Diamagnetic Behavior of Some Aliphatic Molecules in Crystals

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According to Pauling(1) the normal susceptibility in the plane of the aromatic molecules is due to the bound electrons, contributing to the susceptibility equally in all directions, and the electrons which are free to precess only in the plane of the molecule in orbits, provided by the entire molecular ring system, contribute only to the susceptibility along the normal to the molecular plane. When such anisotropic molecules are regularly arranged in crystals, the crystal as a whole will exhibit magnetic anisotropy. Hence anisotropy of the diamagnetic crystals is obviously due to the anisotropy of its constituent molecules.

Krishnan and Banerji(2) and Banerji(3) showed that, if the molecular anisotropy is known, it is possible to obtain much useful information regarding the orientation of the molecules in crystals relative to one another.

In a recent paper (Mookherji et al.)(4) studying the susceptibilities of a few dibasic aliphatic acids and their salts observed that,

a) Unlike the normal aliphatics the maximum diamagnetic susceptibility for the these salts lies normal to the plane of the carboxylic groups.

b) This extra diamagnetism could be attributed to resonance which exists in these molecules.

From X-ray studies and chemical considerations one may be led to think that the carboxylic groups in mono- and dibasic aliphatic acids and their salts can be represented by two or more structures and hence in these molecules resonance will exist. It would be therefore interesting to study the diamagnetic anisotropy of the crystals of the above mentioned acids and their salts and to find whether a similar diamagnetic behaviour like succinic and tartaric acids and their salts could be observed.

Experimental

Crystals were grown out of aqueous solution at room temperature by slow evaporation. The chemicals used were Merk's extra pure reagent quality prewar variety.

The magnetic anisotropy and the orientation of the crystals in magnetic field were carried out by the well known method of Krishnan and Banerji(2). The absolute susceptibility in any convenient direction was measured by a modified quartz balance (Bose)(5). The magnetic field used for the purpose had a constant gradient over a considerable volume by using pole pieces as devised by Dutta Roy(6). The standard crystal for calibration of this balance was a well developed crystal of naphthalene for which mass susceptibility is accurately known (Banerji)(7).

Results

The results of measurements are collected in Tables I and II, and are expressed in the usual units i. e. c. g. s. E. M. units. χ_3 is the gram molecular susceptibility along b-crystallographic axis of a monoclinic crystal; the algebraically greater of the two values in the symmetry plane (010) is denoted by χ_1 and the smaller by χ_2; ϕ is the angle that χ_1-direction makes with c-crystallographic axis taken positive from c-axis towards a-axis through obtuse β.

In orthorhombic crystals, the gram molecular susceptibilities along the crystallographic axes a, b and c are represented by χ_a, χ_b and χ_c, respectively.

Discussion

Magnetic Analysis of Molecular Orientation in Crystals.—We proceed now to discuss the magnetic anisotropy in the light of the orientation of the molecules in the unit cell of the crystal. The crystals are discussed individually.

Oxalic Acid Dihydrate.—Complete X-ray studies by Robertson and Woodword(8) revealed that the crystal is monoclinic in the space group C_{2h}^5 with two molecules in the unit cell. The molecules are centro symmetric, approximately plane, and are magnetically nearly uniaxial.

Let us represent the axes of symmetry of the two molecules by Z_1 and Z_2 and the principal susceptibilities of the molecule by $K_\perp$ and $K_\parallel$ in the plane of the molecule and normal to it respectively.

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1) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

2) K. Krishnan and S. Banerji, *Philos. Trans.*, **A 234**, 265 (1935); *Z. Kristallogr*, **A 99**, 499 (1938).

3) S. Banerji, *Z. Kristallogr.*, **A 100**, 316 (1938).

4) A. Mookherji, R. Mittal and D. Neogy, *Bull. Nat. Inst. Sci. India*, No. 14 (1959).

5) A. Bose, *Ind. Jour. Phys.*, **21**, 275 (1947).

6) S. Datta Roy, idid., **29**, 429 (1955).

7) S. Banerji, *Report Symposium. Ind. Association for the cultivation of Science*, 19 (1957).

8) J. M. Robertson and J. Woodward, *J. Chem. Soc.*, **1936**, 1817.

