

tions between 70 and 100 mole per cent. cyclopentane, while the heat of this transition per mole of mixture decreases from 1165 cal. at 100 mole per cent. cyclopentane to 0 cal. at approximately 68 mole per cent. cyclopentane.

5. The upper transition is found only for the pure components and mixtures between 60 and 100 mole per cent. cyclopentane.

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The Magnetic Anisotropy of Coronene, Naphthazarin, and Other Crystals

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The magnetic constants of crystals have recently proved to be a useful aid in crystal structure analysis,² and the magnetic constants of molecules, which can in many cases be derived from those of the crystal, are of interest theoretically. A semi-classical theory of the magnetic anisotropy of aromatic hydrocarbons has been developed by Pauling,³ and a molecular orbital treatment by London⁴; these agree satisfactorily with experiment for most molecules for which data are available for comparison, but predict widely different values for coronene.⁵ A study was therefore made⁶ of the magnetic constants of coronene, both to pro-

vide experimental data for comparison with theory, and to aid in the determination of the crystal structure. Since these measurements were made, however, a complete analysis of the crystal structure of coronene has been reported⁷; the orientation observed experimentally for the molecules in the crystal is in good agreement with the prediction made from the magnetic data.

The data for other crystals studied at the same time are also reported and discussed here.

Experimental

Apparatus.—Measurements of crystal anisotropy were made by a method developed by Krishnan⁸; the apparatus is shown in Figs. 1 and 2. The crystal was attached to a fine glass thread about 1 inch long by means of a minute amount of glyptal; when necessary this was done in an optical goniometer so that the orientation with respect to the fiber axis could be accurately determined. The glass thread was in turn attached to the lower end of a fine quartz fiber (3-7 μ in diameter⁹) about a meter long. The upper end of the fiber is attached to the pin of a torsion head. The torsion head consisted of a ball bearing (B of Fig. 1), the outer part of which was fixed, while the central part had a 360° protractor attached to it above, and the quartz fiber below. For convenience in handling and centering, the pin to which the fiber was attached was set in a brass disc (D, Fig. 1) which was held to the bearing only by a thin layer of wax. The crystal was suspended centrally between the plane parallel pole pieces (3

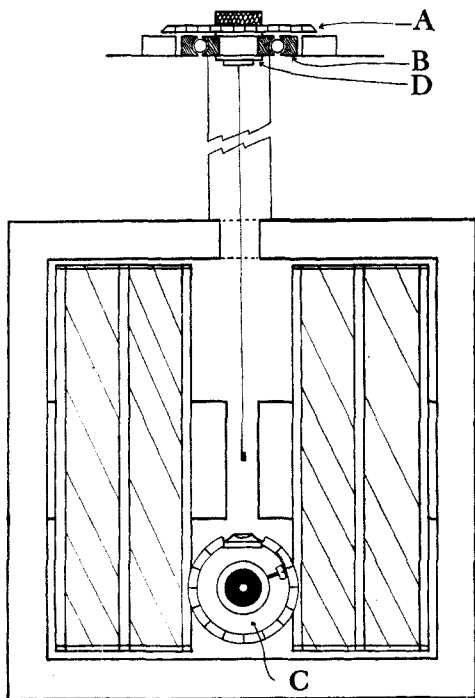


Fig. 1.—Apparatus for measurement of the magnetic anisotropy of crystals: detail of part C shown in Fig. 2.

(1) Present address: Kedzie Chemical Laboratory, Michigan State College, East Lansing, Michigan.

(2) Cf. K. Lonsdale, "Reports on Progress in Physics," Vol. IV, 1937, p. 368.

(3) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

(4) F. London, *J. Phys. Radium*, **8**, 397 (1936).

(5) C. F. Squire, *Compt. rend.*, **206**, 665 (1938).

(6) M. T. Rogers, Thesis, California Institute of Technology, 1941.

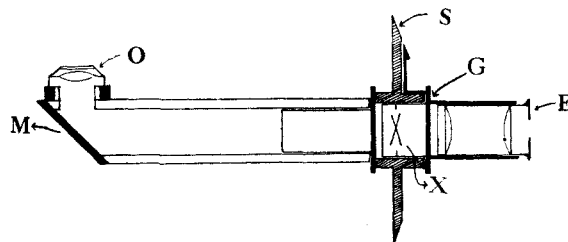


Fig. 2.—Viewing device.

