

Diamagnetic anisotropy and molecular structure of succinimide derivatives

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Abstract : The axial diamagnetic susceptibilities of succinimide $C_4H_5NO_2$ and its derivatives *i.e.* isomorphous pair $C_4H_4NO_2X$ ($X = Cl, Br$), were measured and their molecular values were deduced using the molecular tensor relations. These measurements show that each of these crystals has unique magnetic axis and the molecular plane in succinimide compound lies nearer to (001) plane but in each of its derivatives lies in the vicinity of (010) plane. Effect of substitution of chloride and bromide ions on the magnetic anisotropy of these isomorphous pair were studied. Correlation between these results and other physical properties of these molecular crystals, providing acceptable information on their molecular structure, was established. Effect of the packing forces in these crystals was also discussed.

Keywords : Diamagnetic anisotropy, molecular structure, succinimide derivatives

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Study of the physical properties of molecular crystals having similar structure may be important to give valuable information on the general features of their structures [1–3]. Only in a few cases, this information could be obtained directly from X-ray data. In some other cases, the 'trial and error' structure has been obtained by an intensive study of the X-ray data which is a difficult problem involving much time and labour. Any independent physical methods which indicate the approximate configuration and orientation of the molecules in the crystal are therefore greatly welcomed. Fortunately, crystal structure of the present heterocyclic succinimide and its derivatives *i.e.* isomorphous pair N-chloro and N-bromo succinimide, are known [4,5]. The general structural formula of them is shown in Figure 1.

Succinimide crystal is orthorhombic [4] and the structure is built up through the usual Van der Waals forces. The crystals of isomorphous pair N-chloro and N-bromo succinimide are also orthorhombic [5] and their molecules are significantly planar. The

present work is devoted to provide more information on the molecular structure of these molecular crystals and to investigate the effect of halogen substitution on their diamagnetic anisotropies.

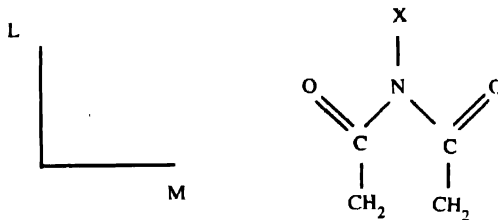


Figure 1. Structural formula of succinimide and its N-chloro and N-bromo succinimide derivatives, $C_4H_4NO_2X$ (where $X = H, Cl, Br$)

Succinimide crystals are grown from a solution of succinimide in methyl ethyl ketone and larger crystal are grown by seeding the solution. The density ρ and molecular weight M are 1.425 g/cm^3 and 99 mol , respectively. N-Chloro succinimide crystal $C_4H_4O_2Cl$ (NCS) are obtained from its solution in benzene by slow evaporation as small tabular plates. This compound has $\rho = 1.66 \text{ g/cm}^3$ and $M = 138.5 \text{ mol}$. Crystals of N-bromo succinimide $C_4H_4O_2Br$ (NBS) are obtained from solution in benzene as thin plates. The method of measurement used in the determination of the magnetic anisotropies of these crystals, has been mentioned elsewhere [6,7]. In this method, the crystal was suspended along one of its principal axes by very fine quartz wire at the centre of a uniform magnetic field to avoid any complications due to lateral forces acting on the crystal. The upper end of the fine quartz is attached to the center of a graduated torsion head which was used to measure the twisting angle of the fibre quartz at the balanced point between the restoring couple due to the field and the crystal anisotropy. Measurements were performed on small crystals, weighing 0.2 and 0.8 mg . In all cases, measurements were carried out on each of these crystals in at least three different orientations in order to calculate the crystal magnetic anisotropies and to compare the calculated and observed values. Each crystal was always weighed accurately just before and after the magnetic measurements, in order to detect any volatilization of the crystal due to its rapid rotation during the experiment and loss of weight subsequently checked.

Study of diamagnetic susceptibility of orthorhombic crystals lies in the determination of the crystal anisotropies, thus :

$$\text{and } \left. \begin{array}{l} \chi_a - \chi_b = A \\ \chi_a - \chi_c = B \end{array} \right\} \quad (1)$$

where A and B are the anisotropy values when the crystal is suspended along c -axis and b -axis respectively. Making use of the relation

$$\chi_a + \chi_b + \chi_c = C, \quad (2)$$

where $\bar{\chi}_M = C/3$ is the gram molecular susceptibility measured by Gouy powder method [8], the values of χ_a, χ_b, χ_c are deduced as follows :

$$\begin{aligned} \chi_a &= \frac{1}{3}(A + B + C) \\ \chi_b &= -\frac{2}{3}A + \frac{1}{3}(B + C) \\ \chi_c &= -\frac{2}{3}B + \frac{1}{3}(A + C) \end{aligned} \tag{3}$$

