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Optical Anisotropies of Some Organic Molecules

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The principal refractive indices of some organic aromatic crystals of known structure have been measured and the principal molecular refractivities deduced from these and the molecular orientation. The substances investigated include aromatic compounds having three rings, two rings or one ring with different substituents. The results give a clear indication that strong magnetic anisotropy is always associated with strong optical anisotropy.

Introduction

Anisotropic properties may often be used to give direct information about the general shape of the molecules in crystals and the way in which the molecules or ions are packed.

The gram molecular refractivity R_M of any crystal can be determined using the Lorentz–Lorenz equation

$$R_M = \frac{(n^2-1) M}{(n^2+2) D}$$

where n is the refractive index of the crystal, M is the molecular weight and D is the density in g.cm^{-3}. n was measured using the Becke method for the sodium D line at room temperature (about 25°C).

The molecular refractivity of benzene, and hence the molecular anisotropy Δr were given by Hartshorne & Stuart (1960) to be,

$$\Delta r = \tfrac{1}{2}(r_L + r_M) - r_N = 15.7$$

where r_L and r_M are the molecular refractivities in the plane of the molecule and r_N perpendicular to it.

In the case of orthorhombic crystals the crystal refractivities are R_a, R_b and R_c in the direction of the a, b and c axes respectively. For monoclinic crystals the crystal refractivity parallel to [010] is taken as R_3, while R_1 and R_2 denote those in the (010) plane. The sum of R_a, R_b and R_c or R_1, R_2 and R_3 for a crystal is equal to the sum of r_L, r_M and r_N for the molecule.

The transformations from crystalline to molecular refractivities 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).

Orthorhombic crystals

(1) *Triphenylbenzene* $(C_6H_5)_3C_6H_3$
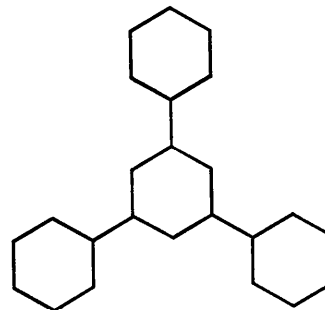
The crystal structure was determined by Farag (1954) who gave:

$a = 7.47$, $b = 19.66$, $c = 11.19$ Å; $Z = 4$; $Pna2_1$.

The crystals used were crystallized from ether.

The principal refractive indices of triphenylbenzene, for the sodium D line are:

Winchell (1943) $n_x = 1.5241$, $n_y = 1.8670$, $n_z = 1.8725$.
Present work $n_a = 1.509$, $n_b = 1.843$, $n_c = 1.849$.

The gram molecular refractivities of triphenylbenzene crystal, where $M = 306.14$ and $D = 1.237$, are

$$R_a = 73.89, \quad R_b = 109.89, \quad R_c = 110.46.$$

Using the calculated direction cosines of the four rings of the molecule, the mean refractivities and the anisotropy of one ring in the triphenylbenzene molecule are:

$$r_L = 28 \cdot 17, \quad r_M = 28 \cdot 91, \quad r_N = 16 \cdot 69, \quad \Delta r = 11 \cdot 85 \ .$$

(2) Acenaphthene $C_{10}H_6(CH_2)_2$
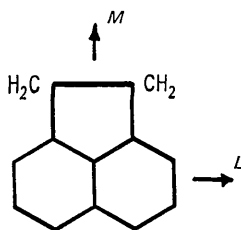
The crystal structure of acenaphthene was determined by Ehrlich (1957) who gave:

$$a = 8 \cdot 290, \quad b = 14 \cdot 000, \quad c = 7 \cdot 225 \ \text{Å}, \quad Z = 4; \quad Pcm2_1.$$

The crystals used in the present work were crystallized from benzene in the form of plates elongated along [001].

The principal refractive indices of acenaphthene are:

Groth (1919) $\alpha = 1 \cdot 4065, \quad \beta = 1 \cdot 4678, \quad \gamma = 1 \cdot 6201$.
Present work $n_a = 1 \cdot 489, \quad n_b = 1 \cdot 642, \quad n_c = 1 \cdot 396$.

