Short Communications

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Diamagnetic anisotropies of some organic molecules. By M. A. Lasheen, *Physics Department, Faculty of Science, Alexandria University, Alexandria, U.A.R.*

The molecular susceptibilities and anisotropies of some aromatic molecules have been deduced from their crystal diamagnetic susceptibilities and their molecular orientations. The molecules investigated are 10,10′-dianthronyl, bi(anthracene-9,10-dimethylene) photo-isomer and potassium acid phthalate. The molecular anisotropy can usually be calculated with a good degree of accuracy even in cases where the mean absolute susceptibility is not known with certainty.

Bi(anthracene-9,10-dimethylene) photo-isomer, $(C_{16}H_{12})_2$

The crystal magnetic anisotropies of this compound were measured by the author (Lasheen, 1964*b*) who found:

$\chi_1 - \chi_2 = 94\cdot9$, $\chi_1 - \chi_3 = 90\cdot7$, $\chi_3 - \chi_2 = 4\cdot2$ (all in 10^{-6} e.m.u. g^{-1}); ψ (angle between χ_1 and [001], positive in obtuse β) $= +30\cdot5°$.
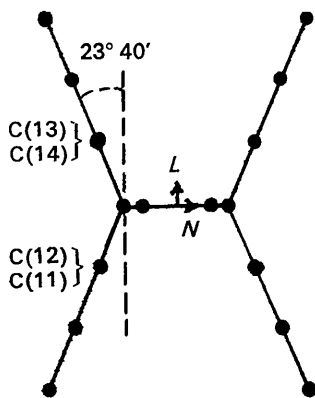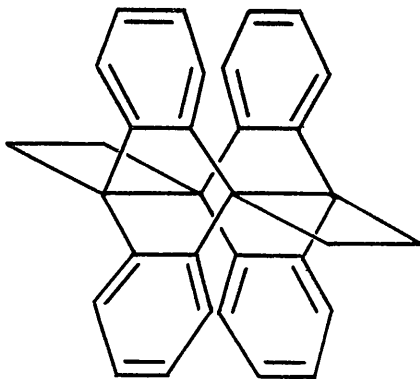

Fig. 1. Projection of the molecule on a plane normal to the molecular axis M (Ehrenberg, 1966).

By the use of Pascal's additive law, the mean molecular susceptibility and hence the crystal magnetic susceptibilities are: $\bar{\chi}_M = -276\cdot32$, $\chi_1 = -214\cdot45 \pm 0\cdot22$, $\chi_2 = -309\cdot35 \pm 0\cdot22$, $\chi_3 = -305\cdot15 \pm 0\cdot32$.

The crystal structure of bi(anthracene-9,10-dimethylene) photo-isomer, $(C_{16}H_{12})_2$, was determined by Ehrenberg (1966) who found: $a = 8\cdot56 \pm 0\cdot07$, $b = 12\cdot99 \pm 0\cdot09$, $c = 9\cdot87 \pm 0\cdot08$ Å, $\beta = 111° 39′$, $Z = 2$, $P2_1/a$.

The molecules lie on centres of symmetry. The angle of bending of the half molecule was found to be $2(23° 40′)$ as shown in Fig. 1, which gives a projection of the molecule on a plane normal to the molecular axis M.

The direction cosines of the molecular axes L, M and N of the plane passing through the atoms C(11), C(12), C(13) and C(14) were calculated referred to the orthogonal axes a', b and c, where a' is perpendicular to both the b and c axes. They are:

	a'	b	c
L	0·2053	−0·1674	0·9643
M	0·7207	0·6925	−0·0332
N	0·6620	−0·7016	−0·2636

Thus the molecular susceptibilities and anisotropy are:

$K_L = -216\cdot7 \pm 1\cdot0$
$K_M = -181\cdot9 \pm 10\cdot1$ $\Delta K = 231\cdot1 \pm 10\cdot4$
$K_N = -430\cdot4 \pm 9\cdot0$

Potassium acid phthalate, C_6H_4 (COOH) (COOK)

Lasheen (1964*a*) measured the crystal magnetic anisotropies and Lasheen & Heddewi (1967) measured the mean molecular susceptibility, These are:

$\chi_b - \chi_a = 35\cdot6$, $\chi_c - \chi_a = 41\cdot7$, $\chi_c - \chi_b = 6\cdot0$, $\bar{\chi}_M = -99\cdot25$. Hence, $\chi_a = -125\cdot02 \pm 0\cdot12$, $\chi_b = -89\cdot42 \pm 0\cdot19$, $\chi_c = -83\cdot32 \pm 0\cdot20$ (10^{-6} e.m.u. g^{-1}).
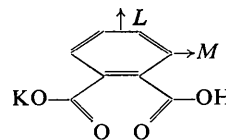
The molecular susceptibilities of this molecule were previously calculated (Lasheen, 1964*a*) by the use of the direction cosines of ammonium acid phthalate, whose crystal

Table 1. *Molecular susceptibilities and anisotropy of half the molecule of* 10,10′-*dianthronyl compared with those of anthraquinone* (*Lasheen,* 1964a)

|	K_L	K_M	K_N	ΔK
Half the molecule of 10,10′-dianthronyl	$-67\cdot1 \pm 1\cdot4$	$-70\cdot7 \pm 1\cdot2$	$-207\cdot4 \pm 0\cdot5$	$138\cdot5 \pm 1\cdot0$
Anthraquinone	$-76\cdot1$	$-64\cdot5$	$-217\cdot9$	$147\cdot6$

structure had been determined by Okaya & Pepinsky (1957).

