‖Tableau 10. *Paramètres d'agitation thermique du cycle benzénique supposé rigide*

Coordonnées du centre de libration dans a, b, c^*: 3,886, 4,656, 0,537.

$$T = \begin{pmatrix} 3,34 & 0,17 & -0,27 \\ & 3,69 & 0,04 \\ & & 3,36 \end{pmatrix} 10^{-2} \text{ Å}^2 \qquad L = \begin{pmatrix} 2,95 & -0,18 & 0,88 \\ & 85,26 & 5,71 \\ & & 6,55 \end{pmatrix} (°)^2$$

$$\sigma(T) = \begin{pmatrix} 0,26 & 0,12 & 0,16 \\ & 0,11 & 0,11 \\ & & 0,16 \end{pmatrix} 10^{-2} \text{ Å}^2 \qquad \sigma(L) = \begin{pmatrix} 0,41 & 1,70 & 0,41 \\ & 6,14 & 0,90 \\ & & 0,48 \end{pmatrix} (°)^2$$

Tableau 11. *Liaisons hydrogènes et plus courtes distances intermoléculaires*

O(2, I)—N(4, V)	2,89 Å		O(2, I)–O(2, V)	3,47 Å
N(4, I)—O(2, V)	2,89		O(2, I)–O(3, IV)	3,50
O(2, I)—O(3, VI)	3,07		N(4, I)–O(3, VI)	3,57
O(3, I)—O(2, VII)	3,07		O(2, I)–C(13, V)	3,59
N(4, I)—O(3, IV)	3,24		C(7, I)–Cl(1, VIII)	3,60
C(11, I)-C(11, IX)	3,42			

I	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	VI	$1-x$	$1-y$	$1-z$
II	x	y	z	VII	$1-x$	$-y$	$1-z$
III	x	$1+y$	z	VIII	$-x$	$1-y$	$-z$
IV	x	$y-1$	z	IX	$-x$	$y-\frac{1}{2}$	$\frac{1}{2}-z$
V	$1-x$	$y-\frac{1}{2}$	$\frac{1}{2}-z$				

Ions cristallins et Monsieur le Professeur Meinnel qui a suscité et dirigé ce travail.

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The Crystal and Molecular Structure of Dibromodulcitol C6H12O4Br2 and Dichlorodulcitol C6H12O4Cl2

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Dibromodulcitol (DBD) and dichlorodulcitol (DCD) are isomorphous and crystallize in the monoclinic space group $P2_1/c$ with 2 molecules in unit cells of dimensions $a=4·874$, $b=5·269$, $c=19·812$ Å and $\beta=98·05°$ for DBD and $a=4·889$, $b=5·119$, $c=19·043$ Å and $\beta=96·8°$ for DCD. Both molecules have Ī symmetry and form planar zigzag carbon chains. The halogen atoms at the end of the chain are outside of the carbon plane in an almost equi-distant position to the two nearest oxygen atoms of the molecule. The molecules form two-dimensional molecular networks parallel to the (001) plane. In the networks each molecule is linked to four neighbouring molecules by two hydrogen bonds, respectively, forming in this way closed circuits with hydrogen bonds. The networks are held together by van der Waals forces. All hydroxyl oxygens act both as donors and acceptors and in the closed circuits the proton positions could be determined. The mean lengths of C–C, C–O and halogen–C bonds are 1·540, 1·413 and 1·975 Å in DBD and 1·534, 1·432 and 1·820 Å in DCD. The C–C–C bond angles are on average 111·0 and 111·5° for DBD and DCD, respectively.

Introduction

Dibromodulcitol (1,6-dibromo-1,6-dideoxy-D-galacti-tol) and dichlorodulcitol (1,6-dichloro-1,6-dideoxy-D- galactitol) were produced for pharmacological purposes (Institoris, 1967, Institoris, Horváth & Csányi, 1967) by substituting OH at the two ends of the galactitol molecule by halogen atoms. The Fischer formula

of these derivatives is

CH₂X
|
H—C—OH
|
HO—C—H
|
HO—C—H
|
H—C—OH
|
CH₂X
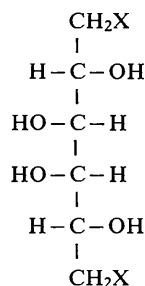
where X represents the place of Br and Cl atoms.

On the basis of both pharmacological and clinical investigations a selective and vigorous antitumoral effect of DBD was reported (Kellner, 1967). The same effect, however, could not be proved for DCD (Institoris, 1970). The present crystal structure determination, giving the molecular conformations, is part of further investigations for detecting the origin of the different behaviour of the two halogen derivatives of dulcitol.

Experimental

The halogen derivatives of galactitol DBD and DCD were dissolved in dimethylformamide. From this solution colourless transparent crystals could be gained by recrystallization for DBD as well as for DCD, which are always thin plates parallel to the (001) crystallographic plane. For DBD the plates are extremely thin and their thickness has never exceeded 0·01 mm. Therefore the other two dimensions could not be reduced sufficiently for avoiding unwanted absorption and thus the reflexion intensities for DBD are less accurate than for DCD.