Thus the gram molecular refractivities of acenaphthene crystal, where $M = 154 \cdot 21$, $D = 1 \cdot 19$, are:
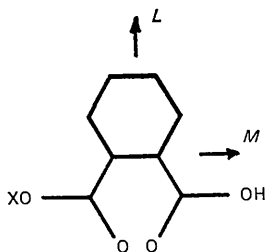
$$R_a = 37 \cdot 39, \ R_b = 46 \cdot 80, \ R_c = 31 \cdot 13 \ .$$

Thus using the direction cosines of the molecule, its molecular refractivities and anisotropy are:

$$r_L = 46 \cdot 80, \quad r_M = 48 \cdot 01, \quad r_N = 20 \cdot 51, \quad \Delta r = 26 \cdot 89 \ .$$

(3) Sodium acid phthalate $C_6H_4(COOH)$ $(COONa)$ and
(4) 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 crystal structure of potassium acid phthalate was determined by Okaya (1965). The cell dimensions are:

	a	b	c	Z	Space group
Sodium acid phthalate	6·76	9·31	26·42 Å	8	B2ab
Ammonium acid phthalate	6·40	10·23	26·14	8	Pcab
Potassium acid phthalate	6·46	9·60	13·85	4	P2₁ab.

Sodium and potassium acid phthalate crystals were obtained from their aqueous solution with (001) as the plate face, the sodium acid phthalate crystals being elongated along [100].

The principal refractive indices of sodium and potassium acid phthalates are:

Sodium acid phthalate, Winchell (1943)
     $n_x = 1 \cdot 485, \quad n_y = 1 \cdot 661, \quad n_z = 1 \cdot 668.$
Sodium acid phthalate (Present work)
     $n_a = 1 \cdot 476, \quad n_b = 1 \cdot 665, \quad n_c = 1 \cdot 678.$
Potassium acid phthalate, Winchell (1943)
     $n_x = 1 \cdot 498, \quad n_y = 1 \cdot 659, \quad n_z = 1 \cdot 663.$
Potassium acid phthalate (Present work)
     $n_a = 1 \cdot 494, \quad n_b = 1 \cdot 632, \quad n_c = 1 \cdot 674.$

Hence the gram molecular refractivities of sodium and potassium acid phthalates are:

	M	D	R_a	R_b	R_c
Sodium acid phthalate	188·13	1·504	35·41	46·66	47·34
Potassium acid phthalate	204·22	1·579	37·65	46·13	48·54.

Thus the molecular refractivities of sodium and potassium acid phthalates are:

	r_L	r_M	r_N	Δr
Sodium acid phthalate	49·59	47·34	32·48	15·98
Potassium acid phthalate	51·03	48·53	33·27	16·51.

(5) m-Dinitrobenzene $C_6H_4(NO_2)_2$
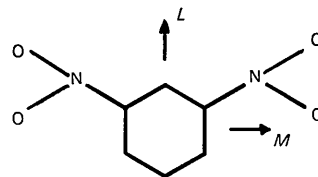
The crystal structure of m-dinitrobenzene was determined by Trotter (1961) who gave:

$$a = 13 \cdot 20, \quad b = 13 \cdot 97, \quad c = 3 \cdot 80 \ \text{Å}; \quad Z = 4; \quad Pbn2_1 \ .$$

The crystals used were crystallized from ethyl alcohol as needles elongated along [001].

The principal refractive indices of m-dinitrobenzene are:

Winchell (1943) $n_x = 1 \cdot 432, \quad n_y = 1 \cdot 765, \quad n_z = 1 \cdot 839$.
Present work $n_a = 1 \cdot 746, \quad n_b = 1 \cdot 841, \quad n_c = 1 \cdot 482$.

