201. *Molecular Polarisability. The Conformations of Cholesteryl Halides as Solutes in Carbon Tetrachloride.*

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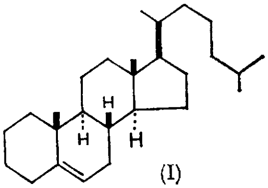
Measurements of molar Kerr constants, dipole moments, and refractivities are reported for cholesterol, cholest-5-ene, cholest-5-en-3-one, cholesteryl chloride, bromide, and iodide, and epicholesteryl chloride. From bond-polarisability data and a C_{27} skeleton based on that deduced from Carlisle and Crowfoot's *X*-ray analysis of cholesteryl iodide, molar Kerr constants appropriate for alternative conformations are calculated and compared with those found. The halogen atoms at position 3 are attached equatorially in the three cholesteryl halides, and axially in epicholesteryl chloride.

OF the methods [1,2] for deciding the disposition of a solitary polar bond in a monosubstituted hydrocarbon system *present in solution*, only those involving the anisotropy of molecular polarisability of the solute appear not to rely on arguments by analogy. The molar Kerr constant, ${}_{\mathrm{m}}K$, of a compound is a convenient property reflecting such anisotropy; it is conformation-dependent and calculable *a priori*.[3,4]

In this paper the ${}_{\mathrm{m}}K$'s of some 3-derivatives of cholest-5-ene (I) are reported and considered against the ${}_{\mathrm{m}}K$'s expected when the 3-substituent is attached either equatorially or axially. The approach is similar to that already adopted for cyclohexyl halides,[5] but the solutes here contain many more bonds and are optically active. The last-named factor prevents realisation of the $\pi/4$ setting between the plane of polarisation and the applied electric field required [3] in measurements of the Kerr effect. Eckert and Le Fèvre [6] have, however, shown that adequate estimates of molar Kerr constants of optically active materials at infinite dilution, ${}_{\infty}({}_{\mathrm{m}}K_2)$, can be achieved by standard techniques, even though the apparent ${}_{\mathrm{m}}K$'s at finite concentrations may become increasingly erroneous as the concentration rises.



(I)

EXPERIMENTAL

General.—Apparatus, procedures, notation, and methods of calculation are described in ref. 3(*a*), (*b*), or (*c*).

Solvent.—The solvent used was freshly distilled, dry ($CaCl_2$) carbon tetrachloride, having ε^{25} 2·2270, d_4^{25} 1·5845, n_D^{25} 1·4575, and 10^7B^{25} 0·070.

Solutes.—These were recrystallised before use. Epicholesteryl chloride was prepared by Shoppee and Summers's method [7] from 3β-hydroxycholestan-6-one (available from cholesterol, 6-nitrocholestanyl acetate, 6-oxocholestan-3β-yl acetate,[8,9] etc.); purification of a pentane solution through a silica gel column and recrystallisation from acetone provided colourless needles, m. p. 107—108°. Cholesteryl chloride and bromide were obtained as in refs. 10 or 11 with m. p.s 95—96° and 96—97°, respectively (both from acetone–methanol); their $[\alpha]_D$'s in benzene were $-26·5°$ and $-18·1°$. Treatment of cholesterol with aluminium iodide (obtained

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[1] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.

[2] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

[3] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*b*) *J.*, 1953, 4041; (*c*) Chap. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459; (*d*) *J.*, 1956, 3549; (*e*) *J.*, 1954, 1577.

[4] Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

[5] Le Fèvre, Le Fèvre, Roper, and Pierens, *Proc. Chem. Soc.*, 1960, 117.

[6] Eckert and Le Fèvre, *J.*, 1961, 2356.

[7] Shoppee and Summers, *J.*, 1952, 1790.

[8] Heilbron, Jackson, Jones, and Spring, *J.*, 1938, 102.

[9] Shoppee and Summers, *J.*, 1952, 3361.

[10] Shoppee and Summers, *J.*, 1952, 1786.

[11] Broome, Brown, and Summers, *J.*, 1957, 2071.

TABLE 1.

Kerr effects, dielectric constants, etc., of solutions in carbon tetrachloride at 25°.

Cholesterol

10^5w_2 ……	171	282	427	619	741	1030	1620	1933
ε^{25}…………	2·2305	2·2327	2·2358		2·2411	2·2473	2·2561	2·2603
d_4^{25} ………	1·58298	1·58147	1·58029	1·57881	1·57714	1·57446	1·56911	1·56619
$10^4\Delta n$ ……	2	2	3	7	7	10	14	19

whence $\Delta\varepsilon = 2{\cdot}13w_2 - 20{\cdot}9w_2^2$; $\Delta d = -0{\cdot}998w_2 + 2{\cdot}58w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}094$.

10^5w_2 ……	172	330	496	571	572
$10^7\Delta B$ ……	0·001	0·003	0·003	0·004	0·004

whence $10^7\sum\Delta B/\sum w_2 = 0{\cdot}70$.

Cholest-5-ene

10^5w_2 ……	387	513	749	1143	1793	2454	[illegible]	3755	4305	4915
ε^{25}…………	2·2297	2·2304	2·2319	2·2344	2·2393	2·2430	2·2460	2·2496	2·2524	2·2554
d_4^{25} ………	1·58043	1·57911	1·57764	1·57252	1·56575	1·55894	1·55345	1·54618	1·54063	1·53446
$10^4\Delta n$ ……	4	5	7	11	18	24	29	37	42	47

whence $\Delta\varepsilon = 0{\cdot}71w_2 - 2{\cdot}71w_2^2$; $\Delta d = -1{\cdot}060w_2 - 0{\cdot}893w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}097$.

10^5w_2 ……	103	192	264	387	493	559	648	749	823	917
$10^7\Delta B$ ……	0·001	0·002	0·003	0·005	0·006	0·007	0·008	0·010	0·011	0·012

whence $10^7\Delta B = 1{\cdot}02w_2 + 31{\cdot}6w_2^2$.