The relations between the axial diamagnetic susceptibilities χ_a, χ_b, χ_c and the molecular diamagnetic susceptibilities K_L, K_M, K_N [9] are given by :

$$\begin{aligned} \chi_a &= K_L \alpha_1^2 + K_M \alpha_2^2 + K_N \alpha_3^2 \\ \chi_b &= K_L \beta_1^2 + K_M \beta_2^2 + K_N \beta_3^2 \\ \chi_c &= K_L \gamma_1^2 + K_M \gamma_2^2 + K_N \gamma_3^2 \end{aligned} \tag{4}$$

where $\alpha_i^2, \beta_i^2, \gamma_i^2$ ($i = 1, 2, 3$) denote the summation of the direction cosines which is taken over all the independently oriented molecules in the unit cell. From eq. (4), the molecular susceptibilities are as follows :

$$\begin{aligned} K_L &= \begin{vmatrix} \chi_a & \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \chi_b & \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \chi_c & \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{vmatrix} + \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{vmatrix} \\ K_M &= \begin{vmatrix} \alpha_1^2 & \chi_a & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \chi_b & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \chi_c & \gamma_2^2 & \gamma_3^2 \end{vmatrix} + \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{vmatrix} \\ K_N &= \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \chi_a & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \chi_b & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \chi_c & \gamma_3^2 \end{vmatrix} + \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{vmatrix} \end{aligned}$$

Substituting for χ_a, χ_b, χ_c from eq. (3), we get

$$\begin{aligned} K_L &= \frac{1}{3D} [(a_1 - 2b_1 + c_1)A - (a_1 + b_1 - 2c_1)B + (a_1 + b_1 + c_1)C], \\ K_M &= \frac{1}{3D} [(a_2 - 2b_2 + c_2)A - (a_2 + b_2 - 2c_2)B + (a_2 + b_2 + c_2)C], \end{aligned} \tag{5}$$

and
$$K_N = \frac{1}{3D} [(a_3 - 2b_3 + c_3)A - (a_3 + b_3 - 2c_3)B + (a_3 + b_3 + c_3)C],$$

where

$$a_1 = \beta_2^2 \gamma_3^2 - \beta_3^2 \gamma_2^2, \quad b_1 = \gamma_2^2 \alpha_3^2 - \gamma_3^2 \alpha_2^2, \quad c_1 = \alpha_2^2 \beta_3^2 - \alpha_3^2 \beta_2^2;$$

$$a_2 = \beta_3^2 \gamma_1^2 - \beta_1^2 \gamma_3^2, \quad b_2 = \gamma_3^2 \alpha_1^2 - \gamma_1^2 \alpha_3^2, \quad c_2 = \alpha_3^2 \beta_1^2 - \alpha_1^2 \beta_3^2;$$

$$a_3 = \beta_1^2 \gamma_2^2 - \beta_2^2 \gamma_1^2, \quad b_3 = \gamma_1^2 \alpha_2^2 - \gamma_2^2 \alpha_1^2, \quad c_3 = \alpha_1^2 \beta_2^2 - \alpha_2^2 \beta_1^2.$$

The molecular diamagnetic anisotropy is given by the relation

$$\Delta K = K_N - \left(\frac{K_L + K_M}{2} \right). \quad (6)$$

The measured axial diamagnetic anisotropies of succinimide and its isomorphous pair derivatives are listed in Table 1.

Table 1. Axial diamagnetic anisotropies ($10^{-6} \text{cm}^3/\text{mole}$).

Crystal	Axial anisotropy		
	$\chi_b - \chi_a$	$\chi_c - \chi_a$	$\chi_c - \chi_b$
S	+6.2	7.1	+0.9
NCS	-7.1	-0.6	+6.5
NBS	-7.2	-0.9	+6.3

To get the values of the crystal diamagnetic susceptibilities χ_a , χ_b , χ_c , the following relation was used

$$\bar{\chi}_M = \frac{1}{3} [\chi_a + \chi_b + \chi_c],$$

where $\bar{\chi}_M$ has been measured several times by familiar Gouy method. The results are listed in Table 2.

