-head would turn round the crystal in the same manner as before. Again, when α just exceeds $\alpha_c + 2\pi$, there will be still another turning round and so on. From any one of these critical values of α , the value of α_c can be readily calculated, and hence $\Delta\chi$.

4—Determination of the Orientation of the Crystal in the Field

With the above experimental arrangement, the *orientation* of the crystal in the magnetic field is also easily determined. Let us consider again the monoclinic crystal suspended with its “ b ” axis vertical, and suppose that one of the $(h0l)$ faces is well developed. It is required to determine the inclination θ of this face to the equatorial plane of the field. The axis of the observation tele-microscope is adjusted to be horizontal and normal to the direction of the field. Starting now with the equilibrium position of the crystal in the field under zero torsion of the fibre, the torsion-head is gradually rotated in the proper direction so as to bring the $(h0l)$ face to the equatorial plane (as tested by observation through the tele-microscope). Let α_1 be the necessary angle of rotation of the torsion-head. Also let α_c be the critical angle of its rotation, as defined in the previous section. Then θ is given

by the simple relation

$$\sin 2\theta = \frac{\alpha_1 - \theta}{\alpha_c - \frac{\pi}{4}}, \quad \dots \dots \dots (6)$$

and hence θ is known.

5—Absolute Susceptibilities

Finally, the absolute susceptibility was measured for a suitable direction in the crystal by the modified form of RABl's null-method described in Parts I and II of this paper. Where, as is usual, the volume susceptibility is numerically less than that of water, a standard solution of NiCl_2 , suitably diluted, was used for magnetically balancing the crystal.* Where the volume susceptibility was numerically higher than that of water, solutions of KCl or KI were used.

6—Results

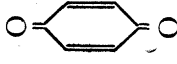
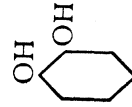
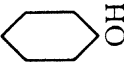
We explain here briefly the notation adopted in the paper. When the crystal has an axis of symmetry, the gram molecular susceptibility along the axis and that along perpendicular directions are denoted by χ_{\parallel} and χ_{\perp} respectively. For the orthorhombic crystal, χ_a , χ_b and χ_c denote the gram molecular susceptibilities along the "a," "b" and "c" axes respectively. For the monoclinic crystal, the gram molecular susceptibility along the "b" axis is denoted by χ_3 , while the greater of the two principal susceptibilities in the (010) plane is denoted by χ_1 and the smaller by χ_2 . The χ_1 axis is inclined at an angle ψ to the "c" axis and at $\beta - \psi$ to the "a" axis, β being the *obtuse* angle between the "c" and "a" axes. For many of the monoclinic crystals the (001) faces were well developed, and their inclination to the χ_2 axis was directly measured. This angle is denoted by θ , its relation to ψ being expressed by the equation $\theta + \psi + \frac{1}{2}\pi = \beta$ (obtuse).

The results of the measurements on magnetic anisotropy are given in Table I. In the third column of the table are given the crystallographic data that have been adopted as basis for the description of the various crystal faces. Where X-ray data are available for the dimensions of the unit cell, these data have naturally been adopted in preference to the goniometric data. For those crystals, however, for which such X-ray measurements are not available, the axes and axial ratios adopted for the crystal are those described in GROTH's 'Chemische Kristallographie.' The other columns of the table need no explanation. As has already been mentioned, the determination of $\Delta\chi$ for any *two* planes in the crystal is, in general, sufficient to give $\chi_1 - \chi_2$ and $\chi_1 - \chi_3$. However, as a check on the accuracy of the measurements, an extra measurement was usually made, using a third plane. The calculated value for this plane is included in the table for comparison with the directly measured value.

In Table II are given the results of the measurements on the absolute susceptibilities.

* We wish to correct here an error which appears on p. 245 of Part I. The susceptibility of MnCl_2 at $28^\circ.5\text{ C}$ should be 114.9×10^{-6} per gram, and not 117.9×10^{-6} as is given there. The other values remain unaffected.

TABLE I

Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
1	<i>p</i> -Benzoquinone 	Monoclinic C_{2h}^5 $Z = 2$ $a = 7.08 \text{ \AA}$ $b = 6.79$ $c = 5.80$ $\beta = 101^\circ 0'$	" <i>b</i> " axis vertical " " " " (001) plane horizontal	$\theta = -20^\circ.2$ " " " " " " " "	40.0 6.0 37.1	$\chi_1 - \chi_2 = 40.0$ $\chi_1 - \chi_3 = 1.2$ $\psi = +31^\circ.2$ Cal. $\Delta\chi = 36.4$
2	Catechol 	Monoclinic C_{2h}^3 $Z = 8$ $a = 17.46 \text{ \AA}$ $b = 10.74$ $c = 5.48$ $\beta = 94^\circ 15'$	" <i>b</i> " axis vertical " " " " (100) plane horizontal	$\psi = +2^\circ.2$ " " " " " " " "	30.5 2.7 27.8	$\chi_1 - \chi_2 = 30.5$ $\chi_1 - \chi_3 = 27.8$ $\psi = +2^\circ.2$ Cal. $\Delta\chi = 27.8$
3	Hydroquinol 	Trigonal C_{3v}^1 $Z = 18$ $a = 22.06 \text{ \AA}$ $c = 5.62$	Trigonal axis horizontal	Trigonal axis along field	1.4	$\chi_{11} - \chi_{11} = 1.4$

MAGNE-CRYSTALLIC ACTION

TABLE I—(continued)

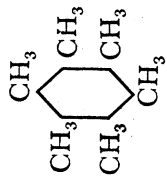
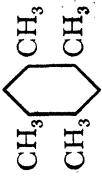
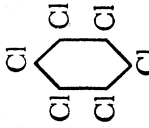
Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
4	Hexamethyl benzene 	Triclinic C_2^1 Z = 1 a = 9·010 Å. b = 8·926 c = 5·344 α = 44° 27' β = 116° 43' γ = 119° 34'	(001) plane horizontal “a” axis vertical . . “b” “ ” (100) plane horizontal	“a” axis at 26½° to field and “b” axis at 93° to field (001) plane along field “(001)” “b” axis practically along field	1·6 61·4 62·3 59·6	$\left\{ \begin{array}{l} \chi_1 - \chi_2 = 1\cdot6 \\ \chi_1 - \chi_3 = 62\cdot7 \end{array} \right.$ χ_1 and χ_2 axes lie in the (001) plane making 26½° with “a” axis and 93° with “b” axis Cal. $\Delta\chi$ = 62·7 ” = 59·5
5	Durene (1, 2, 4, 5-Tetramethyl benzene) 	Monoclinic C_{2h}^5 . . . Z = 2 a = 11·57 Å. b = 5·77 c = 7·03 β = 113°·3	“b” axis vertical . . (001) plane horizontal “a” axis vertical . . “b” “ ”	$\theta = +3^\circ\cdot1$ “a” axis normal to field “b” “ ”	39·7 7·6 31·7	$\left\{ \begin{array}{l} \chi_1 - \chi_2 = 39\cdot7 \\ \chi_1 - \chi_3 = 32\cdot0 \end{array} \right.$ $\psi = +20^\circ\cdot2$ Cal. $\Delta\chi$ = 31·9
6	Hexachlorobenzene 	Monoclinic C_{2h}^5 . . . Z = 2 a = 8·07 Å. b = 3·84 c = 16·61 β = 116° 52'	“b” axis vertical . . (100) plane horizontal “c” axis vertical . . “b” “ ”	$\theta = -25^\circ\cdot7$ “b” axis normal to field “b” “ ”	6·8 37·4 39·4	$\left\{ \begin{array}{l} \chi_1 - \chi_2 = 6\cdot8 \\ \chi_1 - \chi_3 = 41\cdot7 \end{array} \right.$ $\psi = +52^\circ\cdot6$ Cal. $\Delta\chi$ = 39·2

TABLE I—(continued)

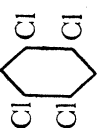
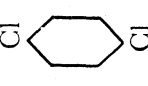
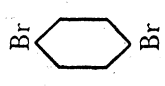
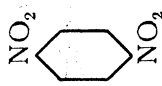
Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
7	1, 2, 4, 5-Tetrachlorobenzene 	Monoclinic prism $a : b : c = 0.9041 : 1 : 0.3650$ $\beta = 99^\circ 22\frac{1}{2}'$	"b" axis vertical "c" " (100) plane horizontal	$\psi = -68^\circ.9$ "b" axis along field "b" " "b" "	41.7 5.6 36.1	$\chi_1 - \chi_2 = 41.7$ $\chi_1 - \chi_3 = 0.2$ $\psi = -68^\circ.9$ Cal. $\Delta\chi = 36.5$
8	<i>p</i> -Dichlorobenzene 	Monoclinic C_{2h}^5 $Z = 2$ $a = 14.83 \text{ \AA.}$ $b = 5.88$ $c = 4.10$ $\beta = 112^\circ 30'$	"b" axis vertical "c" " (100) plane horizontal	$\psi = +86^\circ.9$ "b" axis normal to field "c" " "c" "	36.2 9.8 26.3	$\chi_1 - \chi_2 = 36.2$ $\chi_1 - \chi_3 = 9.9$ $\psi = +86^\circ.9$ Cal. $\Delta\chi = 26.2$
9	<i>p</i> -Dibromobenzene 	Monoclinic C_{2h}^5 $Z = 2$ $a = 15.46 \text{ \AA.}$ $b = 5.80$ $c = 4.11$ $\beta = 112^\circ 38'$	"b" axis vertical "c" " (100) plane horizontal	$\psi = +87^\circ.0$ "b" axis normal to field "c" " "c" "	32.2 9.0 23.3	$\chi_1 - \chi_2 = 32.2$ $\chi_1 - \chi_3 = 9.1$ $\psi = +87^\circ.0$ Cal. $\Delta\chi = 23.0$
10	<i>p</i> -dinitrobenzene 	Monoclinic prism $a : b : c = 2.038 : 1 : 1.043$ $\beta = 92^\circ.3$	"b" axis vertical "c" " (100) plane horizontal	$\psi = -36^\circ.6$ "b" axis normal to field "b" " "b" "	53.6 6.5 21.5	$\chi_1 - \chi_2 = 53.6$ $\chi_1 - \chi_3 = 41.0$ $\psi = -36^\circ.6$ Cal. $\Delta\chi = 21.9$