Hence the gram molecular refractivities of m-dinitro-

benzene crystal, where $M=168\cdot05$, $D=1\cdot593$, are:

$$R_a=42\cdot81, \quad R_b=46\cdot78, \quad R_c=29\cdot87 .$$

Thus the molecular refractivities and anisotropy of m-dinitrobenzene are:

$$r_L=49\cdot55, \quad r_M=42\cdot53, \quad r_N=28\cdot12, \quad \Delta r=17\cdot92 .$$

(6) *Acetanilide* $C_6H_5NHCOCH_3$
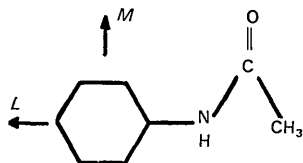
The crystal structure of acetanilide was determined by Brown & Corbridge (1954). The unit cell axes are:

$$a=19\cdot640, \quad b=9\cdot483, \quad c=7\cdot979 \text{ Å}^\circ, \quad Z=8; \quad Pbca.$$

The crystals used were crystallized from ethyl alcohol solution with (100) as the plate face.

The principal refractive indices of acetanilide are:

Winchell (1943) $n_x=1\cdot515$, $n_y=1\cdot620$, $n_z>1\cdot733$.
Brown &
Corbridge (1954) $\alpha=1\cdot51$, $\beta=1\cdot62$, $\gamma=1\cdot73$.
Present work $n_a=1\cdot748$, $n_b=1\cdot612$, $n_c=1\cdot524$.

The gram molecular refractivities of acetanilide crystal, where $M=135\cdot041$ and $D=1\cdot206$, are:

$$R_a=45\cdot49, \quad R_b=38\cdot89, \quad R_c=34\cdot23 .$$

Thus the molecular refractivities and anisotropy of the acetanilide molecule are:

$$r_L=46\cdot54, \quad r_M=43\cdot82, \quad r_N=28\cdot64, \quad \Delta r=16\cdot64 .$$

(7) *Anthranilic acid* $C_6H_4\cdot NH_2\cdot COOH$
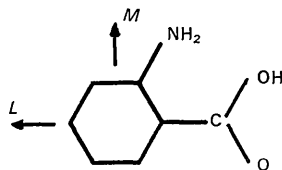
The crystal and molecular structure of anthranilic acid was determined by Brown (1968), who gave:

$$a=12\cdot83, \quad b=10\cdot77, \quad c=9\cdot28 \text{ Å}, \quad Z=8; \quad Pcn2 .$$

The crystals used were crystallized from ethanol in the form of prismatic plates with (100) as the plate face.

The principal refractive indices of anthranilic acid are:

Winchell (1943) $n_x=1\cdot560$, $n_y=1\cdot730$, $n_z=1\cdot760$.
Present work $n_a=1\cdot508$, $n_b=1\cdot768$, $n_c=1\cdot736$.

Thus the gram molecular refractivities of anthranilic acid, where $M=137\cdot1$ and $D=1\cdot42$, are:

$$R_a=28\cdot78, \quad R_b=40\cdot04, \quad R_c=38\cdot77 .$$

Hence the molecular refractivities and anisotropy of

anthranilic acid are:

$$r_L=40\cdot55, \quad r_M=41\cdot29, \quad r_N=25\cdot69, \quad \Delta r=15\cdot23 .$$

Monoclinic crystals

(1) *Anthracene* $C_{14}H_{10}$
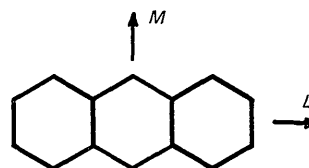
The crystal structure of anthracene was determined by Mathieson, Robertson & Sinclair (1950) and by Sinclair, Robertson & Mathieson (1950) and refined by Cruickshank (1956), who gave:

$a=8\cdot561$, $b=6\cdot035$, $c=11\cdot163$Å, $\beta=124^\circ$ 42'; $Z=2$; $P2_1/a$.