The unit-cell dimensions were determined from Buerger precession photographs around the crystallographic axes with Cu $K\alpha$ radiation. The crystal density was measured by pycnometer. The summarized crystallographic data are as follows:

DBD

$a = 4·874 \pm 0·004$ Å   M.W. 307·994
$b = 5·269 \pm 0·006$ $D_m = 2·05$ g.cm⁻³
$c = 19·812 \pm 0·007$ $D_x = 2·03$
$\beta = 98·05 \pm 0·1°$ $Z = 2$
$F(000) = 300$ μ(Cu $K\alpha$) = 112 cm⁻¹

DCD

$a = 4·889 \pm 0·003$ Å   M.W. 219·076
$b = 5·119 \pm 0·005$ $D_m = 1·58$ g.cm⁻³
$c = 19·043 \pm 0·007$ $D_x = 1·54$
$\beta = 96·8 \pm 0·1°$ $Z = 2$
$F(000) = 228$ μ(Cu $K\alpha$) = 60 cm⁻¹

The space group $P2_1/c$ has been determined from the systematic absences, $h0l$ if l odd and $0k0$ if k odd. From the crystallographic data it became obvious that

Table 1. *The final fractional coordinates of atoms in the asymmetric unit for DBD and DCD*

After each atomic coordinate its estimated standard deviation is given in parentheses and refers to the least significant digits. In the notation of hydrogen atoms the C or O atoms, to which the hydrogen atoms are attached, are given. For the heavier atoms of DCD there are also given the coordinates corrected for libration of molecule as a rigid body.

	DBD			DCD					
	x	y	z	x	y	z	x (corrected)	y (corrected)	z (corrected)
Halogen	0·3316 (6)	0·1184 (5)	0·1929 (1)	0·3369 (4)	0·1196 (4)	0·1924 (1)	0·3378	0·1200	0·1928
O(1)	−0·2484 (27)	−0·3181 (28)	0·0750 (7)	−0·2418 (9)	−0·3148 (10)	0·0812 (3)	−0·2422	−0·3154	0·0814
O(2)	−0·2292 (27)	−0·2587 (29)	0·0117 (6)	−0·2345 (8)	−0·2726 (10)	0·0137 (2)	0·2351	−0·2732	0·0137
C(1)	0·1191 (48)	−0·1817 (53)	0·1558 (11)	0·1362 (15)	−0·1673 (16)	0·1624 (4)	0·1368	−0·1675	0·1627
C(2)	−0·0651 (42)	−0·1158 (38)	0·0909 (10)	−0·0577 (13)	−0·0969 (14)	0·0958 (3)	−0·0578	−0·0970	0·0960
C(3)	0·1028 (36)	−0·0327 (47)	0·0327 (9)	0·0992 (11)	−0·0406 (13)	0·0323 (3)	0·0995	−0·0407	0·0324
H1[C(1)]	−0·010	−0·238	0·193	0·020	−0·220	−0·200			
H2[C(1)]	0·261	−0·322	0·146	0·270	−0·327	0·152			
H[C(2)]	−0·182	0·052	0·098	−0·175	0·050	0·108			
H[C(3)]	0·219	0·137	0·049	0·270	0·100	0·048			
H[O(1)]	−0·242	−0·468	0·044	−0·239	−0·463	0·047			
H[O(2)]	0·423	−0·281	0·035	0·427	−0·288	0·038			

Table 2. *Anisotropic thermal parameters for DBD and DCD with the estimated standard deviations in parentheses*

The b_{ij} are defined by
$$T = \exp[-10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

Crystal		b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
DBD	Br	770 (15)	470 (14)	35 (1)	−38 (23)	−39 (6)	42 (4)
	O(1)	438 (53)	250 (53)	32 (4)	82 (117)	−30 (26)	12 (27)
	O(2)	555 (59)	329 (57)	21 (3)	322 (126)	−13 (23)	16 (25)
	C(1)	610 (92)	467 (104)	29 (5)	240 (214)	−96 (38)	−46 (44)
	C(2)	467 (78)	300 (85)	25 (5)	188 (155)	−75 (33)	14 (33)
	C(3)	413 (72)	434 (93)	22 (4)	238 (187)	35 (32)	69 (38)
DCD	Cl	491 (8)	546 (9)	21 (0)	−97 (15)	−44 (3)	−42 (3)
	O(1)	257 (16)	423 (19)	24 (1)	−100 (33)	12 (7)	−4 (9)
	O(2)	279 (16)	368 (17)	19 (1)	161 (31)	−11 (7)	−31 (8)
	C(1)	408 (27)	471 (30)	20 (2)	−68 (56)	−20 (12)	13 (13)
	C(2)	291 (22)	426 (27)	19 (2)	46 (46)	−1 (10)	−8 (11)
	C(3)	238 (19)	369 (23)	17 (1)	78 (41)	8 (9)	3 (10)

the molecule itself has a centre of symmetry. Though the dimensions of the crystals used reached in some direction 0·3 mm and thus in such direction $\mu.R$ was 3·4 for DBD, no absorption correction was made.

The relative intensities of the reflexions were recorded with STOE equi-inclination Weissenberg camera using multiple-film technique on layers 0 to 3 about both the a and b crystallographic axes. For DCD some more intensities were collected on 0 to 5 layers about the c axis. The intensities were eye-estimated using calibrated intensity scales. For DBD and DCD, 639 and 946 reflexions, respectively, were collected, of which 207 and 225, respectively, were unobserved. The reflexions of zero intensity were taken with a value of $I_0 = \frac{1}{4}I_{min}$. The intensities originating from different films were brought to a common scale by multiple-film scaling, and by interlayer scaling after applying the Lorentz and polarization factors. The absolute scale and approximate overall isotropic temperature factor were determined by a Wilson plot from all the three-dimensional data.

Table 3. *Observed and calculated structure factors*

Table 3 (cont.)

Determination of the structure

The heavy atom positions of DBD and DCD were deduced from the two-dimensional Patterson along the a and b axes. The corresponding approximate coordinates of the heavy atoms with overall isotropic temperature factors $B(DBD) = 3·93$ Å^{-2} and $B(DCD) = 3·52$ Å^{-2} gave a structure factor agreement for all observed reflexions $R(DBD) = 0·43$ and $R(DCD) = 0·51$. All other atoms except hydrogen atoms and one oxygen atom, nearest to the halogen atom, could be deduced from the first three-dimensional Fourier function for DBD, using Domenicano & Vaciago's (1966) program.

