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The Magnetic Anisotropies of some Further Organic Compounds of Unknown Crystal Structure

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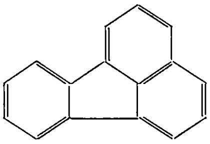
The magnetic anisotropies of several organic crystals of unknown structure have been measured and conclusions are drawn about the probable planarity and orientations of the molecules in the unit cells.

1. Fluoranthene, $C_{16}H_{10}$

The cell dimensions and space group of fluoranthene (I) were determined by Chakravarti (1954) who found $a=18{\cdot}46$, $b=6{\cdot}205$, $c=22{\cdot}11$ Å, $\beta=121^\circ\,45'$; $Z=8$; space group $P2_1/c$; two molecules of fluoranthene form an asymmetric unit in the unit cell.



(I)

The crystals used in the present work were crystallized from ethanol as flat six-sided prisms with (001) as the large face, but more elongated along [010] than along [100]. Three crystals of weights 3·9, 4·4 and 2·7 mg were used.

The magnetic anisotropies of the crystal (in units 10^{-6} e. m. u. g^{-1} throughout) measured by the Krishnan–Banerjee method are shown in Table 1 together with those found by Krishnan & Banerjee (1935).

The large magnetic anisotropy of the fluoranthene crystal indicates that the molecule is probably planar and that the molecular normals make small angles with their projections on the (010) plane; these projections lie along the χ_2 direction at about 9° to [100] in acute β.

The fluoranthene molecules, assumed to be magnetically uniaxial, would be expected to have a magnetic anisotropy equal or near to that of one naphthalene plus one benzene molecule. The reason for supposing that the two nominally single bonds should have no effect on the anisotropy is based on a comparison with the experimental data for biphenyl (found to have an anisotropy equal to that of two benzene molecules) and acenaphthene (found to have an anisotropy equal to or a little less than that of naphthalene) (Lasheen, 1964). Values of ΔK of 114·0 and 119·8 have been reported for naphthalene (Lonsdale & Krishnan, 1936; Lumbroso & Pacault, 1957); that of benzene is 59·7 (Hoarau, Joussot-Dubien, Lemanceau, Lumbroso & Pacault, 1956). Thus a reasonable range for fluoranthene is

$$\Delta K=K_{\parallel}-K_{\perp}=176{\cdot}6\pm2{\cdot}9$$

with

$$K_{\parallel}=-79{\cdot}1\pm1{\cdot}0 \quad\text{and}\quad K_{\perp}=-255{\cdot}7\pm1{\cdot}9\,.$$

If the normals to the two asymmetric molecules are not parallel to each other and make angles of $\pm\alpha_1$ and $\pm\alpha_2$ with χ_2, then

$$2\chi_2=K_{\perp}\,(\cos^2\alpha_1+\cos^2\alpha_2)+K_{\parallel}\,(\sin^2\alpha_1+\sin^2\alpha_2)$$

and

$$2\chi_3=K_{\perp}\,(\sin^2\alpha_1+\sin^2\alpha_2)+K_{\parallel}\,(\cos^2\alpha_1+\cos^2\alpha_2)$$

from which $\sin^2\alpha_1+\sin^2\alpha_2=0{\cdot}614\pm0{\cdot}006$.

If the normals to the two asymmetric molecules are parallel, then $\alpha_1=\alpha_2=\pm33{\cdot}7\pm0{\cdot}2^\circ$.

2. 1,4-Dichloronaphthalene, $C_{10}H_6Cl_2$

1,4-Dichloronaphthalene crystals were obtained from ethyl alcohol solution as prisms and plates with (100)

Table 1. *Magnetic anisotropies and susceptibilities of fluoranthene crystals*

Unit of susceptibility is 10^{-6} e.m.u. g^{-1}

χ_1 and χ_2 lie in (010) and make angles of θ and $\pi/2-\theta$ respectively with [100]; θ is positive in obtuse β

	$\chi_1-\chi_2$	$\chi_3-\chi_2$	$\chi_1-\chi_3$	θ_0	θ_c	χ_M	χ_1	χ_2	χ_3
Krishnan & Banerjee	109·0		40·0	(+87·6)		−138·4	−88·6*	−198·0	−128·6
Present work	109·4	68·1	41·3	+81·9	+81·0	−138·0†	−87·8	−197·2	−129·1

* Absolute value measured directly by Krishnan & Banerjee (1935).

