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Diamagnetic Anisotropies of some Organic Molecules

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The diamagnetic anisotropies of some crystals of aromatic and aliphatic compounds of known structure have been measured and the molecular susceptibilities and anisotropies deduced from these and the molecular orientations. 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. The molecular susceptibilities and anisotropies may be correlated with bond lengths and angles in the hope of presenting some information concerning the effect of substitution on conjugation. This has a strong influence on the values of the molecular susceptibilities and anisotropies of the aromatic compounds and in general markedly decreases the anisotropy. This decrease varies not only with the nature of the substituents (heavy atom, compact group or aliphatic chain) but with their positions on the nucleus.

Introduction

The present work is a part of a project undertaken to provide a quantitative knowledge of the principal susceptibilities and anisotropies of organic molecules, aromatic and aliphatic, of different shapes and containing various electronic groupings. Aromatic compounds containing different numbers of rings with different substituents and aliphatic compounds containing six-membered rings, five-membered rings and open chains have been studied previously (Lasheen, 1964). In this paper some more such compounds are investigated. The aromatic compounds include three rings, two rings or one ring with different substituents while the aliphatic compounds investigated are theophylline, 2,6-dimethyl-γ-pyrone and glycine. Theophylline contains a six-membered ring (a substituted pyrimidine ring) and a five-membered ring (an imidazole ring) sharing a double C=C bond, while 2,6-dimethyl-γ-pyrone contains a six-membered ring (a γ-pyrone ring).

The Krishnan & Banerjee (1935) method was used in the determination of the magnetic anisotropies of the crystals. Several crystals of different weights and sizes were used for each compound when possible and measurements were carried out on every crystal in at least three different orientations. A high-accuracy balance was used to determine the crystal weight just before the magnetic measurements were carried out. Volatilization or loss of weight could always be detected from repeated measurements on the same crystal. In such cases the crystal was weighed just before and just after the magnetic measurements and the average weight used, the measurements being carried out in the least possible time.

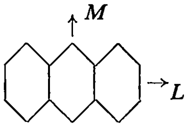
In the case of monoclinic crystals the crystal susceptibility parallel to [010] is taken as χ_3 while χ_1 and χ_2 denote the values in the (010) plane, χ_1 being algebraically greater than χ_2. The molecular susceptibilities are denoted by K_L and K_M in the molecular plane and K_N normal to it, and the molecular anisotropy $\Delta K = (K_L + K_M)/2 - K_N$. The directions taken for K_L and K_M are indicated below for each molecule; K_L is usually along the length of the molecule. The unit of susceptibility or anisotropy is 10^{-6} e.m.u.g^{-1} throughout, and is omitted hereafter.

The unit-cell dimensions and orientation of the crystal of each compound were always determined from X-ray rotation and Laue photographs to be sure that the substance investigated was the one whose crystal structure was assumed as known.

The transition from crystalline to molecular susceptibilities was carried out by the use of molecular direction cosines and the mathematical relations given by Lonsdale & Krishnan (1936).

It was noticed that small experimental errors in the crystal magnetic anisotropies could lead in some cases to very large errors in the molecular susceptibilities and anisotropies and for that reason the variances in the crystal magnetic susceptibilities and the resulting probable errors in the molecular susceptibilities and anisotropies were calculated by the methods given for the study of these errors in orthorhombic crystals by Lasheen & Tadros (1968) and in monoclinic crystals by Walley (1967).

Anthracene, $C_{14}H_{10}$



The crystal structure was determined by Mathieson, Robertson & Sinclair (1950) and by Sinclair, Robertson & Mathieson (1950) and refined by Cruickshank (1956). $a = 8{\cdot}561$, $b = 6{\cdot}035$, $c = 11{\cdot}163$ Å, $\beta = 124°42'$; $Z = 2$; $P2_1/a$.

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The molecular susceptibilities of anthracene have been determined previously by Lonsdale & Krishnan (1936) and by Lumbroso-Bader (1956). The former authors found ΔK=182·6 while the latter gave ΔK= 172·1. One is more than three times that of benzene, ΔK=59·7 (Hoarau, Joussot-Dubien, Lemanceau, Lumbroso & Pacault, 1956), while the other is much lower. ΔK for anthracene is expected to be only a little less than three times that for benzene. Thus it was decided to redetermine the molecular susceptibilities of this substance.