TABLE I—(continued)

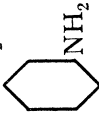


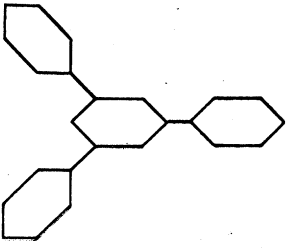
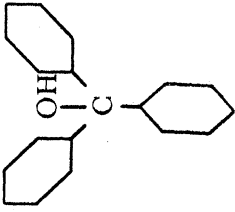


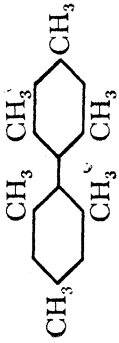
Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
11	<i>m</i> -Nitroaniline 	Rhombic C_{2v}^5 $Z = 4$ $a = 19.23$ A. $b = 6.48$ $c = 5.06$	" <i>c</i> " axis vertical " <i>a</i> " " <i>b</i> "	" <i>a</i> " axis along field " <i>b</i> " " <i>a</i> "	2.0 10.5	$\chi_a - \chi_b = 2.0$ $\chi_a - \chi_c = 12.5$
12	Terphenyl (<i>p</i> -Diphenylbenzene) 	Monoclinic C_{2h}^5 $Z = 2$ $a = 8.08$ A. $b = 5.60$ $c = 13.59$ $\beta = 91^\circ 55'$	" <i>b</i> " axis vertical " <i>a</i> " (001) plane horizontal	$\theta = +16^\circ.2$ " <i>b</i> " axis normal to field " <i>a</i> "	117 39.5 59.8	$\chi_1 - \chi_2 = 117$ $\chi_1 - \chi_3 = 48.6$ $\psi = -14^\circ.3$ Cal. $\Delta\chi = 59.3$
13	Quaterphenyl (4,4'-Diphenyldiphenyl) 	Monoclinic C_{2h}^5 $Z = 2$ $a = 8.14$ A. $b = 5.64$ $c = 18.4$ $\beta = 97^\circ$	" <i>b</i> " axis vertical " <i>a</i> " (001) plane horizontal	$ \theta = 17^\circ.1$ " <i>b</i> " axis normal to field " <i>a</i> "	168 55 82	$\chi_1 - \chi_2 = 168$ $\chi_1 - \chi_3 = 70$ $ \theta = 17^\circ.1$ Cal. $\Delta\chi = 83$
14	1,3,5-Triphenylbenzene 	Rhombic C_{2v}^9 $Z = 4$ $a = 7.55$ A. $b = 19.76$ $c = 11.22$	" <i>a</i> " axis vertical " <i>c</i> " " <i>b</i> "	" <i>c</i> " axis along field " <i>b</i> " " <i>c</i> "	14.9 158 174	$\chi_c - \chi_b = 14.9$ $\chi_c - \chi_a = 173$ Cal. $\Delta\chi = 173$

TABLE I—(continued)

Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
15	Triphenyl carbinol 	Trigonal $Z = 3$ $a = 11.25 \text{ \AA}$ $\alpha = 107^\circ$	Trigonal axis horizontal	Trigonal axis along field	5.3	$\chi_{11} - \chi_{11} = 5.3$
16	4, 4'-Dichlorodiphenyl 	Monoclinic prism $a : b : c = 1.1569 :$ $1 : 0.7078$ $\beta = 96^\circ 48'$	"b" axis vertical (100) plane horizontal "c" axis vertical	$\psi = -28^\circ.5$ "b" axis along field "b"	35.1 33.4 52.4	$\chi_{11} - \chi_{22} = 35.1$ $\chi_{11} - \chi_{33} = -25.4$ $\psi = -28^\circ.5$ Cal. $\Delta\chi = 52.5$
17	4, 4'-Dibromodiphenyl 	Monoclinic prism $a : b : c = 1.1181 :$ $1 : 0.6963$ $\beta = 94^\circ 30'$	"b" axis vertical (100) plane horizontal "c" axis vertical	$\psi = -27^\circ.6$ "b" axis along field "b"	35.9 29.7 49.7	$\chi_{11} - \chi_{22} = 35.9$ $\chi_{11} - \chi_{33} = -22.0$ $\psi = -27^\circ.6$ Cal. $\Delta\chi = 50.2$
18	Dimesityl 	Monoclinic C_{2h}^5 $Z = 4$ $a = 8.19 \text{ \AA}$ $b = 8.54$ $c = 22.1$ $\beta = 95^\circ 46'$	"b" axis vertical (001) plane horizontal	$\theta = +61^\circ.6$ "b" axis along field	27.5 2.4	$\chi_{11} - \chi_{22} = 27.5$ $\chi_{11} - \chi_{33} = 3.8$ $\psi = -55^\circ.8$
			(100)	"b"	14.9	Cal. $\Delta\chi = 15.0$

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TABLE I—(continued)



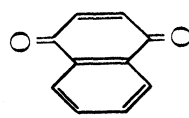
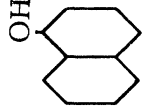
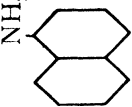
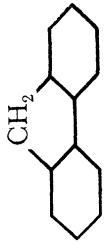
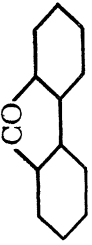
Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
19	Diphenic acid (<i>o,o'</i> -Bi-benzoic acid) 	Monoclinic C_{2h}^5 $Z = 8$ $a = 13.70 \text{ \AA}$ $b = 11.95$ $c = 14.08$ $\beta = 91^\circ 40'$	" <i>b</i> " axis vertical " " " " (100) plane horizontal	$\psi = -3^\circ.4$ " " " " " "	17.8 0.3 17.9	$\chi_1 - \chi_2 = 17.8$ $\chi_1 - \chi_3 = 18.0$ $\psi = -3^\circ.4$ Cal. $\Delta\chi = 17.9$
20	<i>o</i> -Tolidine (4, 4'-Diamido-3, 3'-dimethyl diphenyl) 	Orth. bisphen. $Q^4 (?)$ $Z = 4$ $a = 6.47 \text{ \AA}$ $b = 7.48$ $c = 23.60$	" <i>a</i> " axis vertical " " " " " "	" <i>c</i> " axis along field " " " " " "	79.6 3.3 82.8	$\chi_a - \chi_b = 82.9$ $\chi_a - \chi_c = 3.3$ Cal. $\Delta\chi = 82.9$
21	1, 4-Naphthoquinone 	Monoclinic C_{2h}^5 $Z = 4$ $a = 13.50 \text{ \AA}$ $b = 7.74$ $c = 8.25$ $\beta = 121^\circ 10'$	" <i>b</i> " axis vertical " " " " (100) plane horizontal	$\psi = -62^\circ.5$ " " " " " "	87.9 1.8 51.5	$\chi_1 - \chi_2 = 87.9$ $\chi_1 - \chi_3 = 16.9$ $\psi = -62^\circ.5$ Cal. $\Delta\chi = 52.3$

TABLE I—(continued)

Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
22	α -Naphthol 	Monoclinic prism $Z = 4$ $a = 13.1 \text{ \AA}$ $b = 4.9$ $c = 13.4$ $\beta = 117^\circ 10'$	"b" axis vertical (001) plane horizontal	$\theta = -1^\circ.5$ "b" axis normal to field	51.9 10.0	$\chi_1 - \chi_2 = 51.9$ $\chi_1 - \chi_3 = 61.9$ $\psi = +28^\circ.7$
23	α -Naphthylamine 	Rhombic bipy. $a : b : c = 1.6340 :$ $1 : 0.8156$	"c" axis vertical "a" " "b" "	"b" axis along field "b" " "a" "	3.4 20.1 16.6	$\chi_a - \chi_c = 16.7$ $\chi_b - \chi_c = 20.1$ Cal. $\Delta\chi = 16.7$
24	Fluorene 	Monoclinic C_{2h}^5 $Z = 4$ $a = 8.48 \text{ \AA}$ $b = 5.73$ $c = 19.24$ $\beta = 101^\circ 30'$	"b" axis vertical "a" " "a" " (001) plane horizontal	$\theta = +0^\circ.6$ "b" axis normal to field "a" "	84.0 37.0 47.3	$\chi_1 - \chi_2 = 84.0$ $\chi_1 - \chi_3 = 37.0$ Cal. $\Delta\chi = 47.0$
25	Fluorenone (Fluorene-ketone) 	Rhombic bipy. $a : b : c = 0.5808 :$ $1 : 0.7788$	"a" axis vertical "b" " "c" "	"c" axis along field "a" " "a" "	31.7 25.2 56.5	$\chi_a - \chi_b = 56.9$ $\chi_a - \chi_c = 25.2$ Cal. $\Delta\chi = 56.9$

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TABLE I—(continued)