Table 2. Axial diamagnetic susceptibilities ($10^{-6} \text{cm}^3/\text{mole}$)

Crystal	Axial diamagnetic susceptibilities			Mean value $\bar{\chi}_M$
	χ_a	χ_b	χ_c	
S	56.3	50.1	49.2	51.9
NCS	58.2	65.3	58.8	60.8
NBS	68.3	75.5	69.2	71.0

Maximum diamagnetic susceptibility (χ_a) along $[100]$ direction and small diamagnetic anisotropy ($\chi_b - \chi_c$) in (100) plane, indicate that the S crystal is magnetically uniaxial along $[100]$ direction and the molecular plane is nearer to (100) plane. For the other two isomorphous pair (NCS) and (NBS) crystals, larger χ_b along $[010]$ direction and small axial diamagnetic anisotropies in (010) plane, were obtained. These results, show that these crystal are magnetically uniaxial along $[010]$ direction and the molecular plane is in

the vicinity of (010) plane. It is clear that the substitution of H ion in S crystal by Cl or Br ion, leads to the rotation of the molecular plane from the vicinity of (100) plane to the neighborhood of (010) plane, which in turn affect the physical properties of these molecular crystals. Measurements of the optical anisotropies [10] and the X-ray investigation of these crystals [4,5] show that the molecular plane is in the vicinity of (100) plane in succinimide and of (010) plane in its derivatives which in turn, support the present results. The values of the small inclined angles of molecular planes of these crystals have been discussed later. The calculated direction cosines $\alpha_i, \beta_i, \gamma_i$ ($i = 1, 2, 3$) of the molecular axes L, M, N referred to the axes a, b, c , are given in Table 3.

Table 3. Direction cosines of L, M, N referred to a, b, c .

Compound	Direction cosines			i
	α_i	β_i	γ_i	
S	0.7823	-0.1889	0.5940	3
	0.6282	0.0187	0.7778	2
	-0.1360	0.9836	0.1184	1
NCS & NBS	0.4732	0.8783	0.0675	3
	0.8062	0.3987	0.4370	2
	0.3569	0.2612	-0.8967	1

L is taken parallel to the length of the molecule, M is normal to L in the molecular plane and N is normal to the molecular plane as shown in Figure 1. The molecular diamagnetic susceptibilities K_L, K_M, K_N and the anisotropy ΔK were calculated using eqs. (5) and (6) respectively. The results are given in Table 4.

Table 4. Molecular diamagnetic susceptibilities and anisotropies ($10^{-6} \text{ cm}^3/\text{mole}$).

Compound	Molecular diamagnetic susceptibilities			Anisotropy (ΔK)
	K_L	K_M	K_N	
S	50.0	40.6	63.9	18.15
NCS	59.1	52.6	73.9	18.05
NBS	72.0	59.9	84.3	18.35

Now, after the calculations of the molecular diamagnetic values, it is easy to get the orientational angles of the molecular planes from the relation :

$$\begin{aligned} \chi_a &= K_{\parallel} \sin^2 \theta + K_{\perp} \cos^2 \theta \\ &= K_{\parallel} + (K_{\perp} - K_{\parallel}) \cos^2 \theta \end{aligned}$$

and
$$\chi_b = K_{\parallel} + (K_{\perp} - K_{\parallel}) \cos^2 \theta,$$

where $K_{\parallel} = (K_L + K_M)/2$ and $K_{\perp} = K_N$.

For S compound, $\theta = 41^\circ$ and for NCS and NBS, $\theta = 43.7^\circ$.

The coincidence of the maximum value of the molecular diamagnetic susceptibility in the normal direction of the molecular plane with the minimum molecular optical refractivity for these crystals, indicates that the molecules are planar. X-ray investigation [4,5] indicates identical results. The nearly equal values of anisotropy ΔK of these molecular crystals, suggest the same packing forces in them [11]. Magnetic contribution of bonds (C-Br), (C-Cl) were calculated relative to succinimide molecule, the results are listed in Table 5.

Table 5. Diamagnetic contribution of (C-X) bonds relative to S molecule ($10^{-6} \text{ cm}^3/\text{mole}$)

Bond	Molecular components	
	K_{\parallel}	K_{\perp}
C-Br	10.1	10.0
C-Cl	21.2	20.9

These results show that the substitution of H ion by halogen ion leads to an increase in the value of the diamagnetic susceptibilities in the plane of the molecule. It is also noticed that the substitution by bromide ion increases the diamagnetic susceptibilities further, as compared to that of chloride ion due to the difference of the spreading effect of their electron clouds [2].

These measurements indicate that these crystals are magnetically uniaxial along [100] direction which is the axis of symmetry in S crystal whereas it is along the [010] axis in NCS and NBS crystals. The molecular plane is inclined to (100) plane by 41° in S compound and by 43.7° to (010) plane in its derivatives NCS and NBS. These results show also that the substitution by halogen ions rotates the molecular plane from the vicinity of (100) plane to that of (010) plane and increases the diamagnetic susceptibility in the molecular plane by different values due to the difference of the spreading effect of their electron clouds. The nearly equal values of ΔK suggest equal values of packing forces in these crystals.

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