Thin prismatic six-sided plates with (001) as the plate face were used. Five different crystals of weights 3·5, 2·6, 2·5, 1·7 and 1·6 mg were chosen.

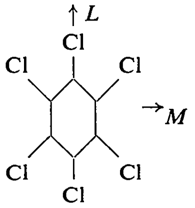
The magnetic measurements together with those found by Lonsdale & Krishnan and by Lumbroso-Bader are shown in Table 1.

The direction cosines of the molecular axes L, M, and N referred to the three orthogonal axes a, b and c' are:

	a	b	c'
L	−0·4960	−0·1248	0·8593
M	−0·3234	−0·8919	−0·3162
N	0·8059	−0·4347	0·4020

The molecular susceptibilities and anisotropy are shown in Table 2 together with those found by Lonsdale & Krishnan and by Lumbroso-Bader.

Hexachlorobenzene, C_6Cl_6



The crystal structure was determined by Tulinsky & White (1958) who gave a=8·08, b=3·87, c=16·65 Å, β=117·0°; Z=2; $P2_1/c$.

The molecule is plane and hexagonal with C–C= 1·39 Å and C–Cl=1·70 Å.

Crystals from benzene solution were long platy needles elongated along [010] with (100) as the plate face.

The magnetic data are shown in Table 3 together with those found by Krishnan & Banerjee (1935). The two sets are in reasonable general agreement except for ψ. The angle between χ_2 and [100] was found to be −25·6° by Krishnan & Banerjee while it is +21·1° in the present work.

Three different sets of direction cosines for the axes L, M and N of the benzene ring were calculated with L parallel to each of the lines joining the two symmetrical carbon atoms *i.e.* parallel to C(1)C(1′), parallel

Table 1. *Magnetic anisotropies and susceptibilities of anthracene crystal compared with those given by Lonsdale & Krishnan* (1936) *and by Lumbroso-Bader* (1956)

ψ(angle χ_1: [001], positive in obtuse β).

	$\chi_1-\chi_2$	$\chi_3-\chi_2$	$\chi_1-\chi_3$	ψ_{obs}	ψ_{calc}	$\bar{\chi}_M$	χ_1	χ_2	χ_3
Present work	140·5	108·1	32·4	+9·45±1·10	+9·4±1·1	−130*	−72·4±2·0	−212·9±2·0	−104·8±1·0
Lonsdale & Krishnan	(136·3)†	(108·9)	(27·4)	+8·0	+8·9	(−130·1)	−75·5	−211·8	−102·9
Lumbroso-Bader	140·3	108·2	(32·1)	+8·0		−134·2‡	−76·7	−217·0	−108·8

* Absolute mean value $\bar{\chi}_M$ determined by Akamatsu & Matsunaga (1956).
† Values between brackets are calculated from given susceptibilities.
‡ Absolute mean value determined by Pacault (1946).

Table 2. *Anthracene molecular susceptibilities and anisotropy compared with those given by Lonsdale & Krishnan* (1936) *and by Lumbroso-Bader* (1956)

	K_L	K_M	K_N	ΔK
Present work	−72·4±2·0	−71·8±1·7	−245·7±2·7	173·6±3·0
Lonsdale & Krishnan	−75·8	−62·6	−251·8	182·6
Lumbroso–Bader	−76·9	−76·6	−248·9	172·1

Table 3. *Magnetic anisotropies and susceptibilities of hexachlorobenzene crystal compared with those found by Krishnan & Banerjee* (1935)

ψ (angle χ_1: [001], positive in obtuse β).

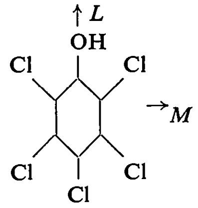
	$\chi_1-\chi_2$	$\chi_2-\chi_3$	$\chi_1-\chi_3$	ψ_{obs}	ψ_{calc}	χ_M	χ_1	χ_2	χ_3
Present work	5·7	34·6	40·3	+5·9±7·3	+7·3±10·2	−147·5*	−132·2±0·4	−137·9±0·4	−172·5±0·6
Krishnan & Banerjee	6·8	(34·9)†	41·7	+52·6		−145·6	−123·4‡	−136·2	−171·1

* Absolute mean value taken from *International Critical Tables.*
† Values between brackets are calculated from given data.
‡ Absolute value measured directly by authors.

to C(2)C(2′) and to C(3)C(3′). M is in each case perpendicular to L in the plane of the ring and N is normal to that plane. These referred to the orthogonal axes a, b and c', and the molecular susceptibilities deduced in each case are as shown in Table 4.