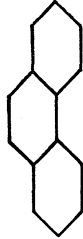
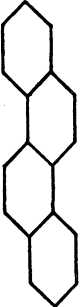
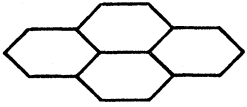
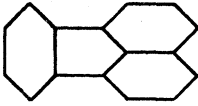
Serial number	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$ \Delta\chi $	Magnetic anisotropy
26	Phenanthrene 	Monoclinic C_{2h}^5 $Z = 4$ $a = 8.60 \text{ \AA}$ $b = 6.11$ $c = 19.24$ $\beta = 98^\circ 15'$	"b" axis vertical "a" "	$\theta = +11^\circ.4$ "b" axis normal to field	126 35.0	$\chi_1 - \chi_2 = 126$ $\chi_1 - \chi_3 = 39.9$ $\psi = -3^\circ.1$
27	Chrysene (1, 2-Benzo-phenanthrene) 	Monoclinic C_{2h}^6 $Z = 4$ $a = 8.34 \text{ \AA}$ $b = 6.18$ $c = 25.0$ $\beta = 115^\circ.8$	"b" axis vertical "a" " (001) plane horizontal	$\theta = +13^\circ.1$ "b" axis normal to field "a" "	170 39.4 114	$\chi_1 - \chi_2 = 170$ $\chi_1 - \chi_3 = 48.1$ $\psi = +12^\circ.7$ Cal. $\Delta\chi = 113$
28	Pyrene 	Monoclinic prism $a : b : c = 1.468 : 1 : 1.781$ $\beta = 100^\circ 53'$	"b" axis vertical (001) plane horizontal "a" axis vertical	$\theta = -14^\circ.1$ "b" axis normal to field "b" "	97.5 33.2 118	$\chi_1 - \chi_2 = 97.5$ $\chi_1 - \chi_3 = 125$ $\psi = +25^\circ.0$ Cal. $\Delta\chi = 119$
29	Fluoranthene 	Monoclinic prism $a : b : c = 1.495 : 1 : 1.025$ $\beta = 97^\circ 10'$	"b" axis vertical "a" " (001) plane horizontal	$\theta = -2^\circ.4$ "b" axis normal to field "a" "	109 39.8 69.9	$\chi_1 - \chi_2 = 109$ $\chi_1 - \chi_3 = 40.0$ $\psi = +9^\circ.6$ Cal. $\Delta\chi = 69$

TABLE II—ABSOLUTE SUSCEPTIBILITIES

Serial number	Crystal	Direction along which susceptibility was measured	Vol susceptibility	Density of the crystal	Corresponding gm mol suscep	Principal gm mol susceps	Mean susceptibility
1	<i>p</i> -Benzoquinone	Along χ_1 — axis .	— 0.330 — 0.327	1.324 1.298	—27.0 —27.2	$\chi_1 = - 27.1$ $\chi_2 = - 67.1$ $\chi_3 = - 25.9$ $\psi = + 31^\circ.2$	— 40.0
2	Catechol . . .	Along χ_1 — axis .	— 0.604	1.370	— 48.5	$\chi_1 = - 48.5$ $\chi_2 = - 79.0$ $\chi_3 = - 76.3$ $\psi = + 2^\circ.2$	— 67.9
3	Hydroquinol .	Along the normal to trigonal axis	— 0.77	1.32	— 64	$\chi_{11} = - 63$ $\chi_{11} = - 64$	— 64
4	Hexamethyl benzene	Along the normal to “ <i>b</i> ” axis in (001) plane	— 0.636	1.020	—101.1	$\chi_1 = - 101.1$ $\chi_2 = - 102.7$ $\chi_3 = - 163.8$ For the directions of the axes see Table I	—122.5
5	Durene . . .	Along χ_1 — axis .	— 0.596	1.034	— 77.3	$\chi_1 = - 77.3$ $\chi_2 = - 117.0$ $\chi_3 = - 109.3$ $\psi = + 20^\circ.2$	—101.2
6	Hexachloro-benzene	Along χ_1 — axis .	— 0.970	2.134	—129.4	$\chi_1 = - 129.4$ $\chi_2 = - 136.2$ $\chi_3 = - 171.1$ $\psi = + 52^\circ.6$	—145.6
7	1, 2, 4, 6-Tetrachlorobenzene	Along χ_1 — axis .	— 0.855	1.829	—100.9	$\chi_1 = - 100.9$ $\chi_2 = - 142.6$ $\chi_3 = - 100.7$ $\psi = - 68^\circ.9$	—114.7
8	<i>p</i> -Dichloro-benzene	Along the normal to “ <i>c</i> ” axis in (010) plane	— 0.720	1.510	— 70.1	$\chi_1 = - 70.0$ $\chi_2 = - 106.2$ $\chi_3 = - 79.9$ $\psi = + 86^\circ.9$	— 85.4
9	<i>p</i> -Dibromo-benzene	Along χ_1 — axis .	— 0.848	2.318	— 86.3	$\chi_1 = - 86.3$ $\chi_2 = - 118.5$ $\chi_3 = - 95.4$ $\psi = + 87^\circ.0$	—100.1

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TABLE II—(continued)

Serial number	Crystal	Direction along which susceptibility was measured	Vol susceptibility	Density of the crystal	Corresponding gm mol suscep	Principal gm mol susceps	Mean susceptibility
10	<i>p</i> -Dinitrobenzene	Along χ_1 — axis .	— 0.366	1.625	— 37.8	$\chi_1 = -37.8$ $\chi_2 = -91.4$ $\chi_3 = -78.8$ $\psi = -36^\circ.6$	— 69.3
11	<i>m</i> -Nitroaniline	Along “ <i>a</i> ” axis .	— 0.662	1.415	— 64.6	$\chi_a = -64.6$ $\chi_b = -66.6$ $\chi_c = -77.1$	— 69.4
12	Terphenyl . .	Along χ_1 — axis .	— 0.516	1.226	— 96.8	$\chi_1 = -96.8$ $\chi_2 = -214$ $\chi_3 = -145.4$ $\psi = -14^\circ.3$	—152
13	1, 3, 5-Triphenyl benzene	Along “ <i>b</i> ” axis .	— 0.607 — 0.609	1.200 1.201	—154.9 —155.2	$\chi_a = -313$ $\chi_b = -155.0$ $\chi_c = -140.1$	—203
14	Triphenyl carbinol	Along trigonal axis	— 0.777 — 0.773	1.191 1.189	—169.7 —169.1	$\chi_{11} = -169.4$ $\chi_{11} = -174.7$	—172.9
15.	4, 4'-Dichorodiphenyl	Along “ <i>b</i> ” axis .	— 0.663 — 0.667	1.417 1.420	—104.3 —104.7	$\chi_1 = -129.9$ $\chi_2 = -165.0$ $\chi_3 = -104.5$ $\psi = -28^\circ.5$	—133.1
16	4, 4'-Dibromodiphenyl	Along “ <i>b</i> ” axis .	— 0.754 — 0.761	1.880 1.911	—125.1 —124.3	$\chi_1 = -146.7$ $\chi_2 = -182.6$ $\chi_3 = -124.7$ $\psi = -27^\circ.6$	—151.3
17	Dimesityl . .	Along χ_1 — axis .	— 0.692	1.023	—161.2	$\chi_1 = -161.2$ $\chi_2 = -188.7$ $\chi_3 = -165.0$ $\psi = -55^\circ.8$	—171.6
18	Diphenic acid .	Along χ_1 — axis .	— 0.698	1.406	—120.2	$\chi_1 = -120.2$ $\chi_2 = -138.0$ $\chi_3 = -138.2$ $\psi = -3^\circ.4$	—132.1
19	<i>o</i> -Tolidine . .	Along “ <i>a</i> ” axis .	— 0.680	1.230	—117.3	$\chi_a = -117.3$ $\chi_b = -200.2$ $\chi_c = -120.6$	—146.0
20	α -Naphthoquinone	Along “ <i>b</i> ” axis .	— 0.494 — 0.497	1.402 1.406	— 55.7 — 55.9	$\chi_1 = -38.9$ $\chi_2 = -126.8$ $\chi_3 = -55.8$ $\psi = -62^\circ.5$	— 73.8

TABLE II—(continued)

Serial number	Crystal	Direction along which susceptibility was measured	Vol susceptibility	Density of the crystal	Corresponding gm mol suscep	Principal gm mol susceps	Mean susceptibility
21	α -Naphthol	Along χ_1 — axis .	— 0.538	1.282	— 60.5	$\chi_1 = - 60.5$ $\chi_2 = - 112.4$ $\chi_3 = - 122.4$ $\psi = + 28^\circ.7$	— 98.4
22	α -Naphthyl-amine	Along “ b ” axis .	— 0.741	1.185	— 89.5	$\chi_a = - 92.9$ $\chi_b = - 89.5$ $\chi_c = - 109.6$	— 97.3
23	Fluorene . . .	Along χ_1 — axis .	— 0.516	1.181	— 72.6	$\chi_1 = - 72.6$ $\chi_2 = - 156.6$ $\chi_3 = - 109.6$ $\psi = + 10^\circ.9$	—112.9
24	Fluorenone .	Along “ a ” axis .	— 0.502	1.254	— 72.1	$\chi_a = - 72.1$ $\chi_b = - 129.0$ $\chi_c = - 97.3$	— 99.5
25	Phenanthrene .	Along χ_1 — axis .	— 0.49	1.172	— 74	$\chi_1 = - 74$ $\chi_2 = - 200$ $\chi_3 = - 114$ $\psi = - 3^\circ.1$	—129
26	Chrysene . .	Along χ_1 — axis .	— 0.490	1.270	— 88.0	$\chi_1 = - 88.0$ $\chi_2 = - 258$ $\chi_3 = - 136.1$ $\psi = + 12^\circ.7$	—160.7
27	Pyrene . . .	Along χ_1 — axis .	— 0.509 — 0.503	1.274 1.264	— 80.7 — 80.4	$\chi_1 = - 80.6$ $\chi_2 = - 178.1$ $\chi_3 = - 206$ $\psi = + 25^\circ.0$	—154.9
28	Fluoranthene .	Along χ_1 — axis .	— 0.542	1.236	— 88.6	$\chi_1 = - 88.6$ $\chi_2 = - 198$ $\chi_3 = - 128.6$ $\psi = + 9^\circ.6$	— 138.4

III—MAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE : BENZENE DERIVATIVES

We proceed to discuss the results obtained in the previous Section, in relation to X-ray and other data concerning molecular and crystalline structure. We shall first consider the benzene derivatives.

