

## Diamagnetic Anisotropy of Some Organic Molecules

M. A. Lasheen

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## DIAMAGNETIC ANISOTROPY OF SOME ORGANIC MOLECULES

By M. A. LASHEEN\*

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The diamagnetic anisotropies of crystals of aromatic and aliphatic compounds, mostly of known structure, have been measured, and the principal molecular susceptibilities deduced from these and the molecular orientations. In a few cases where the absolute susceptibility is not known with certainty, the molecular anisotropy may, nevertheless, be calculated with a good degree of accuracy.

The molecular susceptibilities and anisotropy are related to the molecular shape and constitution, and to the bond character; and in the case of aromatic compounds they are strongly influenced by substitution, which, 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. This may give some information concerning the effect of substitution on conjugation, especially when correlated with changes in bond lengths and angles.

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## INTRODUCTION

Hoarau, Jousot-Dubien, Lemanceau, Lumbroso & Pacault (1956) determined the molecular susceptibilities of benzene and found the molecular anisotropy

$$\Delta K = \frac{1}{2}(K_L + K_M) - K_N = 59.7 \times 10^{-6},$$

where  $K_L$  and  $K_M$  are the molecular susceptibilities in the plane of the molecule and  $K_N$  perpendicular to it.

Lonsdale & Toor (1959) determined the molecular anisotropy of both 1:3:5- $C_6H_3Br_3$  and  $B-B_3N_3H_3Cl_3$  and found that they are respectively  $47 \times 10^{-6}$  and  $18 \times 10^{-6}$  e.m.u./g. They concluded that it seems possible that the reduction in molecular diamagnetic anisotropy might be a good way of measuring the degree of aromatic character of derivatives of conjugated ring compounds. Lonsdale (1959) compared the intermolecular distances of 1:3:5- $C_6H_3Cl_3$  and  $B-B_3N_3H_3Cl_3$  and found that there is a clear indication that Cl and H atoms in  $B$ -trichloroborazole molecule are charged. This would lead to a corresponding reduction in the double-bond character of the ring, in spite of the short B—N distance. This supports the measurements of the diamagnetic anisotropy.

The present investigations were undertaken in the hope of providing quantitative knowledge of the principal magnetic susceptibilities of molecules of different shapes and containing various electronic groupings. Fortunately, the crystal structures of a large number of organic compounds, aromatic and aliphatic, have been determined in the last 10 or 15 years with considerable accuracy. Comparison of the character of their bond lengths with their molecular anisotropies may lead to the understanding of the role of different electron configurations.

The substances investigated include aromatic compounds having three rings, two rings or one ring with different substituents. Aliphatic compounds investigated include one having a six-membered ring, others with five-membered rings and open-chain compounds containing double bonds.

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 every compound, in the different necessary orientations, and means were taken. In most cases measurements were carried out on every crystal in at least three different orientations, in order to calculate the crystal magnetic anisotropies and to compare calculated and observed anisotropies in case of orthorhombic crystals or calculated and observed directions of  $\chi_1$  or  $\chi_2$  in the case of monoclinic crystals. Each crystal was always weighed accurately just before the magnetic measurements. Any volatilization of the crystal could be detected from repeated measurements on the same crystal in the same suspension, and the loss of weight subsequently checked.

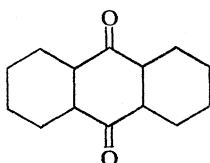
In the case of monoclinic crystals the crystal susceptibility parallel to [010] is taken as  $\chi_3$ , while  $\chi_1$  and  $\chi_2$  denote those in the (010) plane,  $\chi_1$  being algebraically greater than  $\chi_2$ .

The transitions from crystalline to molecular susceptibilities were carried out by the use of the molecular direction cosines obtained from the X-ray crystal structure and the mathematical relations given by Lonsdale & Krishnan (1936).

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## AROMATIC COMPOUNDS

## (a) Three-ring compounds

1. Anthraquinone,  $C_{14}H_8O_2$ 

The crystal structure of anthraquinone was refined by Murty (1960) who gave  $a = 15.810$ ,  $b = 3.942$ ,  $c = 7.865 \text{ \AA}$ ,  $\beta = 102^\circ 43'$ ,  $Z = 2$ , space group  $P2_1/a$ . The different atoms of the anthraquinone molecule were found to conform closely to a planar configuration.

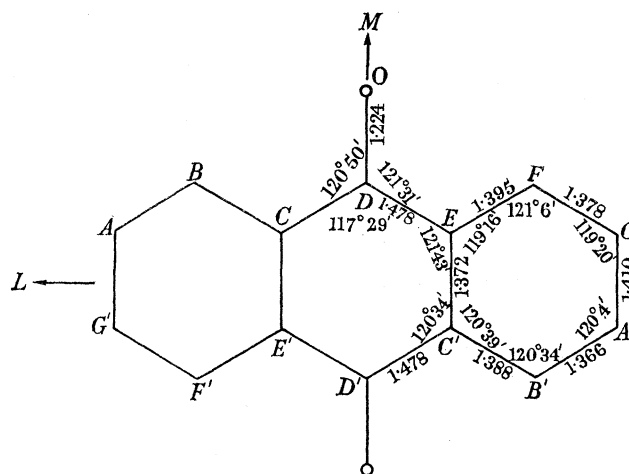


FIGURE 1. Bond lengths ( $\text{\AA}$ ) and angles in anthraquinone (centrosymmetric).

Two crystals were used in the magnetic measurements, of average weight 7 mg and average dimensions  $3.5 \times 2 \times 1 \text{ mm}^3$ .

The magnetic anisotropies of the crystal are:

$$\chi_1 - \chi_2 = 42.2, \quad \chi_1 - \chi_3 = 124.45, \quad \chi_2 - \chi_3 = 82.25$$

(the units throughout this paper being  $10^{-6} \text{ e.m.u./g}$ );

$$\theta \text{ (angle between } \chi_1 \text{ and } [100], \text{ positive in obtuse } \beta)$$

$$= -37.65 \text{ (obs.)}, \quad -37.67 \text{ (calc.)}.$$

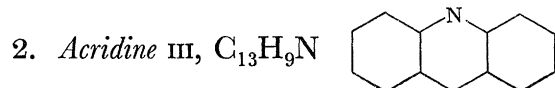
The mean susceptibility of anthraquinone  $\bar{\chi}_M = -119.6$  (Pascal 1911a, corrected). Hence the crystal susceptibilities are:

$$\chi_1 = -64.05, \quad \chi_2 = -106.25, \quad \chi_3 = -188.50.$$

Molecular direction cosines referred to the orthogonal axes  $a$ ,  $b$  and  $c'$ , where  $c'$  is perpendicular to  $a$  in (010), are:

		$a$	$b$	$c'$
(length)	$L$	0.531	0.451	0.713
(breadth)	$M$	0.788	0.036	-0.615
(normal)	$N$	-0.305	0.889	-0.341

Hence the molecular susceptibilities which are shown in table 1.



The crystal structure of acridine III has been determined by Phillips (1956). The cell dimensions are:  $a = 11.375$ ,  $b = 5.988$ ,  $c = 13.647 \text{ \AA}$ ,  $\beta = 98^\circ 58'$ ,  $Z = 4$  and the space group is  $P2_1/n$ . The molecule is not strictly planar but is bent slightly across the line N...C5. It is pseudo-symmetrical, in the crystal.

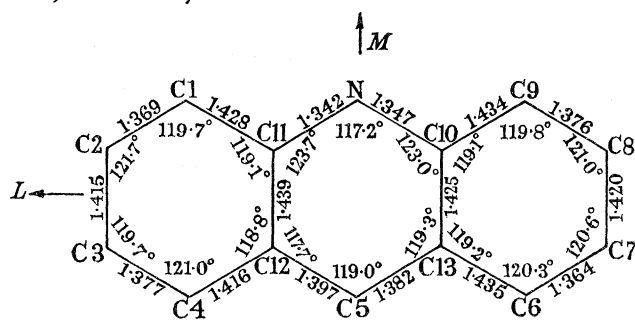


FIGURE 2. Bond lengths ( $\text{\AA}$ ) and angles in acridine.

The crystals used in the present work were crystallized from ethyl alcohol in the form of hexagonal plates with (001) or (100) as the flat face and elongated in the [010] direction. Four different crystals were used with weights varying between 8.1 and 26.4 mg and thickness between 0.7 and 1.5 mm.

The magnetic anisotropies are:

$$\chi_1 - \chi_2 = 147.5, \quad \chi_3 - \chi_2 = 110.0, \quad \chi_1 - \chi_3 = 37.5.$$

$$\psi \text{ (angle between } \chi_1 \text{ and } [001], \text{ positive in obtuse } \beta) = -12^\circ.$$

The mean susceptibility of acridine has been reported as:

$$\bar{\chi}_M = -123.2 \text{ (Pascal 1911 } b)$$

$$-122.82 \text{ (Pacault 1946)}$$

$$-123.3 \text{ (Int. Crit. Tables and Handb. Chem. and Phys.).}$$

The last value was used and hence the crystal susceptibilities are:

$$\chi_1 = -61.63, \quad \chi_2 = -209.13, \quad \chi_3 = -99.13.$$

Phillips gave the atomic co-ordinates and the equation of the best plane through the molecule and of the two planes through the two halves of the molecule. The direction cosines of  $L$ ,  $M$ ,  $N$  for the whole molecule and for each of the two halves were calculated. These referred to the orthogonal axes  $a$ ,  $b$  and  $c'$  are:

<i>the whole molecule</i>							
	$a$	$b$	$c'$		$a$	$b$	$c'$
$L$	0.4725	0.1562	-0.8674	$L$	0.4690	0.1214	-0.8748
$M$	0.4369	-0.8962	0.0766	$M$	0.4184	-0.9029	0.0990
$N$	0.7652	0.4151	0.4921	$N$	0.7758	0.4119	0.4779
<i>first half</i>				<i>second half</i>			
	$a$	$b$	$c'$		$a$	$b$	$c'$
$L$	0.4722	0.1955	-0.8595	$L$	0.4690	0.1214	-0.8748
$M$	0.4567	-0.8882	0.0488	$M$	0.4184	-0.9029	0.0990
$N$	0.7553	0.4162	0.5062	$N$	0.7758	0.4119	0.4779

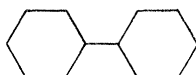
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The differences of the molecular susceptibilities calculated for the two cases are less than the experimental error. These susceptibilities are shown in table 1, together with those of anthraquinone and anthracene (Lonsdale & Krishnan 1936). For acridine, in contrast with anthraquinone, anthracene and most of the aromatic molecules, the numerical value of  $K_L$  is less than that of  $K_M$ . This was also found to hold for the  $\alpha$ -phenazine molecule by Herbstein & Schmidt (1955) who used Lonsdale's unpublished magnetic measurements.

