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**Optical anisotropies of some organic molecules.** By M. A. LASHEEN and M. E. BASSIOUNI, *Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt*

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## Abstract

The principal refractive indices of some organic crystals were obtained. The principal molecular refractivities of these crystals were determined using the equations for transitions from crystalline to molecular refractivities. The results show that strong optical anisotropy is always associated with strong magnetic anisotropy, in good agreement with that predicted by Krishnan, Guha & Banerjee [*Philos. Trans. R. Soc. London Ser. A* (1933), **231**, 235–262]. The results also demonstrate the effect of substitution on the optical anisotropy in the case of aromatic compounds.

## Introduction

The determination of the optical properties of crystals is useful for the identification of substances and makes an important contribution to the study of crystal structures by X-rays.

In the present work, the 'Becke test' for sodium light at room temperature was used in the determination of the

principal refractive indices of the materials investigated. Hence, the gram molecular refractivity for any principal direction of the crystal was calculated using the Lorentz–Lorenz equation

$$[(n^2 - 1)/(n^2 + 2)] (M/D) = R_M,$$

where  $n$  is the refractive index of the crystal for that direction,  $M$  is the molecular weight and  $D$  is the density. In the case of the orthorhombic system, the principal refractivities along the crystal axes  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  are  $R_a$ ,  $R_b$  and  $R_c$  respectively. For the monoclinic system the crystal refractivity parallel to  $\mathbf{b}$  is taken as  $R_3$ , while  $R_1$  and  $R_2$  denote those in the (010) plane.

The mathematical relationships between the crystal and molecular refractivities were given by Lonsdale & Krishnan (1936). The molecular refractivities are denoted by  $r_L$  and  $r_M$  in the molecular plane and  $r_N$  normal to it, and the molecular anisotropy  $\Delta r = (r_L + r_M)/2 - r_N$ ;  $r_L$  is usually taken along the length of the molecule. The experimental errors in the molecular refractivities and anisotropies were calculated in a similar manner to that given by Lasheen & Tadros (1968) for orthorhombic crystals and Walley (1967) for monoclinic

Table 1. *Molecular magnetic and optical anisotropies and their ratios with respect to those of the benzene molecule*

Name	Formula	Molecular susceptibilities					Molecular refractivities				
		$\kappa_x$	$\kappa_y$	$\kappa_z$	$\Delta\kappa$	$\frac{\Delta\kappa}{\Delta\kappa_{\text{benzene}}}$	$r_L$	$r_M$	$r_N$	$\Delta r$	$\frac{\Delta r}{\Delta r_{\text{benzene}}}$
Orthorhombic crystals											
Barbituric acid dihydrate	$C_4H_4N_2O_3 \cdot 2H_2O$	-75.3	-70.0	-90.6	17.95 <sup>(1)</sup>	0.30	34.70 ± 0.04	41.5 ± 0.5	33.9 ± 0.2	4.3 ± 0.5	0.3
Phloroglucinol dihydrate	$C_6H_3(OH)_3 \cdot 2H_2O$	-83.1	-84.1	-120.2	36.6 <sup>(1)</sup>	0.61	43.5 ± 0.4	40.1 ± 0.4	32.7 ± 0.4	9.1 ± 0.8	0.6
1,4-Dimethoxybenzene	$C_8H_8(OCH_3)_2$	66 ± 6	-78.6 ± 0.1	-11.5 ± 0.5	43.7 ± 0.6 <sup>(2)</sup>	0.73	41.8 ± 0.2	41.9 ± 0.1	31.9 ± 0.6	10.0 ± 0.7	0.63
Monoclinic crystals											
Chloroacetamide	$CH_2ClCONH_2$	-51.70	-48.74	-53.37	3.15 <sup>(1)</sup>	0.05	21.1 ± 0.4	21.8 ± 0.1	21.5 ± 0.6	0.60 ± 0.1	0.04
Glycine	$CH_2(NH_2)COOH$	-37.6 ± 0.1	-39.4 ± 0.1	-44.57 ± 0.15	6.6 ± 0.2	0.11	16 ± 2	17.0 ± 2	15.2 ± 0.03	1.6 ± 0.04	0.1
<i>p</i> -Benzoquinone	$C_6H_4O_2$	-23.0	-27.0	-65.2	40.2 <sup>(1)</sup>	0.67	39 ± 2	34 ± 1	22.14 ± 0.01	10 ± 2	0.6
Pentachlorophenol	$C_6Cl_5(OH)$	125.5 ± 0.6	-125 ± 19	-174 ± 19	48 ± 21	0.81	51 ± 0.8	54 ± 4	40 ± 3	12 ± 6	0.8
<i>p</i> -Dibromobenzene	$C_6H_4Br_2$	-97.1	-70.5	-136.7	52.9 <sup>(1)</sup>	0.98	45 ± 5	36 ± 6	27.3 ± 0.1	13 ± 5	0.8
Naphthalene											
tetrachloride	$C_{10}H_6Cl_4$	-147.5	-145.0	-201.2	54.9 <sup>(3)</sup>	0.92	66 ± 2	67.1 ± 0	53 ± 0.9	13.4 ± 0.2	0.9
$\beta$ -Naphthol	$C_{10}H_7(OH)$	-63.9	-51.9	-175.2	117.3 <sup>(1)</sup>	1.96	47 ± 1	57 ± 2	28 ± 0.2	24 ± 1	1.5
1-Naphthoic acid	$C_{10}H_7COOH$	-70.5	-58.95	-192.5	127.8 <sup>(1)</sup>	2.14	49 ± 5	61 ± 5	29.3 ± 0.1	26 ± 5	1.6