† Absolute mean value measured by Bergmann, Hoarau, Pacault, Pullman & Pullman (1952).

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as the flat face but more elongated along [010] than along [001]. The cell dimensions measured from rotation photographs and the angle β from goniometric measurements and from a Weissenberg photograph are: $a=28{\cdot}2$, $b=3{\cdot}95$, $c=16{\cdot}4$ Å, $\beta=93{\cdot}0°$, $D_m=1{\cdot}434$ g.cm^{-3} (flotation method using aqueous zinc chloride solution), $D_x=1{\cdot}434$ g.cm^{-3} for $Z=8$ and M.W. 196·96.

The crystal magnetic anisotropies are:

$$\chi_1-\chi_2=20{\cdot}6$$
$$\chi_1-\chi_3=87{\cdot}5$$
$$\chi_2-\chi_3=66{\cdot}9$$

θ (angle between χ_1 and [100], positive in obtuse β) $=90{\cdot}0°$ obs. and calc.

It is evident from these magnetic data that the normals to the molecular planes make small angles $\pm\alpha$ with [010], and that the molecular plane intersects the (010) plane in a line that lies along χ_1 perpendicular to [100].

The magnetic anisotropy ΔK of the p-dichlorobenzene molecule was found to be 55·9 (Lasheen, 1964) as compared with 59·7 for benzene. Assuming that the difference, $-3{\cdot}8$, is due to the substitution, ΔK for 1,4-dichloronaphthalene may be expected to be less than that for naphthalene by a similar amount. Using the range of ΔK given for naphthalene in the literature, and the relations:

$$\chi_2=K_{\parallel}\cos^2\alpha+K_{\perp}\sin^2\alpha$$

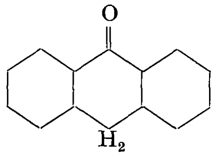
and

$$\chi_3=K_{\parallel}\sin^2\alpha+K_{\perp}\cos^2\alpha$$

it follows that $\alpha=\pm26{\cdot}8\pm0{\cdot}6°$.

3. A new form of anthrone crystallized from ethyl alcohol

In a previous paper (Lasheen, 1963) reference was made to a new form of anthrone crystals, crystallized from acetic acid, $D_m=1{\cdot}255$ g.cm^{-3}, m.p. 254 °C, cell dimensions $a=13{\cdot}6$, $b=7{\cdot}76$, $c=17{\cdot}7$ Å, $\beta=91{\cdot}1°$, which differed from that described by Srivastava (1957*a*, *b*, 1961). It was suggested (without further proof) that the unit cell might contain 6 anthrone (II) and 4 acetic acid molecules.


(II)

Since then a form of similar habit, and having $a=13{\cdot}7$, $b=7{\cdot}76$, $c=18{\cdot}0$ Å, $\beta=91{\cdot}1°$, m.p. 254 °C has been recrystallized from ethyl alcohol solution of the same (British Drug Houses) anthrone of original m.p. 153–159 °C. The measured density is, however, 1·342 g.cm^{-3} and this corresponds to 8 molecules of anthrone and no solvent of crystallization in the unit cell ($D_x=1{\cdot}347$ g.cm^{-3}). It seems probable that the density previously measured was too low. Using the corrected data, the crystal magnetic anisotropies are:

$$\chi_1-\chi_2=127{\cdot}0$$
$$\chi_3-\chi_2=114{\cdot}2$$
$$\chi_1-\chi_3=\ 12{\cdot}8\ ,$$

θ (angle between χ_1 and [100], positive in obtuse β)

$$=+76{\cdot}4 \text{ obs. and } +76{\cdot}8 \text{ calc.}$$

The mean gram molecular susceptibility of anthrone is $\chi_M=-118$ (Matsunaga, 1958), thus the crystal susceptibilities are:

$$\chi_1=\ -71{\cdot}4$$
$$\chi_2=-198{\cdot}4$$
$$\chi_3=\ -84{\cdot}2\ .$$

These magnetic data imply that the anthrone molecular normals project along the χ_2 direction on (010) plane at about 15° to [100] in acute β and make a small angle α with χ_2.