TABLE 1

	$K_L$	$K_M$	$K_N$	$\Delta K$
anthraquinone	-76.1	-64.5	-217.9	147.6
acridine { considering plane of whole molecule	-61.4	-70.5	-238.0	172.1
{ considering planes of two halves	-61.3	-70.7	-237.9	171.9
anthracene (Lonsdale & Krishnan 1936)	-75.8	-62.6	-251.8	182.6

## (b) Two-ring compounds

1. Biphenyl,  $C_{12}H_{10}$  

The crystal and molecular structure of biphenyl have been recently determined in two independent papers by Trotter (1961) and by Hargreaves & Hasan Rizvi (1962). These agree closely. The latter give  $a = 8.12_4$ ,  $b = 5.63_5$ ,  $c = 9.15_3$  Å,  $\beta = 95.1^\circ$ ; space group  $P2_1/a$ ,  $Z = 2$ . The whole molecule is planar within the limits of error of the experimental results. The length of the bond linking the two phenyl rings ( $1.50_6$  Å with estimated standard deviation  $0.017$  Å) indicates that there is little or no conjugation between the rings; and this is confirmed by the fact that in the gaseous state the molecule is no longer planar.

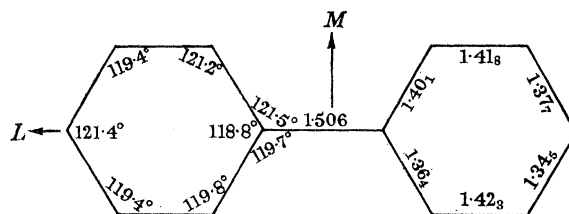


FIGURE 3. Observed dimensions (ångströms and degrees) (centrosymmetric) of biphenyl.

The crystals used in the present work were crystallized from ethyl alcohol in the form of rhombic plates, with (001) as the plate face, and [010] parallel to the shorter diagonal of the rhomb. Crystals were used weighing between 13 and 26 mg, of thickness between 0.5 and 1 mm.

The magnetic data together with those found by Krishnan, Guha & Banerjee (1933) are given in table 2.

TABLE 2

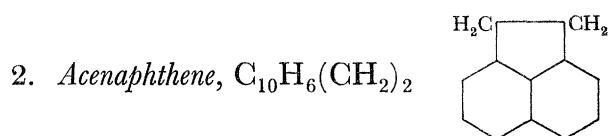
	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$	$\psi$	$\bar{\chi}_M$	$\chi_1$	$\chi_2$	$\chi_3$
Krishnan <i>et al.</i>	83.1	35.5	+20.1	-102.9	-63.4	-146.5	-98.9
					(measured)		
present work	77.5	33.5	{ +22.4 (obs.) } { +21.3 (calc.) }	-104.4 (used) (Pascal 1911 b)	-67.4	-144.9	-100.9

$\psi$  is the angle between  $\chi_1$  and [001], positive in obtuse  $\beta$ .

Molecular direction cosines referred to the orthogonal axes  $a$ ,  $b$ , and  $c'$  are:

	$a$	$b$	$c'$
$L$	0.2966	-0.0256	0.9545
$M$	0.5355	-0.8233	-0.1881
$N$	0.7928	0.5669	-0.2243

From these direction cosines and the crystal susceptibilities quoted in table 2, the molecular susceptibilities were calculated. These are shown in table 5. From these molecular susceptibilities  $\Delta K = 119.1$  and, as the crystal structure suggests no conjugation between the two rings, the magnetic anisotropy for each ring would be  $\Delta K = 59.6$ , in good agreement with  $\Delta K = 59.7$  found by Hoarau *et al.* (1956) for the benzene molecule. This means that the substitution of a benzene ring for a hydrogen atom has no effect, in this case, in reducing the anisotropy; or possibly that a small reduction due to substitution is compensated by a small amount of double-bond character in the central bond.



The crystal structure of acenaphthene has been determined by Ehrlich (1957). The crystal is orthorhombic with cell dimensions, at  $15^\circ\text{C}$ :  $a = 8.290$ ,  $b = 14.000$ ,  $c = 7.225 \text{ \AA}$ ;  $Z = 4$ ; space group  $Pcm2_1$ .

The two independent molecules are both planar and have mirror symmetry about a plane through the bond common to the two aromatic rings and  $N$ , the normal to the molecules. They are of two kinds, crystallographically, both sets having  $L$ , their 'length', parallel to  $[010]$ . One set has  $N$  parallel to  $[001]$ , the other has  $N$  at about  $62^\circ$  to  $[001]$ . For both sets  $M$  is, by symmetry, in  $(010)$ .

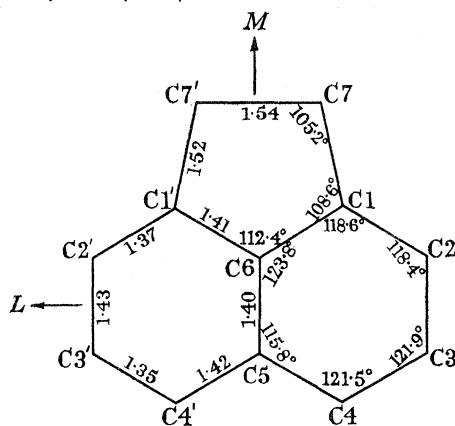


FIGURE 4. The weighted means of the bond lengths ( $\text{\AA}$ ) and angles of the two crystallographically independent acenaphthene molecules.

TABLE 3

	$\chi_b - \chi_a$	$\chi_b - \chi_c$	$\chi_a - \chi_c$	$\bar{\chi}_M$	$\chi_a$	$\chi_b$	$\chi_c$
Krishnan <i>et al.</i>	—	73.5	28.0	-111.8	-117.6	-72.1	-145.6
						(measured)	
present work	42.9	69.4	26.8	-109.3	-114.9	-72.0	-141.1
				(Pacault 1946)			

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The crystals used in the present work were crystallized from benzene in the form of plates elongated along [001] with (010) as the plate face. Three different crystals having weights between 1.5 and 2.1 mg with dimensions between  $5 \times 1.2 \times 0.3 \text{ mm}^3$  and  $6 \times 1.2 \times 0.5 \text{ mm}^3$  were used. It was easy to crystallize very large crystals from this solvent.

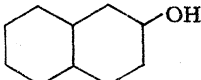
The present magnetic data together with those given by Krishnan *et al.* (1933) are shown in table 3.

The direction cosines of the molecular axes were calculated for the two independent molecules by the use of the Ehrlich (1957) molecular planes and atomic co-ordinates.

These are:

	molecule A				molecule B		
	<i>a</i>	<i>b</i>	<i>c</i>		<i>a</i>	<i>b</i>	<i>c</i>
<i>L</i>	0	1	0	<i>L</i>	0	1	0
<i>M</i>	1	0	0	<i>M</i>	0.4772	0	0.8788
<i>N</i>	0	0	1	<i>N</i>	0.8788	0	-0.4772

The molecular susceptibilities calculated from these direction cosines and the above crystal susceptibilities are shown in table 5.

3. *β*-Naphthol (2-oxynaphthalene)  $\text{C}_{10}\text{H}_7(\text{OH})$  

The crystal structure of *β*-naphthol has been determined by Hargreaves & Watson (1958). They give:  $a = 8.185$ ,  $b = 5.950$ ,  $c = 36.29 \text{ \AA}$ ,  $\beta = 119^\circ 52'$ ;  $Z = 8$ ; space group *Ia*.

The molecules, which are of two kinds, pack in sheets which lie parallel to the (001) plane. All molecules in a given sheet are equivalent to one another and to molecules in alternate sheets.

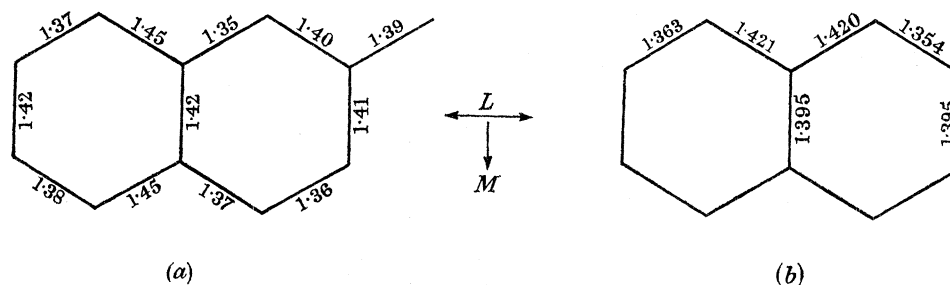


FIGURE 5. Bond lengths in (a) *β*-naphthol (mean of two values obtained for non-equivalent molecules), (b) naphthalene. Hargreaves & Watson (1958) state that no significance is to be attached to the difference in the lengths of the corresponding bonds in the two structures because of the large probable errors in the bond lengths determined for *β*-naphthol.

The crystals used in the magnetic measurements were crystallized from  $\text{CS}_2$  in the form of rhombic plates with (001) as the plate face, and [010] parallel to the shorter diagonal of the rhomb (exactly as found by Hargreaves & Watson). Three different crystals were used of weights between 14.9 and 20.7 mg and of thickness between 0.5 and 0.8 mm.

TABLE 4

	$\chi_1 - \chi_2$	$\chi_3 - \chi_2$	$\chi_1 - \chi_3$	$\psi(\chi_1 \wedge [001], +ve \text{ in obtuse } \beta)$	$\bar{\chi}_M$	$\chi_1$	$\chi_2$	$\chi_3$
Krishnan <i>et al.</i>	86.0	—	18.1	+9.4°	-97.0	-62.3 (meas.)	-148.3	-80.4
present work	85.3	68.0	17.3	{ +11.1 (obs.) +13.8 (calc.) }	-97.0 (Pascal 1911 a)	-62.8	-148.1	-80.1

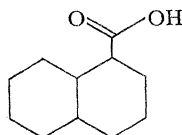


The magnetic data are shown in table 4 together with those found by Krishnan *et al.* (1933). The atomic co-ordinates given by Hargreaves & Watson were used to calculate the direction cosines of the two independent (asymmetric) molecules. These, referred to the orthogonal axes  $a$ ,  $b$  and  $c'$ , are:

	molecule A				molecule B		
	$a$	$b$	$c'$		$a$	$b$	$c'$
$L$	-0.4005	0.2430	0.8835	$L$	-0.4190	-0.1616	0.8936
$M$	0.2913	-0.8918	0.3438	$M$	0.3860	0.8610	0.3305
$N$	0.8625	0.4269	0.2718	$N$	-0.8188	0.4954	-0.2902

Hence the molecular susceptibilities were calculated. When we compare these values (shown in table 5) with those of naphthalene determined by Lonsdale & Krishnan (1936) and by Lumbroso & Pacault (1957), it seems that substitution of a hydrogen by a hydroxyl does not change the molecular anisotropy. Compare phloroglucinol dihydrate (p. 371).

4. 1-Naphthoic acid,  $C_{10}H_7COOH$



The crystal structure of 1-naphthoic acid has been determined by Trotter (1960*b*). The cell dimensions are:  $a = 31.12$ ,  $b = 3.87$ ,  $c = 6.92 \text{ \AA}$ ,  $\beta = 92.2^\circ$ ;  $Z = 4$ ; space group  $P2_1/a$ .

The naphthalene rings are planar (r.m.s. deviation  $0.04 \text{ \AA}$ ), and the oxygen atoms lie one above and one below the aromatic plane at a mean distance of about  $0.20 \text{ \AA}$ . The carboxyl group is thus twisted about the C(aromatic)—C(carboxyl) bond, the angle between the aromatic and carboxyl planes being  $11^\circ$ .