The second series of results is not reasonably regular, since K_L is numerically greater than K_M in the first two cases but less in the third case. Also comparing the three sets of values with those of pentachlorophenol ($K_L = -125{\cdot}5$, $K_M = -125{\cdot}3$ *i.e.* $K_L = K_M$, Table 5), it is clear that the first series of results probably gives the correct values. That is, the molecules of pentachlorophenol and hexachlorobenzene are both magnetically uniaxial. The difference between the three values of K_N is possibly due to the carbon atoms not being exactly coplanar. Taking K_N as the mean of the three values and $K_L = K_M$, the molecular susceptibilities of hexachlorobenzene are shown in Table 5, together with those of some other similar compounds.

Pentachlorophenol, $C_6Cl_5(OH)$



The crystal structure of pentachlorophenol was determined by Sakurai (1962), who gave: $a = 29{\cdot}11$, $b = 4{\cdot}930$, $c = 12{\cdot}09$ Å, $\beta = 93°38'$; $Z = 8$; $C2/c$. All the carbon atoms are coplanar within experimental error. The deviation of the chlorine and oxygen atoms from this plane is also very small.

Crystals of pentachlorophenol suitable for the magnetic measurements were crystallized from ethyl alcohol in the form of prismatic plates elongated along [010] with (100) as the plate face. Four crystals weighing 17·8, 17·4, 8·0 and 2·4 mg were used. The crystal magnetic anisotropies are:

$$\chi_1 - \chi_2 = 24{\cdot}9,\ \chi_1 - \chi_3 = 23{\cdot}5,\ \chi_3 - \chi_2 = 1{\cdot}4$$

$$\psi(\text{angle } \chi_1\text{: [001], positive in obtuse } \beta)$$

$$= +81{\cdot}4 \pm 1{\cdot}5°\text{obs.}$$

$$= +82{\cdot}7 \pm 5{\cdot}5°\text{calc.}$$

Using $\bar{\chi}_M = -194{\cdot}0$ given in *International Critical Tables* for pentabromophenol, Pascal's additive value for pentachlorophenol is $\bar{\chi}_M = -141{\cdot}5$. Thus the crystal susceptibilities are:

$$\chi_1 = -125{\cdot}4 \pm 0{\cdot}7,\ \chi_2 = -150{\cdot}3 \pm 0{\cdot}7,\ \chi_3 = -148{\cdot}9 \pm 0{\cdot}3.$$

The direction cosines of the molecular axes L, M and N, considering the plane of the carbon atoms only, referred to the orthogonal axes a', b and c are:

	a'	b	c
L	0·9814	0·0769	0·1758
M	0·1778	−0·7094	−0·6823
N	0·0651	0·7006	−0·7114

The molecular susceptibilities and anisotropy of pentachlorophenol are shown in Table 5, together with those of tetrachlorohydroquinone (Lasheen, 1964) and hexachlorobenzene.