TABLE I. MAGNETIC ANISOTROPY AT 30°C

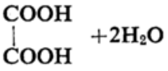
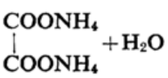
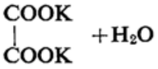
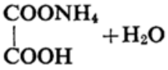
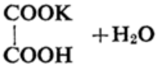
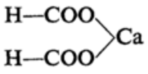
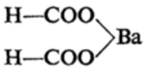
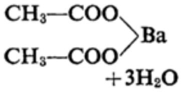
Sl. No.	Name and structural formula of the crystal	Crystallo-graphic data	Mode of suspension	Orientation in the field	$\varDelta\chi \times 10^6$	Magnetic anisotropy
1	2	3	4	5	6	7
1.	Oxalic acid dihydrate	Monoclinic	“ b ” axis vertical	$\theta=15.2°$	2.1	$\chi_1-\chi_2=2.10$
		C^5_{2h}	“ a ” axis vertical	“ b ” axis normal to the field	8.39	$\chi_1-\chi_3=8.53$
	 $\begin{array}{l}\mathrm{COOH}\\ \vert\\ \mathrm{COOH}\end{array}+2H_2O$	$a=6.12$ $b=3.6$ $c=12.0$ $\beta=106°\ 12'$ $z=2$	001 Plane horizontal	“ b ” axis normal to the field	6.56	$\theta_{\mathrm{cal}}=14.7°$ $\theta_{\mathrm{obs}}=15.2°$
2.	Ammonium oxalate monohydrate	Orthorhombic	“ c ” axis vertical	“ a ” axis along the field	1.108	$\chi_a-\chi_b=1.108$
		$P_{2_12_12}$	“ a ” axis vertical	“ c ” axis normal to the field	13.17	$\chi_b-\chi_c=13.17$
	 $\begin{array}{l}\mathrm{COONH_4}\\ \vert\\ \mathrm{COONH_4}\end{array}+H_2O$	$a=8.04$ $b=10.27$ $c=3.82$ $z=2$	“ b ” axis vertical	“ a ” axis along the field	14.16	Cal. $\varDelta\chi=0.99$
3.	Potassium oxalate monohydrate	Monoclinic	“ b ” axis vertical	$\theta=61.0°$	1.6	$\chi_1-\chi_2=1.6$
		$C_{2/c}$	“b” & “c” axes horizontal	“ b ” axis normal to the field	8.8	$\chi_1-\chi_3=10.0$
	 $\begin{array}{l}\mathrm{COOK}\\ \vert\\ \mathrm{COOK}\end{array}+H_2O$	$a=9.32$ $b=6.17$ $c=10.65$ $\beta=110°\ 58'$ $z=4$	“ a ” axis vertical	“ b ” axis normal to the field	9.5	$\theta_{\mathrm{cal}}=59.5°$ $\theta_{\mathrm{obs}}=61.0°$
4.	Ammonium bi-oxalate monohydrate	Orthorhombic	“ b ” axis vertical	“ b ” axis along the field	9.09	$\chi_c-\chi_a=9.09$
		$a:b:c=$ $0.4524:1:0.5593$	“ c ” axis vertical	“ b ” axis along the field	10.78	$\chi_b-\chi_a=10.78$
	 $\begin{array}{l}\mathrm{COONH_4}\\ \vert\\ \mathrm{COOH}\end{array}+H_2O$		“ a ” axis vertical	“ b ” axis along the field	2.06	Cal. $\varDelta\chi=1.70$
5.	Potassium bi-oxalate monohydrate	Monoclinic	“ b ” axis vertical	$\Psi=4.0$	9.00	$\chi_1-\chi_2=9.00$
		$P_{2_1/c}$	“ c ” axis vertical	“ b ” axis along the field	10.2	$\chi_3-\chi_2=10.3$
	 $\begin{array}{l}\mathrm{COOK}\\ \vert\\ \mathrm{COOH}\end{array}+H_2O$	$a=4.32$ $b=12.88$ $c=10.32$ $\beta=133°\ 29'$ $z=4$	“ b ” & “ c ” axes horizontal	“ b ” axis along the field	1.4	$\phi_{\mathrm{cal}}=3.9$ $\phi_{\mathrm{obs}}=4.0$
6.	Calcium formate	Orthorhombic P_{Cab}	“ b ” axis vertical	“ c ” axis along the field	1.722	$\chi_c-\chi_a=1.722$
	 $\left.\begin{array}{l}\mathrm{H{-}COO}\\ \mathrm{H{-}COO}\end{array}\right\rangle\mathrm{Ca}$	$Z=8$ $a=10.16$	“ c ” axis vertical	“ a ” axis normal to the field	1.287	$\chi_b-\chi_a=1.287$
		$b=13.38$ $c=6.27$	“ a ” axis vertical	“ b ” axis normal to the field	0.3118	Cal. $\varDelta\chi=0.435$
7.	Barium formate	Orthorhombic	“ c ” axis vertical	“ a ” axis along the field	0.621	$\chi_a-\chi_b=0.621$
		$a:b:c=$ $0.765:1:0.8638$	“ b ” axis vertical	“ b ” axis normal to the field	1.729	$\chi_c-\chi_b=1.729$
	 $\left.\begin{array}{l}\mathrm{H{-}COO}\\ \mathrm{H{-}COO}\end{array}\right\rangle\mathrm{Ba}$		“ b ” axis vertical	“ c ” axis along the field	0.9279	Cal. $\varDelta\chi=1.108$
8.	Barium acetate trihydrate	Monoclinic	“ b ” axis vertical	$\theta=33.5°$	1.18	$\chi_1=\chi_2=1.18$
		$a:b:c=$ $2.1362:1:1.222$	“ a ” axis vertical	“ b ” axis along the field	0.776	$\chi_1-\chi_3=0.458$
	 $\left.\begin{array}{l}\mathrm{CH_3{-}COO}\\ \mathrm{CH_3{-}COO}\end{array}\right\rangle\mathrm{Ba}+3H_2O$	$\beta=113°\ 27'$	001 Plane horizontal	“ b ” axis along the field	1.27	$\phi_{\mathrm{cal}}=33.5°$