1—*p*-Benzoquinone

This crystal has been analysed by X-ray methods,* and it is assigned to the space group C_{2h}^5 ($P2_1/a$) in the monoclinic prismatic class, with 2 molecules in the unit cell, the molecules possessing a centre of symmetry. The X-ray measurements are not sufficient to locate the orientations of the two molecules in the unit cell. They can, however, be determined easily from the magnetic data.† As will be seen from Table I, the χ_1 axis makes an angle of $31^\circ.2$ with the “*c*” axis and one of $69^\circ.8$ with the “*a*” axis, while, from the cell dimensions given by CASPARI, the $(20\bar{1})$ plane is found to be inclined at an angle of $34^\circ.1$ to the “*c*” axis and $66^\circ.9$ to the “*a*” axis. Thus the χ_1 axis lies practically in the $(20\bar{1})$ plane, which contains of course the χ_3 axis as well, the third magnetic axis, viz., χ_2 , being along the normal to $(20\bar{1})$. Moreover, since χ_1 and χ_3 are nearly equal, the normal to the $(20\bar{1})$ plane is an axis of approximate magnetic symmetry. Further, the ratio of the susceptibility of the crystal along this axis to that along perpendicular directions, is equal to $2\chi_2/(\chi_1 + \chi_3) = 2.5$, which is nearly the same as the value for the benzene molecule. We may, therefore, conclude that the molecular planes in benzoquinone crystal practically coincide with the $(20\bar{1})$ plane.

The optical properties of the crystal also support the molecular orientations suggested here. Since the optical polarizability of the benzene ring for light vibrations along the normal to its plane is much less than for directions in the plane, we should expect α to be much smaller than either β or γ , and further the vibration direction of α to be normal to $(20\bar{1})$. This is actually so, since the crystal exhibits a strong negative birefringence, and the acute bisectrix is nearly perpendicular to $(20\bar{1})$.‡

* W. A. CASPARI, ‘Proc. Roy. Soc.,’ A, vol. 136, p. 82 (1932).

† A preliminary report on the analysis of molecular orientations in this crystal by the magnetic method was published in ‘Nature,’ vol. 131, p. 653 (1933).

‡ Since the present paper was written, ROBERTSON (‘Nature,’ vol. 134, p. 138, July 28 (1934)) has published the results of a complete X-ray analysis of this crystal. He finds that the molecular planes are inclined to the $(20\bar{1})$ plane at an angle between 3° and 7° towards the “*c*” axis, in agreement with the 3° obtained by us from the magnetic data. Besides giving the inclinations of the molecular planes, his X-ray analysis gives complete information regarding the orientations of the molecules. Let us call for convenience the line joining the two O atoms of the molecule as its K_1 axis, the line perpendicular to the K_1 axis in the plane of the molecule as its K_2 axis, and the line normal to its plane as its K_3 axis. ROBERTSON finds that the K_1 axis of the molecule makes 79° with the “*a*” axis of the crystal, $37^\circ.5$ with the “*b*” axis, and $54^\circ.5$ with the normal to the (001) plane, while the K_2 axis makes 70° , 127° and 44° respectively with these crystal directions. These correspond, in the notation adopted in the later portions of this paper, to $\lambda = 8^\circ.6$, $\mu = +29^\circ.2$, and $\nu = 52^\circ.5$. (The magnetic value of $\mu = +31^\circ.2$.) From these orientations the principal susceptibilities of the benzoquinone molecule along its K_1 , K_2 and K_3 axes can be readily calculated; they are

$$K_1 = -24.2$$

$$K_2 = -27.9$$

$$K_3 = -68.0.$$

It is clear that the presence of the two oxygen atoms in the para positions produces a small anisotropy in the plane of the molecule, the susceptibility along the line joining the oxygen atoms being numerically the smaller.

2—*Catechol and Hydroquinol*

Catechol (*o*-dioxo-benzene) has also been studied by CASPARI.* It crystallizes in the monoclinic prismatic class in the space group C_{2h}^3 with 8 asymmetric molecules in the unit cell. Regarding the molecular planes, it has been tentatively suggested that they are parallel to (010) plane. The magnetic data, however, point to a different orientation. As will be seen from Table I, two of the principal magnetic susceptibilities of this crystal, viz., χ_2 and χ_3 are nearly equal, so that the χ_1 axis, which almost coincides with the “*c*” axis (actually inclined to it at $2^\circ\cdot2$), is an axis of approximate magnetic symmetry. Further, the susceptibility along this axis is numerically smaller than along perpendicular directions by about 29, which is nearly one half of the anisotropy of the benzene molecule, viz., $54/2$. This shows that the molecular planes in the unit cell are all parallel to the above symmetry axis, but are orientated relatively to one another in such a manner as to make the two principal susceptibilities perpendicular to the above axis nearly equal. Because, if $K_1 = K_2$ are the two principal susceptibilities of the $C_6H_4(OH)_2$ molecule in its plane, and K_3 that along the normal to its plane, the molecular orientations proposed above will give the following susceptibilities for the crystal :

$$\chi_1 = K_1$$

$$\chi_2 = \chi_3 = \frac{K_1 + K_3}{2};$$

$$\text{therefore } \chi_1 - \chi_2 = \chi_1 - \chi_3 = \frac{K_1 - K_3}{2}.$$

Now, since the anisotropy, $K_1 - K_3$, of the $C_6H_4(OH)_2$ molecule must be the same as for C_6H_6 molecule, and since for the latter it is equal to $53\cdot9$, it follows with the molecular orientations proposed here that for catechol crystal both $\chi_1 - \chi_2$ and $\chi_1 - \chi_3$ should be equal to 27, which is about the value required by observation.

These molecular orientations are also supported by the optical properties of the crystal. On the basis of these orientations we should expect first the two refractive indices α and β to be nearly equal and to be much smaller than γ , and secondly, the vibration direction of γ to be nearly along the χ_1 axis. Both these conclusions are experimentally verified ; the principal refractive indices of the crystal for the D lines are :

$$\alpha = 1\cdot60, \quad \beta = 1\cdot61, \quad \gamma = 1\cdot73 ;$$

and further the γ vibration direction makes 6° to 7° with the “*c*” axis, as compared with $2^\circ\cdot2$ made by the χ_1 axis.

Hydroquinol (*p*-dioxo-benzene), in one of its hexagonal modifications (α , in CASPARI's notation) was also studied. It is found to be almost isotropic, $\chi_{||} - \chi_{\perp}$ being only 1·4. Also optically ω and ε are very close to each other, their values for the D lines being 1·632 and 1·626 respectively.

* ‘J. Chem. Soc.’ vol. 129, p. 573 (1926).

3—*Hexamethyl Benzene*

This crystal is of exceptional interest. A complete X-ray analysis has been made by Mrs. LONSDALE,* and the unit cell contains only one molecule. The benzene ring has a plane regular hexagonal structure, and the aliphatic carbon atoms also lie in the same plane. These molecular planes are all parallel to (001) plane of the crystal. Preliminary magnetic measurements on this crystal have been made by BHAGAVANTAM† in this laboratory.

As will be seen from Table I, two of the principal susceptibilities, viz., χ_1 and χ_2 are nearly equal, so that the χ_3 axis, which is normal to the (001) plane, is an axis of magnetic symmetry, as we should expect from the parallelism of the benzene planes to (001). The difference between the susceptibilities along and perpendicular to the symmetry axis is about 61·9, which is slightly higher than the corresponding difference for the benzene molecule, viz., 53·9. This shows that the numerical increase in susceptibility that occurs when a hydrogen atom in benzene is replaced by a methyl group, is not quite isotropic, but has a small preponderance along the normal to the molecular plane. This can be expressed more precisely in the following manner. Consequent on replacing an H by CH_3 , let s_1 be the increase in susceptibility along the line of attachment of the CH_3 group to the C atom in benzene, s_2 the increase in a perpendicular direction in the benzene plane, and s_3 the increase along the normal to the benzene plane. The greater anisotropy of $\text{C}_6(\text{CH}_3)_6$ as compared with that of C_6H_6 shows that s_3 is greater than $\frac{1}{3}(s_1 + s_2 + s_3)$, being actually found, on calculation, to be equal to 0·36 ($s_1 + s_2 + s_3$). The magnetic data for $\text{C}_6(\text{CH}_3)_6$ do not, however, give us any information regarding the relative values of s_1 and s_2 owing to the hexagonal symmetry of orientation of the s_1 and s_2 axes of the different CH_3 groups.

Before closing this article we should draw attention to the small but definite anisotropy in the (001) plane. Its origin is not clear.