(7) J. M. Robertson, *J. Chem. Soc.*, 607 (1945).

(8) K. S. Krishnan, *Trans. Roy. Soc. (London)*, **A231**, 235 (1933); **A232**, 99 (1933); **A234**, 267 (1935).

(9) For preparation of fibers see Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1938.

inches in diameter) of an electromagnet, and observed from below. The viewing device (Fig. 2) enables the angle of rotation of the crystal in the field to be observed directly. An objective lens (O, Fig. 2) is focused on the illuminated crystal which is then observed in the eyepiece (E), the mirror (M) being set at exactly 45° ; the rotation of the crystal is followed by reference to the cross-hairs (X), the angle of rotation being read directly on the eyepiece scale (S). The crystal and fiber were protected from air currents by a glass case.

Method.—The crystal was suspended in a known orientation and the torsion head adjusted initially so no motion of the crystal was observed on turning on the field. The torsion head was now turned, with the field on, until the crystal had been rotated through 45° ; at this point the couple is a maximum and a further rotation of the fiber causes a sudden easily observed spinning of the crystal. From the angle (c) through which the torsion head was rotated, the torsion constant (k) of the fiber, the field strength (H), the mass (m) of the crystal, and its molecular weight (M), the anisotropy was calculated by the equation²

$$\Delta\chi = \frac{Mk}{mH^2} (\alpha_c - \pi/4)$$

where $\Delta\chi$ is the anisotropy (c. g. s. units per mole) in the plane perpendicular to the axis of suspension. The torsion constant of the fiber was obtained from the period of oscillation of an object of known moment of inertia; the field strength was measured by a fluxmeter; small crystals were weighed on a microbalance. With monoclinic crystals a direct measurement was made of the angle, ψ , between the a -axis and χ_1 , the axis of greatest magnetic susceptibility in the basal plane; this defines the orientation of the magnetic ellipsoid with respect to the crystal axes. The anisotropy, $\Delta\chi$, was determined, for each crystal, in three orientations; these values, along with the average susceptibility, enable the principal crystal susceptibilities to be calculated. The tensor algebra has been developed in detail by Lonsdale and Krishnan.¹⁰ Since only two measurements of $\Delta\chi$ are required, the third serves as an independent check on the values. Measurements of $\Delta\chi$ were always made at field strengths of 6000 and 8375 gauss (occasionally also at 4600 gauss) and the values so obtained averaged.

The largest error in the measurements results from the couple exerted on an irregularly shaped crystal by the inhomogeneous component of the field. Where the shape anisotropy is large, as with long needle, this error is important unless the field is quite homogeneous.

Results and Discussion

Coronene.—Crystals of coronene (hexabenzobenzene, $C_{24}H_{12}$) were kindly provided by Prof.

(10) (a) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. (London)*, **A156**, 597 (1936); their symbols have been retained here; (b) see also Wooster, "Textbook of Crystal Physics," Macmillan Co., New York, N. Y., 1938.

Melvin S. Newman, who had synthesized them.¹¹ The crystals are monoclinic prismatic, $a_0 = 16.10$ Å., $b_0 = 4.695$ Å., $c_0 = 10.15$ Å., $\beta = 110.8^\circ$ and $Z = 2$ molecules⁷; the largest available crystals weighed only 0.25 mg. and were long yellow-brown laths with the b -axis the needle axis.

The mean of several measurements gave for the anisotropies

$$\chi_1 - \chi_2 = 180 \times 10^{-6}, \chi_1 - \chi_3 = 210 \times 10^{-6}, \frac{\chi_2 - \chi_3}{30} = 10^{-6}$$

and $\psi = 20^\circ$. Since no measurements of χ mean have been made a value, χ mean = -220×10^{-6} , estimated from Pascal's constants, has been used^{11a}; this leads to principal crystal susceptibilities $\chi_1 = -90 \times 10^{-6}$, $\chi_2 = -270 \times 10^{-6}$ and $\chi_3 = -300 \times 10^{-6}$. Because of the large shape anisotropy of the crystals and the lack of homogeneity of the field, the probable error in these measurements is several per cent.