TABLE II. ABSOLUTE SUSCEPTIBILITIES

Sl. No.	Name of the crystal	Temp. °C	Direction along which suscept. was measured	Volume suscept.	Corresponding χ_M	Principal gram molecular suscept.	Mean suscept. $\overline{\chi}_m$	Pascal's value $\overline{\chi}_m$
1	2	3	4	5	6	7	8	9
1.	Oxalic acid dihydrate, Monoclinic	33.00	Along "b" axis	−0.4214	−53.1	$\chi_1=-53.1$ $\chi_2=-55.2$ $\chi_3=-61.63$	−56.64	−60.42
2.	Ammonium oxalate monohydrate, orthorhombic	33.00	Along "b" axis	−0.4257	−60.4	$\chi_a=-60.4$ $\chi_b=-61.51$ $\chi_c=-74.68$	−65.33	−68.20
3.	Potassium oxalate monohydrate, monoclinic	33.00	Along "b" axis	−0.3740	−68.82	$\chi_1=-68.82$ $\chi_2=-70.42$ $\chi_3=-78.82$	−72.68	−67.20
4.	Ammonium bi-oxalate monohydrate, orthorhombic	33.00	Along "b" axis	−0.3417	−42.72	$\chi_a=-42.72$ $\chi_b=-31.94$ $\chi_c=-33.63$	−36.09	−56.83
5.	Potassium bi-oxalate monohydrate, monoclinic	33.00	Along "b" axis	−0.2954	−43.13	$\chi_1=-43.13$ $\chi_2=-52.13$ $\chi_3=-41.93$	−45.73	−57.33
6.	Calcium formate orthorhombic	33.00	Along "b" axis	−0.2650	−34.46	$\chi_c=-34.46$ $\chi_a=-36.182$ $\chi_b=-34.895$	−35.179	−44.70
7.	Barium formate orthorhombic	33.00	Along "b" axis	−0.2892	−65.77	$\chi_c=-65.77$ $\chi_b=-67.50$ $\chi_a=-66.88$	−66.71	−65.40
8.	Barium acetate trihydrate, monoclinic	33.00	Along "b" axis	−0.3772	−116.7	$\chi_1=-116.7$ $\chi_2=-117.88$ $\chi_3=-116.242$	−116.94	−128.00

Then χ_1 will lie in the direction, normal to the plane containing Z_1 and Z_2 axes and χ_2 will be the internal bisector of the angle 2Ψ between Z_1 and Z_2 and hence,

$$\left.\begin{aligned}\chi_1&=K_\perp\\ \chi_2&=K_\parallel\cos^2\Psi+K_\perp\sin^2\Psi\\ \chi_3&=K_\parallel\sin^2\Psi+K_\perp\cos^2\Psi\end{aligned}\right\}\qquad(1)$$

and $$\overline{\chi}=(\chi_1+\chi_2+\chi_3)/3=\frac{K_\parallel+2K_\perp}{3}$$

substituting the values of $(\chi_1-\chi_2)$ and $(\chi_1-\chi_3)$ in Eq. 1 we have $(K_\perp-K_\parallel)=10.7\times10^{-6}$ and $\Psi=63.5°$, which agrees well with X-ray findings, i. e. 61.9°.