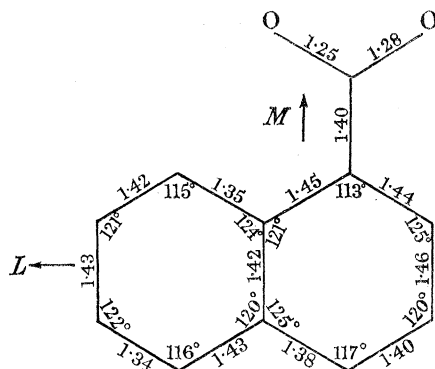


FIGURE 6. Bond lengths ( $\text{\AA}$ ) and valency angles in 1-naphthoic acid.

The crystals used in the present work were crystallized from aqueous ethanol as colourless plates elongated along  $[010]$  with  $(100)$  as the plate face. Three crystals weighing 2.8, 3.7 and 4 mg and of average dimensions  $8 \times 1.5 \times 0.4 \text{ mm}^3$  were used in the magnetic measurements. The anisotropies are:

$$\chi_1 - \chi_2 = 19.8, \quad \chi_1 - \chi_3 = 106.4, \quad \chi_2 - \chi_3 = 86.6;$$

$$\theta \text{ (angle between } \chi_1 \text{ and } [100], \text{ positive in obtuse } \beta) \\ = -9.95^\circ \text{ (obs.)}, \quad -9.90^\circ \text{ (calc.)}.$$

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Using the experimental values of the mean susceptibilities of benzene ( $\bar{\chi}_M = -54.86$ ) and benzoic acid ( $\bar{\chi}_M = -70.28$ ) given by French (1954) and of naphthalene ( $\bar{\chi}_M = -91.9$ ) given in the *International critical tables*, that of naphthoic acid  $\bar{\chi}_M = -107.32$ . Thus the crystal susceptibilities are:

$$\chi_1 = -65.25, \quad \chi_2 = -85.05, \quad \chi_3 = -171.65.$$

From the atomic co-ordinates and the plane of the naphthalene rings given by Trotter the direction cosines of the three molecular axes were calculated. These, referred to the orthogonal axes used by Trotter,  $a'$ ,  $b$  and  $c$ , where  $a'$  is perpendicular to  $c$  in (010), are:

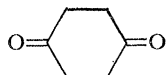
	$a'$	$b$	$c$
$L$	0.7646	0.2472	0.5952
$M$	0.6441	-0.3217	-0.6939
$N$	0.0238	0.9152	-0.4022

Hence the molecular susceptibilities were calculated (table 5). Taking  $\Delta K = 8.8$  for the carboxyl group as found in ammonium hydrogen *d*-tartrate (p. 381) and allowing for the angle  $11^\circ$  between the aromatic and carboxyl planes, the magnetic anisotropy of the naphthalene residue alone would be  $\Delta K = 119.3$ ; which is very close to that found for naphthalene by Lumbroso & Pacault (1957) and shown in table 5.

TABLE 5

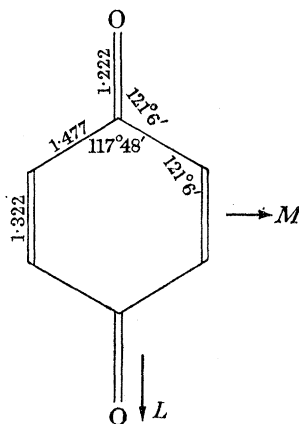
	$K_L$	$K_M$	$K_N$	$\Delta K$
naphthalene (Lonsdale & Krishnan 1936)	-56.1	-53.9	-169.0	114.0
naphthalene (Lumbroso & Pacault 1957)	-54.7	-52.6	-173.5	119.8
biphenyl	-67.7	-61.7	-183.8	119.1
acenaphthene	-72.0	-70.5	-185.5	114.25
$\beta$ -naphthol	-63.9	-51.9	-175.2	117.3
1-naphthoic acid	-70.5	-58.95	-192.5	127.8

## (c) One-ring compounds

1. *p*-Benzoquinone,  $C_6H_4O_2$ 

The crystal structure of *p*-benzoquinone was redetermined by Trotter (1960*a*). The cell dimensions are:  $a = 7.055$ ,  $b = 6.795$ ,  $c = 5.767$  Å,  $\beta = 101^\circ 28'$ ;  $Z = 2$ ; space group  $P2_1/a$ .

The *p*-benzoquinone molecule is planar within the limits of experimental error, the maximum deviation from the mean plane being only 0.007 Å. Molecular symmetry: *mmm*; in crystal,  $\bar{1}$  only.

FIGURE 7. Molecular configuration of *p*-benzoquinone.

Thin six-sided plates, tabular on (001), were crystallized from petroleum ether; short prismatic {110} plates with (001) as the plate face were obtained from benzene. Seven crystals from the two crops, of weights varying between 6.0 and 61.2 mg and of thicknesses between 0.5 and 1.2 mm, were used in the magnetic measurements. The crystals were losing weight rather quickly due to volatilization, so in each suspension the crystal was weighed just before and just after the measurements and the mean weight used; the measurements being carried out in the least possible time.

Experimental values of the mean susceptibility  $\bar{\chi}_M$  recorded are:

$$\begin{aligned}\bar{\chi}_M = & -41.28 \text{ (Pascal 1911 } a) \\ & -33.31 \text{ (Palacios \& Foz 1935)} \\ & -40.0 \text{ (Krishnan \& Banerjee 1935, based on measurements} \\ & \quad \text{of anisotropy and of } \chi_{\min.}) \\ & -38.2 \text{ (Mikhail \& Baddar 1944)} \\ & -38.4 \text{ (Matsunaga 1956)}\end{aligned}$$

The last, most recent, result was adopted and the magnetic data together with those found by Krishnan & Banerjee (1935) are shown in table 6.

TABLE 6

	$\chi_1 - \chi_2$	$\chi_3 - \chi_1$	$\chi_3 - \chi_2$	$\psi$	$\chi_M$	$\chi_1$	$\chi_2$	$\chi_3$
Krishnan & Banerjee (1935)	40.0	1.2	—	$\left\{ \begin{array}{l} +31.2 \text{ (obs.)} \\ +30.5 \text{ (calc.)} \end{array} \right\}$	-40.0	-27.1 (meas.)	-67.1	-25.9
present work	39.5	1.45	40.95	$\left\{ \begin{array}{l} +30.7 \text{ (obs.)} \\ +30.4 \text{ (calc.)} \end{array} \right\}$	-38.4	-25.7	-65.2	-24.3

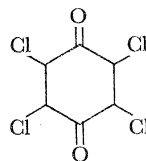
$\psi$  is the angle between  $\chi_1$  and [001], positive in obtuse  $\beta$ .

Trotter (1960*a*) gave the following direction cosines for the three molecular axes referred to the orthogonal axes  $a'$ ,  $b$  and  $c$ :

	$a'$	$b$	$c$
$L$	0.3120	0.8178	0.4835
$M$	0.4207	-0.5740	0.7025
$N$	0.8522	-0.0153	-0.5229

The molecular susceptibilities are shown in table 8 together with related compounds investigated and the values found for *p*-benzoquinone by Lonsdale & Krishnan (1936), who used Krishnan & Banerjee (1935) crystal susceptibilities.

2. *Tetrachloro-p-benzoquinone* (*chloranil*),  $C_6Cl_4O_2$



The crystal structure of tetrachloro-*p*-benzoquinone has been determined by Chu, Jeffrey & Sakurai (1962).  $a = 8.708$ ,  $b = 5.755$ ,  $c = 8.603 \text{ \AA}$ ,  $\beta = 105^\circ 51'$ ;  $Z = 2$ ; space group  $P2_1/a$ .

Within the accuracy of the analysis, the quinoid ring is planar. The deviations of the substituents out of the plane are significant. They correspond to a bending of the C—Cl and C—O bonds out of the plane by  $1.5^\circ$  and  $2.1^\circ$ , respectively, so that the substituent atoms alternate  $0.05 \text{ \AA}$  above and below the plane around the ring.

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Crystals were grown from acetone as well-developed transparent yellow rhombic plates with (001) as the plate face and [100] and [010] along the diagonals. Crystals of weights varying between 6.3 and 12.3 mg and thicknesses between 0.3 and 0.5 mm were used. The magnetic data together with those found by Banerjee (1938) are shown in table 7.

TABLE 7

	$\chi_1 - \chi_2$	$\chi_3 - \chi_2$	$\chi_1 - \chi_3$	$\theta$	$\bar{\chi}_M$	$\chi_1$	$\chi_2$	$\chi_3$
Banerjee (1938)	22.3	20.1	2.3	+90°	—	-93.9 (meas.)	-116.2	-96.2
present work	23.2	20.6	2.6	+90°	-107.12	-98.52	-121.72	-101.12

$\theta$  is the angle between  $\chi_1$  and [100], positive in obtuse  $\beta$ .

The values of the mean susceptibility recorded are:

$$\bar{\chi}_M = -112.6 \text{ (Int. Crit. Tables)}$$

$$-102.1 \text{ (Banerjee's (1938) mean value for his crystal susceptibilities)}$$

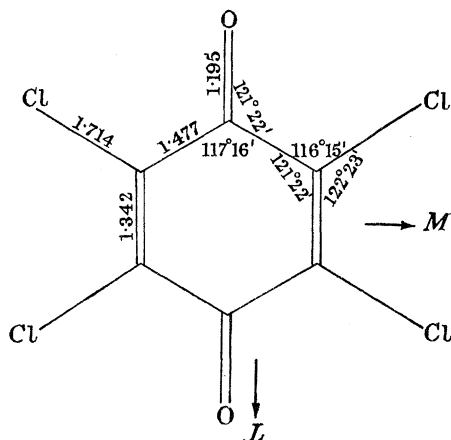
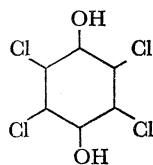
$$-107.12 \text{ (Pascal's additive value derived from the experimental value of } p\text{-benzoquinone, } \bar{\chi}_M = -38.4 \text{ (Matsunaga 1956))}$$

The third value, which is almost the mean of the other two values, was used.

Chu *et al.* (1962) gave direction cosines of the molecular axes referred to the orthogonal axes  $a'$ ,  $b$  and  $c$ :

	$a'$	$b$	$c$
$L$	0.5390	0.8306	-0.1399
$M$	0.2604	-0.0064	0.9655
$N$	-0.8011	0.5569	0.2197

The molecular susceptibilities are shown in table 8.

FIGURE 8. Molecular configuration of tetrachloro-*p*-benzoquinone.3. *Tetrachloro-hydroquinone*,  $C_6Cl_4(OH)_2$ 

The crystal structure of tetrachloro-hydroquinone has been determined by Sakurai (1962):  $a = 8.214$ ,  $b = 4.843$ ,  $c = 12.441$  Å,  $\beta = 123^\circ 49'$ ;  $Z = 2$ ; space group  $P2_1/c$ . The molecule is planar, its plane making an angle of  $44.8^\circ$  with the (010) plane.

The crystals were grown by the slow evaporation of alcoholic solution. They were light brown in colour and of parallelepipedal shape elongated along  $[010]$ ,  $(10\bar{4})$  being the plate face. Three different crystals were used of weights varying between 18.8 and 24.2 mg and of average dimensions  $9 \times 2.2 \times 0.6 \text{ mm}^3$ .