Assuming that the susceptibilities K_1 and K_2 in the plane of the molecule are equal, we obtain¹⁰

$$K_1 = K_2 \cong \chi_1 = -90 \times 10^{-6}; K_3 = \chi_2 + \chi_3 - K_1 = -480 \times 10^{-6}$$

and

$$\beta_3 = \sqrt{\frac{\chi_2 - K_3}{K_3 - K_1}} = 0.734$$

Here β_3 is the direction cosine of the angle between the normal to the plane of the molecule and the monoclinic b -axis, hence this angle as determined magnetically is $42^\circ 16'$; this is in excellent agreement with the crystal structure value,⁷ 43.7° .

The anisotropy of the molecule, $\Delta K = K_{\perp} - K_{\parallel} = -390 \times 10^{-6}$, is considerably larger than the value $\Delta K = 4.56 \Delta K_{\text{benzene}} = -246 \times 10^{-6}$ calculated by Squire⁵ on the basis of the London theory. Although the semi-classical theory of Pauling³ predicts a higher value, $\Delta K = -572 \times 10^{-6}$, for the anisotropy, the experimental results are in qualitative agreement with that theory in that both K_3 and ΔK are found to be much larger for coronene than for any other molecule yet studied; considerably larger even than condensed polynuclear aromatic hydrocarbons of about the same molecular weight but of lower symmetry (*e. g.*, for 1,2-5,6-dibenzanthracene, $C_{22}H_{14}$, $K_3 = -358 \times 10^{-6}$, $\Delta K = -248 \times 10^{-6}$ are observed). Although the experimental values of K_3 and ΔK are lower than the theoretical values, it is interesting to note that the ratio, $\Delta K/K_1 = 4.33$, is the same.

It seems likely that the theoretical values of K_1 , K_3 and ΔK for large aromatic hydrocarbons tend to be too high (thus for perylene,¹² $C_{20}H_{12}$, $\Delta K = -240 \times 10^{-6}$ and $K_3 = -350 \times 10^{-6}$ are observed while the theoretical values are $\Delta K = -314 \times 10^{-6}$ and $K_3 = -428 \times 10^{-6}$). It is possible that the value of χ mean obtained here from Pascal's constants may be low although values

(11) M. S. Newman, *THIS JOURNAL*, **62**, 6612 (1940).

(11a) The values of χ atomic employed were C(member of one aromatic ring) = -6.24×10^{-6} , C(member of two or three aromatic rings) = -9.1×10^{-6} , H = -3.0×10^{-6} .

(12) S. Banerjee, *Z. Krist.*, **A100**, 316 (1938).

calculated with these constants agree within about five per cent. with the measured values of all the condensed polynuclear aromatic hydrocarbons for which data are available.

Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone, $C_{10}H_6O_4$).—Dark red crystals of a modification of naphthazarin not previously studied were obtained from benzene solution. They are monoclinic prismatic,¹³ $a_0 = 5.41 \text{ \AA.}$, $b_0 = 6.40 \text{ \AA.}$, $c_0 = 12.81 \text{ \AA.}$, $\beta = 91^\circ 32'$, and $Z = 2$ molecules. The anisotropies observed are $\chi_1 - \chi_2 = 63.0 \times 10^{-6}$, $\Delta\chi(100)$ horizontal = 10.4×10^{-6} , $\Delta\chi(100)$ vertical = 12.9 and $\psi = 41^\circ 40'$. From these and the mean susceptibility,¹² χ mean = -84.7 , we obtain $\chi_1 = -57.3 \times 10^{-6}$, $\chi_2 = -120.3 \times 10^{-6}$, $\chi_3 = -77.1 \times 10^{-6}$. Assuming the susceptibilities K_1 and K_2 in the plane of the molecule to be equal, we find¹⁰ $K_1 = K_2 \cong \chi_1 = -57.3 \times 10^{-6}$, K_3 (perpendicular to plane of molecule) = -140.1×10^{-6} and $\beta_3 = 0.489$. The angle between the normal to the plane of the molecule and the b -axis of the crystal is, then, $60^\circ 48'$. Banerjee¹² found, for another modification of naphthazarin, $K_1 = K_2 = -60.7 \times 10^{-6}$ and $K_3 = -132.8 \times 10^{-6}$.