(1) Lasheen (1964); (2) Lasheen (1968); (3) Lasheen (1966).

crystals. The results obtained are summarized in Table 1. The calculations are similar to those described by Lasheen & Ibrahim (1975) and Lasheen & Abdeen (1972).\*

### Conclusion

It is clear from Table 1, which shows the comparison between the molecular refractivities and molecular susceptibilities of crystals of several molecules, that strong magnetic anisotropy ( $\Delta\kappa$ ) is always associated with strong optical anisotropy ( $\Delta r$ ), in good agreement with that predicted by Krishnan, Guha & Banerjee (1933). It is also clear that the optical anisotropy of each of the molecules investigated divided by that of the benzene molecule is smaller than the corresponding ratio for the magnetic anisotropy; this is due to the fact that the induced magnetic dipoles do not interact appreciably whereas the optically induced dipoles are very strong and exert a considerable interaction on one another (cf. Lasheen & Ibrahim, 1975).

It may be noticed that organic substances containing double bonds have higher average refractive indices than

\* Full details of the calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34818 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**Etude des défauts d'empilement dans un cristal moléculaire  $[V(C_6H_5CN)_2Cl_3O]$ .** Par A. GOURDON et Y. JEANNIN, *Laboratoire de Chimie des Métaux de Transition, Equipe de Recherche Associée n° 608, Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris CEDEX 05, France*

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### Abstract

Bis(benzonitrile)trichloromonooxovanadium(V),  $[V(C_6H_5CN)_2Cl_3O]$ , crystallizes in the tetragonal system with  $a = b = 10.18 \pm 0.02$  Å,  $c = 31.58 \pm 0.04$  Å,  $Z = 8$ . In this crystal, stacking faults ( $\mathbf{a} + \mathbf{b}$ )/2 occur, giving diffraction lines with  $h + k = 2n + 1$ .

La présence de fautes d'empilement a souvent été constatée dans le cas de cristaux métalliques. Elle est néanmoins beaucoup plus rare dans le cas de cristaux moléculaires. L'objet de cette note est de montrer son existence dans le cas du composé moléculaire  $[V(C_6H_5CN)_2Cl_3O]$ .

L'étude des conditions de cristallisation du bis(benzonitrile)trichloromonooxovanadium (Daran, Gourdon & Jeannin, 1980) a montré l'existence de deux types de cristaux. La résolution de la structure de la première variété, de type monoclinique, a permis de déterminer l'environnement du métal: l'atome de vanadium a un environnement octaédrique déformé très voisin de celui du niobium dans  $[Nb(CH_3CN)_2Cl_3O]$  (Chavant, Daran, Jeannin, Constant &

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singly linked compounds and the refractive index for light vibrating along the double bond is higher than for other directions, thus the molecular refractivities and anisotropy are related to the bond character and constitution; and in the case of aromatic compounds they are strongly influenced by substitution, which markedly decreases the anisotropy.

In some special cases small experimental errors in the refractive indices could lead to very large errors in the molecular refractivities and anisotropies of the crystals; these probable errors were calculated in this work for all the substances investigated.

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Moranco, 1975). Ce composé est préparé par addition sous atmosphère inerte du benzonitrile au trichlorure oxyde de vanadium. Le précipité obtenu, porté à 308 K sous une pression de 0,3 mm de mercure dans un doigt de sublimation, donne lieu en quelques minutes à la formation de cristaux pyramidaux sur la paroi froide maintenue à 295 K. Un microdosage élémentaire du vanadium, du chlore, du carbone et de l'hydrogène conduit à la même formule brute  $VOCl_3 \cdot 2C_6H_5CN$  que celle du composé de maille monoclinique.

Les clichés de précession (Fig. 1) de ce composé montrent l'existence d'une part d'un réseau de taches bien définies et d'autre part de lignes continues de diffraction. La Fig. 2 représente le réseau réciproque tel qu'il peut être construit à partir de ces clichés. Les 'lignes' de diffraction sont parallèles à l'axe  $\mathbf{c}^*$  et passent par le centre des mailles. Si l'on considère le système qui fait intervenir ce réseau et les intersections des 'lignes' de diffraction avec les plans  $\mathbf{a}^*\mathbf{b}^*$ , la maille élémentaire obtenue à partir de la maille réciproque  $ABCD A'B'C'D'$  est quadratique, avec:  $a = b = 10,18 \pm 0,02$  Å,  $c = 31,58 \pm 0,04$  Å,  $Z = 8$ ,  $d_m = 1,51 \pm 0,03$ ,  $d_x = 1,54$  Mg m<sup>-3</sup>.

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