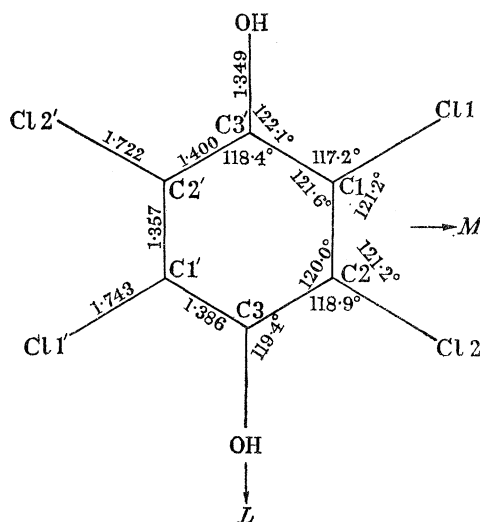


FIGURE 9. Molecular configuration of tetrachloro-hydroquinone.

The magnetic anisotropies are:

$$\chi_1 - \chi_2 = 25.7, \quad \chi_2 - \chi_3 = 0.2, \quad \chi_1 - \chi_3 = 25.9;$$

$$\theta \text{ (angle between } \chi_1 \text{ and } [100], \text{ positive in obtuse } \beta)$$

$$= +29.9^\circ \text{ (obs.)}, \quad +31.8 \text{ (calc.)}.$$

Pascal's additive law gives the mean susceptibility  $\bar{\chi}_M = -120.7$ , hence the crystal susceptibilities are:

$$\chi_1 = -103.5, \quad \chi_2 = -129.2, \quad \chi_3 = -129.4.$$

The direction cosines of the molecular axes referred to the orthogonal axes  $a'$ ,  $b$  and  $c$  were given by Sakurai. These are:

	$a'$	$b$	$c$
$L$	0.982	-0.108	0.155
$M$	-0.201	-0.694	0.691
$N$	-0.035	0.710	0.703

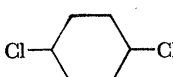
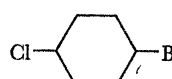
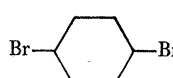
The molecular susceptibilities are shown in table 8.

TABLE 8

	$K_L$	$K_M$	$K_N$	$\Delta K$
<i>p</i> -benzoquinone (Lonsdale & Krishnan 1936)	-24.3	-28.7	-67.1	40.6
<i>p</i> -benzoquinone (present work)	-23.0	-27.0	-65.2	40.2
tetrachloro- <i>p</i> -benzoquinone (chloranil) (present work)	-84.4	-98.5	-138.5	47.0
tetrachloro-hydroquinone (present work)	-103.0	-114.3	-144.9	36.3

From all these results, a marked reduction of  $\Delta K$  on substitution, implying a stabilization of the double bonds, is observed. Compare the marked reduction for the hydroquinone with that for phloroglucinol (p. 371).

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4. *p*-Dichlorobenzene,  $C_6H_4Cl_2$  
5. *p*-Bromochlorobenzene,  $C_6H_4ClBr$  
6. *p*-Dibromobenzene,  $C_6H_4Br_2$  

The crystal structures of *p*-dichlorobenzene, *p*-bromochlorobenzene and *p*-dibromobenzene are isomorphous. The structures have been determined, *p*-dichlorobenzene by Croatto, Bezzi & Bua (1952), *p*-bromochlorobenzene by Klug (1947) and *p*-dibromobenzene by Bezzi & Croatto (1942). The cell dimensions are:

<i>p</i> -dichlorobenzene	$a = 14.80, b = 5.78, c = 3.99 \text{ \AA},$ $\beta = 113^\circ; Z = 2; P2_1/a;$
<i>p</i> -bromochlorobenzene	$a = 15.20, b = 5.86, c = 4.11 \text{ \AA},$ $\beta = 113^\circ 12'; Z = 2; P2_1/a;$
<i>p</i> -dibromobenzene	$a = 15.36, b = 5.75, c = 4.10 \text{ \AA},$ $\beta = 112^\circ 38'; Z = 2; P2_1/a.$

The molecules are planar and centro-symmetrical (disordered in the case of  $C_6H_4ClBr$ ), the benzene ring being a regular hexagon within the limits of experimental error given. In *p*-bromochlorobenzene  $C-X = 1.77 \text{ \AA}$ , intermediate between  $C-Cl$  and  $C-Br$ .

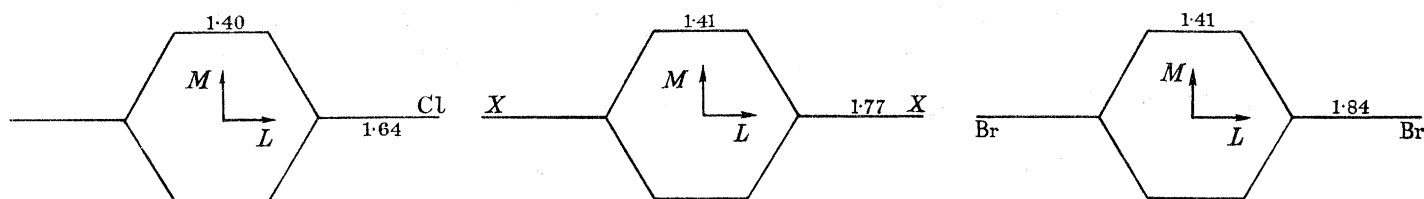


FIGURE 10. Bond lengths ( $\text{\AA}$ ) in the three molecules, whose benzene rings are regular hexagons within the limits of experimental error.

Acetone and ethyl alcohol were used to crystallize *p*-dichlorobenzene. The other two compounds were crystallized from ethyl alcohol. The crystals are prisms, platy on (100) and elongated along [001]. In some crystals of *p*-dichlorobenzene (001) was the plate face.

The crystals of all three compounds were very volatile; *p*-dichlorobenzene more so than *p*-bromochlorobenzene which also exceeds *p*-dibromobenzene. To mitigate this difficulty the crystals were weighed just before and just after each experiment and the mean of the two weights was used. Four crystals of *p*-dichlorobenzene (of weights between 8.3 and 60.1 mg), three crystals of *p*-dibromobenzene (17.7 to 25.9 mg) and four crystals of *p*-bromochlorobenzene (9.1 to 41.7 mg) were measured. The magnetic anisotropies of the three compounds together with those found by Krishnan & Banerjee (1935) for *p*-dichlorobenzene and *p*-dibromobenzene are shown in table 9.

The mean susceptibility of *p*-dichlorobenzene is  $\bar{\chi}_M = -82.93$  (French 1945) and that of dibromobenzene is  $\bar{\chi}_M = -101.4$  (Bose 1936), but the mean susceptibility of bromochlorobenzene is not reported; it is taken as the mean of the other two values;  $\bar{\chi}_M = -92.16$ . The

values of the resulting crystal susceptibilities of the three compounds are shown in table 10 together with those found for *p*-dichlorobenzene and *p*-dibromobenzene by Krishnan & Banerjee (1935) who measured the absolute susceptibility along a known crystal direction in each of the two compounds.

TABLE 9

	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$	$\chi_3 - \chi_2$	$\psi$ ( $\chi_1 \wedge [001]$ , positive in obtuse $\beta$ )	
<i>p</i> -dichlorobenzene { (Krishnan <i>et al.</i> )	36.2	9.9	—	+86.9	
(present work)	36.4	10.3	26.1	+87.4 (obs.)	+87.0 (calc.)
<i>p</i> -bromochlorobenzene	35.0	9.7	25.3	+87.2 (obs.)	+86.9 (calc.)
<i>p</i> -dibromobenzene { (Krishnan <i>et al.</i> )	32.2	9.1	—	+87.0	
(present work)	33.7	9.4	24.3	+87.1 (obs.)	+86.9 (calc.)

TABLE 10

	present work			Krishnan & Banerjee		
	$\chi_1$	$\chi_2$	$\chi_3$	$\chi_1$	$\chi_2$	$\chi_3$
<i>p</i> -dichlorobenzene	-67.36	-103.76	-77.66	-70.0	-106.2	-79.9
<i>p</i> -bromochlorobenzene	-77.3	-112.3	-86.9	—	—	—
<i>p</i> -dibromobenzene	-87.0	-120.7	-96.4	-86.3	-118.5	-95.4

The atomic co-ordinates for the three compounds given in their structure determinations were used to calculate the direction cosines of the molecular axes of each compound. Differences between the corresponding direction cosines, which caused unexpected differences in the values of  $\Delta K$ , are probably due to inaccuracies in the structure determinations, perhaps because of the rapid evaporation of the crystals. The mean of the corresponding direction cosines of *p*-dichlorobenzene and *p*-dibromobenzene gave reasonable results. These, referred to the orthogonal axes *a*, *b* and *c'*, are:

<i>p</i> -dichlorobenzene			<i>p</i> -dibromobenzene				
	<i>a</i>	<i>b</i>	<i>c'</i>		<i>a</i>	<i>b</i>	<i>c'</i>
<i>L</i>	0.7898	-0.6116	0.0474	<i>L</i>	0.8092	-0.5871	-0.0213
<i>M</i>	0.4417	0.6206	0.6478	<i>M</i>	0.4752	0.6328	0.6112
<i>N</i>	0.4255	0.4909	-0.7602	<i>N</i>	0.3527	0.4993	-0.7915

mean direction cosines			
	<i>a</i>	<i>b</i>	<i>c'</i>
<i>L</i>	0.7995	-0.5994	0.0131
<i>M</i>	0.4585	0.6267	0.6295
<i>N</i>	0.3891	0.4951	-0.7759

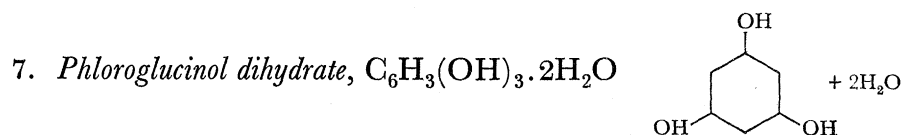
These give the three sets of molecular susceptibilities shown in table 11.

TABLE 11

	$K_L$	$K_M$	$K_N$	$\Delta K$
<i>p</i> -dichlorobenzene	-78.3	-50.3	-120.2	55.9
<i>p</i> -bromochlorobenzene	-87.6	-59.9	-129.0	55.2
<i>p</i> -dibromobenzene	-97.1	-70.5	-136.7	52.9

Thus para-substitution decreases  $\Delta K$  the molecular magnetic anisotropy.

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The crystal structure of phloroglucinol dihydrate has been determined by Wallwork & Powell (1957). The crystal is orthorhombic:  $a = 6.73$ ,  $b = 13.58$ ,  $c = 8.09$  Å;  $Z = 4$ ; space group  $Pnma$ . The molecule is planar and has mirror-symmetry across (010). The whole structure consists of layers parallel to (100).

An aqueous solution gave good rhombic plates with (010) as the plate face, and [100] parallel to the shorter diagonal. Four crystals of weights between 3.1 and 52.3 mg and dimensions between  $3 \times 2 \times 0.6$  and  $7.5 \times 6 \times 2$  mm<sup>3</sup> were used in the magnetic measurements.