Cholest-5-en-3-one

10^5w_2 ……	575	706	1077	1304	1412	2029
ε^{25}…………	2·2594	2·2681	2·2903	2·3035	2·3083	2·3409

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}75$.

10^5w_2 ……	46	97	134	213	220	292	480	611
d_4^{25} ………		1·58353	1·58321	1·58238		1·58167	1·57944	1·57789
$10^4\Delta n$ ……			1	1	2	4	6	6
$10^7\Delta B$ ……	0·003	0·007			0·016		0·043	0·054

whence $\sum\Delta d/\sum w_2 = -1{\cdot}046$; $\sum\Delta n/\sum w_2 = 0{\cdot}109$; $10^7\Delta B = 6{\cdot}93w_2 + 329w_2^2$.

Cholesteryl iodide

10^5w_2 ……	172	183	236	312	343	402	455	540	737	774	1030
ε^{25}…………	2·2308				2·2355		2·2381	2·2395	2·2448		2·2516
d_4^{25} ………	1·58363	1·58358	1·58332	1·58297	1·58272					1·58059	
$10^4\Delta n$ ……	2		3	5				7		10	
$10^7\Delta B$ ……	0·019	0·020	0·025		0·036	0·048					

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}39$; $\sum\Delta d/\sum w_2 = -0{\cdot}516$; $\sum\Delta n/\sum w_2 = 0{\cdot}133$; $10^7\Delta B = 9{\cdot}74w_2 + 428w_2^2$.

Cholesteryl bromide

10^5w_2 ……	424	460	555	621	765	912
ε^{25}…………	2·2370	2·2374	2·2399	2·2424	2·2454	2·2496
d_4^{25} ………	1·58186	1·58145	1·58070	1·58038	1·57943	1·57832
$10^4\Delta n$ ……	3	4	5	5	6	11

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}40$; $\sum\Delta d/\sum w_2 = -0{\cdot}672$; $\sum\Delta n/\sum w_2 = 0{\cdot}091$.

10^5w_2 ……	91	132	147	206	300	399	495
$10^7\Delta B$ ……	0·008	0·015	0·016	0·023	0·033	0·047	0·058

whence $10^7\Delta B = 10{\cdot}22w_2 + 319w_2^2$.

Cholesteryl chloride

10^5w_2 ……	235	423	541	615	730	874
ε^{25}…………	2·2328	2·2374	2·2408	2·2425	2·2445	2·2500
d_4^{25} ………	1·58253	1·58074	1·57983	1·57895	1·57768	1·57675
$10^4\Delta n$ ……	3	4	6	6	7	9

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}52$; $\sum\Delta d/\sum w_2 = -0{\cdot}900$; $\sum\Delta n/\sum w_2 = 0{\cdot}102$.

10^5w_2 ……	49	150	175	225	376	418	487
$10^7\Delta B$ ……	0·003	0·017	0·020	0·024	0·042	0·050	0·057

whence $10^7\Delta B = 10{\cdot}03w_2 + 372w_2^2$.

Epicholesteryl chloride

10^5w_2 ……	68	222	307	524	1006
ε^{25}…………	2·2286	2·2324	2·2356	2·2414	2·2523
d_4^{25} ………	1·58401	1·58282	1·58198	1·58029	1·57628
$10^4\Delta n$ ……	1	3	3	5	12
$10^7\Delta B$ ……	−0·001	−0·003	−0·005		

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}60$; $\sum\Delta d/\sum w_2 = -0{\cdot}815$; $\sum\Delta n/\sum w_2 = 0{\cdot}113$; $10^7\sum\Delta B/\sum w_2 = -1{\cdot}41$.

TABLE 2.

Calculations of results.

	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_T$ (c.c.)	R_D (c.c.)	μ* (D)	$10^{12}{}_\infty({}_mK_2)$
Cholesterol	2·13	−0·630	0·064	10	202·4	120·0	1·93	30
Cholest-5-ene	0·71	−0·669	0·067	15	140·9	117·8	0·92	44
Cholest-5-en-3-one	5·75	−0·660	0·075	99	350·8	123·7	3·28	282
Cholesteryl iodide	2·39	−0·326	0·091	139	246·0	134·3	2·26	517
Cholesteryl bromide	2·40	−0·424	0·062	146	231·3	123·5	2·23	492
Cholesteryl chloride	2·52	−0·568	0·070	143	224·0	122·8	2·15	435
Epicholesteryl chloride ...	2·60	−0·514	0·077	−20	223·7	120·2	2·18	−60

* Calc. for distortion polarisation of 1·05 R_D.

by gradual addition of iodine in ether to amalgamated aluminium powder) yielded cholesteryl iodide [11] as colourless needles, m. p. 106—107°, $[\alpha]_D$ −12° (in CCl_4), after chromatographic purification through alumina. Oxidation of cholesterol dibromide with hot sodium dichromate–acetic acid gave the dibromo-ketone which was suspended in ether containing a little acetic acid and debrominated [12] with zinc dust; from methanol, cholest-5-en-3-one appeared as leaflets, m. p. 124—126°, $[\alpha]_D$ −3° (in $CHCl_3$). Cholest-5-ene was prepared by the action of sodium and pentyl alcohol on cholesteryl chloride [13] and after repeated crystallisation from ether–ethanol had m. p. 90—91°, $[\alpha]_D$ −56° (in $CHCl_3$). The cholesterol used had m. p. 146—147°, $[\alpha]_D$ −32·1° (in ether).

Measurements.—These are listed under usual headings in Table 1; quantities calculated therefrom, including dipole moments and molar Kerr constants at infinite dilution, are in Table 2.