Table 4. *Direction cosines and molecular susceptibilities in hexachlorobenzene*

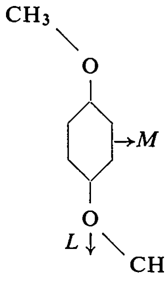
		Direction cosines			Molecular susceptibilities	
(1)		a	b	c'	First series	Second series
C(1)–C(1′)	L	0·9253	0·1988	0·3229	$K_L = -132{\cdot}4 \pm 0{\cdot}6$	$K_L = -135{\cdot}5 \pm 6{\cdot}8$
	M	0·2590	0·2907	−0·9212	$K_M = -132{\cdot}7 \pm 0{\cdot}8$	$K_M = -129{\cdot}4 \pm 6{\cdot}8$
	N	0·2691	−0·9375	−0·2202	$K_N = -177{\cdot}6 \pm 0{\cdot}7$	$K_N = -177{\cdot}7 \pm 0{\cdot}6$
					$\Delta K = 45{\cdot}05 \pm 0{\cdot}76$	$\Delta K = 45{\cdot}25 \pm 4{\cdot}85$
(2)		a	b	c'		
C(2)–C(2′)	L	0·2183	−0·1902	0·9571	$K_L = -132{\cdot}4 \pm 0{\cdot}4$	$K_L = -137{\cdot}7 \pm 13{\cdot}8$
	M	0·9396	0·3057	−0·1534	$K_M = -133{\cdot}7 \pm 0{\cdot}5$	$K_M = -128{\cdot}0 \pm 14{\cdot}2$
	N	0·2691	−0·9375	−0·2202	$K_N = -176{\cdot}5 \pm 0{\cdot}7$	$K_N = -176{\cdot}9 \pm 0{\cdot}7$
					$\Delta K = 43{\cdot}45 \pm 0{\cdot}79$	$\Delta K = 44{\cdot}05 \pm 9{\cdot}96$
(3)		a	b	c'		
C(3)–C(3′)	L	0·6646	0·3456	−0·6625	$K_L = -132{\cdot}2 \pm 0{\cdot}5$	$K_L = -125{\cdot}7 \pm 0{\cdot}5$
	M	0·6972	0·0319	0·7161	$K_M = -132{\cdot}3 \pm 0{\cdot}4$	$K_M = -137{\cdot}9 \pm 0{\cdot}4$
	N	0·2691	−0·9375	−0·2202	$K_N = -178{\cdot}1 \pm 0{\cdot}7$	$K_N = -179{\cdot}0 \pm 0{\cdot}7$
					$\Delta K = 45{\cdot}85 \pm 0{\cdot}79$	$\Delta K = 47{\cdot}20 \pm 0{\cdot}76$

Table 5. *Molecular susceptibilities and anisotropies of tetrachlorohydroquinone* (*Lasheen*, 1964) *hexachlorobenzene and pentachlorophenol*

	K_L	K_M	K_N	ΔK
Tetrachlorohydroquinone	−103·0	−114·3	−144·9	36·3
Hexachlorobenzene	−132·3 ± 0·3	−132·3 ± 0·3	−177·4 ± 0·4	44·8 ± 0·5
Pentachlorophenol	−125·5 ± 0·6	−125·3 ± 18·8	−173·8 ± 18·9	48·4 ± 21·1

It was found that small experimental errors in the crystal magnetic anisotropies of this compound lead to very large probable errors in its molecular susceptibilities and anisotropies as shown in Table 5.

1,4-Dimethoxybenzene, $C_6H_4(OCH_3)_2$



The crystal structure of 1,4-dimethoxybenzene was determined by Goodwin, Przybylska & Robertson (1950) who gave: $a=7{\cdot}29$, $b=6{\cdot}30$, $c=16{\cdot}55$ Å; $Z=4$; *Pbca*. The molecule is centrosymmetrical and planar.

The *p*-dimethoxybenzene crystals were obtained from its solution in methyl alcohol as six-sided flat prisms elongated along [100] with (001) as the plate face. Three crystals of weights 44·8, 19·7 and 4·4 mg were used in the measurements. The crystals were losing weight slowly by volatilization, so the necessary precautions were considered.

The crystal magnetic anisotropies are:

$$\chi_c-\chi_a=35{\cdot}3,\ \chi_b-\chi_a=18{\cdot}2,\ \chi_c-\chi_b=17{\cdot}1 \text{ obs.}\quad (17{\cdot}1 \text{ calc.})\,.$$

French (1945) found $\bar{\chi}_M=-86{\cdot}65$, thus the crystal susceptibilities are:

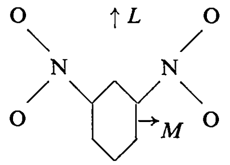
$$\chi_a=-104{\cdot}5\pm0{\cdot}2,\ \chi_b=-86{\cdot}3\pm0{\cdot}3,\ \chi_c=-69{\cdot}2\pm0{\cdot}3.$$