The difference Fourier synthesis, removing the Br atom revealed also the oxygen atom missing in the first Fourier function. As the heavy atom positions of DBD and DCD, deduced from the two-dimensional Patterson functions agreed quite well, the isomorphy of the two crystals was assumed and therefore the positions of common atoms of the two crystals were taken from the determination of DBD. With these atomic positions, using all observed reflexions, agreement factors of $R=0.27$ and $R=0.28$ could be attained for DBD and DCD respectively. From this point on, the refinement of the two structures was carried out separately by full-matrix least-squares using Albano, Domenicano & Vaciago's (1966), program minimizing the function

$$\Phi=\sum_h w_h(F_{oh}-\frac{1}{G}|F_{ch}|)^2,\text{ where } G\text{ is the scaling factor.}$$

The weighting factor of Cruickshank (1961a), $w_h= 1/(a+b.F+c.F^2)$ was used with $a=4.0$, $b=1$ and $c=0.01$. The refinement of coordinates and temperature parameters was carried out only for the heavy (halogen, O, C) atoms and no refinement was made for hydrogen parameters. Three cycles with isotropic and three cycles with anisotropic temperature parameters resulted, with all observed reflexions, in agreement factors of $R=13.1\%$ and $R=11.0\%$ for DBD and DCD, respectively.

After least-squares refinement the atomic coordinates of hydrogen atoms, except those of the hydroxyls, have been generated geometrically for both crystals. Including these generated hydrogen atoms into struc-

ture factor calculation we found that the agreement factors decreased to $R(\text{DBD})=12.9\%$ and $R(\text{DCD})= 10.8\%$. At this stage of refinement the F_o-F_c difference Fourier function was calculated only for DCD, removing all atoms but the hydrogen. In this Fourier function definite electron density peaks could be found very well approximating all the generated hydrogen positions and two further peaks at distances of 1.0 and 0.6 Å from the two hydroxyl oxygens belonging to the asymmetric part of the molecule. Including also these hydrogen atoms of the hydroxyls, increasing the distance of 0.6 to 1.0 Å and replacing the generated hydrogen atoms by those experimentally determined we could achieve a further slight decrease of the R value, which is significant if we take into consideration that this decrease takes place in the presence of heavy Cl atoms. Thus the hydrogen positions of the hydroxyls in DCD can be considered as confirmed and on the basis of isomorphy the same hydrogen positions can be generated in DBD. The final atomic parameters are summarized in Table 1 and Table 2.

Structure factors calculated from the final atomic parameters are given in Table 3. The atomic scattering factors of all atoms are taken from *International Tables for X-ray Crystallography* (1962). For the hydrogen atoms, the temperature factors of these nearest atoms to which they are bonded are used. The final R values for all observed reflexions are $R=12.9\%$ for DBD and in the case of DCD, omitting 9 reflexions with high extinction, $R=9.9\%$.

Table 4. *Constants of least-squares plane* $(Ax+By+Cz=D)$ *formed by the carbon atoms of the molecule and distances to this plane for all asymmetric atoms of the molecule, excluding* H

The plane is referred to crystal axes and coordinates are considered in Å.

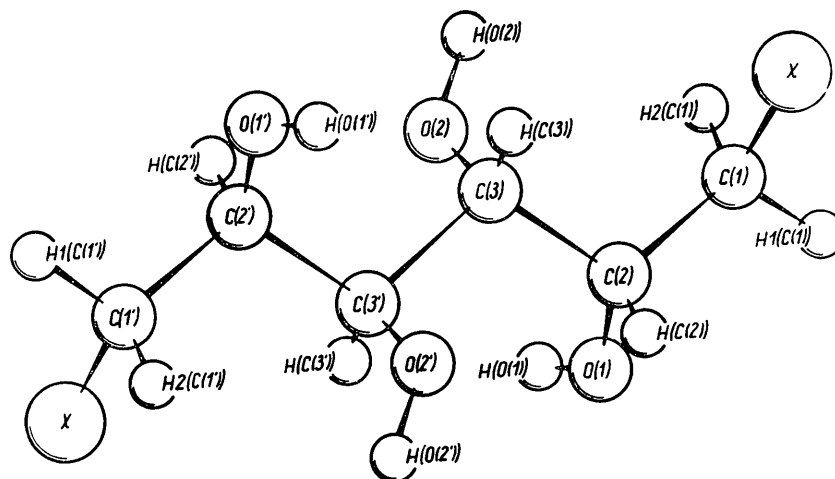| Crystal		A	B	C	D	Distance to plane (Å)
DBD	C(1), C(2) C(3)	−0.0738	0.9560	0.3088	0.0	0.0004, −0.0004, −0.0007
	O(1), O(2), Br					−1.0450, −1.3066, 1.6522
DCD	C(1), C(2), C(3)	0.0381	0.9626	0.2618	0.0	0.0105, −0.0107, −0.0206
	O(1), O(2), Cl					−1.1915, −1.2313, 1.6111

Fig. 1. Perspective view of the DBD molecule with identifications of the atoms. No significant difference arises with DCD.

The geometry of the molecule

The molecule of DBD as well as of DCD form zigzag carbon chains with a centre of symmetry at the midpoint of the central C(3)–C(3') bond (Fig. 1). This *meso* conformation is in accordance with the optical inactivity of both molecules. The six carbon atoms of the molecule form a plane with observed mean deviations of 0·0005 and 0·014 Å for DBD and DCD, respectively (Table 4). All other atoms are outside the plane according to the tetrahedral configuration. The terminal tetrahedra of the molecule are twisted about the C(2)–C(1) and its *meso*-related bond, compared to dulcitol, so that the Br and Cl atoms, respectively, come far from the plane and take positions at almost equal distances farthest from O(1) and O(2) atoms of the molecule. The bond lengths and bond angles and some non-bonding interatomic distances of the molecule were calculated from atomic positions given in Table 1 and are summarized in Table 5. For DCD the interatomic distances were also corrected for thermal libration of the molecule as rigid body and are included in Table 5. The symmetry of the molecules is $\bar{1}$.

