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The magnetic anisotropies of some organic compounds of unknown crystal structure. By

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1. 2,4-Dinitroaniline $C_6H_3(NO_2)_2.NH_2$

2,4-Dinitroaniline was described by Groth (1917) as monoclinic prismatic with $a:b:c=0{\cdot}9913:1:0{\cdot}6985$, $\beta=94°\,58'$. The Barker Index (Porter & Spiller, 1956) gives $a:b:c=0{\cdot}9747:1:0{\cdot}6985$, $\beta=94°\,58'$.

Siddiq, Saraogi & Ali (1959) gave $a=8{\cdot}46$, $b=12{\cdot}50$, $c=7{\cdot}40$ Å, $\beta=101°\,54'$ ($a:b:c=0{\cdot}6768:1:0{\cdot}5920$), $Z=4$ and space group $P2_1/m$.

The crystals used in the present work were crystallized from a mixture of acetone and chloroform. They are thin six-sided plates tabular on (010), with (100) as a perfect cleavage plane exactly as described in the Barker Index.

The axial lengths measured from rotation photographs and the angle β from Laue photographs are however $a=12{\cdot}8$, $b=12{\cdot}9$, $c=9{\cdot}07$ Å, $\beta=95°$, giving $a:b:c=0{\cdot}992:1:0{\cdot}703$ in good agreement with Groth.

The magnetic anisotropies of the crystal were measured by the Krishnan–Rabi method which gives:

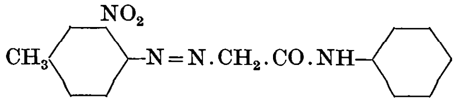
$$\chi_1-\chi_2=65{\cdot}5\times10^{-6}\ \text{c.g.s.e.m.u.}$$
$$\chi_3-\chi_2=69{\cdot}0\times10^{-6}\ \text{c.g.s.e.m.u.}$$
$$\chi_3-\chi_1=3{\cdot}5\times10^{-6}\ \text{c.g.s.e.m.u. (obs. and calc.)}$$
$$\psi\ \text{(angle between}\ \chi_1\ \text{and [001])}=0°.$$

Using the experimental values of the mean susceptibilities given by Pascal (1911*a*, *b*) for dinitrobenzene, benzene and aniline, that of 2,4-dinitroaniline is $\bar{\chi}_M=74{\cdot}3\times10^{-6}=\frac{1}{3}(\chi_1+\chi_2+\chi_3)$. Hence

$$\chi_1=-53{\cdot}6,\quad \chi_2=-119{\cdot}1,\quad \chi_3=-50{\cdot}1\quad (10^{-6}\ \text{c.g.s.e.m.u.}).$$

It is evident from these results that the benzene ring is parallel to the (100) cleavage plane. Also as $\chi_1-\chi_2=65{\cdot}5\times10^{-6}$ and $\chi_3-\chi_2=69{\cdot}0\times10^{-6}$, both of which are greater than the anisotropy of a benzene ring, there is a great probability that the nitro groups are coplanar with the benzene ring; that is, that the molecule as a whole is planar and parallel to (100).

2. 4-Methyl-2-nitrophenylazoacetanilide



The crystals, which were kindly supplied by Dr C. J. Brown, are thin laths elongated along [010] with predominant $\{20\bar{1}\}$ plate faces. The faces {001} are also developed. The largest crystal weighed about 4·6 mg and had dimensions $6\times1{\cdot}7\times0{\cdot}5$ mm^3.

Dr Brown (unpublished data) found $a=23{\cdot}20$, $b=5{\cdot}90$, $c=12{\cdot}20$ Å, $\beta=121°$, $Z=4$; space group $P2_1/a$.

The magnetic anisotropies are:

$$\chi_1-\chi_2=94{\cdot}2\times10^{-6}\ \text{c.g.s.e.m.u.}$$
$$\chi_1-\chi_3=35{\cdot}3\times10^{-6}\ \text{c.g.s.e.m.u.}$$
$$\chi_3-\chi_2=58{\cdot}9\times10^{-6}\ \text{c.g.s.e.m.u.}$$
$$\theta\ \text{(angle between}\ \chi_1\ \text{and [100], positive in obtuse}\ \beta)=48°.$$

The anisotropy of two benzene rings is expected to be about $120{\cdot}10^{-6}$, which is not much greater than $\chi_1-\chi_2$. It is fairly clear from these data that χ_1 lies in or near to the planes of the two benzene rings and that probably the whole molecule is planar. The normal to the two benzene rings lies between [010] and χ_2, but is nearer to χ_2. Now χ_1 is nearly along the trace of the plane $(40\bar{3})$ (and of all planes $\{4k\bar{3}\}$) on (010). Hence it seems probable that the plane of the molecule, which intersects (010) in the direction χ_1, lies not far from $(40\bar{3})$. This agrees with Dr C. J. Brown's observation that the $40\bar{3}$ and $41\bar{3}$ X-ray reflexions are both intense.

3. o-Tolidine, $C_{14}H_{16}N_2$

The crystals of *o*-tolidine (4,4′-diamino-3,3′-dimethylbiphenyl) are orthorhombic. The unit-cell dimensions were redetermined by Quader (1958) who found:

$$a=6{\cdot}412,\ b=7{\cdot}490,\ c=23{\cdot}758\ \text{Å};\ Z=4,$$

space group $P2_12_12_1$.

The crystals used in the present work were crystallized from ethyl alcohol as small rectangular tablets with (001) as the plate face. The cell dimensions were checked by rotation photographs and were found to be in good agreement with the above values.