Note on results in Table 2. The dipole moments listed are much as expected. Kumler *et al.*[14] reported the polarities of more than two dozen steroids and related substances, but the only overlap with present determinations is with cholesterol for which, in dioxan at 25°, $_\infty P_2$ was given as 204·6 c.c., $_D P$ as 121·4 c.c., and μ as 1·99 D. The refractivities of cholestene and cholesterol as solutes in benzene were examined by Tschugaeff and Koch,[15] R_D's of 117·0 and 118·65 c.c., respectively, being found; from the bond refractions of Vogel *et al.*[16] values of 118·1 (cholest-5-ene) and 119·6 c.c. (cholesterol) are forecast.

The moments now obtained for the cholesteryl halides are similar to those for the corresponding cyclohexyl derivatives.[3d, 5] The value $3{\cdot}2_8$ D for cholest-5-en-3-one is slightly greater than that ($3{\cdot}1_4$ D) for cyclohexanone; [3d] therefore, because of the possibility that the cholestenone used had rearranged to the (conjugated) Δ^4-isomer, its infrared spectrum was taken. Ketonic absorption occurred at 1720 cm.$^{-1}$, showing no evidence of conjugation between C=C and C=O. Moreover, at the end of a run of measurements a check of the specific rotation gave −2·4° (in CCl_4) in contrast to *ca.* +80° (in $CHCl_3$) for cholest-4-en-3-one.

DISCUSSION

The literature of the Kerr effect contains no reference to steroids, although the early discovery by Reinitzer [17] that cholesteryl acetate and benzoate form " liquid crystals " with marked birefringence [18] implied [19, 20] that these molecules are likewise anisotropically refractive and probably elongated. Bernal [21] in 1932 confirmed the last point by *X*-ray methods, showing a number of sterols [22] to have the approximate dimensions 5 × 7·2 ×

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[11] Fieser, *Org. Synth.*, 1955, **35**, 43.

[13] von Fürth and Felsenreich, *Biochem. Z.*, 1915, **69**, 416.

[14] Kumler, *J. Amer. Chem. Soc.*, 1945, **67**, 1901; Kumler and Fohlen, *ibid.*, 437.

[15] Tschugaeff and Koch, *Annalen*, 1911, **385**, 352.

[16] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

[17] Reinitzer, *Monatsh.*, 1888, **9**, 435.

[18] Lehmann, *Z. phys. Chem.*, 1889, **4**, 468; *Ann. Phys.*, 1900, **2**, 649.

[19] Bose, *Phys. Z.*, 1909, **10**, 32, 230.

[20] Bernal and Wooster, *Ann. Reports*, 1931, **28**, 280.

[21] Bernal, *Nature*, 1932, **129**, 277.

[22] Bernal, Crowfoot, and Fankuchen, *Phil. Trans.*, 1940, *A*, **239**, 135.

17—20 Å. Co-ordinates for the atomic positions in cholesteryl iodide,[23] calciferyl 4-iodo-3-nitrobenzoate,[24] lanostenyl iodoacetate,[25] etc., have since become available and provide the geometrical data needed for calculating molecular polarisability semiaxes from the polarisabilities of the various bonds concerned in such structures. For the cholestene derivatives of this paper, Carlisle and Crowfoot's analysis [23] of cholesteryl iodide is taken as a basis. Bond polarisabilities are adopted as follows:

Bond *	C–H	C–C	C–I	C–Br	C–Cl	C=C	C=O
b_L	0·064	0·099	0·882	0·598	0·396	0·280	0·230$_5$
b_T	0·064	0·027	0·423	0·258	0·158	0·073	0·140$_5$
b_V	0·064	0·027	0·423	0·258	0·158	0·077	0·046

* Longitudinal, transverse, and "vertical" polarisabilities of bonds are here and throughout this paper given as 10^{-23} c.c. units; molecular principal polarisabilities, b_1, b_2, and b_3 cited elsewhere are also in these units.

Derivation of the first five sets is found in ref. 3(*a*), and that of values for the C=C and C=O links in refs. 26 and 27, respectively.

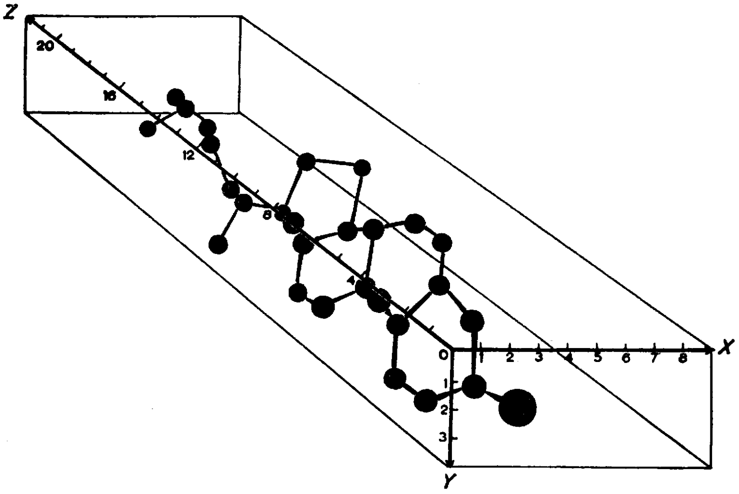

FIG. 1. *X*-Ray atomic position co-ordinates for cholesteryl iodide. $\alpha = \gamma = 90°$; $\beta = 149°$. Numbers represent Å.

Computational procedures are outlined generally on pp. 2483—2486 of ref. 3(*c*): for a given conformation, b_1, b_2, b_3, and the components of μ_{res} along the directions to which b_1, b_2, and b_3 relate, are estimated *a priori* and appropriately united to yield the corresponding molar Kerr constant, ${}_{\text{m}}K$ (calc.); comparisons of the ${}_{\text{m}}K$'s (calc.) for alternative conformations with the ${}_{\text{m}}K$ (obs.) should then assist a choice of the correct space formula. As already stated, the argument is essentially that used in the equatorial–axial problem for cyclohexyl halides,[3d,5] although the present cases involve 75 or 76 bonds instead of only 18, and thus provide the most severe tests yet made of the usefulness of the Kerr effect in stereochemistry.