4—*Durene (1, 2, 4, 5-Tetramethylbenzene)*

A complete X-ray analysis of this crystal has recently been made by ROBERTSON.‡ It belongs to the space group C_{2h}^5 ($\text{P2}_1/a$) in the monoclinic prismatic class, and the unit cell contains two molecules, which are centro-symmetric. ROBERTSON finds its structure to be a plane hexagonal benzene ring with the four methyl groups also in the plane of the ring.

For convenience in description, let us call the line joining the two carbon atoms at positions 3 and 6 (not attached to methyl groups) as the K_1 axis of the molecule, and the perpendicular direction in the plane of the benzene ring as the K_2 axis, and the normal to the molecular plane as the K_3 axis. In order to obtain from the magnetic data the orientations of these molecular axes in the unit cell, let us first place both the molecules with their K_1 axes along the “ c ” axis of the crystal, and

* ‘Proc. Roy. Soc.,’ A, vol. 123, p. 494 (1929); ‘Trans. Faraday Soc.,’ vol. 25, p. 352 (1929).

† ‘Proc. Roy. Soc.,’ A, vol. 126, p. 143 (1929).

‡ ‘Proc. Roy. Soc.,’ A, vol. 142, p. 659 (1933).

their K_2 axes along “ b .” Let us now suppose that, in order to bring them to their final orientations, we have to perform the following rotations :

- (1) about the “ c ” axis : one of the molecules by an angle λ and the other by an angle $-\lambda$;
- (2) about the “ b ” axis : both the molecules through an angle μ , in the direction from “ c ” axis to “ a ” axis through the obtuse angle β ;
- (3) about an axis in the (010) plane perpendicular to the direction of the K_1 axis of the molecule obtaining after rotation (2) has been performed : one of the molecules through an angle ν and the other through $-\nu$.

Evidently $\mu = \psi = +20^\circ.2$.

As for λ and ν , we have the following relations*

$$\left. \begin{aligned} \chi_1 &= K_1 \cos^2 \nu + (K_2 \cos^2 \lambda + K_3 \sin^2 \lambda) \sin^2 \nu \\ \chi_2 &= K_2 \sin^2 \lambda + K_3 \cos^2 \lambda \\ \chi_3 &= K_1 \sin^2 \nu + (K_2 \cos^2 \lambda + K_3 \sin^2 \lambda) \cos^2 \nu \end{aligned} \right\}, \quad \dots \dots \dots (7)$$

from which, if the K 's are known, λ and ν can be calculated.

K_3 is readily obtained from the following considerations. We have the relation $K_1 + K_2 + K_3 = \chi_1 + \chi_2 + \chi_3 = -303.6$, and further we can obtain the value of $\frac{1}{2}(K_1 + K_2) - K_3$ by interpolating between the anisotropies of C_6H_6 and $C_6(CH_3)_6$ molecules,

$$\frac{1}{2}(K_1 + K_2) - K_3 = 53.9 + \frac{4}{6}(61.9 - 53.9) = 59.2 ;$$

whence

$$K_3 = -140.7.$$

As regards K_1 and K_2 , if we take them to be equal, as we might to a first approximation, we obtain for K_1 the value 81. Since it is nearly the value of χ_1 , we obtain directly $\cos^2 \nu = 1$, *i.e.*, $\nu = 0$, and from the latter two equations in (7) $\lambda = 41^\circ$.

On closer examination, however, we find that the small difference between χ_1 and K_1 , which to a first approximation we neglected in the previous paragraph, is in such a direction as to give for $\cos^2 \nu$ a value slightly in *excess* of unity. This is evidently due to the uncertainty in the assumption made above, that $K_1 = K_2$. Conversely, taking $\cos^2 \nu$ to be actually unity, we can calculate the values of K_1 and K_2 more exactly. We thus obtain†

$$K_1 = -77.3$$

$$K_2 = -85.6,$$

* See Part I of this paper, p. 256.

† In an earlier section we found that when a CH_3 group replaces an H atom in benzene, of the total increase in susceptibility, equal to $s_1 + s_2 + s_3$ taken in all directions together, about 36% was directed along the s_3 direction, and the remaining 64% along s_1 and s_2 . The difference obtained in this section between K_1 and K_2 of durene shows that of the latter 64%, about 38% is along the s_1 direction, and 26% along s_2 .

which, when substituted in (7), give $\lambda = 41^\circ\cdot 0$. We thus have finally

$$\lambda = 41^\circ\cdot 0$$

$$\mu = + 20^\circ\cdot 2$$

$$\nu = 0 ;$$

i.e., the K_1 axes of both the molecules lie in the (010) plane in the obtuse angle β making an angle of $20^\circ\cdot 2$ with the “ c ” axis and $93^\circ\cdot 1$ with the “ a ” axis. Their K_2 axes are inclined at $+ 41^\circ\cdot 0$ and $- 41^\circ\cdot 0$ respectively, to the “ b ” axis.

With these may be compared the values obtained by ROBERTSON by X-ray analysis, which correspond to

$$\lambda = 41^\circ\cdot 4$$

$$\mu = + 16^\circ\cdot 5$$

$$\nu = 1^\circ\cdot 2.$$

The values of λ and ν agree well with the magnetic values, whereas μ is definitely smaller.*

We may mention here that for naphthalene and anthracene crystals also, the values of μ obtained by X-ray analysis differ slightly from the magnetic values. The X-ray values† are $6^\circ\cdot 7$ and $5^\circ\cdot 1$ respectively, whereas the magnetic values‡ are $12^\circ\cdot 0$ and $8^\circ\cdot 0$.

4—Hexachlorobenzene

The structure of this crystal has been analysed by Mrs. LONSDALE.§ This crystal also belongs to the space group C_{2h}^5 ($P2_1/c$) in the monoclinic prismatic class, with two centro-symmetric molecules in the unit cell. From observations on the structure-factors in the [010] zone, she finds that this zone has a pseudo-hexagonal structure. This is reflected in the magnetic properties of the crystal, since the two principal susceptibilities in the (010) plane, viz., χ_1 and χ_2 are nearly equal, and differ considerably from the susceptibility along the “ b ” axis.

As regards the positions of the carbon atoms in the unit cell, we can approximately locate them with the help of the magnetic data. Let us assume that the benzene ring in C_6Cl_6 has the same structure as in C_6H_6 , and that the chlorine atoms are magnetically isotropic ; the anisotropy of the C_6Cl_6 molecule will then be the same as that of the C_6H_6 molecule. This assumption may not be wholly justified, especially in view of the fact that Mrs. LONSDALE's X-ray results for this crystal

* We should remark here that μ in the magnetic case is the angle ψ which the χ_1 axis makes with the “ c ” axis. Its measurement is simple and involves merely the suspending of the crystal in the magnetic field with its “ b ” axis vertical, and finding the orientation of the (001) face, which is usually well developed ; the measurement is, therefore, capable of yielding accurate values for μ .

† ROBERTSON, ‘Proc. Roy. Soc.,’ A, vol. 142, p. 675, and vol. 140, p. 79 (1933).

‡ See Part I of this paper, p. 249.

§ ‘Proc. Roy. Soc.,’ A, vol. 133, p. 536 (1931).

throw some doubt on the regular hexagonal structure of the C_6Cl_6 molecule ; the assumption, however, would not be far from the truth. We should then get for the two principal susceptibilities of C_6Cl_6 in the plane of its benzene ring

$$K_1 = K_2 = -128,$$

and for the susceptibility along the normal to the plane of the ring

$$K_3 = -182.$$

Introducing the same angular parameters λ , μ , and ν as before to define the orientations of the two benzene rings in the unit cell, we obtain by a correlation of the above K 's with the χ 's for the crystal, with the help of equations (7),

$$\lambda = 66^\circ$$

$$\mu = +52^\circ.6$$

$$\nu = 10^\circ.$$

Thus the molecular benzene rings make angles of about 26° with the (010) plane. This is not very different from the angle obtained by Mrs. LONSDALE.

Optically, from the above orientations we should expect the “ b ” axis, which is nearly perpendicular to the molecular planes, to be the vibration direction of the fast ray, and the vibration direction of the slow ray to be close to the χ_1 axis. Experimentally, the axial plane is found to be perpendicular to (010), the obtuse bisectrix making an angle of 74° with the “ c ” axis in the obtuse angle β .

5—1, 2, 4, 5-Tetrachlorobenzene

This crystal does not seem to have been studied by X-ray methods. The orientations of the molecular planes in the crystal lattice can, however, be easily determined from the magnetic data. As will be seen from Tables I and II, two of the principal susceptibilities of the crystal, viz., χ_1 and χ_3 are almost identical, and thus the χ_2 axis, which makes $78^\circ.3$ with the “ a ” axis and $21^\circ.1$ with “ c ”, is an axis of approximate magnetic symmetry. Further, the susceptibility along this axis is numerically greater than along perpendicular directions by 41.8 , which is not much short of the anisotropy of the benzene ring, viz., 53.9 . This shows that the molecular planes in the crystal must be orientated about the plane* containing the χ_1 and χ_3 axes, making with it small angles θ , given by the relation

$$\cos^2 \theta - \frac{1}{2} \sin^2 \theta = \frac{41.8}{53.9},$$

$$\text{i.e., } \theta = 23^\circ.$$

Optically, we should expect from the above orientations the two principal refractive indices β and γ to be much greater than α , and the vibration direction of α

* This is not a lattice plane.

to be close to the χ_2 magnetic axis. Sufficient optical observations on the crystal are not available to test these conclusions.