The principal refractive indices of anthracene are: Winchell (1943)

$$n_x=1\cdot556, \qquad n_y=1\cdot786, \quad n_z=1\cdot959 .$$

Present work

$$n_1 \text{ (assumed)}=1\cdot959, \ n_2=1\cdot485. \ n_3=1\cdot837 .$$

The gram molecular refractivities of anthracene, where $M=178\cdot2$ and $D=1\cdot026$, are:

$$R_1=84\cdot43, \quad R_2=49\cdot78, \quad R_3=76\cdot73 .$$

Thus the molecular refractivities and the anisotropy of anthracene are:

$$r_L=84\cdot55, r_M=85\cdot05, r_N=41\cdot58, \Delta r=43\cdot22 .$$

(2) *Biphenyl* $C_{12}H_{10}$
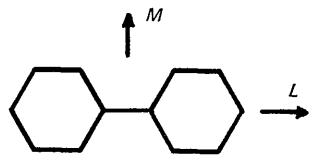
The crystal structure of biphenyl has been determined in two independent papers, by Trotter (1961) and by Hargreaves & Hasan Rizvi (1962). The latter gave:

$a=8\cdot63$, $b=5\cdot63$, $c=9\cdot15$ Å, $\beta=95\cdot1^\circ$, $Z=2$; $P2_1/a$.

The crystals used 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.

The principal refractive indices of biphenyl are: Winchell (1943)

$$n_x=1\cdot561, \qquad n_y=1\cdot658, \quad n_z=1\cdot945 .$$

Present work

$$n_1\text{(assumed)}=1\cdot945, \ n_2=1\cdot550, \ n_3=1\cdot661 .$$

The gram molecular refractivities of the biphenyl crystal, where $M=154\cdot2$ and $D=1\cdot224$, are:

$$R_1=60\cdot62, \quad R_2=40\cdot13, \quad R_3=46\cdot56 .$$

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

Orthorhombic crystals

Compound	Formula	Molecular susceptibilities					Molecular refractivities				
		K_L	K_M	K_N	ΔK	$\dfrac{\Delta k_{mol}}{\Delta k_{benz}}$	r_L	r_M	r_N	Δr	$\dfrac{\Delta r_{mol}}{\Delta r_{benz}}$
Triphenylbenzene (for one ring only)	$(C_6H_5)_3C_6H_3$	-33.7	-32.5	-85.9	$52.8*$	0.91	28.17	28.91	16.69	11.85	0.75
Acenaphthene	$C_{10}H_6(CH_2)_2$	-72.0	-70.5	-185.5	$114.25\dagger$	1.91	46.80	48.01	20.51	26.89	1.71
Sodium acid phthalate	$C_6H_4(COOH)(COONa)$	-59.1	-76.5	-134.1	$66.3\dagger$	1.11	49.5	47.37	32.48	15.98	1.02
Potassium acid phthalate	$C_6H_4(COOH)(COOK)$	-73.92	-79.12	-144.79	$68.27\ddagger$	1.14	51.03	48.53	33.27	16.51	1.05
m-Dinitrobenzene	$C_6H_4(NO_2)_2$	-50.0	-41.7	-119.8	$74.0\S$	1.28	49.55	42.53	28.12	17.92	1.14
Acetanilide	$C_6H_5NHCOCH_3$	-55.8	-44.3	-116.6	$66.55\dagger$	1.15	46.54	43.52	28.64	16.64	1.06
Anthranilic acid	$C_6H_4NH_2COOH$	-57.7	-58.8	-120.5	$62.25\dagger$	1.08	40.55	41.29	25.69	15.23	0.97

Monoclinic crystals

| Compound	Formula	Molecular susceptibilities					Molecular refractivities				
		K_L	K_M	K_N	ΔK	$\dfrac{\Delta k_{mol}}{\Delta k_{benz}}$	r_L	r_M	r_N	Δr	$\dfrac{\Delta r_{mol}}{\Delta r_{benz}}$
Anthracene	$C_{14}H_{10}$	-72.4	-71.8	-245.7	$173.6\S$	2.99	84.55	85.05	41.58	43.22	2.75
Biphenyl	$C_{12}H_{10}$	-67.7	-61.7	-183.8	$119.1\dagger$	2.06	62.27	53.79	31.25	26.78	1.71
Hexachlorobenzene	C_6Cl_6	-132.3	-132.3	-177.4	$44.8\S$	0.75	62.78	62.52	52.16	10.49	0.67
p-Dichlorobenzene	$C_6H_4Cl_2$	-78.3	-50.3	-120.2	$55.9\dagger$	0.97	38.37	40.66	26.29	13.23	0.84

* Lasheen (1966).
† Lasheen (1964).
‡ Lasheen (1969).
§ Lasheen (1968).