Calculation of Molar Kerr Constants.—From the fractional position co-ordinates given by Carlisle and Crowfoot,[23] by multiplication by the unit-cell dimensions, are obtained the atomic position co-ordinates (*x*, *y*, *z*) within axes *X*, *Y*, *Z* which coincide with the edges of the unit cell and are monoclinic (see Fig. 1; this shows the *trans*-disposition of all

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[23] Carlisle and Crowfoot, *Proc. Roy. Soc.*, 1945, *A*, **184**, 64.
[24] Crowfoot and Dunitz, *Nature*, 1948, **162**, 608.
[25] Curtis, Fridrichsons, and Mathieson, *Nature*, 1952, **170**, 321.
[26] Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.
[27] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

the rings, the *cis*-attachment of the 10- and 13-methyl groups and of the 17-side-chain, a *cis* relation between the 3-iodo- and the 10-methyl group, and distortion in the region of the 5,6-double bond which makes carbon atoms 4, 5, 6, 7, 8, and 10 almost coplanar). For such a system, any point (x, y, z) may be expressed in terms of corresponding cartesian co-ordinates (x', y', z') as $x' = x \sin \beta$, $y' = y$, and $z' = z + x \cos \beta$. The disposition of any bond can now be specified by the cartesian co-ordinates of its terminal atoms, *viz.*, (x_1', y_1', z_1') and (x_2', y_2', z_2') so that relations are deducible which give the direction cosines of the principal axes (L, T, V) in terms of co-ordinates $x' = (x_2' - x_1')$, $y' = (y_2' - y_1')$, $z' = (z_2' - z_1')$. Let the nine directions cosines be, for L, l_x, l_y, l_z for T, t_x, t_y, t_z, and for V, v_x, v_y, v_z. The direction of the longitudinal axis L of any link along OA in Fig. 2 is, thus defined by:

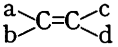
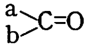
$$l_x = x'/\sqrt{[(x')^2 + (y')^2 + (z')^2]};$$
$$l_y = y'/\sqrt{[(x')^2 + (y')^2 + (z')^2]};$$
$$l_z = z'/\sqrt{[(x')^2 + (y')^2 + (z')^2]}.$$

For bonds in which $b_T = b_V$ the transverse and the vertical axes may be chosen in any mutually perpendicular planes intersecting along axis L. If axis T is placed in the OAA′ plane of Fig. 2 it follows that axis V lies in the ZX plane, with

$$t_x = -x'l_y/\sqrt{[(x')^2 + (z')^2]},$$
$$t_y = \sqrt{[(x')^2 + (z')^2]}/\sqrt{[(x')^2 + (y')^2 + (z')^2]},$$
$$t_z = -z'l_y/\sqrt{[(x')^2 + (z')^2]},$$

and

$$v_x = -z'/\sqrt{[(x')^2 + (z')^2]},$$
$$v_y = 0,$$
$$v_z = x'/\sqrt{[(x')^2 + (z')^2]}.$$

For links where $b_L \neq b_T \neq b_V$ the planes containing the transverse and the vertical axes, T and V, are no longer arbitrary and must be determined by considering the bond in relation to its environment. In the present series the axes T and V of the double bonds of  $\overset{a}{\underset{b}{>}}C{=}C\overset{c}{\underset{d}{<}}$ and  $\overset{a}{\underset{b}{>}}C{=}O$ are respectively in, and perpendicular to, the planes abC.

Let the 5,6-double bond be represented by AB in Fig. 3 in which carbon atoms 5, 6, and 10 correspond to points A, B, and C with co-ordinates (x_5', y_5', z_5'), (x_6', y_6', z_6'), and $(x_{10}', y_{10}', z_{10}')$, respectively. Then l_x, l_y, and l_z for $b_L^{C=C}$ may be calculated as above, but $b_T^{C=C}$ is required by molecular geometry to be taken in the ABC plane at right-angles to AB (*i.e.*, along AD); t_x, t_y, and t_z therefore result from solution of the three simultaneous equations:

$$t_x l_x^{5:6} + t_y l_y^{5:6} + t_z l_z^{5:6} = \cos 90,$$
$$t_x l_x^{5\cdot10} + t_y l_t^{5\cdot10} + t_z l_z^{5\cdot10} = \cos (\mathrm{CAB} - 90),$$
$$t_x^2 + t_y^2 + t_z^2 = 1,$$

where $l_x^{5:6}$, $l_y^{5:6}$, $l_z^{5:6}$, $l_x^{5\cdot10}$, $l_y^{5\cdot10}$, $l_z^{5\cdot10}$ have been calculated above, and $\cos \mathrm{CAB} = l_x^{5:6}l_x^{5\cdot10} + l_y^{5:6}l_y^{5\cdot10} + l_z^{5:6}l_z^{5\cdot10}$.

The remaining direction cosines v_x, v_y, and v_z may be obtained by application of the appropriate orthogonality conditions, thus:

$$v_x = \sqrt{[1 - (l_x^2 + t_x^2)]},$$
$$v_y = \sqrt{[1 - (l_y^2 + t_y^2)]},$$
$$v_z = \sqrt{[1 - (l_z^2 + t_z^2)]}.$$

The axis of the carbonyl group in cholest-5-enone is assumed to lie in a plane perpendicular to the ZX plane and at 54° 44′ to $C_{(3)}$–I in equatorial cholesteryl iodide, *i.e.*, along AC in Fig. 4, in which A (x_3', y_3', z_3') and B (x_I', y_I', z_I') correspond to the positions of $C_{(3)}$ and iodine, respectively; then the position co-ordinates (x', y', z') of C are derived as follows: $(AB)^2 = (x_3' - x_I')^2 + (y_3' - y_I')^2 + (z_3' - z_I')^2$, $AD = y_3' - y_I'$, sin ABD = AD/AB, ACB = (180° − 54° 44′ − ABC), and BC = AB sin BAC/sin ACB; accordingly $x' = x_I'$, $y' = y_I' + BC$, and $z' = z_I'$. Since $b_T^{C=O}$ lies in the ABC plane, all nine direction cosines needed to specify the carbonyl group may be computed from expressions given above.