The direction cosines of the molecular axes *L*, *M* and *N* referred to the crystal axes and hence the molecular susceptibilities are:

	a	*b*	*c*
L	0·0290	0·3635	0·9313
M	0·5499	−0·7836	0·2887
N	0·8348	0·5038	−0·2228

$$\begin{aligned} K_L &= -65{\cdot}6\pm0{\cdot}4\\ K_M &= -78{\cdot}6\pm0{\cdot}7\\ K_N &= -115{\cdot}8\pm0{\cdot}5\\ \Delta K &= 43{\cdot}7\pm0{\cdot}6 \end{aligned}$$

m-Dinitrobenzene, $C_6H_4(NO_2)_2$



The crystal structure of *m*-dinitrobenzene was determined by Trotter (1961). $a=13{\cdot}20$, $b=13{\cdot}97$, $c=3{\cdot}80$ Å; $Z=4$; $Pbn2_1$. The carbon and nitrogen atoms are all coplanar but the nitro groups are twisted out of this plane about the C–N bonds by 11·8° for N(1)O(1)O(2) and 9·6° for N(2)O(3)O(4).

Needles elongated along [001] with (100) as the plate face were crystallized from ethyl alcohol. Four crystals of weights 16·2, 12·0, 8·9, 8·6 mg were used in the measurements.

The magnetic data together with those found by Banerjee (1938) and by Banerjee & Bhattacharjya (1938) are shown in Table 6.

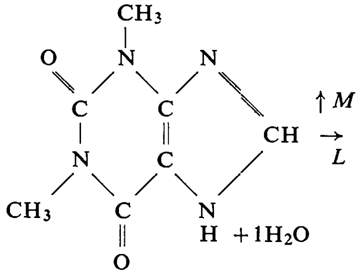
The direction cosines of the three molecular axes *L*, *M* and *N* where *N* is normal to the plane of the benzene ring, *M* is parallel to the line joining the two carbon atoms connected to the nitro groups and *L* perpendicular to *M* in the plane of the ring, are:

	a	*b*	*c*
L	0·5786	−0·7238	0·3744
M	0·8109	0·5596	−0·1713
N	0·0871	−0·4048	−0·9103

Thus the molecular susceptibilities are:

$$K_L=-50{\cdot}0\pm6{\cdot}9,\ K_M=-41{\cdot}7\pm2{\cdot}1,\ K_N=-119{\cdot}8\pm6{\cdot}7,\ \Delta K=74{\cdot}0\pm7{\cdot}6\,.$$

Theophylline, $C_7H_8N_4O_2.H_2O$



The crystal structure of theophylline, which contains a six-membered ring (a substituted pyrimidine ring)

Table 6. *Magnetic anisotropies and susceptibilities of m-dinitrobenzene crystal compared with those found by S. Banerjee* (1938) *and by K. Banerjee & Bhattacharjya* (1938)

	$\chi_a-\chi_c$	$\chi_b-\chi_c$	$\chi_a-\chi_b$ obs.	$\chi_a-\chi_b$ calc.	$\bar{\chi}_M$	χ_a	χ_b	χ_c
Present work	62·4	48·6	13·8	13·8	−70·53*	−45·1±2·3	−58·9±2·4	−107·5±4·6
S. Banerjee	62·2	48·5	13·8	13·7	−68·9	−43·6†	−57·3	−105·8
K. Banerjee & Bhattacharjya	59·92	49·80	10·25					

* Absolute mean value measured by French (1945).
† Absolute value measured directly by authors.

and a five-membered ring (an imidazole ring), was determined by Sutor (1958). $a=13{\cdot}3$, $b=15{\cdot}3$, $c=4{\cdot}50$ Å, $\beta=99{\cdot}5^\circ$; $Z=4$; $P2_1$. The whole molecule is planar with the exception of a carbon atom in one of the methyl groups; other deviations are not significant.

Two crystals weighing 44·7 and 16·0 mg were used in the magnetic measurements. They were crystallized from aqueous solution as needles elongated along [001] with faces {110}. The suspension of the crystal with [010] vertical or with (100) horizontal was made possible by setting the crystal by X-ray diffraction with [010] vertical and then attaching to it a very fine glass fibre of negligible weight. Measurements were carried out with the fibre attached and then without to be sure that it had no effect on the results.