The crystal structure of potassium acid phthalate was later determined by Okaya (1965) who found:

$a = 6\cdot46_6$, $b = 9\cdot60_9$, $c = 13\cdot85_7$ Å, $Z = 4$, $P2_1ab$.

The angles between the plane of the benzene ring and those of the two carboxyl groups are $31\cdot7$ and $75\cdot4°$ respectively.

10,10′-Dianthronyl, $(C_{14}H_9O)_2$

Crystals of 10,10′-dianthronyl were obtained during the crystallization of anthrone from both acetic acid and ethyl alcohol. It was assumed (Lasheen, 1963, 1964b) that these crystals belonged to a new form of anthrone. Ehrenberg (1967) found that it was a dimer and determined its crystal structure. The unit-cell dimensions are: $a = 13\cdot68 \pm 0\cdot04$, $b = 7\cdot751 \pm 0\cdot003$, $c = 17\cdot92 \pm 0\cdot04$ Å, $\beta = 91\cdot1° \pm 0\cdot3°$, $Z = 4$, space group $I2/a$.
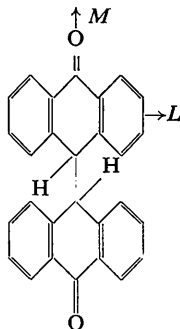
Each molecule has a twofold axis of symmetry perpendicular to the C(10)–C(10′) bond connecting the two halves of the molecule, coinciding with the twofold axis in the unit cell. C(10) is $0\cdot321$ Å from the best plane through the half-molecule, indicating a considerable pull towards the second half of the molecule.

The crystal magnetic anisotropies (all in 10^{-6} e.m.u. g.$^{-1}$) are:

$\chi_1 - \chi_2 = 252\cdot6$, $\chi_3 - \chi_2 = 227\cdot3$, $\chi_1 - \chi_3 = 25\cdot3$; ψ (angle between χ_1 and [001], positive in obtuse β) = $+14\cdot9° \pm 1\cdot1°$ observed, $= +14\cdot3° \pm 1\cdot3°$ calculated.

The mean susceptibility of 10,10′-dianthronyl was calculated by using Pascal's additive law and the mean susceptibility of anthrone, $\bar{\chi}_M = -118$, determined by Matsunaga (1958). Thus, $\bar{\chi}_M = -230\cdot14$ and hence, $\chi_1 = -137\cdot5 \pm 1\cdot9$, $\chi_2 = -390\cdot1 \pm 1\cdot9$, $\chi_3 = -162\cdot8 \pm 1\cdot8$.

The direction cosines of the axes L, M and N for half of the molecule referred to the orthogonal axes a', b and c, where a' is perpendicular to both the b and c axes are:

	a'	b	c
L	0·0175	0·6020	−0·7983
M	0·3705	0·7364	0·5660
N	−0·9303	0·3011	0·2079

The molecular susceptibilities and anisotropy, calculated by Lonsdale & Krishnan's (1936) method, are shown in Table 1 together with those of anthraquinone (Lasheen, 1964a).

It was expected that the molecular anisotropy of half the molecule of 10,10′-dianthronyl would be just less than that of anthraquinone by the value contributed by the $\verb|>|C=O$ bond, which is equal to $3\cdot1$ e.m.u. g^{-1} (Lasheen, 1964a, p. 380). This still leaves a small difference and also K_L is less than K_M in the case of the 10,10′-dianthronyl molecule. This may be a result of the C(10) atom being displaced from the best plane of the half molecule by $0\cdot321$ Å towards the second half.

The direction cosines of the molecular axes L, M and N are:

	a	b	c
L	0·1609	0·4349	0·8858
M	0·5148	−0·8029	0·3006
N	−0·8399	−0·4111	0·3543

Thus the molecular susceptibilities and anisotropy are:

$$K_L = -73\cdot92 \pm 0\cdot10$$
$$K_M = -79\cdot12 \pm 0\cdot13 \qquad \Delta K = 68\cdot27 \pm 0\cdot12$$
$$K_N = -144\cdot79 \pm 0\cdot08$$

The variances in the crystal magnetic susceptibilities and the resulting probable errors in the molecular susceptibilities and anisotropies were calculated by the method given for orthorhombic crystals by Lasheen & Tadros (1968) and for monoclinic crystals by Walley (1967).

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