7—*p*-Dichloro and *p*-Dibromo Benzenes

These two crystals have recently been analysed by HENDRICKS.* They belong to the space group C_{2h}^5 ($P2_1/a$) in the monoclinic prismatic class. Their unit cells, which contain two molecules each, have nearly the same dimensions, and the two crystals are isomorphous. The molecular orientations can be determined from the magnetic data in the same manner as in the other crystals. We shall merely mention here that the orientations of the benzene rings thus obtained are practically the same for the two crystals, and they differ from those suggested in HENDRICK's paper. The complete analysis of the orientations in these two crystals will be published elsewhere.


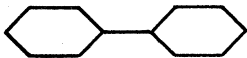
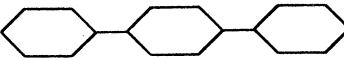
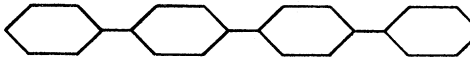
We shall not consider here the nitro-derivatives of benzene since they do not offer any points of special interest.

IV—MAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE : DIPHENYL AND TRIPHENYL DERIVATIVES

1—*Diphenyl*,† *Terphenyl*, and *Quaterphenyl*

These three compounds form an interesting series. The first compound has been analysed by Dhar,‡ and all the three by Miss PICKETT,§ and by HERTEL and RÖMER.|| They all crystallize in the monoclinic prismatic class in the space group C_{2h}^5 ($P2_1/a$), the unit cell containing two centro-symmetric molecules. The benzene rings are found to have a plane hexagonal structure. All the benzene rings in a molecule lie in a plane, and their centres lie on a line. Let us denote by K_1 the susceptibility of the molecule along the line joining the centres of the constituent benzene rings, and by K_2 the susceptibility along a direction in the plane of the benzene rings perpendicular to the K_1 axis, and by K_3 the susceptibility along the normal to the plane of the benzene rings. The K 's can be calculated from the known anisotropy of the benzene molecule, and are as given in Table III.

TABLE III

	Benzene	Diphenyl	Terphenyl	Quaterphenyl
				
$K_1 = K_2$	— 37·3	— 67	— 98	— 129
K_3	— 91·2	— 175	— 260	— 345

* 'Z. Kristallog,' vol. 84, p. 85 (1933).

† Diphenyl has already been considered in detail in Part I of this paper. For the sake of completeness, the results obtained with this crystal are included in this Section.

‡ 'Ind. J. Phys.,' vol. 7, p. 43 (1932).

§ 'Nature,' vol. 131, p. 513 (1933) ; 'Proc. Roy. Soc.,' A, vol. 142, p. 333 (1933).

|| 'Z. phys. Chem.,' B, vol. 22, p. 292, and vol. 23, p. 226 (1933).

Defining the orientations of the K_1 , K_2 , and K_3 axes of the last three molecules in their unit cells by the usual parameters λ , μ , and ν , the values of these angles can be readily calculated from the magnetic data. The calculated values are given in Table IV, along with the X-ray values for comparison.

TABLE IV

	Diphenyl		Terphenyl		Quaterphenyl*	
	Magnetic	X-ray	Magnetic	X-ray	Magnetic	X-ray†
λ	31°	32°	$32\frac{1}{2}^\circ$	34°	$31\frac{1}{2}^\circ$	—
μ	$+ 20^\circ \cdot 1$	$+ 20^\circ$	$- 14^\circ \cdot 3$	$- 15^\circ \cdot 3$	$ \theta = 17^\circ \cdot 1$	—
ν	0	0	0	0	0	—

The agreement with the X-ray values is very satisfactory, and emphasizes the powerfulness of the magnetic method for the determination of the orientations of the benzene rings in the crystal lattice.

For all the three molecules, we should expect the K_3 axis, which is normal to the plane of the benzene rings, to be the vibration direction of the fast ray, and the K_1 axis to be that of the slow ray. Since in the crystal, the K_1 molecular axes coincide with the χ_1 axes and since the inclinations of the K_3 axes to the (010) plane are small (about 30°), we should expect the vibration directions of γ and α to lie in the (010) plane, and to be close to the χ_1 and χ_2 magnetic axes respectively. This is actually so, as has been pointed out by Miss PICKETT; the (010) plane is the axial plane for all the three crystals, and further the directions of the bisectrices are nearly as predicted.

* We are indebted to Dr. P. C. GUHA and Mr. B. H. IYER, of the Indian Institute of Science, Bangalore, for the supply of this compound, and to Miss PICKETT for dimesityl, and we take this opportunity to express our thanks to them.

† [Note added in proof, February 19, 1935.—Through the kindness of Miss PICKETT we are able to give here the results of some unpublished X-ray studies by her on the structure of quaterphenyl. She finds that the long axes of the molecules lie in the (010) plane in the acute angle β , making $11^\circ \cdot 5$ with the “ c ” axis, and that the molecular planes are inclined at 34° to the “ b ” axis. She finds further that β is about 95° . These X-ray results would correspond, in our notation, to

$$\lambda = 34^\circ \quad \mu = -11^\circ \cdot 5, \text{ i.e., } \theta = +16\frac{1}{2}^\circ \quad \nu = 0,$$

which are in close agreement with the values deduced from our magnetic data (see Table IV),

$$\lambda = 31\frac{1}{2}^\circ \quad |\theta| = 17^\circ \cdot 1 \quad \nu = 0.$$

The ambiguity in the sign of magnetic θ is due to the circumstance that in the crystals studied by us, none of the prismatic faces was developed, and it was therefore not possible to decide whether the χ_2 — axis, which is inclined at $17^\circ \cdot 1$ to the (001) plane, lies in the acute angle β or in the obtuse angle β .]

2—1, 3, 5-Triphenyl Benzene and Triphenyl Carbinol

s-Triphenyl benzene has recently been analysed by ORELKIN and Mrs. LONSDALE* and is assigned to the space group C_{2v}^9 (Pna) in the orthorhombic hemihedral class. The crystal axes and axial ratios adopted in the following descriptions are those given by ORELKIN and Mrs. LONSDALE, and are slightly different from those given by GROTH for this crystal.

The crystal is found to have a pseudo-hexagonal structure, with “ a ” as the pseudo-principal axis. This is reflected in the magnetic data for the crystal, since “ a ” is an axis of approximate magnetic symmetry, χ_b and χ_c being nearly equal. The actual susceptibilities are

$$\chi_a = -313$$

$$\chi_b = -155$$

$$\chi_c = -140.$$

The above large anisotropy of the crystal suggests that the benzene planes must be either parallel to the (100) plane of the crystal or make small angles with it. Their actual orientations can be calculated in the following manner.† We have seen (see Table III) that the susceptibility of the benzene molecule for directions in the plane of the molecule is -37.3 , while along the normal to its plane it is -91.2 . The difference is thus equal to -54 . If in the crystal all the four benzene rings of the molecules were orientated parallel to the (100) plane, we should have

$$\chi_a - \chi_b = \chi_a - \chi_c = -216,$$

whereas actually $\chi_a - \chi_b$ and $\chi_a - \chi_c$ are equal to only -166 . This shows, in agreement with the conclusions of Mrs. LONSDALE, that the benzene rings cannot be all parallel to the (100) plane, but must make small angles with it.

Assuming that all the rings are inclined at the same angle θ to (100), the value of θ can be calculated from the relation

$$\cos^2 \theta - \frac{1}{2} \sin^2 \theta = \frac{166}{216},$$

$$i.e., \theta = 23^\circ.$$

The optical properties of the crystal also support these orientations. The principal refractive indices of the crystal for vibrations along the “ a ,” “ b ” and “ c ” axes are 1.524, 1.867, and 1.872 respectively for the D lines. The corresponding gram molecular refractivities, defined as usual by the LORENTZ Constant $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho}$, are

$$R_a = 77.6, R_b = 115.0 \text{ and } R_c = 115.5.$$

* ‘Proc. Roy. Soc.,’ A, vol. 144, p. 630 (1934).

† A preliminary report on the analysis of molecular orientations in this crystal by the magnetic method was published in ‘Nature,’ vol. 133, p. 497 (1934).

The latter two refractivities, which correspond predominantly to vibrations in the plane of the benzene rings, are nearly equal, and are, as we should expect, much greater than R_a , which corresponds predominantly to vibrations along the normal to the benzene planes. Indeed, just as in the magnetic case, we may find the actual inclinations of the benzene rings to the (100) plane by correlating the observed birefringence, $R_b - R_a$ or $R_c - R_a$ of the crystal with the known birefringence of the benzene rings. The gram molecular refractivities of the benzene molecule for vibrations along the normal to its plane, and along directions in its plane, are 16.4 and 32.6 respectively,* so that the birefringence of the benzene molecule = 16.2. If all the four benzene rings of the molecules were orientated parallel to (100), and if *further it is assumed that the optical moments induced in the different benzene rings exert no influence on one another*, we should have

$$R_b - R_a = R_c - R_a = 65.$$

The actual values, on the other hand, are

$$R_b - R_a = R_c - R_a = 38.$$

From these data, we can calculate θ as in the magnetic case, and we obtain

$$\cos^2 \theta - \frac{1}{2} \sin^2 \theta = \frac{38}{65},$$

or

$$\theta = 32^\circ.$$

The assumption that the optical dipole moments induced in the different benzene rings do not influence one another is not quite justifiable. The value of θ obtained from the optical constants is, therefore, not inconsistent with the value obtained from the magnetic data, viz., $\theta = 23^\circ$.

In strong contrast with this crystal, in which the benzene rings are orientated more or less parallel to one another, is *triphenyl carbinol*, whose low anisotropy, namely, $\Delta\chi = 5.4$, shows that the benzene rings in its unit cell must be so orientated as to form a more or less isotropic group.