Ammonium Oxalate Monohydrate.—Fine structure studies by X-ray methods (Hendricks, and Hendricks and Jefferson[9,10]) reveal that there are two molecules in the unit cell in space group $P_{2_12_12}$ and that the two parts of the $\begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{matrix}$ group are in planes making an angle of 20° whereas in oxalic acid both parts are in the same plane. The planes containing the oxygens of the oxalate groups are almost parallel to (001) plane. Following Mookherji[11] we can attribute the abnormal diamagnetism to oxygen atoms of the oxalate groups. Hence according to X-ray findings (001) plane should approximately be a plane of magnetic symmetry, whereas normal to this plane we should expect algebraically maximum susceptibility. From Table I we find that in the (001) plane $\Delta\chi=\chi_a-\chi_b=1.1\times10^{-6}$, whereas it is 14.2×10^{-6} in the plane normal to it.

We may therefore conclude that for oxalate molecules, which are in strained condition because of its two parts being in two different planes $\Delta K=K_\perp-K_\parallel=14.0\times10^{-6}$, more by 4 units for the oxalate groups, where both the parts are in the same plane.

Ammonium Bi-oxalate.—From Table I it is seen that the two susceptibilities in the (001) plane are nearly equal and numerically less than the third susceptibility by about 10 units, which is almost equal to the value of the oxalate group in oxalic acid dihydrate. Thus we conclude that in this crystal all the oxalate groups are oriented parallel with (001) plane. At present no X-ray data are available to verify the above conclusions.

Potassium Oxalate Monohydrate.—Hendricks[9] by X-ray methods found that the crystal is

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[9] S. B. Hendricks, *Z. Kristallogr.*, **91**, 48 (1935).

[10] S. B. Hendricks and M. E. Jefferson, *J. Chem. Phys.*, **4**, 102 (1936).

[11] A. Mookherji, *Acta Cryst.*, **10**, 25 (1957).

monoclinic in the space group of $C_{2/c}$ with four molecules in the unit cell; they form a set of two pairs with the two molecular planes in each pair being parallel. If the slight tilt between the two pairs is neglected then the molecules may be taken oriented parallel to the plane (010).

Evidently, $K_{\parallel}=\chi_3,\ K_{\perp}\approx\chi_2\approx\chi_1$

Hence, $1/2\,[(\chi_1-\chi_3)+(\chi_2-\chi_3)]=K_{\perp}-K_{\parallel}$

Thus it is observed that $(K_{\perp}-K_{\parallel})$ for oxalate group in the crystal is 9.2 as against 10.7 for that in the oxalic acid. This is evidently due to the neglect of the tilt. On calculating the tilt comes out as 15.0° with the (010) plane.

Potassium Bi-oxalate. — According to Hendricks⁹⁾, the crystal has four molecules in the unit cell and the molecular planes are oriented parallel to (100) plane. Hence $K_{\perp}-K_{\parallel}=10.0\times10^{-6}$, which is almost the same as found with other oxalate groups.

Calcium Formate.—It crystallises in the orthorhombic system in the space group P_{Cab} with eight molecules in the unit cell (Nitta and Osaki¹²⁾). If n, m and l are the direction cosines of the normal to the formate group, following Banerji³⁾ we have,

$$l^2-m^2=\frac{\chi_b-\chi_a}{K_{\perp}-K_{\parallel}},\qquad l^2-n^2=\frac{\chi_c-\chi_a}{K_{\perp}-K_{\parallel}}$$

and $l^2+m^2+n^2=1$

In order to calculate m, l and n one must know $(K_{\perp}-K_{\parallel})=\Delta K$ for COOH group. This may be estimated as follows:

According to Pauling and Sherman¹³⁾ resonance energy in monobasic acids is 1.20 electron volts. Now according to Pauling¹⁴⁾, if one attributes to ΔK this resonance energy then,

$$\Delta K=\frac{E\times M}{3.22\times\rho}=8.36\times10^{-6}$$

where E is kinetic energy, M the molecular weight and ρ the density. On substituting this value and $(\chi_b-\chi_a)$ and $(\chi_c-\chi_a)$ from Table I we find that the formate groups are inclined at 48.1, 56.0 and 59.8° to a, b and c crystallographic axes respectively.