The crystal magnetic anisotropies are:

$$\chi_1-\chi_2=59{\cdot}2,\ \chi_3-\chi_2=56{\cdot}6,\ \chi_1-\chi_3=2{\cdot}6$$

$$\psi(\text{angle } \chi_1:[001], \text{ positive in obtuse } \beta)=$$
$$-48{\cdot}8\pm0{\cdot}9 \text{ obs.}$$
$$(-48{\cdot}0\pm3{\cdot}0 \text{ calc.})\,.$$

Pascal's additive value for the mean molecular susceptibility using the correction constants found by Pacault (1946) for the pyrimidine ($\lambda=+6{\cdot}5$) and the imidazole ($\lambda=+8{\cdot}0$) rings is $\bar{\chi}_M=-84{\cdot}2$. The experimental value determined recently by Lasheen & Korayem (1967) is $\bar{\chi}_M=-84{\cdot}28$. Thus the crystal susceptibilities are:

$$\chi_1=-63{\cdot}6\pm1{\cdot}0,\ \chi_2=-122{\cdot}8\pm1{\cdot}0,\ \chi_3=-66{\cdot}2\pm2{\cdot}0\,.$$

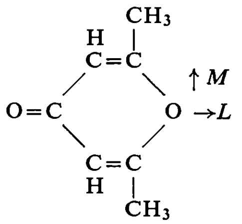
The direction cosines of the molecular axes L, M and N referred to orthogonal axes a', b and c are:

	a'	b	c
L	0·7525	−0·0959	−0·6515
M	0·1783	0·9816	0·0615
N	0·6344	−0·1598	0·7562

Hence the molecular susceptibilities are:

$$K_L=-63{\cdot}4\pm1{\cdot}0,\ K_M=-64{\cdot}7\pm2{\cdot}1,$$
$$K_N=-124{\cdot}5\pm1{\cdot}1,\ \Delta K=60{\cdot}4\pm1{\cdot}6\,.$$

2,6-Dimethyl-γ-pyrone, $C_7H_8O_2$



The crystal structure of 2,6-dimethyl-γ-pyrone was determined by Brown, Norment & Levy (1957) who gave $a=7{\cdot}672$, $b=7{\cdot}212$, $c=13{\cdot}92$ Å, $\beta=120^\circ59'$; $Z=4$; $P2_1/c$. The carbon–oxygen skeleton of the molecule is planar. It may be concluded from the bond lengths that the most important resonance structure for the molecule is the normal covalent ketonic structure.

Large prismatic crystals of 2,6-dimethyl-γ-pyrone were obtained from its aqueous solution with (100) and ($20\bar{1}$) as the prominent faces; (001) appeared occasionally. After some trials it was possible to grow small platy crystals with (100) as the plate face which are just suitable for magnetic measurements. Four crystals of weights 134·6, 16·6, 15·3 and 8·1 mg were used. The crystal magnetic anisotropies are:

$$\chi_1-\chi_2=21{\cdot}2,\ \chi_1-\chi_3=5{\cdot}4,\ \chi_3-\chi_2=15{\cdot}8$$

$$\psi(\text{angle } \chi_1:[001], \text{ positive in obtuse } \beta)=$$
$$+21{\cdot}3\pm2{\cdot}3 \text{ obs.}$$
$$(+20{\cdot}7\pm4{\cdot}5 \text{ calc.})\,.$$

Pascal's additive value for the mean susceptibility $\chi_M=-69{\cdot}7$ was calculated with use of the correction constant ($\lambda=-1{\cdot}4$) for γ-pyrone ring found by Pacault (1946). Thus,

$$\chi_1=-60{\cdot}85\pm0{\cdot}35,\ \chi_2=-82{\cdot}05\pm0{\cdot}35,$$
$$\chi_3=-66{\cdot}25\pm0{\cdot}67\,.$$