Fig. 5 relates to the calculation of direction cosines for bonds attached axially at position 3 and assumed to be situated in a plane perpendicular to the ZX plane and at 109° 28′ to $C_{(3)}$–I, *i.e.*, along AC. [A and B, as before, are the locations (x_3', y_3', z_3') and (x_I', y_I', z_I') of $C_{(3)}$ carbon and of iodine in equatorial cholesteryl iodide; AC is of unit length.] Then CAE = 360° − (109° 28′ + 90° + DAB), DAB = 90° − ABD = 71° 17′ (see argument for ketone group), CE = sin CAE, $(A'B')^2 = (x_3' - x_I')^2 + (z_3' - z_I')^2$, $B'G = z_3' - z_I'$, cos A′B′G = cos A′C′F = B′G/A′B′, AE = A′C′ = cos CAE, A′F = A′C′ sin A′C′F, and C′F = A′C′ cos A′C′F, so that the position co-ordinates of C (x', y', z') are $x' = x_3' + A'F$, $y' = y_3' + CE$, and $z' = z_3' + C'F$. Again, since $b_L^{C-X} \neq b_T^{C-X} = b_V^{C-X}$ the nine necessary direction cosines are calculable by formulæ already given.

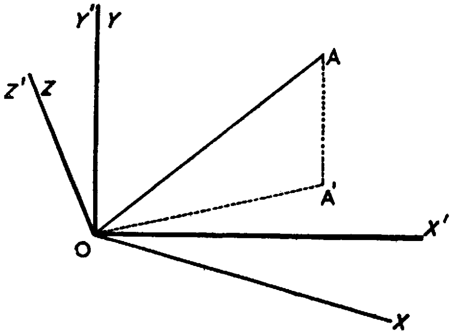


Fig. 2.

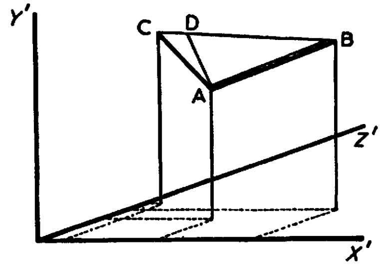


Fig. 3.

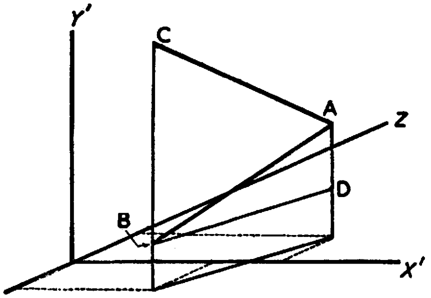


Fig. 4.

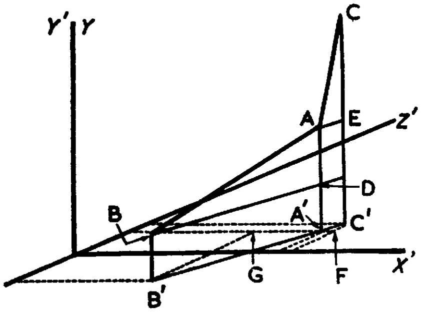


Fig. 5.

Constructions used in the calculations of direction cosines: Figs. 1 and 2, single bonds; Fig. 3, the 5,6-double bond; Fig. 4, the C=O bond.

Subsequent procedure is straight-forward though tedious: the polarisability of every bond in each of the directions X′, Y′, and Z′ (see Fig. 2) is computed and summed over all constituent bonds, *e.g.*, for one bond

$$b_{X'} = (b_L l_x^2 + b_T t_x^2 + b_V v_x^2) + (b_L l_x l_y + b_T t_x t_y + b_V v_x v_y) + (b_L l_x l_z + b_T t_x t_z + b_V v_x v_z)$$
$$b_{Y'} = (b_L l_x l_y + b_T t_x t_y + b_V v_x v_y) + (b_L l_y^2 + b_T t_y^2 + b_V v_y^2) + (b_L l_y l_z + b_T t_y t_z + b_V v_y v_z)$$
$$b_{Z'} = (b_L l_x l_z + b_T t_x t_z + b_V v_x v_z) + (b_L l_y l_z + b_T t_y t_z + b_V v_y v_z) + (b_L l_z^2 + b_T t_z^2 + b_V v_z^2)$$

The nine totals thus obtained form the molecular polarisability tensor, referred to the arbitrary axes X', Y', and Z', the matrix of which is

$$\begin{vmatrix} b_{xx} & b_{yx} & b_{zx} \\ b_{xy} & b_{yy} & b_{zy} \\ b_{xz} & b_{yz} & b_{zz} \end{vmatrix} = Q'$$

This does not have zero off-diagonal terms, except when X', Y', and Z' happen to coincide with the directions in which the molecular principal polarisability axes b_1, b_2, and b_3 are measured, in which case

$$\begin{vmatrix} b_1 & 0 & 0 \\ 0 & b_2 & 0 \\ 0 & 0 & b_3 \end{vmatrix} = Q$$

Q' and Q are related by the orthogonal transformation $Q' = LQL^{-1}$, where L corresponds to

$$\begin{vmatrix} l_{x_1} & l_{x_2} & l_{x_3} \\ l_{y_1} & l_{y_2} & l_{y_3} \\ l_{z_1} & l_{z_2} & l_{z_3} \end{vmatrix}$$

and L^{-1} to the transpose of L

$$\begin{vmatrix} l_{x_1} & l_{y_1} & l_{z_1} \\ l_{x_2} & l_{y_2} & l_{z_2} \\ l_{x_3} & l_{y_3} & l_{z_3} \end{vmatrix}$$