3—4, 4'-Dichlorodiphenyl and 4, 4'-Dibromodiphenyl

These two di-halogen derivatives of diphenyl crystallize in the monoclinic prismatic class, and are isomorphous. They do not seem to have been studied by X-ray methods. The magnetic data for these crystals are very similar, as will be seen from Table V, and they show that the orientations of the benzene rings in the unit cells of these two crystals must also be very similar.

* KRISHNAN, 'Proc. Roy. Soc.,' A, vol. 126, p. 155 (1929).

TABLE V

Crystal	$\chi_1 - \chi_2$	$\chi_3 - \chi_2$	ψ
4, 4'—Dichlorodiphenyl . .	35.1	60.5	— 28°·5
4, 4'—Dibromodiphenyl . .	35.9	57.9	— 27°·6

The actual orientations can be determined from the magnetic data in the same manner as for the other crystals described before. It is found that in both the crystals the different benzene planes in the unit cell are inclined at small angles to the “*b*” axis.

4—*o*-Tolidine

We shall consider here only one more diphenyl derivative *o*-tolidine (4, 4'-diamido : 3, 3'-dimethyl diphenyl). Its structure has been analysed by CLARK and PICKETT* and it probably belongs to the space group Q^1 in the orthorhombic bisphenoidal class. They tentatively place the molecular planes nearly parallel to (010). The magnetic data definitely confirm this orientation. As will be seen from Table I, the “*b*” axis is an axis of approximate magnetic symmetry, the susceptibility along this axis being numerically greater than along perpendicular directions by about 81. Had all the benzene planes in the unit cell been orientated parallel to (010), the above anisotropy would have been about 110. We may, therefore, conclude that the benzene planes are inclined to (010) at small angles

$$\theta = \arcsin \sqrt{\frac{2}{3} \left(1 - \frac{81}{110} \right)} = 25^\circ.$$

Whether the pair of benzene rings constituting a molecule are orientated the same way or not, it is not possible to say from the magnetic data.

The above orientation would correspond optically to the α vibration direction lying along the “*b*” axis, and further α being considerably smaller than either β or γ . Optical observations do not appear to have been made on the crystal.

V—MAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE : NAPHTHALENE DERIVATIVES

1—1, 4-Naphthoquinone

An X-ray analysis of this crystal has been made by CASPARI,† and he assigns it to the space group C_{2h}^5 in the monoclinic class, with 4 molecules in the unit cell. From considerations of the dimensions of the molecules and of the unit cell, he places the molecules with their widths (perpendicular to the line joining the two benzene nuclei) along the “*a*” axis, and their lengths nearly along “*b*,” the molecular

* ‘J. Amer. Chem. Soc.,’ vol. 53, pp. 167 and 3826 (1931).

† ‘Proc. Roy. Soc.,’ A, vol. 136, p. 86 (1932).

planes being thus near about (001). The magnetic data are in accord with these orientations. In the first place two of the principal susceptibilities of the crystal, viz., χ_1 and χ_3 , are numerically much smaller than the third, so that the plane containing them must be nearly about the molecular planes. Further, this plane practically coincides with (001) (being inclined to it at $3^\circ\cdot7$). Thus the molecular planes must be inclined at small angles to (001).

On calculation from the magnetic data we find that the molecular planes are tilted from (001) by about 31° .

Optically, we should expect α to be much smaller than either β or γ , and the vibration direction of α to be nearly along the normal to (001). Observations are not available which may enable us to check this conclusion.

2— α -Naphthol

In Part I β -naphthol was discussed in detail. The molecular orientations in the α -compound can be determined in the same manner. We shall give here the final results only. Denoting by K_1 the long axis of the molecule, by K_2 the short axis in its plane, and by K_3 that along the normal to its plane, the angular parameters λ , μ , and ν that define in the usual manner the orientations of these axes, are as given in Table VI.

TABLE VI

Crystal	λ	μ	ν
α -Naphthol	$49\frac{1}{2}^\circ$	$+ 28^\circ\cdot7$	22°
β -Naphthol	34°	$+ 9^\circ\cdot4$	34°

VI—MAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE : POLYNUCLEAR COMPOUNDS

1—Fluorene and Phenanthrene

Diphenyl, fluorene, and phenanthrene form an interesting series. From the striking similarity in the dimensions of their unit cells (see Table VII) it has been suggested by HENGSTENBERG and MARK* that the molecular orientations in these crystals must be very similar, the lengths of the molecules being nearly along the “ c ” axis, and their breadths at small angles to “ b .” For diphenyl, the precise orientations have since been determined, as we mentioned in an earlier section, and the long axes of the molecules are found to lie in the (010) plane making 20° with “ c ” axis, their planes being inclined at 32° to the “ b ” axis. We shall proceed to inquire what information the magnetic measurements can give us regarding the molecular orientations in the other two crystals.

Let us first consider fluorene. Its χ_1 axis is inclined at $+ 10^\circ\cdot9$ to “ c ,” and the susceptibility along it, namely $- 72\cdot6$, is only slightly higher than that of the

* ‘Z. Kristallog.’ vol. 80, p. 283 (1929).

diphenyl molecule along its length, namely -67 (see Table III). Since the fluorene molecule contains one carbon atom more than diphenyl, the above value of -72.6 might very well be the susceptibility K_1 of the fluorene molecule along its length, and the χ_1 — axis the direction of the long axes of the molecules in the unit cell.

TABLE VII

	Dimensions of the unit cell in A.				Molecular susceptibilities		μ	λ
	a	b	c	β	$K_1 = K_2$	K_3		
Diphenyl . . .	8.22	5.69	9.50	$94^\circ 8'$	-67	-175	$+20^\circ 1'$	31°
Fluorene . . .	8.48	5.73	9.62×2	$101^\circ 30'$	-72.6	-193.6	$+10^\circ 9'$	$33\frac{1}{2}^\circ$
Phenanthrene .	8.60	6.11	9.62×2	$98^\circ 15'$	-74	-240	$-3^\circ 1'$	$29\frac{1}{2}^\circ$

If now we know the susceptibility of the molecule along its width, K_2 , and that along the normal to its plane, K_3 , then we can locate their orientations also, from the known values of χ_2 and χ_3 . The value of K_2 can be obtained from the following considerations. We have seen that for diphenyl, terphenyl, naphthalene and anthracene molecules, the two principal susceptibilities in the molecular plane are nearly the same, so that for fluorene also we may, to a first approximation, take K_2 to be equal to K_1 . We thus obtain for this molecule

$$K_2 = K_1 = -72.6$$

$$K_3 = -193.6,$$

from which the inclination of the K_2 axes to “ b ” comes out as

$$\lambda = \frac{1}{2} \arccos \frac{\chi_2 - \chi_3}{K_3 - K_2} = 33\frac{1}{2}^\circ.$$

That is, the lengths of the fluorene molecules in the unit cell lie in the (010) plane making $10^\circ 9'$ with the “ c ” axis in the obtuse angle β , and the molecular planes are inclined at plus and minus $56\frac{1}{2}^\circ$ to (010).

Coming to phenanthrene, adopting a similar course of reasoning, we obtain $K_1 = K_2 = -74$ and $K_3 = -240$, which correspond to the following molecular orientations. The K_1 axes (lengths) lie in the (010) plane in the acute angle β at $3^\circ 1'$ to the “ c ” axis, and the molecular planes are inclined at plus and minus $60\frac{1}{2}^\circ$ to (010).

It is remarkable that in many of the monoclinic crystals containing benzene rings, the inclinations of the benzene planes to (010) should be nearly the same, namely, about 60° ; naphthalene, anthracene, diphenyl, terphenyl, quaterphenyl, dibenzyl, fluorene, phenanthrene, and chrysene may be cited as examples.

Before closing this article we may mention that in both fluorene and phenanthrene we should expect the (010) plane to contain the vibration directions of both γ and α , the latter being close to the χ_2 axis.

2—*Chrysene* (1, 2-Benzophenanthrene)

A structural analysis of this crystal by X-ray methods has recently been made by IBALL and ROBERTSON.* The crystal belongs to the space group C_{2h}^6 in the monoclinic prismatic class. The dimensions of the unit cell are $a = 8.34$, $b = 6.18$, $c = 25.0$ A., $\beta = 115^\circ.8$, and it contains 4 molecules. Let OA be the long axis, and OB the cross axis, of the molecule, which is assumed to have a plane structure as shown in fig. 1. IBALL and ROBERTSON find that in the crystal the OA molecular axis "is tilted about 10° away from the normal to (001) towards the "c" axis, but remains practically in the plane of the (010), and the cross axis OB makes an angle of about 16° with the "b" axis of the crystal."

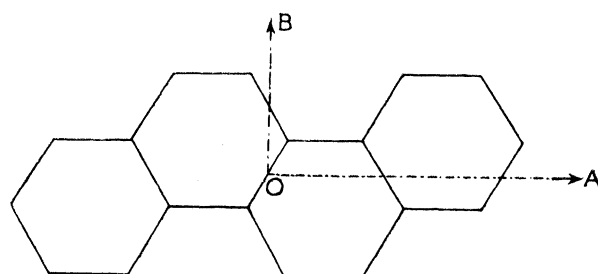


FIG. 1

Now OA and OB will be practically the two principal magnetic axes of the molecule in its plane and let us denote them by K_1 and K_2 respectively, and the third magnetic axis, which would be along the normal to the plane of the molecule, by K_3 . Adopting our usual angular parameters λ , μ , and ν , the above molecular orientations would correspond to

$$\begin{aligned}\lambda &= 16^\circ \\ \mu &= +15^\circ.8 \\ \nu &= 0.\end{aligned}$$

Coming to the magnetic evidence, we find that $\mu = \psi = +12^\circ.7$. The other two angles are obtained by adopting the same kind of reasoning as for fluorene and phenanthrene. In the first place we may reasonably take K_1 to be the same as K_2 (both of which would of course be numerically much less than K_3). Evidently its value can not be numerically greater than the lowest of the crystal susceptibilities, viz., $\chi_1 = -88.0$. It cannot also be appreciably less than this value, since even for phenanthrene which contains one benzene ring less, $K_1 = -74$. We thus obtain $\nu = 0$.