Table 5. *Bond lengths and bond angles and some non-bonding intramolecular atomic distances with their estimated standard deviations in parentheses applied to the least significant digits*

The distances of DCD have also been corrected for thermal libration.

Atoms	DBD	Distances DCD	DCD (corrected)
C(1)–C(2)	1·502 (32) Å	1·534 (10) Å	1·537 Å
C(2)–C(3)	1·567 (28)	1·535 (9)	1·537
C(3)–C(3')	1·561 (28)	1·531 (9)	1·536

Table 5 (*cont.*)

Atoms	DBD	Distances DCD	DCD (corrected)
C(2)–O(1)	1·398 (24)	1·439 (8)	1·442
C(3)–O(2)	1·429 (24)	1·425 (8)	1·428
C(1)–Halogen	1·975 (25)	1·820 (8)	1·824
O(1)–Halogen	4·110 (14)	4·001 (5)	4·011
O(2)–Halogen	4·072 (14)	3·931 (5)	3·941
O(1)–O(2)	2·812 (19)	2·799 (7)	2·805
O(2)–O(2')	3·514 (19)	3·610 (6)	3·619

	Angles DBD	DCD
C(1)–C(2)–C(3)	112·5 (17)°	112·2 (6)°
C(2)–C(3)–C(3')	109·4 (16)	110·8 (5)
C(1)–C(2)–O(1)	107·6 (17)	106·8 (5)
C(3)–C(2)–O(1)	115·5 (16)	110·7 (5)
C(2)–C(3)–O(2)	105·8 (15)	109·3 (5)
C(3')–C(3)–O(2)	101·3 (15)	107·2 (5)
C(2)–C(1)–Halogen	110·7 (16)	109·1 (5)

The thermal motion analysis

The root-mean-square amplitudes and vectors of the principal axes of thermal vibration ellipsoids for the individual atoms were calculated from their anisotropic thermal parameters given in Table 2. The origin of the vectors of principal axes is positioned at the site of the corresponding atom. Thus the data of principal axes given in Table 6 can directly be used to follow the drawing of the thermal ellipsoids in Fig. 2 giving the molecule in orthogonal projection on the plane (010).

The thermal motion of DBD and DCD molecules have also been analysed as rigid body molecular vibration on the basis of Cruickshank's (1961a) procedure using the program of Schomaker & Trueblood (1967). The U tensors of the individual atoms calculated from rigid body thermal motion (U_{calc}) and gained from the structure analysis (U_{obs}) are compared in Table 7. As can be seen, the agreement is quite satisfying for DCD
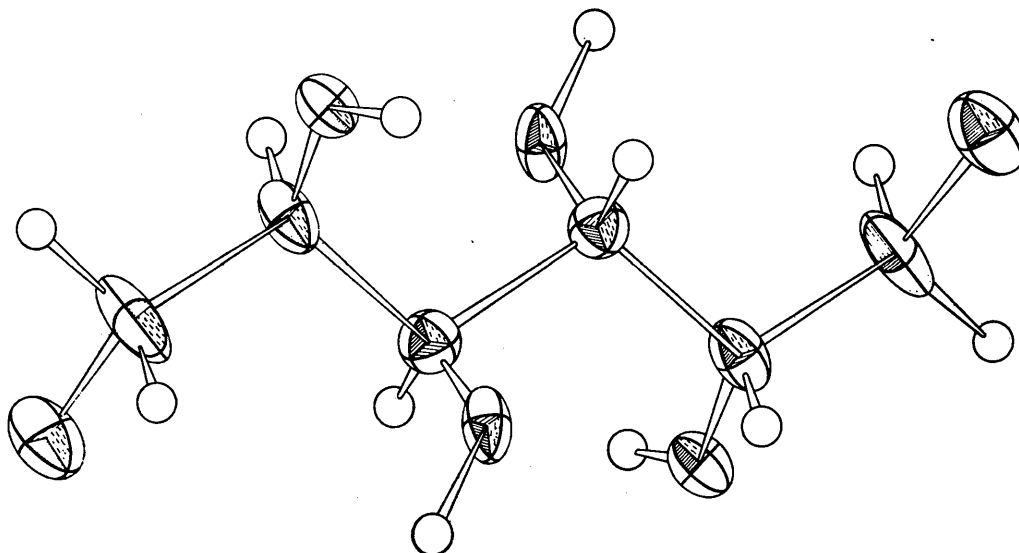

Fig. 2. Perspective view of the DBD molecule. Atoms are represented by their thermal vibration ellipsoids.

and supports the rigid body assumption of this derivative.

The translational **T** and librational ω tensors for DCD are given in Table 8. The estimated standard deviations referred to the least significant digits are in parentheses. The principal axes of **T** and ω tensor ellipsoids are given in Table 9 by their lengths and direction cosines referred to the orthogonalized axial system. The last two columns show the angles of the principal axes to the plane formed by the C atoms and to the direction of the C(1)–Cl bond, respectively. From these data it can be stated that the principal axis of greatest libration has an inclination angle of 12·3° to the plane of the carbon atoms and is almost rectangular to the C(1)–Cl bond (92·3°). The next greatest librational axis is nearly parallel to the C(1)–Cl bond (167·4°).

The atomic coordinates of the DCD molecule were corrected for rigid body thermal libration and are given

Table 6. *Principal axes of the thermal vibration ellipsoids for the asymmetric atoms of the molecule given by their lengths and coordinates of their end points (in fractions) referred to the crystal axes*

The origins of principal axes are considered to be at the site of the corresponding atoms.