The molecular anisotropy of anthrone is expected to be approximately of the same value as that of anthraquinone, *i.e.*

$$\Delta K=K_{\parallel}-K_{\perp}=147{\cdot}6 \text{ (Lasheen, 1964).}$$

Thus

$$\chi_2=K_{\perp}\cos^2\alpha+K_{\parallel}\sin^2\alpha$$

and

$$\chi_3=K_{\perp}\sin^2\alpha+K_{\parallel}\cos^2\alpha$$

from which $\alpha=\pm19{\cdot}6°$.

Table 2. *Magnetic anisotropies and susceptibilities of α-trans-cinnamic acid*

Unit of susceptibility is 10^{-6} e.m.u. g^{-1}

χ_1 and χ_2 lie in (010) and make angles of ψ and $\pi/2-\psi$ respectively with [001]; ψ is positive in obtuse β

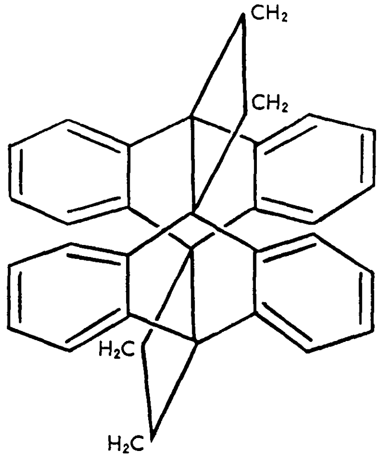
	$\chi_1-\chi_2$	$\chi_2-\chi_3$	$\chi_1-\chi_3$	ψ_o	ψ_c	χ_M	χ_1	χ_2	χ_3
Lonsdale (1939)	26·8	36·2	63·0	−74·4°		−88·3	−58·4*	−85·2	−121·4
Present work	22·7	30·9	53·6	−73·7°	−73·7°	−78·2†	−52·8	−75·5	−106·4

* Absolute value measured directly by Lonsdale.

† Absolute mean value measured by Pacault & Gay (1948).

4. Bi(anthracene-9,10-dimethylene), $C_{32}H_{24}$

Two small prismatic crystals of weights 4·7 and 3·1 mg of the photo-isomer (form VI; Golden, 1961) of bi(anthracene-9,10-dimethylene) (III) were kindly supplied by Dr M. Ehrenberg. They were crystallized from chloroform and had well-developed (001) and (010) faces. The cell dimensions determined by Dr Ehrenberg (unpublished data) are: $a = 8{\cdot}56$, $b = 12{\cdot}96$, $c = 9{\cdot}87$ Å, $\beta = 111°\,39'$; $Z = 2$; space group $P2_1/a$.



(III)

The crystal magnetic anisotropies are:

$$\chi_1 - \chi_2 = 94{\cdot}9$$
$$\chi_1 - \chi_3 = 90{\cdot}7$$
$$\chi_3 - \chi_2 = 4{\cdot}2$$

ψ (the angle between χ_1 and [001], positive in obtuse β) $= +30{\cdot}5°$.

These magnetic data are in good general agreement with the structure determined by Dr Ehrenberg. When the refinement of the structure is completed, it will be of great interest to see what precise effect the non-planarity of the anthracene groups has on the molecular susceptibilities.

5. *α-trans*-Cinnamic acid, $C_6H_5\cdot CH{:}CH\cdot COOH$

A preliminary report on the crystal structure of *α-trans*-cinnamic acid was published by Ladell, McDonald & Schmidt (1956) who stated that full details of the structure would be discussed later. They gave: $a = 7{\cdot}79$, $b = 18{\cdot}07$, $c = 5{\cdot}67$ Å, $\beta = 97°$; $Z = 4$; space group $P2_1/n$.

The crystals used in the magnetic measurements were crystallized from ethyl alcohol as plates with (010) as the plate face. They were elongated along either [100] or [001].

The magnetic measurements are shown in Table 2 together with those found by Lonsdale (1939), who remarked that her value of the mean susceptibility was higher than might have been expected on the basis of the usual additive constants.

These magnetic data agree well with the [001] projection of electron density given by Ladell *et al.* (1956).

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