Since the diagonal elements (eigenvalues, b_i) of Q and the columns of L (eigenvectors, $l_{\cdot i}$) relate to polarisability semiaxes in magnitude and direction, respectively, the problem centres on the conversion of Q' (calculable from bond polarisabilities and molecular geometry) into Q, *i.e.*, on diagonalising Q'. This requires solving the equations

$$(Q' - b_1E)l_{\cdot 1} = 0, \qquad (1)$$

$$(Q' - b_2E)l_{\cdot 2} = 0, \qquad (2)$$

and

$$(Q' - b_3E)l_{\cdot 3} = 0, \qquad (3)$$

(where E is the unit matrix, $L^{-1}L$, of dimension 3), *i.e.*, of finding the three roots of the trinomial:

$$\begin{vmatrix} b_{xx}-\lambda & b_{yx} & b_{zy} \\ b_{xy} & b_{yy}-\lambda & b_{zy} \\ b_{xz} & b_{yz} & b_{zz}-\lambda \end{vmatrix} = 0$$

The eigenvalues thus produced, substituted into (1), (2), and (3), lead to a further nine equations which, when considered in conjunction with the orthogonality condition, $\sum l_{\cdot i}^2 = 1$, permit evaluation of the eigenvectors $l_{\cdot i}$.

These last stages, too lengthy for ordinary " long hand " methods, are readily performed by the Sydney University digital computer Silliac, for which a standard eigenvalue-eigenvector programme is available. Data tapes are prepared containing the matrix elements of Table 3; the machine prints results as in Table 4.

TABLE 3.

Elements of Q' derived from bond polarisabilities and molecular geometry.

Structure	b_{xx}	$b_{xy} = b_{yx}$	b_{yy}	$b_{xz} = b_{zx}$	$b_{yz} = b_{zy}$	b_{zz}
eq-$C_{27}H_{45}I$	5·0408	0·0163	4·6523	0·1064	0·1768	5·5534
eq-$C_{27}H_{45}Br$..................	4·8752	0·0135	4·4750	0·0983	0·1407	5·2824
eq-$C_{27}H_{45}Cl$	4·7747	0·0111	4·3645	0·0913	0·1098	5·0915
ax-$C_{27}H_{45}I$	5·0410	$0{\cdot}0060_5$	5·0641	0·0750	0·0436	5·1471
ax-$C_{27}H_{45}Br$	4·8750	0·0059	4·7801	0·0750	0·0421	4·9811
ax-$C_{27}H_{45}Cl$..................	4·7744	0·0058	4·5781	0·0750	0·0408	4·8805
Cholest-5-enone	4·6921	−0·0011	4·2278	0·0770	−0·0498	4·8240
Cholesteryl skeleton	4·6155	0·0056	4·1820	0·0750	0·0377	4·7215

TABLE 4.

Principal polarisabilities and direction cosines relating them to axes *X′*, *Y′*, and *Z′*.

	eq-$C_{27}H_{45}I$	*ax*-$C_{27}H_{45}I$	*eq*-$C_{27}H_{45}Br$	*ax*-$C_{27}H_{45}Br$	*eq*-$C_{27}H_{45}Cl$	*ax*-$C_{27}H_{45}Cl$	Cholest-5-enone	Cholesteryl skeleton
b_1	5·607	5·199	5·328	5·027	5·131	4·924	4·863	4·763
b_2	5·020	5·055	4·854	4·839	4·751	4·737	4·658	4·577
b_3	4·619	4·998	4·451	4·771	4·348	4·573	4·224	4·179
l_{x_1}	+0·1866	+0·4192	+0·2140	+0·4430	+0·2496	+0·4495	+0·4106	+0·4553
l_{y_1}	+0·1819	+0·2967	+0·1623	+0·1613	+0·1408	+0·1122	−0·0720	+0·0621
l_{z_1}	+0·9655	+0·8580	+0·9633	+0·8819	+0·9581	+0·8862	+0·9089$_5$	+0·8882
l_{x_2}	+0·9824	−0·3610	+0·9768	+0·8894	+0·9683	+0·8930	+0·9117	+0·8903$_5$
l_{y_2}	−0·0437	+0·9216	−0·0431	−0·2032	−0·0421	−0·0812	+0·0450	−0·0307
l_{z_2}	−0·1816	−0·1423	−0·2097	−0·4095	−0·2461	−0·4427	−0·4083	−0·4542
l_{x_3}	+0·0092	+0·8330	+0·0075	+0·1132	+0·0057	+0·0223	−0·0115	−0·0009
l_{y_3}	+0·9823	+0·2501$_5$	+0·9858	+0·9657$_5$	+0·9891	+0·9904	+0·9964	+0·9976
l_{z_3}	−0·1869	−0·4935	−0·1677	−0·2335	−0·1468	−0·1367	+0·0841	−0·0692$_5$

The " anisotropy " and " dipole " terms,[3] θ_1 and θ_2, which contribute to the molar Kerr constants of polar molecules, now have to be calculated. The former, times 10^{35}, can be drawn at once from Table 4 as:

eq-$C_{27}H_{45}I$	8·403	*eq*-$C_{27}H_{45}Br$	6·558	*eq*-$C_{27}H_{45}Cl$	5·218
ax- ,,	0·365	*ax*- ,,	0·598	*ax*- ,,	1·050
Cholest-5-enone	3·623			Cholest-5-ene	3·029

The " dipole " terms have some magnitudes which depend on the disposition of the resultant moment within the framework of the principal axes. If, as an initial approximation, μ_{res} in the equatorial halides acts parallel to the b_1 direction, and in the axial chloride at 20° to b_3 in the b_1b_3 plane, ${}_{m}K$'s (calc.) emerge as follows:

	$10^{35}\theta_2$	$10^{35}(\theta_1 + \theta_2)$	$10^{12}{}_{m}K$ (calc.)	$10^{12}{}_{m}K$ (obs.)
eq-$C_{27}H_{45}I$	105·6	114·0	479	517
eq-$C_{27}H_{45}Br$	88·2	94·8	399	492
eq-$C_{27}H_{45}Cl$	70·6	75·8	319	435
ax-$C_{27}H_{45}Cl$	−24·4$_5$	−23·4	−98	−60

In each case the observed ${}_{m}K$ is algebraically more positive than that calculated.