			DBD						DCD		
	i	U_i(Å)	x	y	z		i	U_i(Å)	x	y	z
Br	1	0·326	0·277	0·112	0·201	Cl	1	0·275	0·345	0·068	0·196
	2	0·270	0·309	0·160	0·187		2	0·264	0·383	0·120	0·186
	3	0·226	0·312	0·094	0·184		3	0·167	0·355	0·128	0·200
O(2)	1	0·285	0·180	−0·285	0·014	O(2)	1	0·243	0·213	−0·310	0·019
	2	0·213	0·226	−0·236	0·020		2	0·180	0·229	−0·254	0·021
	3	0·169	0·210	−0·238	0·007		3	0·166	0·204	−0·264	0·010
O(1)	1	0·275	−0·219	−0·317	0·064	O(1)	1	0·240	−0·231	−0·360	0·082
	2	0·214	−0·215	−0·299	0·081		2	0·212	−0·240	−0·314	0·070
	3	0·179	−0·233	−0·348	0·078		3	0·171	−0·208	−0·307	0·083
C(3)	1	0·279	0·077	−0·075	0·026	C(3)	1	0·224	0·089	−0·083	0·032
	2	0·212	0·069	−0·028	0·038		2	0·177	0·087	−0·038	0·041
	3	0·176	0·087	−0·013	0·026		3	0·164	0·068	−0·034	0·028
C(2)	1	0·288	−0·023	−0·106	0·083	C(2)	1	0·240	−0·065	−0·143	0·097
	2	0·217	−0·054	−0·081	0·097		2	0·197	−0·084	−0·089	0·103
	3	0·154	−0·044	−0·131	0·096		3	0·175	−0·085	−0·096	0·089
C(1)	1	0·335	0·073	−0·208	0·165	C(1)	1	0·256	0·157	−0·211	0·159
	2	0·237	0·104	−0·141	0·159		2	0·228	0·172	−0·146	0·158
	3	0·189	0·093	−0·182	0·148		3	0·178	0·155	−0·168	0·171

Table 7. *The observed and calculated components of U tensors of the individual atoms, in the asymmetric part of the molecule, referred to the orthogonalized axial system as specified in International Tables for X-ray Crystallography (1959) in* 10^{-2} Å²

Crystal		U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
		obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
DBD	Br	9·68	9·66	6·61	7·09	6·74	4·40	−0·10	0·20	−1·90	−2·71	−1·09	−0·13
	O(2)	6·85	6·00	4·63	5·06	4·02	5·43	2·03	1·39	−0·89	−1·29	0·41	0·41
	O(1)	5·60	6·24	3·51	4·61	6·26	5·77	0·49	1·16	−1·61	−0·99	0·32	0·02
	C(3)	4·82	5·72	6·11	4·86	4·43	5·12	1·29	1·04	0·23	−1·75	1·82	0·06
	C(2)	6·23	6·24	4·22	4·64	4·92	5·19	1·21	1·28	−2·50	−1·43	0·38	0·08
	C(1)	8·11	7·42	6·57	5·38	5·69	5·14	1·73	1·59	−3·12	−1·62	−1·20	0·21
DCD	Cl	6·24	6·29	7·25	7·18	3·78	3·63	−0·49	−0·42	−1·49	−1·50	−1·03	−0·67
	O(2)	3·48	3·19	4·89	4·92	3·53	4·07	1·11	0·73	−0·67	−0·57	−0·76	−0·45
	O(1)	3·11	3·71	5·61	5·84	4·43	4·07	−0·62	−0·35	−0·24	−0·28	−0·09	0·17
	C(3)	2·88	2·79	4·91	4·70	3·04	3·30	0·48	0·34	−0·17	−0·50	0·08	−0·46
	C(2)	3·58	3·48	5·66	5·46	3·47	3·34	0·32	0·17	−0·44	−0·27	−0·20	−0·33
	C(1)	5·11	4·95	6·25	6·47	3·58	3·44	−0·47	0·14	−0·89	0·79	0·32	0·07

Table 8. *The translational* **T** (10^{-2} Å²) *and librational* ω (10^{-2} rad²) *tensors of the DCD molecule as rigid body referred to the orthogonalized axial system*

The e.s.d.'s referred to the least significant digits are given in parentheses.

$$\mathbf{T} = \begin{pmatrix} 2\cdot70\,(13) & 0\cdot36\,(11) & -0\cdot43\,(09) \\ & 4\cdot61\,(13) & -0\cdot50\,(09) \\ & & 3\cdot24\,(09) \end{pmatrix} \qquad \omega = \begin{pmatrix} 0\cdot21\,(2) & 0\cdot04\,(2) & 0\cdot06\,(2) \\ & 0\cdot25\,(2) & -0\cdot05\,(2) \\ & & 0\cdot26\,(5) \end{pmatrix}$$

in Table 1. The corrections were calculated on the basis of Cruickshank's (1961b) procedure with the peak shape parameter $q^2 = 0.13$. All calculations of distances and angles are based on the uncorrected coordinates.

Discussion of the structure

The DBD and DCD molecules are formed by the halogenization of dulcitol (galactitol) and therefore it seems reasonable to discuss the structures in compar-

Table 9. *The r.m.s. amplitudes (principal axes) of the translational* T *and librational* ω *tensor ellipsoids of the DCD molecule as rigid body and the directional cosines of the amplitudes referred to the orthogonalized axial system*

In the last two columns the angles of the principal axes to the plane of carbon atoms of the molecule and to the C(1)–Cl bond are listed.

