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Optical anisotropy of succinimide derivatives

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A study of the optical properties of molecular crystals by some authors (Lasheen and Abdeen 1972, Lasheen and Ibrahim 1975, Lasheen and Tadros 1975, Manghi et *al* 1967, Gaafar et *al* 1989), cannot lead to a detailed knowledge of the crystal structures, but it can give valuable information on the general features of them. Fortunately, crystal structure of the present heterocyclic compounds succinimide and its derivatives isomorphous pair N-chloro- and N-bromo-succinimide are known (Mason 1956, Brown·1961). The general structural formula of them is shown in Figure 1, where X = H, Cl, Br.

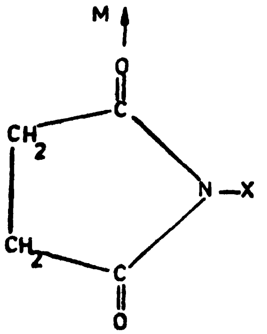

Figure 1. Structural formula of succinimide and its chloro- and bromo succinimide derivatives, $C_4H_4NO_2X$ (where X = H, Cl, Br).

Succinimide crystal is orthorhombic bipyramides with faces [111,] (Mason 1956). The structure is built up through the usual Van der Waals forces. Short intramolecular C – C distances are observed and C – N distances are less than those usually found in analogous compounds. The crystals of isomorphous pair N-chloro- and N-bromo-succinimide are also orthorhombic (Brown 1961). The molecular bond-lengths and angles are bilaterally symmetrical, but the molecule is significantly a planer. The present work may often be used to give direct information on the configuration and orientation of molecules in these crystals.

In this work, the axial refractivities of succinimide $C_4H_5NO_2$ (S) and its derivatives isomorphous pair N-chloro-$C_4H_4NO_2Cl$ (N.C.S.) and N-bromo-succinimide

$C_4H_4NO_2Br$ (N.B.S.) are investigated by "Becke line" method at 24°C. A sodium lamp ($\lambda=589$ nm) is used as light source. The "Becke test" is demonstrated at the extinction position in the crystal planes (axial direction in present orthorhombic crystals). The refractive indices of the immersion media are measured in Abbe refractometer. Succinimide crystals are grown from a solution of succinimide in methyl-ethyl-ketone, larger crystals are grown by seeding the solution. The density (ρ) and molecular weight (M) are 1.425 g cm^{-3} and 99 mol respectively. N.C.S. crystals are obtained from benzene by slow evaporation as small tabular plates. This compound has $\rho=1.66$ g cm^{-3} and $M=133.5$ mol. Crystals of N.B.S. ($\rho=2.122$ g cm^{-3} and $M=178$ mol) are obtained from solution in water as thin plates.

I. Succinimide ($C_4H_5O_2N$) :

The principal polarizabilities, b_i can be calculated from the tensor sum of the ellipsoids of the polarizabilities for the molecular bonds by the formula (Manghi *et al* 1967) :

$$b_{xy}=\sum_{n=1}^{N}\sum_{m=1}^{3} b_{nm}\,(\cos nm,\ y)(\cos nm,\ x). \tag{1}$$

where

b_{nm} = principal polarizability for the n bond,

$m=1, 2, 3$; $m=1$ in the direction parallel to the bond and

$m=2, 3$ in the direction normal to the bond.

xyz = arbitrary orthogonal axes.

The molecular refractivity R_i is closely related to the principal polarizability b_i by the relation :

$$b_i=\frac{3R_i}{4\pi N_0}\ (i=1, 2, 3). \tag{2}$$

where N_0 is Avogadro's number and, R_i is given by Lorentz-Lorenz formula :

$$R_i=\frac{n_i^2-1}{n_i^2+2}\,\frac{M}{\rho}\ (i=1, 2, 3). \tag{3}$$

Relation (2) is valid to a first approximation, when the mutual effect of neighbouring molecules is regarded as negligible.

To get the theoretical values for axial refraction indices n_a, n_b and n_c, knowledge on the molecular orientations with respect to the principle axes a, b and c are required (Mason 1956). L, M and N are molecular axes.

	a	*b*	*c*
L	0.7823	0.1889	−0.5940
M	0.6282	−0.0187	0.7778
N	−0.1360	0.9836	0.1184

Using eq. (1), the principal polarizabilities for S compound in the principle axes a, b and c are (78.5, 3.3 and 112.4)$\times 10^{-25}$ cm^3 respectively. The results of the theoretical values of n_a, n_b and n_c are given in Table 1 together with those obtained experimentally.

As can be seen, there is a good agreement between the n_i measured and those calculated with our b_i.

This agreement is expected for the present highly birefringent crystals because the contributions of differently directed bonds weakly neutralize each other. The gram molecular refractivities are then calculated, in the same directions as the principle indices, using eq. (3), and the results are given in Table 1.

Table I. Axial refractive indices.

Compound	Refractive index	Axial direction		
		a	b	c
S	n obs.	1.507	1.521	1.652
	cal.	1.482	1.517	1.752
	R (cm^3 mol)	20.67	21.15	25.40

Known molecular orientations permit calculation of the indices R_L, R_M and R_N in the molecular directions L, M, N, Figure 1, by tensor relations similar to those given for monoclinic system (Aly *et al* 1986) but with extinction angle $\phi=0$. Variances and relative uncertainties in determination of these molecular indices in the present case of orthorhombic crystals are also discussed (Lasheen and Ibrahim 1975, Lasheen and Tadros 1975). By diagonalization or the molecular tensor, the molecular indices are deduced as diagonal values in this tensor. The results together with the molecular anisotropy ΔR are given in Table 3.