Attempts to locate μ_{res} less speculatively have been made by regarding the measured dipole moment μ_{res} as the resultant of the link moment μ_L appropriate for the substituent at the 3-position and a " skeleton " moment μ_S, the last being taken to act along the 5,6-double bond and to interact with μ_L (*i.e.*, with the $C_{(3)}$–X bond) at ϕ°; $\cos \phi = \sum l_i l_i'$ for the bonds $C_{(3)}$–X and $C_{(5)}{=}C_{(6)}$. Then $\mu_{res}^2 = \mu_L^2 + \mu_S^2 + 2\mu_L\mu_S \cos \phi$, and α (the angle between μ_{res} and μ_L) follows as arctan $[\mu_S \sin \phi/(\mu_L + \mu_S \cos \phi)]$. By using moments of the corresponding methyl derivatives [28] as a first approximation to μ_L, a mean value for μ_S (0·67 D) was obtained; with this the μ_L's were recalculated, thus allowing estimates of the α's to be made. The direction cosines needed to specify μ_{res} within the axes *X′*, *Y′*, and *Z′* were then computed by methods similar to those described above; numerical results are in Table 5.

TABLE 5.

Locations of μ_{res} in axes *X′*, *Y′*, and *Z′*.

Cholest-5-ene deriv.	ϕ°	μ_L (D)	α°	l_x	l_y	l_z
eq-3-I	56° 55′	1·82	14° 23′	−0·3155	−0·2735$_5$	−0·9086
ax-3-I	86° 48′	2·12	17° 13′	0·2582	0·9530$_5$	0·1587
eq-3-Br	56° 55′	1·79	14° 35′	−0·3190	−0·2725	−0·9077
ax-3-Br	86° 48′	2·09	17° 27′	0·2615	0·9522	0·1603
eq-3-Cl	56° 55′	1·71	15° 8′	−0·3280$_5$	−0·2704	−0·9052
ax-3-Cl	86° 48′	2·01	18° 8′	0·2715	0·9478	0·1660
3-Ketone	64° 53′	2·94	10° 40′	−0·2327	0·5167$_5$	−0·8239

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[28] Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

From the combined results of Tables 4 and 5 molar Kerr constants are deducible as follows:

	$10^{35}\theta_2$	$10^{35}(\theta_1 + \theta_2)$	$10^{12}{}_mK$ (calc.)
eq-$C_{27}H_{45}I$	101·46	109·86	462·0
ax- ,,	0·60	0·97	4·1
eq-$C_{27}H_{45}Br$	84·68	91·24	383·7
ax- ,,	−12·70	−12·10	−50·9
eq-$C_{27}H_{45}Cl$	67·46	72·68	305·6
ax- ,,	−21·98	−20·93	−88·0
Cholest-5-en-3-one	62·92	66·54	279·8
Cholest-5-ene	6·71	9·73	40·9

Conformations Indicated by Molar Kerr Constants.—Equatorial or axial attachment of halogen at the 3-position should be revealed by ${}_mK$'s which are large and positive or near-zero to negative, respectively. The ${}_mK$'s now reported (Table 2) thus show each of the cholesteryl halides to have equatorial conformations; epicholesteryl chloride is evidently the axial isomer. Where cholesteryl chloride is concerned this conclusion is in accord with that reached in 1946 by Shoppee [29] through consideration of the mechanisms and steric orientations of substitution in cholestane and cholestene, whereby the chlorine atom in cholesteryl chloride was assigned to the 3(β) class of substituents (*i.e.*, to those lying on the same side of the plane 2,3,7,8 as the angular 10-methyl group); epicholesteryl chloride was unknown until 1952 (Shoppee and Summers [7]). Since the hydroxyl group of cholesterol undergoes replacement by chlorine with retention of configuration (Shoppee [29]) the present work also provides indirect physical support for the long-held [30] view that hydroxyl in this sterol is attached by an equatorial C–O link.

Comparison of Calculated and Observed ${}_mK$'s.—The calculated molar Kerr constants for the iodide, bromide, and chloride fall short of those observed by 11%, 22%, and 30%, respectively. Such deficiencies seem too great to be wholly attributed to incorrectnesses of measurement; in the worst case (cholesteryl chloride) the standard error in the factor which predominantly affects ${}_\infty({}_mK_2)$, *viz.*, 10·03 in the equation $10^7\Delta B = 10{\cdot}03w_2 + 372w_2^2$, is by only ±3·9%; this value is not outside the range of past experience [3e] with optically inactive solutes, and whereas in previous comparisons [6] of (+)- or (−)-solutes with their (±)-varieties the maximum disagreement between the ${}_\infty({}_mK_2)$'s observed was 10%.