Barium Formate.—The crystal is orthorhombic. The orientation of the formate group is calculated following the same method as in the case of calcium formate, which show that the normal to the formate group is inclined at 54.0° to a-axis 35.8° to b-axis and 38.8° to c-axis.

Diamagnetic Anisotropy and Resonance Energy.—According to Pauling, mono- and dicarboxylic acids and their salts exhibit resonance with two contributing forms and the actual resonance structure is a resonance hybrid intermediate between the contributing forms. Taking into account the empirical values of the polar effect and the dissociation constants of fatty acids Pauling calculated the resonance energy in carboxylic groups. One direct consequence of such resonance is the abnormal diamagnetism normal to the plane of the groups. Therefore it would be very interesting to correlate the measured abnormal diamagnetism with the resonance energy as obtained empirically. As already stated the kinetic energy E of the resonating electron is related to ΔK by expression

$$E=3.22\times\frac{\Delta K\times\rho}{M}$$

Using the above relation we have calculated the resonance energy for formates, oxalates, succinates and tartrates using ΔK-values which are given in Table III. We have also taken some of the ΔK-values for some typical aromatics as determined by Krishnan and Banerji²⁾ and calculated resonance energy. The agreement between the observed and calculated values is very encouraging.

TABLE III

Substances	$\Delta K\times10^6$	Extra resonance energy calculated	
		By Pauling	From magnetic values
	Aromatics		
Diphenyl	118.6	86.88	84.65
Naphthalene	114.0	74.66	82.62
Anthracene	182.6	104.70	100.30
Stilbene	141.6	94.26	101.00
	Aliphatics		
Succinic acid	10.7	54.86	52.00
Tartaric acid	9.6	54.86	52.00
Oxalic acid	10.7	54.86	53.31

Influence of Resonance Energy on Diamagnetism.—Adopting the conventional structural formulae for oxalates, formates and acetates, we have calculated mean gram molecular susceptibilities $\overline{\chi}_m$ for them on the basis of Pascal's additive law which are given in Table II. On comparing with our measured values of $\overline{\chi}_m$ a lowering is observed. This lowering is well understood if we recall that the resonance occuring in these groups impart on them some amount of double bond character (unsaturated) which lowers $\overline{\chi}_m$. A similar comparison of $\overline{\chi}_m$ deduced on the basis of Pascal's law and those measured by Krishnan and Banerji²⁾ for a number of aromatic substances

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12) I. Nitta and K. Osaki, *X-Rays*, 5, 37 (1948).

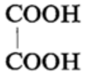
13) L. Pauling and J. Sherman, *J. Chem. Phys.*, 1, 679 (1933).

14) L. Pauling, *Phys. Rev.*, 34, 954 (1929).

points to the same findings. Matsunaga[15] found with azobenzene the same value as Banerji[3] which is lower than Pascal's value Thus one can safely conclude that resonance lowers diamagnetic values.

The above point of view is further strengthened by our findings that for molten oxalic acid dihydrate $\overline{\chi}_m$ is -60.89×10^{-6} (100°C) while that for the powder state is -56.4×10^{-6} (30°C). In molten state the crystal lattice completely breaks down so that the double bond character almost vanishes and hence there is an increment of $\overline{\chi}_m$ approaching Pascal's value.

Summary

The principal magnetic susceptibilities of single crystals of some aliphatic mono- and di-basic acids and their salts have been measured and the results have been correlated with the fine structure studies of the crystals by X-ray methods. It is observed that the anisotropy per –COOH group is 5 units, which increases by nearly 2 units if two parts of  $\begin{matrix}\mathrm{COOH}\\|\\\mathrm{COOH}\end{matrix}$ groups are not in the same plane.

The observed extra diamagnetism normal to the plane of the carboxylic groups, if attributed to resonance, the calculated energy compares very favourably with that deduced by Pauling from a consideration of the heat of formation of molecules and the lowering of the susceptibility from Pascal's value is then well understood.

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[15] Y. Matsunaga, This Bulletin, 29, 308 (1956).