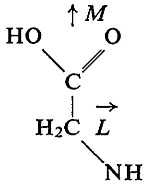
The direction cosines of the molecular axes L, M and N where L is parallel to the line joining the oxygen atom of the ring and the opposite carbon atom connected to the second oxygen atom, N is normal to the molecular plane and M perpendicular to L in that plane were calculated. These referred to the three orthogonal axes a', b and c are:

	a'	b	c
L	0·5667	0·7090	0·4193
M	0·1025	−0·5657	0·8180
N	0·8156	−0·4231	−0·3948

Thus the molecular susceptibilities and anisotropy are:

$$K_L=-62{\cdot}9\pm3{\cdot}0,\ K_M=-59{\cdot}7\pm2{\cdot}5,$$
$$K_N=-86{\cdot}6\pm0{\cdot}7,\ \Delta K=25{\cdot}3\pm2{\cdot}1\,.$$

Glycine, $CH_2(NH_2).COOH$



The crystal structure of the usual α form of glycine was refined by Marsh (1958), who gave $a=5{\cdot}102$, $b=11{\cdot}97$, $c=5{\cdot}4575$ Å, $\beta=111{\cdot}7^\circ$; $Z=4$; $P2_1/n$. The carbon and oxygen atoms are nearly planar.

Glycine crystals grown by slow evaporation from aqueous solution were prismatic elongated along [001] with the edge [100] apparent. Three crystals of weights 30·4, 12·9 and 10·3 mg were used. The crystal magnetic anisotropies are shown in Table 7 together with those found by Gordon (1960).

The mean molecular susceptibility determined by Perceau (1953) and hence the crystal susceptibilities are:

$$\bar{\chi}_M = -40{\cdot}3,\ \chi_1 = -37{\cdot}67 \pm 0{\cdot}08,$$
$$\chi_2 = -39{\cdot}37 \pm 0{\cdot}08,\ \chi_3 = -43{\cdot}87 \pm 0{\cdot}13\ .$$

The interesting part of this molecule is the carboxyl group, which is the only part where resonance may be expected.

The direction cosines of the molecular axes referred to the orthogonal axes a', b and c and the resulting molecular susceptibilities and anisotropy are:

(1) Considering the plane of the carboxyl group COO only:

		a'	b	c
$>C=O$	L	0·8739	−0·2903	0·3899
	M	0·4107	0·0120	−0·9117
	N	0·2611	0·9563	0·1302

$$K_L = -37{\cdot}02 \pm 0{\cdot}10$$
$$K_M = -39{\cdot}41 \pm 0{\cdot}08$$
$$K_N = -44{\cdot}57 \pm 0{\cdot}15$$
$$\Delta K = 6{\cdot}355 \pm 0{\cdot}159$$

(2) Considering the plane of the four carbon and oxygen atoms:

(*a*)

		a'	b	c
$>C=O$	L	0·8739	−0·2903	0·3899
	M	0·4127	0·0195	−0·9105
	N	0·2616	0·9550	0·1390

$$K_L = -36{\cdot}92 \pm 0{\cdot}10$$
$$K_M = -39{\cdot}40 \pm 0{\cdot}08$$
$$K_N = -44{\cdot}68 \pm 0{\cdot}15$$
$$\Delta K = 6{\cdot}52 \pm 0{\cdot}16$$

(*b*)

		a'	b	c
C–C	L	0·0312	−0·1589	0·9863
	M	0·9648	−0·2536	−0·0712
	N	0·2616	0·9550	0·1390

$$K_L = -39{\cdot}31 \pm 2{\cdot}48$$
$$K_M = -37{\cdot}28 \pm 2{\cdot}55$$
$$K_N = -44{\cdot}42 \pm 0{\cdot}00$$
$$\Delta K = 6{\cdot}13 \pm 1{\cdot}78$$

These values may be compared with those found before (Lasheen, 1964) for the carboxyl group in half of the ammonium hydrogen D-tartrate molecule, which are:

$$K_L = -37{\cdot}41,\ K_M = -38{\cdot}57,$$
$$K_N = -46{\cdot}80,\ \Delta K = 8{\cdot}81\ .$$

Conclusion

In some of the above cases where the mean susceptibility has not been measured absolutely, it has been estimated from semi-empirical considerations. This may result in some errors in the absolute values of K_L, K_M and K_N but it is found that even a ten per cent error in $\bar{\chi}_M$ makes an almost negligible difference in ΔK. The molecular anisotropy may therefore be taken as far more accurate than the absolute values of the three molecular susceptibilities, in such cases.

In some special cases small experimental variances in the crystal magnetic anisotropies may lead to large apparent errors in the molecular susceptibilities and anisotropies. These probable errors were calculated in this paper for all the substances investigated (Table 8).