In part the causes for the inadequacies in the ${}_mK$'s (calc.) must lie in the calculations themselves. Improper locations of μ_{res} cannot be responsible, since reasonable variations of these alter the ${}_mK$'s (calc.) by only a few percent (cf. effects of taking μ_{res} parallel to b_1 above). It is possible that the structural specifications for all the dissolved cholesteryl halides should not be taken from that reported for crystalline cholesteryl iodide: the literature [31] appears to contain no rigorous demonstration that replacing iodine by bromine or chlorine leaves an attached carbon skeleton completely undistorted (Bowen, Gilchrist, and Sutton [32] give the C–C–C angles in t-butyl chloride, bromide, and iodide as 109·2° ± 1·5°, 108·9° ± 2°, and 109·2° ± 1·5°, respectively; Wiebenga and Krom [33] state that intervalency angles listed for chloro-, bromo-, and cyano-camphor may have standard deviations of about 4°); Robertson,[34] commenting on the cholesteryl iodide analysis, pointed out that the accuracy claimed for the final atomic positions was not high; molecular configurations in the solid may not be retained in the dissolved state (contrast the planar *trans*-arrangement of 1,4-dimethoxybenzene in the crystal (M 217 of ref. 31) with the polarity of 1·8 D as a solute in carbon tetrachloride.[35] To estimate *a priori* the effects on b_1, b_2, and b_3 of

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[29] Shoppee, *J.*, 1946, 1138, 1147.

[30] Ruzicka, Fürter, and Goldberg, *Helv. Chim. Acta*, 1938, **21**, 498.

[31] Cf., *e.g.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. Sutton, *Chem. Soc. Special Publ.*, No. 11, 1958.

[32] Bowen, Gilchrist, and Sutton, *Trans. Faraday Soc.*, 1955, **51**, 1341.

[33] Wiebenga and Krom, *Rec. Trav. chim.*, 1946, **65**, 663; personal communication from Professor Wiebenga.

[34] Robertson, *Ann. Reports*, 1945, **42**, 54.

[35] Aroney, Le Fèvre, and Shu-Sing Chang, *J.*, 1960, 3173.

varying the C–C–C angles by, say, ±1·5—2·0° would be lengthy and speculative; such operations have not been undertaken.

Because of the numerous bonds in these structures it is possible that neglect of secondary induction effects [cf. p. 268 of ref. 3(*a*)] has become significant, leading to forecasts of lower anisotropies than in fact occur. No way exists of "correcting" our calculations of b_1, b_2, and b_3 for these omissions. Relatively small changes in the semiaxes would reconcile "theory" and experiment. In illustration we mention that, as a check on the formal calculations outlined above, a three-dimensional scale model was built as accurately as possible to Carlisle and Crowfoot's specification for cholesteryl iodide. By stretching threads through the model and measuring by hand all the thread-bond angles, a direction was—after several trials—discovered which produced a maximum value for b_1 and a minimum for b_3; the $C_{(3)}$–X bond lay at 6° to the b_1 direction. Retaining the same $b_{\max}$ direction in the chloride and bromide then gave:

	b_1	b_2	b_3	$10^{12}{}_{\mathrm{m}}K$ (calc.)
eq-Cholesteryl chloride	5·18	4·67	4·34	360
,, bromide	5·38	4·77	4·44	447
,, iodide	5·66	4·94	4·61	532

It is seen that the ${}_{\mathrm{m}}K$'s (calc.) for cholesteryl chloride and bromide are thus brought nearer to those found by experiment, whilst that for the iodide now exceeds ${}_{\mathrm{m}}K$ (obs.), although the individual b_i's have magnitudes within 1% of the corresponding data in Table 4.

Because variations in b_1 of this order could also originate in the anisotropic polarisabilities adopted for the C–X links, the infrared C–X stretching frequencies were checked on ethereal solutions of the three halides and found to agree with those recorded by Barton, Page, and Shoppee[36] for carbon disulphide solutions (*viz.*, for C–Cl, C–Br, and C–I, absorptions noted at 760, 704, and 672 cm.$^{-1}$, respectively). The Le Fèvre equation,[37] connecting ν (cm.$^{-1}$) for the link C–X with $b_L^{\mathrm{C-X}}$, requires knowledge also of the inter-centre separation r_{CX}, which for the cholesteryl halides is available only with the iodide. Since ν is sensitively affected by r_{CX}, by using the equation in reverse (*i.e.*, by calculating r_{CX} from $b_L^{\mathrm{C-X}}$) a test of the reasonableness or otherwise of $b_L^{\mathrm{C-X}}$ can be made: thus $b_L^{\mathrm{C-X}}$'s of 0·396, 0·598, and 0·882 correspond to $r_{\mathrm{C-X}}$'s of $1{\cdot}79_8$, $1{\cdot}93_1$, and $2{\cdot}07_8$ Å. The last of these is identical, to three significant figures, with $r_{\mathrm{C-I}} = 2{\cdot}08$ Å deduced[23] by Carlisle and Crowfoot, while the others are within the ranges reported (M 172 of ref. 31) for $r_{\mathrm{C-X}}$ in Me_3CCl (1·78—1·80 Å) and Me_3CBr (1·92—1·94 Å).

Finally, we mention that the totals, $b_1 + b_2 + b_3$, are close to those forecast by summation of the "bond electronic polarisations" listed recently[38] by Le Fèvre and Steel:

	Σb_i from Table 4	Σb_i from ref. 38
Cholesteryl chloride	14·23	14·35
,, bromide	14·63	14·67
,, iodide	15·25	$15{\cdot}24_5$

Since the b_i's of Table 4 incorporate all the bond polarisabilities now used, and because of the large number of two of the bonds involved, this agreement is reassuring, at least where $b_L + b_T + b_V$ for C–H and C–C are concerned. Incidentally, the present cases provide further examples (cf. ref. 38) of the dangers in assuming ${}_{\mathrm{E}}P = 0{\cdot}95R_{\mathrm{D}}$: on such a basis Σb_i for the chloride, bromide, and iodide would be 13·9, $13{\cdot}9_5$, and 15·2, respectively.

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[36] Barton, Page, and Shoppee, *J.*, 1956, 331.

[37] Le Fèvre, *Proc. Chem. Soc.*, 1959, 363.

[38] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.