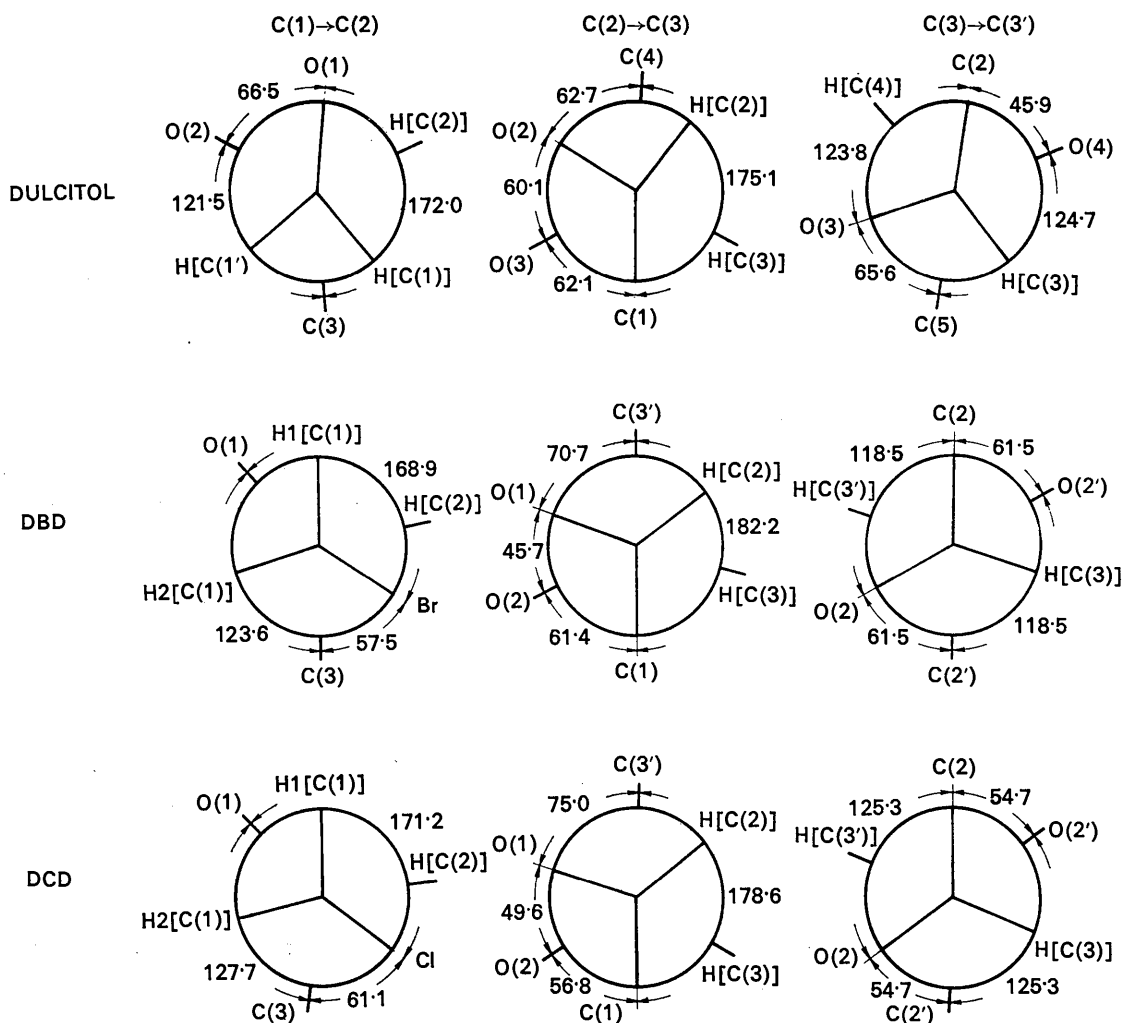| Tensor	i	$(u^2)^{1/2}$	x	y	z	Angle to plane	Angle to bond
T	1	0.221 Å	−0.218 Å	−0.915 Å	0.338 Å	127.2°	137.8°
	2	0.179	−0.411	0.401	0.819	36.2	68.2
	3	0.157	−0.885	0.040	−0.464	173.1	123.7
ω	1	0.056 (rad)	−0.313	0.465	−0.828	12.3	92.3
	2	0.052	−0.643	−0.745	−0.175	127.9	167.4
	3	0.037	−0.699	0.478	0.533	35.2	78.4

Fig. 3. Newman projections of the three C–C bonds in the asymmetric part of DBD and DCD molecules compared with the corresponding ones in dulcitol. For the comparison one has to consider that the atoms O(2), O(3) and O(4) of dulcitol correspond to the atoms O(1), O(2) and O(3), respectively, in the halogen derivatives.

ison with galactitol, the structure of which has been determined by Berman & Rosenstein (1968).

The molecular conformation of the halogen derivatives differs from that of galactitol. In the latter the terminal oxygen atoms, substituted by halogen atoms in DBD and DCD, conform fairly well to the plane of carbon atoms. After substitution of these oxygen atoms by halogen atoms the terminal tetrahedra of the chain molecules are twisted about the C(1)–C(2) and its *meso*-related bond so that the halogen atoms turn out of the plane and at equilibrium of intramolecular forces the halogen atoms are in positions nearly equidistant from the nearest oxygen atoms of the molecule as can be seen in Table 5. At the same time the C(1)–halogen bond and its *meso*-related one are almost perpendicular to the plane. The distortion of the carbon plane is considerably reduced after halogen substitution, especially in the case of DBD. Consequently the O(2)–O(2′) intramolecular distance of the halogen derivatives approximates more the ideal 3·5 Å with its val-

ues of 3·51 Å and 3·61 Å for DBD and DCD, respectively, than for galactitol, where the corresponding O(3)–O(4) distance is 3·68 Å. (The distance of 2·8 Å, reported in Berman and Rosenstein's (1968) paper is a clerical error.*) The other intramolecular non-bonding O–O distances are 2·81 and 2·80 Å for the two halogen derivatives, being slightly shorter than in galactitol which are 2·83 and 2·84 Å. The alterations of the molecular conformation caused by halogen substitution are expressed quite well by the conformational angles which can be seen in the Newman projections of DBD and DCD compared with those of galactitol (Fig. 3).