The magnetic data are shown in table 12 together with those found by Banerjee (1938).

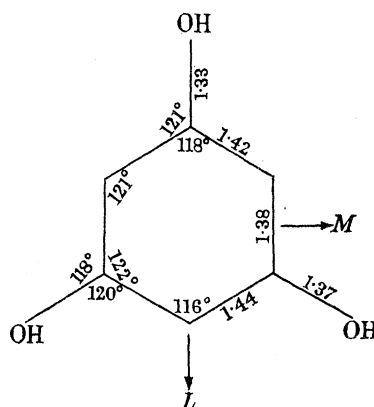


FIGURE 11. Bond lengths (Å) and angles in phloroglucinol dihydrate.

TABLE 12

	$\chi_c - \chi_a$	$\chi_b - \chi_a$	$\chi_c - \chi_b$	$\chi_a$	$\chi_b$	$\chi_c$
Banerjee's data	37.0	36.0	—	-120.1	-84.1	-83.1
present work	37.1	36.1	1.1	-120.2	-84.1	-83.1
						(measured)
						(assumed)

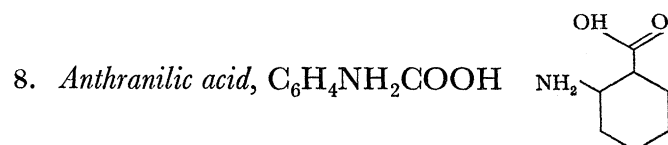
The direction cosines of the molecular axes are:

	$a$	$b$	$c$
$L$	0.016	0	~1
$M$	0	1	0
$N$	~1	0	0.016

Hence the molecular susceptibilities are:

$$K_L = -83.1, \quad K_M = -84.1, \quad K_N = -120.2, \quad \Delta K = 36.6.$$

Symmetrical 1:3:5 substitution thus reduces the anisotropy markedly.



The crystal structure of anthranilic acid has been determined by Dr C. J. Brown (unpublished). The crystal is orthorhombic:  $a = 12.83$ ,  $b = 10.77$ ,  $c = 9.28$  Å;  $Z = 8$ ; space group  $Pcn2$ .



The benzene rings are not quite planar, having carbon atoms alternately 0.015 Å above and below the mean plane of the ring. The bond lengths show considerable deviation from regularity, for which the most satisfactory explanation is that the anthranilic acid molecules are linked together in pairs, one of which is a neutral molecule and one zwitterion. Analysis of the thermal vibrations indicates that they are not particularly anisotropic. Corrections to the bond lengths for thermal libration do not amount to more than 0.005 Å on average. The total bond orders in the two molecules come to 9.3 and 9.1 instead of the 9.0 which would be expected for a normal benzene ring. The angles between the planes of the benzene rings and of the carboxyl groups are 6.85° for molecule *A* and 2.3° for molecule *B*.

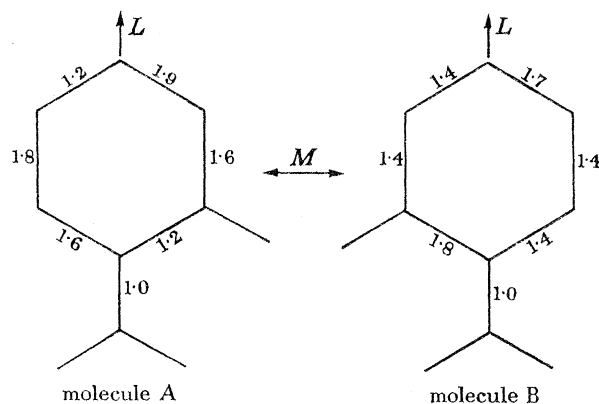


FIGURE 12. Bond-orders in the two independent anthranilic acid molecules. (C. J. Brown, private communication.)

The crystals used in the present work were kindly supplied by Dr Brown. They were crystallized from ethanol in the form of prismatic plates with (100) as the plate face and (010) developed.

The magnetic anisotropies are:

$$\chi_b - \chi_a = 53.2, \quad \chi_c - \chi_a = 47.2, \quad \chi_b - \chi_c = 6.1.$$

Pascal's additive value for the mean susceptibility  $\bar{\chi}_M = -79.0$ . Hence

$$\chi_a = -112.5, \quad \chi_b = -59.3, \quad \chi_c = -65.3.$$

The atomic co-ordinates and the planes of the two independent molecules were kindly supplied by Dr Brown before their publication. The direction cosines for the two independent molecules are:

	molecule <i>A</i>			molecule <i>B</i>		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
<i>L</i>	0.3109	-0.2934	0.9038	-0.2897	0.3713	0.8823
<i>M</i>	0.1865	0.9470	0.2624	0.2138	0.9295	-0.3014
<i>N</i>	-0.9304	0.0837	0.3568	0.9356	-0.1045	0.3388

giving *mean* molecular susceptibilities:

$$K_L = -57.7, \quad K_M = -58.8, \quad K_N = -120.5, \quad \Delta K = 62.5.$$

This  $\Delta K$  is larger than the anisotropy 59.7 of unsubstituted benzene (Hoarau *et al.* 1956). Taking  $\Delta K = 8.8$  for the carboxyl group as found from ammonium hydrogen *d*-tartrate

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(p. 381) and allowing for the angles between the benzene rings and the carboxyl groups in the two molecules, the anisotropy of the anthranilic acid molecule less the carboxyl group would be  $\Delta K = 53.5$  which is less than that of unsubstituted benzene.



The crystal structure of acetanilide was determined by Brown & Corbridge (1954). The crystal is orthorhombic bipyramidal:  $a = 19.640$ ,  $b = 9.483$ ,  $c = 7.979 \text{ \AA}$ ;  $Z = 8$ ; space group  $Pbca$ .

A single molecule lies approximately in two planes, one containing the aniline portion and the other the acetyl group, inclined to each other at  $37.9^\circ$ . Crystalline acetanilide

exists in the amido  $\begin{array}{c} \text{O} \\ \parallel \\ \text{—N—C—} \\ | \\ \text{H} \end{array}$  and not the imidol  $\begin{array}{c} \text{OH} \\ | \\ \text{—N=C—} \end{array}$  form.

Large well-defined crystals were grown from ethyl alcohol solution with (100) as the plate face and (001) developed. The crystals used in the magnetic measurements were of weights varying between 25.7 and 49.0 mg and of average dimensions  $6.2 \times 4.5 \times 1.3 \text{ mm}^3$ . The magnetic anisotropies are:

$$\chi_a - \chi_c = 35.6, \quad \chi_a - \chi_b = 9.0, \quad \chi_b - \chi_c = 26.6.$$

Pascal's additive law gives  $\bar{\chi}_M = -72.24$ , thus the crystal susceptibilities are:

$$\chi_a = -57.4, \quad \chi_b = -66.4, \quad \chi_c = -93.0.$$

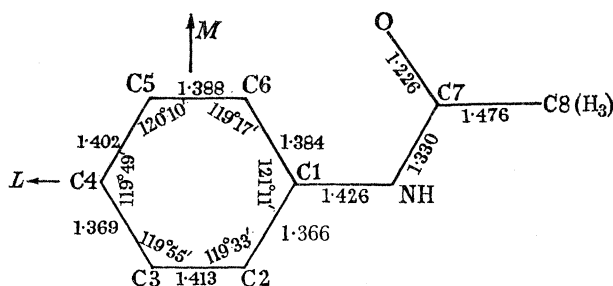


FIGURE 13. Bond lengths ( $\text{\AA}$ ) and angles in acetanilide.

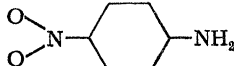
The direction cosines of the axes of the aniline nucleus are:

		$a$	$b$	$c$
(along C4—C1—N)	$L$	0.9289	-0.1404	0.3428
(parallel C3—C5 or C6—C2)	$M$	0.3073	0.8211	-0.4811
	$N$	0.2074	-0.5512	-0.8082

The molecular susceptibilities are therefore:

$$K_L = -55.8, \quad K_M = -44.3, \quad K_N = -116.6, \quad \Delta K = 66.55.$$

The anisotropy is surprising, since the acetyl group is twisted out of the plane of the benzene ring by nearly  $38^\circ$ . The structure determination did not include thermal vibration anisotropy, but gave a residual  $R = 11.2\%$  for 1513 reflexions, not including unobserved values.

10. 4-(*p*-)Nitroaniline,  $C_6H_4(NO_2) \cdot NH_2$  

The crystal structure of 4-(*p*-)nitroaniline has been determined by Trueblood, Goldish & Donohue (1961).  $a = 12.336$ ,  $b = 6.07$ ,  $c = 8.592 \text{ \AA}$ ,  $\beta = 91.45^\circ$ ;  $Z = 4$ ; space group  $P2_1/n$ .

The aromatic ring is planar and at  $1.9^\circ$  with the plane passing through C4 and the nitro group, and at  $16^\circ$  with the plane passing through C1 and the amino group.

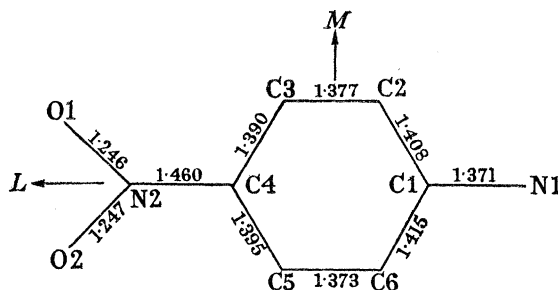


FIGURE 14. Bond lengths ( $\text{\AA}$ ) in the 4-(*p*-) nitroaniline molecule.

Crystals of 4-nitroaniline were obtained as thin, bright yellow plates by slow evaporation of a chloroform solution. They are very fragile and cleave easily parallel to (101). Four crystals were used in the magnetic measurements having weights ranging between 6.3 and 17 mg and of average thickness 0.5 mm.

The magnetic anisotropies are:

$$\chi_1 - \chi_2 = 44.8, \quad \chi_1 - \chi_3 = 4.9, \quad \chi_3 - \chi_2 = 39.9;$$

$$\theta \text{ (angle between } \chi_1 \text{ and } [100], \text{ positive in obtuse } \beta)$$

$$= -47.0^\circ \text{ (obs.)}, \quad -46.0 \text{ (calc.)}.$$

The mean susceptibility of 4-nitroaniline had been determined several times:

$$\bar{\chi}_M = -66.5 \text{ (Garssen 1933),}$$

$$-66.85 \text{ (Baddar \& Sugden 1950),}$$

$$-66.43 \text{ (Mikhail 1953).}$$

Pascal's additive value from experimental values of nitrobenzene, benzene and aniline (Pascal 1911 *b, c*) is  $\bar{\chi}_M = -68.93$ . Using  $\bar{\chi}_M = -66.6$ , the crystal susceptibilities are:

$$\chi_1 = -50.0, \quad \chi_2 = -94.8, \quad \chi_3 = -54.9.$$

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

	$a'$	$b$	$c$
$L$	0.7501	-0.4334	-0.4994
$M$	0.0730	0.8030	-0.5915
$N$	0.6563	0.4077	0.6348

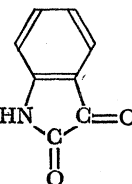
Thus the molecular susceptibilities are:

$$K_L = -52.0, \quad K_M = -43.0, \quad K_N = -104.8, \quad \Delta K = 57.3.$$

## DIAMAGNETIC ANISOTROPY OF SOME ORGANIC MOLECULES 375

The anisotropy is of about the same value as that of benzene (compare the high value for anthranilic acid, and the low value for *p*-benzoquinone). Trueblood *et al.* found significantly short C2—C3 and C5—C6 bonds parallel to *L*, suggesting a minor contribution from a quinoid resonance form to the structure of the molecule. They also found a large ( $14^\circ$  r.m.s. amplitude) torsional oscillation of the nitro-group.