For the molecular susceptibilities we have then

$$\begin{aligned}K_1 &= K_2 = -88 \\ K_3 &= -306,\end{aligned}$$

* 'Nature,' vol. 132, p. 750 (1933).

from which we obtain $\lambda = 28^\circ$. Collecting the angle values from magnetic data

$$\lambda = 28^\circ$$

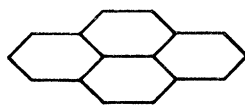
$$\mu = +12^\circ \cdot 7$$

$$\nu = 0.$$

We find both μ and ν agree with the X-ray values, but λ differs considerably.*

3—Pyrene

An X-ray study of this interesting four-ringed compound



has recently been started in this laboratory, and a detailed discussion will be attempted when the preliminary results of the X-ray analysis become available. There are, however, some points of interest in the magnetic data which should be mentioned here. In the first place, we should expect the molecule to have an exceptionally large magnetic anisotropy, the susceptibility along the normal to the plane, say K_3 , being several times greater than either K_1 or K_2 along the two axes in the plane. Further, as with the other polynuclear compounds, K_1 and K_2 may be expected to be nearly the same. If we examine the magnetic data for the crystal, we find that the smallest numerical value of its susceptibility, viz., along its χ_1 axis, is equal to 80·6, and this fixes the upper limit to $|K_1| = |K_2|$. When, however, we remember that for phenanthrene which has only three rings, $|K_1| = 74$, we can reasonably conclude that for pyrene K_1 cannot differ much from the limiting value — 80·6, and is most probably equal to it. We thus obtain

$$K_1 = K_2 = -80 \cdot 6$$

$$K_3 = -303.$$

From these data we can deduce the molecular orientations. To quote only the final results, the molecular planes are inclined at plus and minus 42° to (010),

* Since this was written, IBALL, 'Proc. Roy. Soc.,' A, vol. 146, p. 140 (1934) has published the results of a complete X-ray analysis of this crystal. He finds that the OA molecular axis makes $102^\circ \cdot 0$ with the "a" axis of the crystal, and $90^\circ \cdot 5$ with the "b" axis, and $12^\circ \cdot 0$ with the normal to (001), while the cross axis OB of the molecule makes $118^\circ \cdot 4$, $29^\circ \cdot 0$ and $95^\circ \cdot 4$ respectively with the same crystal directions. These correspond to

$$\lambda = 29^\circ \cdot 0$$

$$\mu = +13^\circ \cdot 8$$

$$\nu = 0^\circ \cdot 5,$$

which are in close agreement with our magnetic values.

intersecting the latter along a line making $75^{\circ} \cdot 9$ with the “*a*” axis and $25^{\circ} \cdot 0$ with “*c*.”

Optically, we should expect from these orientations, the vibration direction of γ to be close to the above line in (010). Actually one of the bisectrices lies in (010), making about 37° with “*c*” in the obtuse angle β .

4—*Fluoranthene*

The crystal data given in GROTH's ‘*Kristallographie*’* for the compound of this name, to which he assigns formula (i) ($C_{15}H_{10}$), most probably refer to the compound $C_{16}H_{10}$ having formula (ii), namely, 7, 8-benzo-acenaphthylene† (see fig. 2).

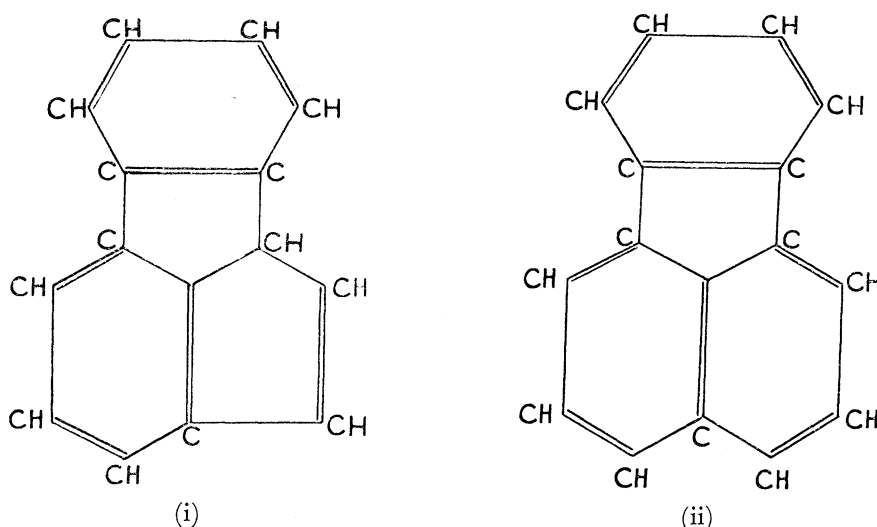


FIG. 2

The magnetic data for the crystal suggest that the χ_1 axis, which makes $87^{\circ} \cdot 6$ with the “*a*” axis and $9^{\circ} \cdot 6$ with “*c*,” cannot deviate much from parallelism to the benzene planes of the molecules, and that the latter are inclined at about 55° to (101).

The magnetic data further suggest that the two optic axes of the crystal should lie in the (010) plane, one of the bisectrices being nearly along the χ_2 axis, *i.e.*, close to “*a*” axis. This is verified by observation.

VII—MOLECULAR ORIENTATIONS IN CRYSTALS AND THEIR OPTICAL PROPERTIES

In the foregoing discussions we have tried wherever possible to correlate the molecular orientations with the optical properties of the crystals also. With the optical properties, however, we are working under serious limitations. We cannot assume, as we do with the magnetic properties, that the crystal polarizability in any

* Vol. 5, p. 430.

† See J. v. BRAUN, ‘*Ber. deuts. chem. Ges.*,’ B, vol. 62, p. 145 (1929).

direction is the same as that obtained by the simple superposition of those of the individual molecules constituting it, because of their strong mutual influence. Hence, even under favourable conditions, the optical data can give only qualitative indications. As an example of the uncertainty attendant on the use of the optical data for this purpose, we shall mention *p*-dichloro- and *p*-dibromobenzenes, recently analysed by HENDRICKS (*loc. cit.*). The unit cells of these crystals have practically the same dimensions, and the available X-ray data give the positions of only the halogen atoms in the lattice, which are found to be nearly identical in the two crystals. They do not, however, enable us to choose uniquely the pair of halogen atoms which belong to the same molecule. But we can estimate, from considerations of interatomic distances, the distance between the halogen atoms belonging to the same molecule, and use that knowledge as a guide for properly pairing the halogen atoms. It so happens that there are two alternative ways of so pairing, both of which give the Cl-Cl or Br-Br distance looked for. Now the experimental fact that the optical extinction directions in the (010) plane are very different for the two crystals is used as the basis for choosing the pairs in one way for *p*-dichlorobenzene and in the other way for *p*-dibromobenzene. The result is, the molecular planes in the two crystals are assigned different orientations. On the other hand, as we mentioned in an earlier section, we have definite reasons to believe that the orientations in the two crystals should be very similar. This discrepancy arises from the large mutual influence between the strongly refractive halogen atoms, which has been ignored, and which further is not easily taken into account. On the other hand in the magnetic case, the mutual influence of the neighbouring molecules is negligible, and this is responsible in a large measure for the success of the magnetic method.

Extensive optical measurements on organic crystals are being made in this laboratory, and a detailed discussion of the optical results in relation to crystal structure, in a manner analogous to the treatment presented here of the magnetic problem, will be published shortly.

An optical observation made recently in this laboratory, which is of significance to the present problem,* is that *in compounds containing benzene nuclei, the absorption bands characteristic of the compounds appear much more intensely when the light vibrations (electric vector) are in the plane of the benzene ring than when they are along the normal to the plane.* Observations on the polarizations of the absorption bands in crystals thus supply another useful guide for locating the orientations of the benzene planes.

VIII—CONCLUSION

From the numerous examples worked out in the foregoing pages it will be clear that a knowledge of the magnetic properties of a crystal offers an effective check on the results of the X-ray analysis. In many organic crystals containing benzene rings the orientations of the benzene rings can be predicted successfully from the magnetic data, and the results are found to agree well with those obtained by ROBERTSON and

* KRISHNAN and SESHAN, 'Current Science,' vol. 3, p. 26 (1934).

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others by their latest methods of X-ray analysis. The values of the angular parameters defining the orientations of the benzene rings, deduced from the magnetic data, besides being more readily obtained, are sometimes even more accurate than the X-ray values, as for example that of the parameter μ in monoclinic crystals, which is obtained in the magnetic method by the direct measurement of an angle. Thus the magnetic method forms a powerful supplement to the X-ray methods of structural analysis.

IX—SUMMARY

In the present part a new method is described of measuring the magnetic anisotropies of crystals, which can be adopted for even such small crystals as weigh only a fraction of a milligram. By this method the principal susceptibilities of a large number of organic crystals, specially selected for their structural interest, have been determined. For many of them the molecular orientations in the crystal lattice are deduced from the magne-crystallic data, and are in general found to agree with the X-ray determinations. The principal susceptibilities of individual molecules have also been computed for a number of compounds.