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Table 7. *Magnetic anisotropies of glycine crystals compared with those determined by Gordon* (1960)

ψ (angle χ_1: [001], positive in obtuse β).

	$\chi_1-\chi_2$	$\chi_1-\chi_3$	$\chi_2-\chi_3$	ψ_{obs}	ψ_{calc}
Present work	1·7	6·2	4·5	+48·0 ± 1·1°	+48·5 ± 1·0°
Gordon	1·59	6·17	4·58	+46 ± 2°	

Table 8. *Molecular susceptibilities and anisotropies with probable errors resulting from the experimental variances*

Less symmetrical planar or non-planar molecules which have only approximate principal molecular magnetic axes are marked *. The directions of these chosen molecular axes are not far from the real molecular magnetic axes for most of these marked molecules.

Compound†	K_L	K_M	K_N	ΔK
Aromatic compounds				
Anthracene	−72·4 ± 2·0	−71·8 ± 1·7	−245·7 ± 2·7	173·6 ± 3·0
Hexachlorobenzene	−132·6 ± 0·3	−132·6 ± 0·3	−177·4 ± 0·4	44·8 ± 0·5
Pentachlorophenol	−125·5 ± 0·6	−125·3 ± 18·8	−173·8 ± 18·9	48·4 ± 21·1
1,4-Dimethoxybenzene	−65·6 ± 0·4	−78·6 ± 0·7	−115·8 ± 0·5	43·7 ± 0·6
m-Dinitrobenzene	−50·0 ± 6·9	−41·7 ± 2·1	−119·8 ± 6·7	74·0 ± 7·6
Aliphatic compounds				
Theophylline*	−63·4 ± 1·0	−64·7 ± 2·1	−124·5 ± 1·1	60·4 ± 1·6
2,6-Dimethyl-γ-pyrone	−62·9 ± 3·0	−59·7 ± 2·5	−86·6 ± 0·7	25·3 ± 2·1
Glycine*	−37·02 ± 0·10	−39·41 ± 0·08	−44·57 ± 0·15	6·355 ± 0·159

† See text for formulae and directions of L and M.

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Crystal Diffraction Profiles for Monochromatic Radiation*

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The instrumental window of a double crystal spectrometer in the dispersive (1, +1) position has been determined experimentally with a Mössbauer source and compared with theoretical predictions. The experiment was done at a wavelength of 0·86 Å* with the 14·4 keV γ ray that follows the ^{57}Co→^{57}Fe decay. The crystals employed were quartz ($10\bar{1}1$), silicon (111), germanium (111), and calcite (211) ($10\bar{1}4$), where the indices refer to the structural cells. The theoretical expression for the double-crystal window was calculated as the convolution of the appropriate single-crystal monochromatic profiles predicted by the Darwin–Prins dynamical theory of X-ray diffraction. The agreement between theory and experiment was good and clearly shows the necessity for crystal asymmetry corrections to precision wavelength determinations in certain cases.

Introduction

Less than two years after von Laue had suggested the possibility of crystal diffraction of X-rays, Darwin (1914) published a pair of papers outlining the dynamics of the process. A number of years later this theory was expanded by Prins (1930) to include absorption effects; but, because of the difficulty in obtaining a monochromatic radiation source in the X-ray region, it has only recently become possible to test the theory adequately. Moreover, the theory predicts asymmetric diffraction profiles under certain conditions, and such profiles are of considerable importance in the determination of X-ray wavelengths with the precision now required for studies such as the atomic constants evaluation.

Investigations with the two-crystal spectrometer permit certain aspects of the theory to be checked, such as the widths of the diffraction profiles in the non-dispersive spectrometer configurations (Parratt, 1932; Allison, 1932; Parratt & Miller, 1936). These experiments, however, give little information as to the shape of these patterns. In fact, for a pair of identical crystals they can yield no information at all about the asymmetry of either the single-crystal profiles or the double-crystal patterns in the dispersive positions of the spectrometer (the configurations required for wavelength determination).

The first step toward the solution of this problem came with DuMond's suggestion in 1937 for a multiple (3 or more) crystal spectrometer (DuMond, 1937; Boll-

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