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* With the authorization of H. Berman and R. D. Rosenstein we are giving here the correction of the clerical error. In the article cited (Berman & Rosenstein, 1968) the next to last sentence on p. 439 is incorrectly written as, 'The distortion is enough that the O(3)–O(4) contact which is ideally 3·5 Å reduces to 2·8 Å'. The correct sentence is as follows: 'The distortion is enough that the O(3)–O(4) contact which is ideally 3·5 Å increases to 3·7 Å.

Table 10. *Hydrogen bond distances and angles in the closed circuit of hydrogen bonding*

The estimated standard deviations are in parentheses.

From atom	In position			To atom	In position			Distances for	
								DBD	DCD
O(2)	x,	y,	z	O(1)	$1+x$,	y,	z	2·694 (19) Å	2·733 (7) Å
O(1)	$1+x$,	y,	z	O(2′)	$1-x$,	$-1-y$,	$-z$	2·824 (19)	2·783 (7)
O(2′)	$1-x$,	$-1-y$,	$-z$	O(1′)	$-x$,	$-1-y$,	$-z$	2·694 (19)	2·733 (7)
O(1′)	$-x$,	$-1-y$,	$-z$	O(2)	x,	y,	z	2·824 (19)	2·783 (7)

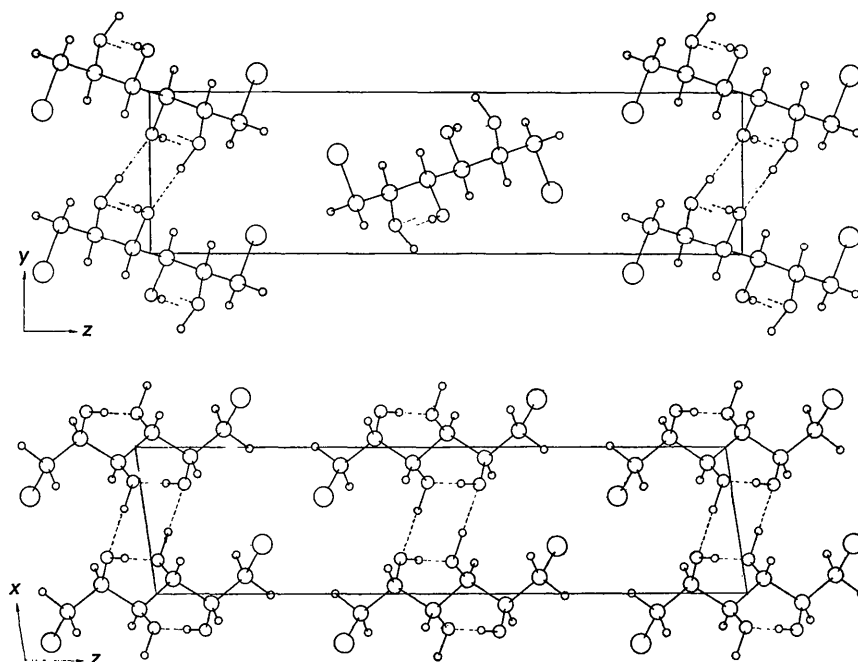|								Angles	
O(1′)–O(2)–O(1)								94·7 (6)°	99·3 (2)°
O(2)–O(1)–O(2′)								85·3 (6)	80·7 (2)

Fig. 4. The structure of DBD in two orthogonal projections, (a) on the (010), (b) on the (100) plane. The spatial packing of the molecules and arrangement of hydrogen bonds is visualized.

The most significant difference can be found in projection of the C(1)–C(2) bond. After substituting in galactitol the O(1) and O(6) atoms by halogen atoms the CH_2X group belonging to C(1) atom turned around the C(2)–C(1) bond by about 120° resulting in a *trans* position for X and O(1) atoms and a *gauche* position for X and C(3) atoms. The same is true for the other CH_2X group at the other end of the molecule. Another remarkable phenomenon can be found in projection of the C(2)–C(3) bond. The conformational angle O(1)–O(2) is 60·1° for galactitol but decreases rapidly in the direction: galactitol → DCD → DBD.

The C–C and C–O bond lengths are on average 1·540 and 1·413 Å for DBD, and 1·534 Å and 1·432 Å for DCD respectively, and are more reliable for DCD. In latter case the e.s.d. are about the third of those of

DBD as can be seen in Table 5. The C–C and C–O bond lengths of DCD are in good agreement with those reported for galactitol (1·527 and 1·432 Å) if we disregard the shorter terminal C–C bonds of galactitol. The discrepancy found for the bond lengths in DBD can be attributed to the fact that in spite of high absorption and unfavorable crystal size, no absorption correction was used. Taking the more reliable data of DCD, there could not be found any sign that the terminal C–C bonds of the molecule were shorter than the internal ones as had been found for galactitol.

The C–Br and C–Cl bond lengths are found to be 1·975 and 1·820 Å, respectively. In the literature several numerical data of these bond lengths, originating from different determinations, can be found. These vary between 1·91 Å (Griffiths, 1969) and 2·01 Å (Gopala-

Table 11. *The shortest intermolecular distances of the extreme* H *and halogen atoms between the two-dimensional molecular networks*

The sums of the van der Waals radii are given in parentheses.