11. *Isatin* (2,3-indolinedione; *isatic acid lactam*),  $\text{CH}:\text{CH}:\text{C} \text{---} \text{CO}$   
 $\text{CH}:\text{CH}:\text{C} \cdot \text{NH} \cdot \text{CO}$



Goldschmidt & Llewellyn (1950) determined the structure of isatin and gave the following cell dimensions:  $a = 6.19$ ,  $b = 14.46$ ,  $c = 7.17 \text{ \AA}$ ,  $\beta = 94^\circ 49'$ ;  $Z = 4$ ; space group  $P2_1/c$ . The molecule is planar.

The crystals used in the present work were crystallized from acetone in the form of prismatic needles elongated along [001] with (010) as the predominant face. Four different crystals of weights differing between 6.1 and 17.1 mg and of average dimensions  $7 \times 1.3 \times 0.8 \text{ mm}^3$  were used.

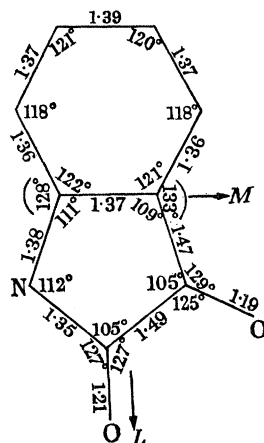


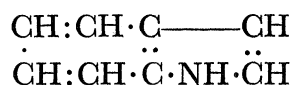
FIGURE 15. Bond lengths ( $\text{\AA}$ ) and angles in isatin.

The magnetic anisotropies are:

$$\chi_1 - \chi_2 = 66.4, \quad \chi_3 - \chi_2 = 61.7, \quad \chi_1 - \chi_3 = 4.7;$$

$$\theta \text{ (angle between } \chi_1 \text{ and } [100], \text{ positive in obtuse } \beta) = 21.5^\circ.$$

Pascal's additivity value for the mean susceptibility using Pacault's (1946) experimental value  $\bar{\chi}_M = -85.0$  for indole



is  $\bar{\chi}_M = -81.15$ .

Thus the crystal susceptibilities are:

$$\chi_1 = -57.45, \quad \chi_2 = -123.85, \quad \chi_3 = -62.15.$$

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

	$a$	$b$	$c'$
$L$	0.1814	-0.9815	0.0611
$M$	0.9095	0.1911	0.3694
$N$	0.3736	0.0123	-0.9261

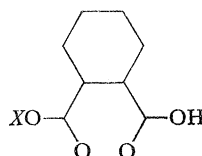
Thus the molecular susceptibilities are:

$$K_L = -62.0, \quad K_M = -57.3, \quad K_N = -124.2, \quad \Delta K = 64.6.$$

12. *Sodium acid phthalate*,  $C_6H_4(COOH)(COONa)$

and

13. *Potassium acid phthalate*,  $C_6H_4(COOH)(COOK)$



The cell dimensions and space groups of several acid phthalates including sodium and potassium phthalates and the crystal structure of ammonium acid phthalate were determined by Okaya & Pepinsky (1957). The cell dimensions are:

	<i>a</i>	<i>b</i>	<i>c</i>	<i>Z</i>	space group
sodium acid phthalate	6.76	9.31	26.42 Å	8	<i>B2ab</i>
ammonium acid phthalate	6.40	10.23	26.14	8	<i>Pcab</i>
potassium acid phthalate	6.47	9.61	13.26	4	<i>P2<sub>1</sub>2<sub>1</sub>2</i>

The unit-cell dimensions appear to be related although the structures are not isomorphous.

In ammonium acid phthalate the benzene ring and the two carbon atoms of the carboxyl groups lie in a plane, but the planes of the two carboxyl groups are inclined to the benzene ring by angles of  $21^\circ$  and  $65^\circ$ . The benzene ring is slightly distorted from a regular hexagon, with C—C distances ranging from 1.35 to 1.40 Å.

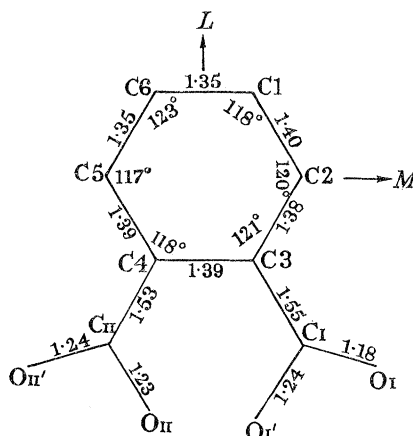


FIGURE 16. Bond distances and angles in the phthalic ion, as found in the crystal structure of the  $NH_4$  acid salt.

No ammonium acid phthalate was available. Sodium and potassium acid phthalate crystals were obtained from their aqueous solutions with (001) as the plate face, the sodium acid phthalate crystals being elongated along [100]. Four crystals of sodium acid phthalate (13.0 to 46.8 mg) and three crystals of potassium acid phthalate (18.5 to 22.9 mg) were used in the magnetic measurements. The measured magnetic anisotropies are:

	$\chi_b - \chi_a$	$\chi_c - \chi_a$	$\chi_c - \chi_b$
sodium acid phthalate	36.3	40.3	4.0
potassium acid phthalate	35.6	41.7	6.0

The mean susceptibilities of sodium and potassium acid phthalate by Pascal's additive law using the experimental value of phthalic acid  $\bar{\chi}_M = -83.6$  (French 1945) are:

$$\bar{\chi}_M = -89.9 \text{ for sodium acid phthalate} \quad \text{and} \quad \bar{\chi}_M = -99.2 \text{ for potassium acid phthalate.}$$

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Thus the crystal susceptibilities are:

	$\chi_a$	$\chi_b$	$\chi_c$
sodium acid phthalate	-115.4	-79.1	-75.1
potassium acid phthalate	-124.95	-89.35	-83.25

The direction cosines of the three molecular axes of ammonium acid phthalate were calculated from the equation of the plane of the benzene ring and the atomic co-ordinates given by Okaya & Pepinsky. These direction cosines are:

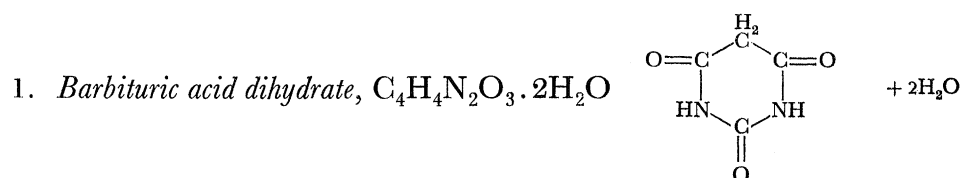
	$a$	$b$	$c$
$L$	0.2382	0.4578	-0.8565
$M$	0.4873	-0.8192	-0.3024
$N$	0.8368	0.3390	0.4300

Using these direction cosines for both sodium and potassium acid phthalates, the resulting molecular susceptibilities are:

	$K_L$	$K_M$	$K_N$	$\Delta K$
sodium acid phthalate	-59.1	-76.5	-134.1	66.3
potassium acid phthalate	-66.4	-87.9	-143.3	66.1

The plausibility of these results imply that the molecules of Na and K acid phthalates probably do have orientations very close to those of the ammonium derivative.

## ALIPHATIC COMPOUNDS



The crystal structure of barbituric acid dihydrate was determined by Jeffrey, Ghose & Warwick (1961). The crystal is orthorhombic;  $a = 12.74$ ,  $b = 6.24$ ,  $c = 8.89$  Å;  $Z = 4$ ; space group  $Pnma$ .

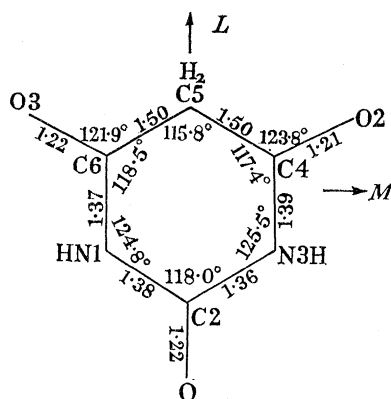


FIGURE 17. Bond lengths (Å) and angles in the barbituric acid molecule, crystallized as a dihydrate.

According to Jeffrey *et al.* barbituric acid dihydrate crystals have a hydrogen-bonded layer structure in which the barbituric acid and water molecules lie on the mirror planes of the space group  $Pnma$ , the normals  $N$  being along  $[010]$ . The barbituric acid is in the tri-keto form and within the accuracy of analysis, has  $mm$  symmetry. The water molecules

are hydrogen-bonded in pairs and their hydrogen-bond combination is unusual in that it is planar and approximately trigonal.

Very beautiful shiny crystals of barbituric acid dihydrate were obtained from aqueous solution. They are prismatic with (100) and (010) well developed. As the crystals decompose slowly in air to become white and opaque after one or two days, the magnetic measurements were carried out on the day of selecting them out of solution. Two crystals weighing 24.1 and 51.7 mg were used in the measurements. The magnetic anisotropies are:

$$\chi_a - \chi_b = 17.5, \quad \chi_c - \chi_b = 18.4, \quad \chi_c - \chi_a = 1.2.$$

The mean susceptibility of barbituric acid dihydrate is  $\bar{\chi}_M = -78.6$  (Sato 1956). Thus the crystal susceptibilities are:

$$\chi_a = -73.1, \quad \chi_b = -90.6, \quad \chi_c = -72.2.$$

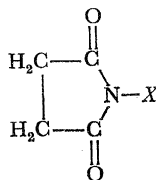
The direction cosines of the molecular axes  $L$ ,  $M$ ,  $N$  are:

	$a$	$b$	$c$
$L$	0.7650	0	0.6439
$M$	-0.6440	0	0.7651
$N$	0	1	0

This gives molecular susceptibilities:

$$K_L = -75.3, \quad K_M = -70.0, \quad K_N = -90.6, \quad \Delta K = 17.95.$$

2. *N*-Chloro-succinimide,  $C_4H_4O_2NCl$
- and
3. *N*-Bromo-succinimide,  $C_4H_4O_2NBr$



The crystal structure of *N*-chloro-succinimide and the unit cell dimensions and space-group of *N*-bromo-succinimide were determined by R. N. Brown (1961). The two crystals form an isomorphous pair, of unit-cell dimensions:

$$\textit{N}$$
-chloro-succinimide:  $a = 6.41, \quad b = 7.11, \quad c = 11.69 \text{ \AA};$

$$Z = 4; \quad \text{space group } P2_12_12_1.$$

$$\textit{N}$$
-bromo-succinimide:  $a = 6.48, \quad b = 7.25, \quad c = 11.86 \text{ \AA};$

$$Z = 4; \quad \text{space group } P2_12_12_1.$$

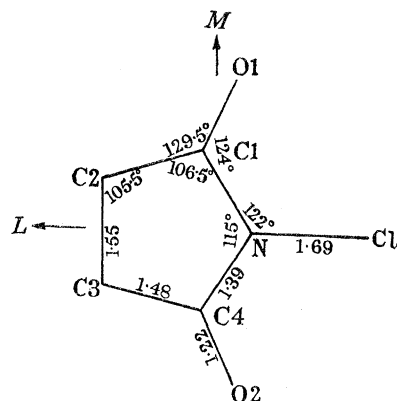


FIGURE 18. Averaged symmetrical dimensions of *N*-chloro-succinimide.