Thus the molecular refractivities and anisotropy of biphenyl are:

$$r_L = 62.27, \ r_M = 53.79, \ r_N = 31.25, \ \Delta r = 26.78 \ .$$

(3) *Hexachlorobenzene* C_6Cl_6
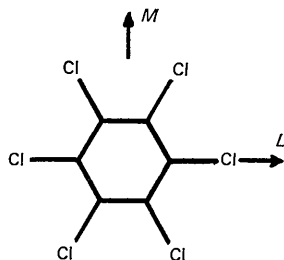
The crystal structure of hexachlorobenzene was determined by Tulinsky & White (1958) who gave:
$a = 8.08, \ b = 3.87, \ c = 16.65$ Å, $\beta = 117.0°$; $Z = 2$; $P2_1/c$. The principal refractive indices of hexachlorobenzene are found to be:

$$n_1 = 1.738, \ n_2 = 1.701, \ n_3 = 1.601 \ .$$

Thus the gram molecular refractivities of hexachlorobenzene crystal, where $M = 284.74$ and $D = 1.816$, are:

$$R_1 = 63.10, \ R_2 = 60.66, \ R_3 = 53.70 \ .$$

Three different sets of direction cosines for the axes L, M and N of the benzene ring were calculated with L parallel to C(1)–C(1′), to C(2)–C(2′) and to C(3)–C(3′). M is, in each case, perpendicular to L in the plane of the ring and N is normal to that plane.

The mean refractivities and the anisotropy of the molecule are:

$$\bar{r}_L = 62.78, \ \bar{r}_M = 62.52, \ \bar{r}_N = 52.16, \ \Delta \bar{r} = 10.49 \ .$$

It is clear from the resemblance of the values of the molecular refractivities and anisotropies for the three sets of direction cosines that the molecule of hexachlorobenzene is optically uniaxial. It has been found before, by one of us (Lasheen, 1968), that it is also magnetically uniaxial.

(4) *p-Dichlorobenzene* $C_6H_4 \ Cl_2$
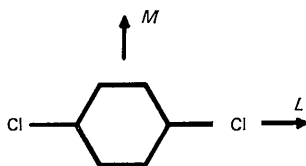
The optical properties of p-dichlorobenzene were determined by Manchi, de Caroni, de Benyacar & de Abeledo (1967) who gave:

$$\alpha = 1.52, \ \beta = 1.69, \ \gamma = 1.75, \ 2V = 54° \ .$$

The crystal structure of p-dichlorobenzene has been determined by Croatto, Bezzi & Bua (1952) who gave:

$$a = 14.80, \ b = 5.78, \ c = 3.99 \ \text{Å}, \ \beta = 113°; \ Z = 2; \ P2_1/a \ .$$

The crystals used were crystallized from acetone and ethyl alcohol.

The principal refractive indices of p-dichlorobenzene crystal are:

$$n_1 = 1.752, \ n_2 = 1.528, \ n_3 = 1.679 \ .$$

The gram molecular refractivities of p-dichlorobenzene crystal, where $M = 146.95$ and $D = 1.526$, are:

$$R_1 = 39.31, \ R_2 = 29.65, \ R_3 = 36.35 \ .$$

Thus the molecular refractivities and anisotropy of p-dichlorobenzene are:

$$r_L = 38.37, \ r_M = 40.66, \ r_N = 26.29, \ \Delta r = 13.23 \ .$$

Conclusion

When the molecular refractivities of the molecules are compared with their molecular susceptibilities (Table 1) it is seen·that strong magnetic anisotropy (ΔK) is always associated with strong optical anisotropy (Δr).

It can also be seen that the optical anisotropy of each of the molecules of these crystals divided by that of benzene (Table 1) is smaller than the corresponding ratio for the magnetic anisotropy. This is because the influence of optical dipoles induced in neighbouring molecules in a crystal is stronger than the corresponding influence of induced magnetic dipoles.

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