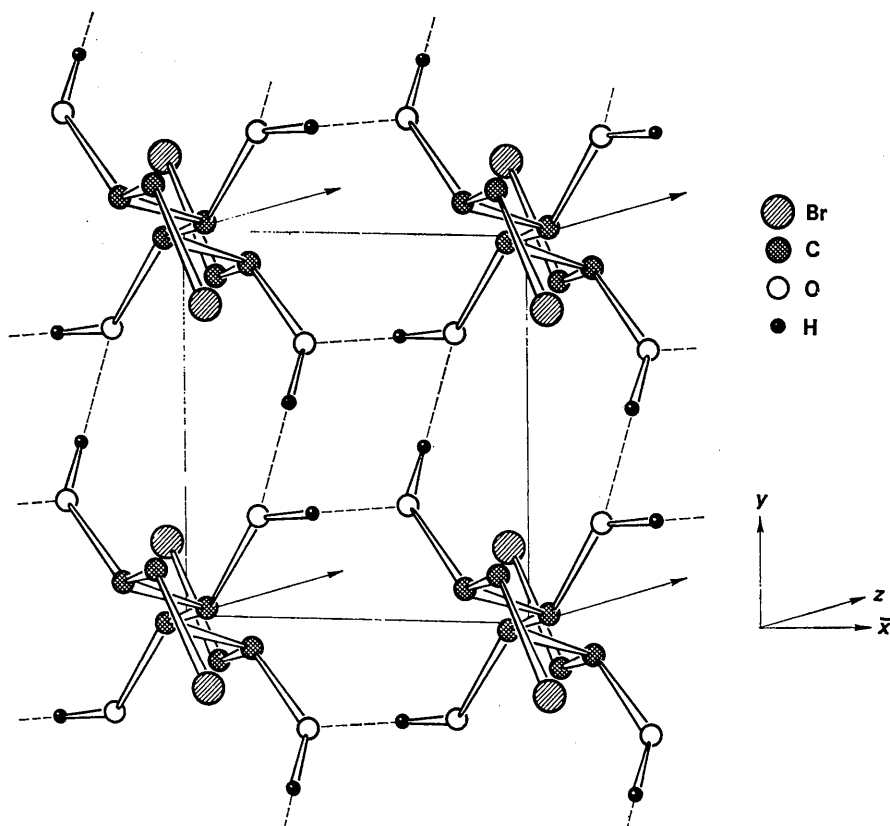| From atom in x,y,z	To atom	In position	Distances for DBD	DCD
Halogen	Halogen	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	3·703 (3·90) Å	3·616 (3·60) Å
	Halogen	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	3·703 (3·90)	3·616 (3·60)
	H1[C(1)]	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	3·029 (3·12)	2·961 (2·97)
	H2[C(1)]	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	3·530 (3·12)	3·346 (2·97)

Fig. 5. Perspective view of the front part of the unit cell of DBD visualizing the closed circuits of hydrogen bonds.

krishna, 1969) for C–Br and between 1·73 Å (Schaefer, 1970) and 1·81 Å (Dejace, 1955) for C–Cl, taking only one example of the extreme cases. The present determinations seem to confirm the higher values.

The C–C–C bond angles with a mean value of 111·0 and 111·5° for DBD and DCD, respectively (Table 5), are in fairly good agreement with the mean value of 111·5° found for galactitol, verifying earlier observations of the widening of C–C–C bond angles in chain carbon molecules. The C–C–O bond angles, however, average 107·6 and 108·5° for DBD and DCD, respectively, being less than the tetrahedral angle as well as those reported for galactitol.

All oxygen atoms have two intermolecular oxygen neighbours in two directions nearly parallel to plane (001) and in hydrogen bond distances as it can be realized from Fig. 4 and Table 10. In this scheme of hydrogen bonding all oxygen atoms are involved as donors as well as acceptors resulting in closed circuits of hydrogen bondings. These closed circuits are all congruent and have their oxygen atoms at the corners of a parallelogram with an angle of 99·3° (Fig. 5, Table 10). From Figs. 4 and 5 it can be made clear that every molecule is always linked to four neighbouring molecules by two-two hydrogen bonds. In this way the closed circuits of hydrogen bondings result in two-dimensional networks of molecules. These networks are parallel to the (001) plane and are held together only by van der Waals forces.

The packing of the two-dimensional molecular networks is visualized in Fig. 4, from which it can also be realized that the neighbouring networks are contacted by the terminal halogen and hydrogen atoms of the chain molecules. The shortest intermolecular distances of these atoms are summarized for the two derivatives in Table 11. From these data it can be ascertained that

between two neighbouring networks every molecule contacts three molecules of the neighbouring network. Two of these contacts are halogen–halogen and the third is halogen–hydrogen. The distances of these contacting atoms agree very well with the sum of the van der Waals radii in the case of DCD and are little shorter in DBD.

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Structure Determination of Mg3TeO6

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The structure of Mg_3TeO_6 has been determined by X-ray methods. Single crystals could be grown from NaCl or Na_2SO_4. Mg_3TeO_6 represents a new pseudocubic structure type; it is rhombohedral with $a_R = 6·05$ Å, $\alpha_R = 90°50'$, $Z = 2$, $D_x = 4·46$ g.cm^{-3}, space group $R\bar{3}$. The final R value was equal to 4·8 %. Tellurium has a regular octahedral oxygen surrounding with Te–O = 1·91 Å. The coordination of Mg is a distorted octahedron with Mg–O distances varying between 2·02 and 2·28 Å. The thermal expansion characteristics were measured up to 820°C.

Introduction

Previous investigations on the crystal chemistry of tellurium oxides (Bayer, 1969) proved the existence of

compounds $M_3^{2+}Te^{6+}O_6$ which can be derived from orthotelluric acid H_6TeO_6. Among these Ni_3TeO_6 has a corundum-type structure (Bayer, 1967; Newnham & Meagher, 1967; Kasper, 1968) and Cu_3TeO_6 crystal-