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The molecular bond lengths and angles of *N*-chloro-succinimide are assumed to be bilaterally symmetrical. The molecule is planar.

*N*-Chloro-succinimide crystals were obtained from solution in benzene by slow evaporation and cooling from about 40 °C. They are fine prismatic large plates with (001) as the plate face and (110), (010) and (011) well developed. One crystal only having the above habit was obtained from *N*-bromo-succinimide solution in benzene under the same conditions as those of *N*-chloro-succinimide. Other crystals of *N*-bromo-succinimide were also obtained from the same solution having a somewhat complicated habit. The two crystal habits were described by Steff (1915). Two crystals of *N*-chloro-succinimide weighing 14.4 and 65.5 mg and the crystal of *N*-bromo-succinimide which weighs 47.5 mg were used in the magnetic measurements. The magnetic anisotropies of the two compounds are:

	$\chi_a - \chi_b$	$\chi_c - \chi_b$	$\chi_a - \chi_c$
<i>N</i> -chloro-succinimide	12.91	9.96	3.03
<i>N</i> -bromo-succinimide	13.07	9.035	4.035

The *International critical tables* give the specific susceptibility of succinimide  $C_4H_5NO_2$  (mol. wt. = 99.047) as  $\chi = -0.477$ , thus the gram-molecular susceptibility of succinimide  $\bar{\chi}_M = -47.24$ . Pascal's additive values using this value are:

$$\textit{N-chloro-succinimide: } \bar{\chi}_M = -64.38$$

$$\textit{N-bromo-succinimide: } \bar{\chi}_M = -74.96.$$

Thus the crystal susceptibilities of the two compounds are:

	$\chi_a$	$\chi_b$	$\chi_c$
<i>N</i> -chloro-succinimide	-59.1	-72.6	-62.1
<i>N</i> -bromo-succinimide	-69.3	-82.3	-72.3

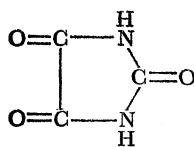
The direction cosines of the molecular axes of *N*-chloro-succinimide are:

	<i>a</i>	<i>b</i>	<i>c</i>
<i>L</i>	0.3569	0.2612	-0.8967
<i>M</i>	0.8062	0.3987	0.4370
<i>N</i>	-0.4732	0.8783	0.0675

Using these direction cosines for both *N*-chloro- and *N*-bromo-succinimide, the molecular susceptibilities of the two compounds are:

	$K_L$	$K_M$	$K_N$	$\Delta K$
<i>N</i> -chloro-succinimide	-64.50	-51.76	-76.96	18.83
<i>N</i> -bromo-succinimide	-76.03	-61.57	-87.31	18.51

#### 4. *Parabanic acid*, $CO(NH \cdot CO)_2$



The crystal structure of parabanic acid has been determined by Davies & Blum (1955). The cell dimensions are:  $a = 10.685$ ,  $b = 8.194$ ,  $c = 5.054 \text{ \AA}$ ;  $\beta = 92^\circ 44'$ ;  $Z = 4$ ; space group  $P2_1/n$ .



There are two planes each containing six atoms (the five ring atoms and one oxygen atom) which can be defined in the molecule, and the atom O1 is displaced by a significantly large distance from each of these planes.

Tabular crystals elongated along [001] were obtained from the aqueous solution of parabanic acid with (100) as the plate face and (010) developed. (010) is the cleavage plane. Six crystals of weights between 3.6 and 30.6 mg and of average thickness 0.4 mm were used in the magnetic measurements. The magnetic anisotropies of parabanic acid crystal are:

$$\begin{aligned}\chi_1 - \chi_2 &= 8.34, & \chi_1 - \chi_3 &= 15.22, & \chi_2 - \chi_3 &= 6.88; \\ \psi \text{ (angle between } \chi_1 \text{ and [001], positive in obtuse } \beta) \\ &= -76.6 \text{ (obs.)}, & & -76.55 \text{ (calc.)}.\end{aligned}$$

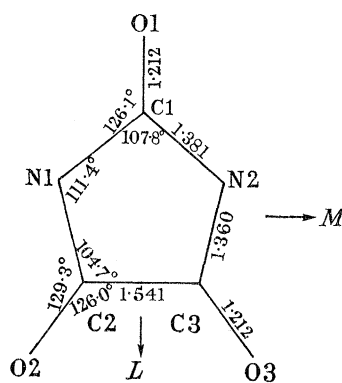


FIGURE 19. Bond lengths (Å) and angles in parabanic acid.

Pascal's additive value for the mean susceptibility of parabanic acid, calculated from  $\bar{\chi}_M = -47.24$  for succinimide, which is also a five-membered ring, is  $\bar{\chi}_M = -35.34$ . Thus the crystal susceptibilities are:

$$\chi_1 = -27.5, \quad \chi_2 = -35.8, \quad \chi_3 = -42.7.$$

The direction cosines of the three axes of parabanic acid molecule, referred to the orthogonal axes  $a$ ,  $b$  and  $c'$  are:

	$a$	$b$	$c'$
$L$	0.0547	0.5758	-0.8158
$M$	-0.9904	0.1191	0.0176
$N$	0.1076	0.8094	0.5768

Thus the molecular susceptibilities are:

$$K_L = -28.6, \quad K_M = -27.5, \quad K_N = -49.9, \quad \Delta K = 21.9.$$

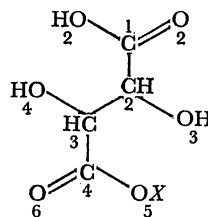
Both  $N$ -chloro-succinimide (or  $N$ -bromo-succinimide) and parabanic acid contain a five-membered ring and  $\text{>C=O}$  double bonds. There are three  $\text{>C=O}$  double bonds in parabanic acid and two in  $N$ -chloro-succinimide. The difference in their molecular anisotropy is  $3.1 \times 10^{-6}$ . This agrees well with the anisotropy found for the chloro-acetamide molecule (p. 383)  $\Delta K = 3.15 \times 10^{-6}$ , which may be largely due to the  $\text{>C=O}$  double bond.

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5. Ammonium hydrogen *d*-tartrate,  $C_4H_4O_6(NH_4) \cdot H$

and

6. Potassium hydrogen *d*-tartrate,  $C_4H_4O_6 \cdot K \cdot H$



The crystal structure of ammonium hydrogen *d*-tartrate and the cell dimensions and space group of potassium hydrogen *d*-tartrate were determined by van Bommel & Bijvoet (1958). The cell dimensions are:

ammonium hydrogen *d*-tartrate:  $a = 7.648$ ,  $b = 11.066$ ,  $c = 7.843 \text{ \AA}$ ;

$Z = 4$ ; space group  $P2_12_12_1$ ;

potassium hydrogen *d*-tartrate:  $a = 7.64$ ,  $b = 10.62$ ,  $c = 7.75 \text{ \AA}$ ;

$Z = 4$ ; space group  $P2_12_12_1$ .

As in the crystal structures of all tartrates so far examined, the carbon chain and the oxygen and carbon atoms of each half —CHOH—COOH of the tartaric acid molecule are nearly planar. From the anisotropic vibration parameters it appears that the oxygen atoms of the carboxyl groups oscillate around the C1—C2 and C3—C4 axes, respectively. The structure is also in agreement with the fact that in aliphatic carboxyl groups the only resonance is between C=O and C—O.

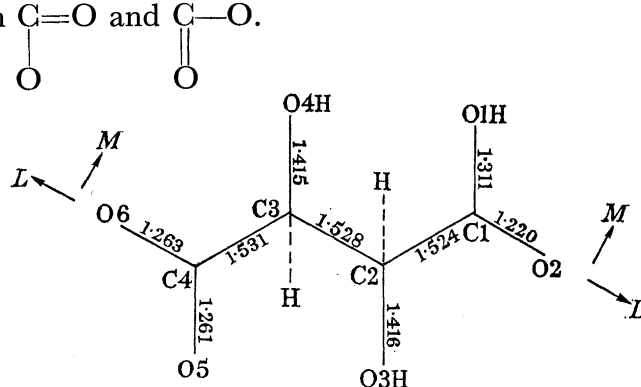


FIGURE 20. Bond lengths ( $\text{\AA}$ ) in the tartaric acid ion.

Large fine crystals of the ammonium salt and small crystals of the potassium salt were obtained from the solutions of the two salts in water and tartaric acid; (after the salt is dissolved in water tartaric acid is added). Both crystals are prismatic plates with (010) as the plate face and (011) developed only in the ammonium salt crystals.

One crystal of ammonium hydrogen *d*-tartrate weighing 81.0 mg and three crystals of potassium hydrogen *d*-tartrate of weights between 5.7 and 6.3 mg were used in the magnetic measurements. The magnetic anisotropies are:

	$\chi_a - \chi_b$	$\chi_a - \chi_c$	$\chi_c - \chi_b$
ammonium hydrogen <i>d</i> -tartrate	7.68	6.19	1.47
potassium hydrogen <i>d</i> -tartrate	7.69	6.15	1.56

Pascal's additivity values for the mean susceptibility of both ammonium and potassium hydrogen *d*-tartrates obtained from the experimental value of tartaric acid  $C_4H_6O_6$ ,  $\bar{\chi}_M = -67.5$  (Joussot-Dubien *et al.* 1956) are:

ammonium hydrogen *d*-tartrate:  $\bar{\chi}_M = -81.85$ ;  
 potassium hydrogen *d*-tartrate:  $\bar{\chi}_M = -83.07$ .