II. Isomorghous N-chloro- and N-bromo-succinimide $C_4H_4NO_2X$ ($X=Cl$ *or Br*)

To study the effect of H-substitution in the succinimide crystal on its optical anisotropy, we selected its isomorphous pair, N.C.S. and N.B.S. derivatives. The variances in their crystal refractivities (Brown 1961, Lasheen and Ibrahim 1975, Lasheen and Tadros 1975) lead to the present measurements, which are the mean values of several measurements for good crystals. It is obvious from Table 2 that the present results approach those of Brown (1961). The gram molecular refractivities were calculated and given in Table 2.

The direction cosines of the molecular axes L, M, N referred to the principle axes a, b, c are calculated from the atomic parameters (Brown 1961). The refractivities R_L, R_M and R_N in the molecular directions L, M, N, Figure 1 are then calculated as diagonal values in the molecular tensor, and the results are given with the molecular anisotropies in Table 3.

This work shows that these crystals are biaxial with two directions of apparent isotropies. They show relatively high positive and negative birefringence for S-compound and its isomorphous pair respectively, which show that, the contributions of differently directed bonds weakly neutralize each other. On the other hand, these results exhibit that the minimum crystal refractive index is in [100]-direction and hence the molecular plane in S-compound lies near (100)-plane.

Table 2. Gram molecular refractivities.

Compound	Refractive index	Axial direction *a*	Axial direction *b*	Axial direction *c*
N.C.S.	*n*	1.625[1]	1.492	1.669
		1.688[2]	1.616	1.661
		1.606[3]	1.533	1.697
	R (cm^3 mol)	27.75	24.95	30.98
N.B.S.	*n*	1.661[1]	1.520	1.732
		1.706[2]	1.641	1.681
		1.651[3]	1.577	1.732
	R (cm^3 mol)	30.64	27.80	33.55

(1) Brown (1961) ; (2) Lasheen *et al* (1975) ; (3) Present work.

Small axial diamagnetic anisotropy in (100)-plane and large crystal diamagnetic susceptibility in [100] direction (Mason 1956), also the unitary values of [100]-reflections (Mason 1956) offer some confirmation for these results. For similar reasons, the molecular plane in the isomorphous pair N.C.S. and N.B.S. lies near (010) plane. It is clear that the substitution of H-ion in S-compound by Cl- or Br-ion lead to the rotation of the molecular plane from the vicinity of the axial plane (100) to the neighbourhood of (010) plane which in turn affect the physical property of these crystals. These results show that the maximum refractivity is along the length of molecule and nearly elongated molecule is expected. The molecule in these molecular crystals are easily polarized by light in the plane of the molecule. As can be seen, halogen substitution increases the molecular polarizability.

Table 3. Optical molecular refractivities and anisotropies (cm^3 mol).

Compound	R_L	R_M	R_N	ΔR
S	25.58	23.81	18.03	6.67
N.C.S.	31.74	28.33	23.82	6.22
N.B.S.	34.03	31.09	26.74	5.82

It is noticed that, presence of (N-Br)-bond in the conjugation increases the molecular polarizability more than (N-Cl) bond which is in good agreement with published data (Gaafar et *al* 1989). The smaller molecular optical anisotropies of these crystals, in comparison with 15 cm^3 mol, for benzene molecule (Pauling 1948) indicate high polarization in the molecular plane. These smaller optical anisotropies with smaller magnetic anisotropies of these crystals suggest nearly parallel molecules containing conjugated bonds (Gaafar et *al* 1989).

The present crystals are optically biaxial with two directions of apparent isotropies. Strongly.positive and negative birefrengences are observed and may be attributed to that, the differently directed bonds weakly neutralize each other. These results exhibit maximum refractivity along the length of the molecule and nearly elongated.molecule is expected. The results show also, that the molecular plane lies near (100)-plane in succinimide crystals but near (010), in chloro and bromo succinimide crystals. Small optical anisotropies are observed and high polarization in the molecular plane is expected. These smaller optical anisotropies are associated with smaller magnetic anisotropies to suggest nearly parallel molecules containing conjugated bonds.

References

Aly A A, Gaafar M, Aly N S and Abd El-Gawad 1986 *Phys. Stat. Sol. (a)* **96** K181
Brown R N 1961 *Acta Cryst.* **14** 711
Gaafar M, Lasheen M A, Aly A A and Ahmed A M 1989 *Phys. Stat. Sol. (a)* **111** K259
Lasheen M A and Abdeen A M 1972 *Acta Cryst.* **A28** 245
Lasheen M A and Ibrahim I 1975 *Acta Cryst.* **A31** 136
Lasheen M A and Tadros S 1975 *Acta Cryst.* **A31** 390
Manghi E, De Caroni C A, De Benyacar M R and De Abeldo M J 1967 *Acta Crys.* **23** 205
Mason R 1956 *Acta Cryst.* **9** 405
Pauling L 1948 *The Nature of the Chemical Bond* (New York : Cornell Univ. Press) p 175