The present magnetic data together with those found by Krishnan & Banerjee (1955) are shown in Table 1.

The mean susceptibility $\bar{\chi}_M=-144{\cdot}9\times10^{-6}$ calculated from the present magnetic anisotropies and Krishnan & Banerjee's measured χ_a agrees with Pascal's additive value $\bar{\chi}_M=-144{\cdot}6\times10^{-6}$, which uses Pascal's experimental data (1911*a*) for biphenyl.

The magnetic data show that [010] is an axis of approximate symmetry. If the two benzene rings of the

Table 1. *Magnetic data for o-tolidine*

(All $\times10^{-6}$)

	$\chi_a-\chi_b$	$\chi_c-\chi_b$	$\chi_a-\chi_c$	χ_a	χ_b	χ_c	$\bar{\chi}_M$
Krishnan & Banerjee	82·9	79·6	3·3	−117·3 (meas.)	−200·2	−120·6	−146·0
Present work	79·4	75·9	3·5	−117·3 (assumed)	−196·7	−120·8	−144·9

molecule are planar, the molecular planes should make only small angles with (010). Adopting the molecular anisotropy $K_{\|}-K_{\perp}=119\cdot6$ found for biphenyl (unpublished data) and taking α and $-\alpha$ as the angles which the molecular planes make with (010), then

$$\chi' = K_{\|}\cos^2\alpha+K_{\perp}\sin^2\alpha;\quad \chi' = \chi_a+\chi_b/2$$

and

$$\chi_b = K_{\|}\sin^2\alpha+K_{\perp}\cos^2\alpha$$

from which $\alpha=\pm24\cdot5$.

4. Anthrone crystallized from acetic acid

The unit-cell dimensions, space group and crystal structure of anthrone, $C_6H_4.CO.CH_2.C_6H_4$, crystallized from ethyl alcohol, were determined by Srivastava (1957*a*, *b*; 1961). His latest values are:

$$a=15\cdot80,\ b=3\cdot998,\ c=7\cdot86\ \text{Å};\ \beta=101^\circ\ 40';\ Z=2\ .$$

The melting point is 153°. He determined the crystal structure (1961) on the assumption that the space group is $P2_1/a$ and found the residual $R=0\cdot267$.

The crystals used in the present work were recrystallized from acetic acid, two crops being grown independently. They are monoclinic platy prisms elongated along [010] with the plate face (001) and the face (100) well developed in the rectangular large plates (average weight 5 mg) of the first crop. Those of the second crop were six-sided small (2 mg) plates with (100) as the plate face and (001) face developed. The axial lengths determined from rotation photographs round the three axes and the angle β determined goniometrically are

$$a=13\cdot6,\ b=7\cdot76,\ c=17\cdot7\ \text{Å};\ \beta=91\cdot1^\circ.$$

The melting point is 254 °C, which is much higher than that of anthrone; that of the original material (British Drug Houses) was checked and found to be 158 °C as stated on the bottle (153–159 °C). The density was measured, with aqueous zinc chloride solution by the flotation method, and found to be 1·255 g.cm^{-3}.

The density calculated from the cell dimensions for 6 anthrone molecules (mol.wt. 194·08) and 4 acetic acid molecules (mol.wt. 60·03) in the unit cell is 1·244 g.cm^{-3}.

There is no proof that this molecular constitution (which would involve hemimorphy or disorder) is correct: nor has the space-group been determined.

Taking $nM=dN.abc\sin\beta=1411\cdot7$ instead of M, the magnetic anisotropies are:

$$\chi_1-\chi_2=909\cdot6\,.\,10^{-6}\ \text{c.g.s.e.m.u.}$$
$$\chi_3-\chi_2=795\cdot0\,.\,10^{-6}\ \text{c.g.s.e.m.u.}$$
$$\chi_1-\chi_3=114\cdot6\,.\,10^{-6}\ \text{c.g.s.e.m.u.}$$

θ (angle between χ_1 and [100], positive in obtuse β) = 73·0°.

Acetic acid may be expected to have a small anisotropy (about 5.10^{-6}) but the above anisotropy will be mainly due to the 6 anthrone molecules, if the molecular constitution suggested is the correct one.

This agrees reasonably well with the measured molecular anisotropy of anthraquinone (unpublished) $K_{\perp}-K_{\|} = -147\cdot6.10^{-6}$ ($6\times147\cdot6 = 885\cdot6$) and would imply that the anthrone molecular normals lie nearly along the χ_2 direction, at 17° to [100] in acute β, and probably make a small angle with (010). The mean susceptibility of anthrone is $\bar{\chi}_M=-118.10^{-6}$ (Matsunaga, 1958).

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Bemerkung zur Terminologie des Begriffes Epitaxie.

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Der Begriff Epitaxie umfasst jede gesetzmässige und strukturabhängige Verwachsung von zwei unterschiedlichen kristallinen oder subkristallin geordneten Substanzen, gleich welcher Art sie sonst sein mögen. Orientierte Substanzabscheidungen im Sinne der Epitaxie unterscheiden sich grundsätzlich vom reinen Eigenwachstum, einschliesslich Zwillingsbildung, Parallelverwachsung und Fortwachsung gleicher oder isomorpher Partner durch partielle Isotypie oder verschiedenartige Atomzustände der entsprechenden Bausteine. Texturbildungen von Gastsubstanzen auf amorphen Trägern gehören nicht zu diesen echten azimutalen Orientierungen.

Durch das wachsende Interesse breiter Kreise der Technik an diesem Phänomen vervollständigte sich der