Thus the crystal susceptibilities of the two isomorphous crystals are:

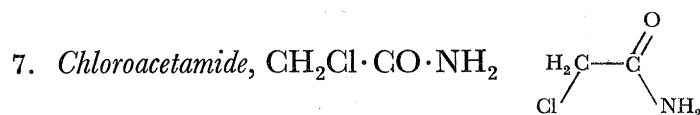
	$\chi_a$	$\chi_b$	$\chi_c$
ammonium hydrogen <i>d</i> -tartrate	-77.23	-84.91	-83.42
potassium hydrogen <i>d</i> -tartrate	-78.46	-86.15	-84.61

The interesting part of these molecules from the point of view of this work is the carboxyl group which is the only part where resonance may be expected. Thus the direction cosines of the axes *L*, *M*, *N* of each halfmolecule were calculated with *L* along C1—O2 and C4—O6 in the two halves respectively, *N* normal to the plane of the carboxyl group and *M* perpendicular to *L* in that plane. The two sets of direction cosines for the three axes of each of the two half-molecules of ammonium hydrogen *d*-tartrate are:

<i>first half</i>				
		<i>a</i>	<i>b</i>	<i>c</i>
(along C1—O2)	<i>L</i>	0.3773	0.8325	0.4056
	<i>M</i>	0.8684	-0.4702	0.1574
	<i>N</i>	0.3218	0.2929	-0.9005
<i>second half</i>				
		<i>a</i>	<i>b</i>	<i>c</i>
(along C4—C6)	<i>L</i>	0.7324	-0.1655	-0.6605
	<i>M</i>	0.6786	0.0988	0.7278
	<i>N</i>	0.0551	0.9808	-0.1845

With these direction cosines for both ammonium and potassium hydrogen *d*-tartrate molecules, the molecular susceptibilities for only *half* of each molecule are:

	$K_L$	$K_M$	$K_N$	$\Delta K$
ammonium hydrogen <i>d</i> -tartrate	-37.41	-38.57	-46.80	8.81
potassium hydrogen <i>d</i> -tartrate	-38.31	-39.04	-47.26	8.59



The crystal structures of two forms of chloroacetamide have been reported. The first form prepared from ethyl alcohol or from benzene was analyzed by Dejace (1955) who found the following cell dimensions:  $a = 10.26$ ,  $b = 5.15$ ,  $c = 7.41 \text{ \AA}$ ,  $\beta = 98^\circ 49'$ ;  $Z = 4$ ; space group  $P2_1/c$ .

The second form crystallized by the slow evaporation of chloroacetamide aqueous solution was analyzed by Katayama (1956) who found the cell dimensions:  $a = 10.27$ ,  $b = 5.15$ ,  $c = 7.45 \text{ \AA}$ ,  $\beta = 102.5^\circ$ ;  $Z = 4$ ; space group  $P2_1/a$ .

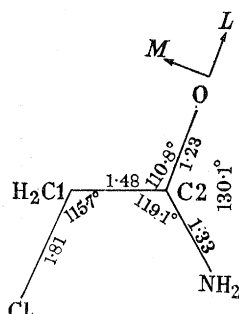


FIGURE 21. Bond lengths ( $\text{\AA}$ ) and angles in the chloroacetamide molecule as found by Dejace.

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The crystals used in the present work were crystallized from ethyl alcohol as flat thin plates elongated along [010] with (100) as the plate face. The axial lengths checked by rotation photographs and the angle  $\beta$  determined from Laue photographs are in good agreement with those found by Dejace. The chloroacetamide molecule as analyzed by Dejace is almost planar.

Four crystals of weights between 2.1 and 10.7 mg and of average thickness 0.4 mm were used in the magnetic measurements. The crystal magnetic anisotropies are:

$$\begin{aligned}\chi_1 - \chi_2 &= 4.73, & \chi_1 - \chi_3 &= 2.045, & \chi_3 - \chi_2 &= 2.685; \\ \psi \text{ (angle between } \chi_1 \text{ and [001], positive in obtuse } \beta) \\ &= -55.5^\circ \text{ (obs.)}, & & -55^\circ 40' \text{ (calc.)}.\end{aligned}$$

Pascal's additive value for the mean susceptibility of chloroacetamide using the experimental value for acetamide  $C_2H_5ON$  ( $\bar{\chi}_M = -34.1$ ) given in the *International critical tables* is  $\bar{\chi}_M = -51.27$ . Thus the crystal susceptibilities are:

$$\chi_1 = -49.01, \quad \chi_2 = -53.74, \quad \chi_3 = -51.06.$$

The direction cosines of the molecular axes  $L, M, N$  ( $L$  along  $C=O$ ,  $N$  normal to the molecular plane and  $M$  perpendicular to both  $L$  and  $N$ ), referred to the orthogonal axes  $a, b$  and  $c'$  are:

		$a$	$b$	$c'$
(along $C=O$ )	$L$	0.3516	-0.9190	-0.1780
	$M$	0.8890	0.3873	-0.2439
	$N$	0.2788	-0.0355	0.9597

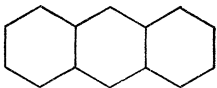
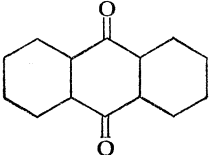
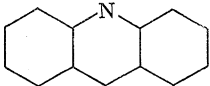
Thus the molecular susceptibilities are:

$$K_L = -51.70, \quad K_M = -48.74, \quad K_N = -53.37, \quad \Delta K = 3.15.$$

It is probable that the magnetic anisotropy  $\Delta K = 3.15$  is due only to the presence of the  $\text{>C=O}$  double bond (compare parabanic acid, p. 380).

## SUMMARY OF RESULTS

*Aromatic compounds*

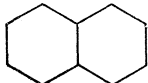
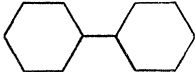
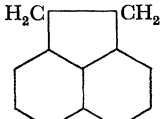
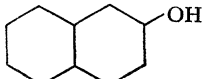
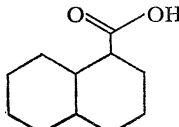
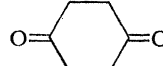
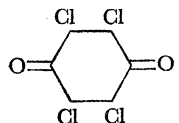
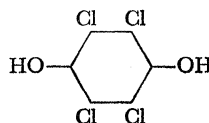


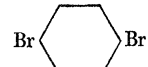
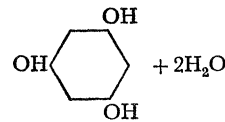
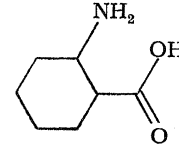
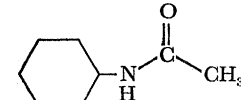
name and formula ( $L \leftrightarrow$ and $M \updownarrow$ in each case)		$K_L$	$K_M$	$K_N$	$\Delta K$
anthracene (Lonsdale & Krishnan 1936)		-75.8	-62.6	-251.6	182.6
anthraquinone		-76.1	-64.5	-217.9	147.6
*acridine		{ † -61.4 ‡ -61.3	-70.5 -70.7	-238.0 -237.9	172.1 171.9

\* See note at end of table.

† One plane.

‡ Two planes.

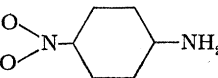
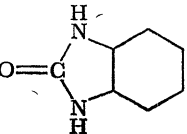
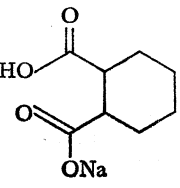
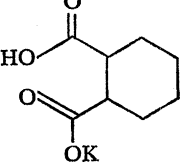
*Aromatic compounds (cont.)*

name and formula ( <i>L</i> ↔ and <i>M</i> ↓ in each case)	$K_L$	$K_M$	$K_N$	$\Delta K$	
naphthalene (Lonsdale & Krishnan 1936) (Lumbroso & Pacault 1957)		-56.1 -54.7	-53.9 -52.6	-169.0 -173.5	114.0 119.8
biphenyl		-67.7	-61.7	-183.8	119.1
acenaphthene		-72.0	-70.5	-185.5	114.25
* $\beta$ -naphthol		-63.9	-51.9	-175.2	117.3
*1-naphthoic acid		-70.5	-58.95	-192.5	127.8
<i>p</i> -benzoquinone (Lonsdale & Krishnan 1936) (present work)		-24.3 -23.0	-28.7 -27.0	-67.1 -65.2	40.6 40.2
tetrachloro- <i>p</i> -benzoquinone (chloranil)		-84.4	-98.5	-138.5	47.0
tetrachloro-hydroquinone		-103.0	-114.3	-144.9	36.3
<i>p</i> -dichlorobenzene		-78.3	-50.3	-120.2	55.9
<i>p</i> -bromochlorobenzene		-87.6	-59.9	-129.0	55.2
<i>p</i> -dibromobenzene		-97.1	-70.5	-136.7	52.9
phloroglucinol dihydrate		-83.1	-84.1	-120.2	36.6
*anthranilic acid		-57.7	-58.8	-120.5	62.25
*acetanilide		-55.8	-44.3	-116.6	66.55

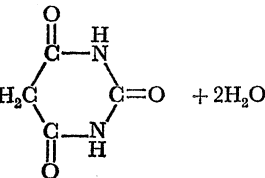
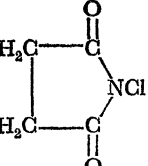
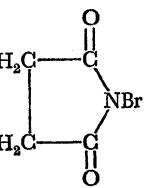
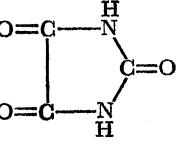
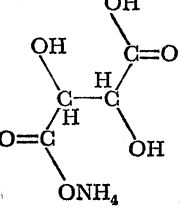
\* See note at end of table.

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*Aromatic compounds (cont.)*

name and formula ( $L \leftrightarrow$ and $M \updownarrow$ in each case)	$K_L$	$K_M$	$K_N$	$\Delta K$
4-( <i>p</i> -)nitroaniline 	-52.0	-43.0	-104.8	57.3
*isatin 	-62.0	-57.3	-124.2	64.6
*sodium acid phthalate 	-59.1	-76.5	-134.1	66.3
*potassium acid phthalate 	-66.4	-87.9	-143.3	66.1

*Aliphatic compounds*

barbituric acid dihydrate 	-75.3	-70.0	-90.6	17.95
<i>N</i> -chloro-succinimide 	-64.50	-51.76	-76.96	18.83
<i>N</i> -bromo-succinimide 	-76.03	-61.57	-87.31	18.51
parabanic acid 	-28.6	-27.5	-49.9	21.9
*ammonium hydrogen <i>d</i> -tartrate 	-37.41	-38.57	-46.80	8.81
	for half the molecule			

\* See note at end of table.

*Aliphatic compounds (cont.)*

name and formula  
( $L \leftrightarrow$  and  $M \updownarrow$  in each case)

*potassium hydrogen <i>d</i> -tartrate		<p>—38·31    —39·04    —47·26    8·59 for half the molecule</p>
*chloroacetamide		<p>—51·70    —48·74    —53·37    3·15</p>

\* *Note.* The majority of molecules dealt with in this paper are planar and of sufficiently high symmetry that  $K_L$ ,  $K_M$ ,  $K_N$  and  $\Delta K$  represent the real mean molecular susceptibilities on principal axes and the real molecular anisotropy. As regards other molecules marked \* in the final summary table which are less symmetrical planar or non-planar molecules the choice of some or all of the molecular axes is arbitrary and thus they are only approximately principal molecular magnetic axes; with the consequence that the conclusions drawn are less rigorous.

## CONCLUSION

In some of the above cases where the mean or minimum 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  $K_L$ ,  $K_M$ ,  $K_N$ , but it is found that even a 10% error in  $\bar{\chi}_M$  makes an almost negligible difference to  $\Delta K$ . The molecular anisotropy may therefore be taken as far more accurate than the absolute values of the three molecular susceptibilities, in such cases.

I am very grateful to Professor Dame Kathleen Lonsdale, F.R.S., for her interest and encouragement and for permission to use the facilities of her department; to Dr C. J. Brown for a gift of crystals and for his kind co-operation. Thanks are also due to The Science Council of the U.A.R., Cairo, for a grant (Amein Lofty Prize) and to Alexandria University for leave of absence.

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