Potassium Nickelocyanide.—Large, regular, orange-yellow crystals of potassium nickelocyanide, $K_2Ni(CN)_4 \cdot H_2O$, were obtained from aqueous solution. They are monoclinic prismatic,⁶ $a_0 = 13.7 \text{ \AA.}$, $b_0 = 15.4 \text{ \AA.}$, $c_0 = 18.6 \text{ \AA.}$, $\beta = 107^\circ 16'$ and $Z = 16$ molecules.

The observed anisotropies are $\chi_1 - \chi_2 = 20.3 \times 10^{-6}$, $\Delta\chi(001)$ vertical = 15.5×10^{-6} , $\Delta K(001)$ horizontal = 2.9×10^{-6} , $\psi = 0^\circ$; using¹⁴ χ mean = -140×10^{-6} , we obtain $\chi_1 = -127.8 \times 10^{-6}$, $\chi_2 = -148.0 \times 10^{-6}$ and $\chi_3 = -144.2 \times 10^{-6}$. The anisotropy no doubt arises from the anisotropy of the planar $Ni(CN)_4^{2-}$ groups, but the large number of molecules in the unit cell of this crystal and lack of knowledge of the crystal structure make detailed interpretation impossible.

Copper Imidazole.—Deep blue crystals of copper imidazole, $Cu(C_3H_4N_2)_4 \cdot 2H_2O$, from aqueous solution are orthorhombic,¹⁵ $a_0 = 9.1 \text{ \AA.}$,

(13) The crystals were prepared by Dr. William Shand, Jr., and the X-ray data quoted here are from a preliminary X-ray investigation by him.

(14) W. Biltz, *Z. anorg. allgem. Chem.*, **170**, 80 (1928).

(15) The author is indebted to Dr. P. A. Shaffer, Jr., for providing

$b_0 = 13.8 \text{ \AA.}$, $c_0 = 12.5 \text{ \AA.}$ and $Z = 4$ molecules. The anisotropies observed are $\chi_1 - \chi_3 = 228 \times 10^{-6}$, $\chi_2 - \chi_3 = 293 \times 10^{-6}$, and $\chi_2 - \chi_1 = 65 \times 10^{-6}$.

Copper Phenylpropiolate.—Deep green crystals of copper phenylpropiolate, $(C_6H_5C \equiv C - COO)_2Cu \cdot 4H_2O$, from aqueous solution are orthorhombic,¹⁶ $a_0 = 6.5 \text{ \AA.}$, $b_0 = 30.1 \text{ \AA.}$, and $c_0 = 9.0 \text{ \AA.}$, $Z = 4$. We find $\chi_1 - \chi_2 = 630 \times 10^{-6}$, $\chi_1 - \chi_3 = 10.4 \times 10^{-6}$ and $\chi_2 - \chi_3 = 620 \times 10^{-6}$; estimating χ mean = 1165×10^{-6} gives approximate values of $\chi_1 = 1377 \times 10^{-6}$, $\chi_2 = 747 \times 10^{-6}$ and $\chi_3 = 1367 \times 10^{-6}$. The crystals are nearly uniaxial magnetically, with the b -axis the unique axis. The large anisotropy observed may be ascribed to the anisotropy of the crystalline field in which the copper ion is located. Thus, in copper sulfate pentahydrate¹⁷ there is approximately tetragonal symmetry of the coordination sphere of the copper ion, and the anisotropy of the ion and its octahedral coordination group has been found experimentally ($K_{11} - K_{\perp} = 550 \times 10^{-6}$). If the coordination were similar in these complex copper compounds, the magnetic data would give information on the orientation of the coordination octahedra in the crystal.

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Summary

The magnetic anisotropies of coronene, naphthazarin, potassium nickelocyanide, copper phenylpropiolate and copper imidazole have been measured. For coronene and naphthazarin the principal susceptibilities of the crystals and of the molecules have been calculated and the orientation of the molecules in the crystal predicted. The magnetic anisotropy of coronene has been compared with theoretical values.

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the crystals used, and for the results of his preliminary X-ray investigation.

(16) The dimensions of the unit cell were determined by Dr. R. W. Spitzer, who supplied the crystals used in this investigation.

(17) K. S. Krishnan and A. Mookherji, *Phys. Rev.*, **54**, 841 (1938).