

strong reflexion (I_{\max}). This trend strongly supports the intensity change being due to the secondary extinction effect.

In Fig. 4, for each strong, low-angle reflexion of category (i), the value of I/I_{\max} corresponding to the value of the extinction factor is plotted as a function of irradiation time. The time dependence of I/I_{\max} differs from reflexion to reflexion; in particular, 002 increases linearly with time and shows no saturation. The rates of change of I/I_{\max} with irradiation time are similar if the reciprocal-lattice points lie close to each other; for example, 040, 230 and 250 behave similarly and so do 210 and 430. In addition, the rate of change of 131 is intermediate between 002 and other reflexions. This seems to indicate an anisotropic change in the extinction effect.

The change in the extinction effect may be caused by a small loss of water molecules under irradiation. As can be seen from Fig. 1, the water molecules are enclosed in a channel parallel to **c**, forming a helical structure around a screw diad. The water molecules are weakly hydrogen-bonded to the N and O atoms of the complex ions forming the wall of the channel. Such a structure suggests that the water molecules can easily come out of the channel. In fact, a crystal specimen not sealed in a glass capillary showed different unit-cell dimensions after one day: $a' = 16.092 (-0.617)$, $b' = 18.001 (-0.138)$, $c' = 7.610 (+0.041)$ Å. Such contraction in the **a** and **b** directions and elongation along **c** may reasonably correspond to the loss of water molecules from the channels parallel to **c**. The small change

of cell dimension along **c** may be related to the slow change in the extinction effect of 002.

The observed intensities of very strong, low-angle reflexions of category (i), except 002, decreased slowly with irradiation time until 20 h and then began to increase. This change cannot be accounted for.

The authors are grateful to Professor M. Shibata of Kanazawa University for supplying the specimens. All the computations were carried out on the FACOM 230-48 computer at this Institute. Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

References

- AOKI, T., MATSUMOTO, K., OOI, S. & KUROYA, H. (1973). *Bull. Chem. Soc. Japan*, **46**, 159–162.
- BUTLER, K. R. & SNOW, M. R. (1971). *Chem. Commun.* pp. 550–551.
- BUTLER, K. R. & SNOW, M. R. (1976). *J. Chem. Soc. Dalton*, pp. 251–258.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- ITO, T. & SHIBATA, M. (1976). *Inorg. Chem.* In the press.
- MATSUMOTO, K. & KUROYA, H. (1972). *Bull. Chem. Soc. Japan*, **45**, 1755–1759.
- SHINTANI, H., SATO, S. & SAITO, Y. (1976). *Acta Cryst.* **B32**, 1184–1188.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1977). **B33**, 1384–1389

The Crystal Structures of Two Enol Acetates

BY ARNAUD DUCRUIX AND CLAUDINE PASCARD-BILLY

Institut de Chimie des Substances Naturelles, Laboratoire de Cristallochimie, CNRS, 91190 Gif/Yvette, France

(Received 8 September 1976; accepted 24 October 1976)

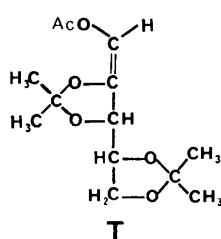
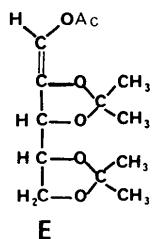
The crystal structures of 1-*O*-acetyl-2,3:4,5-di-*O*-isopropylidene- δ -*erythro*-pent-1-enitol and of the corresponding *threo* compound ($C_{13}H_{20}O_6$) were solved by application of the phase function. Crystals of the *erythro* compound are monoclinic, $a = 5.435$ (2), $b = 14.703$ (6), $c = 9.332$ (4) Å, $\beta = 104.15$ (9)°, $Z = 2$, space group $P2_1$. The *threo* crystals are orthorhombic, space group $P2_12_12_1$, $a = 5.543$ (2), $b = 8.240$ (3), $c = 32.336$ (10) Å, $Z = 4$. Intensities were collected on a four-circle diffractometer with Cu $K\alpha$ radiation. The final *R* values are 0.04 for the *erythro* compound and 0.05 for the *threo*. In both structures the stereochemistry about the double bond is *Z*.

Introduction

In the course of a general study of the acyclic sugar derivatives (Ducruix & Pascard-Billy, 1974, 1975a,b)

and in collaboration with Professor Horton's Laboratory, we have undertaken the determination of the crystal structures of two enol acetates. The aim was to assign a precise geometry at the double bond

by X-ray analysis for 1-*O*-acetyl-2,3:4,5-di-*O*-isopropylidene-*D*-*erythro*-pent-1-enitol (hereafter compound E) and to compare it with the corresponding *threo* compound (hereafter T).



Experimental

Crystals were provided by Dr Eitelman and grown from ether-pentane for compound E and from ab-

solute ethanol for compound T. Intensities were recorded with a Philips PW 1100 automatic four-circle diffractometer, Cu $K\alpha$ radiation, and a graphite monochromator. No absorption correction was made; crystal data are given in Table 1. [$\omega-2\theta$ scan; scan width 1.5° (E), 1.3° (T); scan speed $0.075^\circ \text{ s}^{-1}$ (E), $0.05^\circ \text{ s}^{-1}$ (T); background measurement on either side of the peak: 5 s (E), 10 s (T).]

Structure determination and refinement

Both structures were solved and refined in the same way and will be depicted together. The phase function was used to assign numerical values to a set of symbolic phases (Riche, 1973). The tangent refinement procedure was then used and the first *E* map showed nearly all the atoms.

Full-matrix least-squares refinement was carried out with a local version of ORFLS. Atomic scattering factors for C, N and O were those of Doyle & Turner (1968) and for H atoms those of Stewart, Davidson & Simpson (1965) were used.

Heavy atoms were refined anisotropically and all H atoms were located on difference Fourier syntheses and introduced with the corresponding isotropic *B* values of the bonded C atoms. Their coordinates were refined and final *R* values were 0.04 for (E) and 0.05 for (T). The positional coordinates and thermal parameters of the heavy atoms are listed in Tables 2 and 3, and the coordinates of the H atoms are in Table 4.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32246 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic coordinates of the heavy atoms ($\times 10^4$)*

	Compound E			Compound T		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	3883 (4)	3940 (0)	4112 (2)	903 (5)	6412 (3)	3031 (1)
O(2)	3474 (4)	2967 (2)	6548 (3)	3499 (4)	8961 (3)	3370 (1)
O(3)	1358 (5)	3261 (2)	8302 (3)	5960 (5)	9091 (3)	3930 (1)
O(4)	-859 (5)	5428 (2)	6636 (3)	3468 (4)	5247 (2)	4273 (1)
O(5)	-2679 (5)	5673 (2)	8524 (3)	222 (4)	6596 (3)	4518 (1)
O(6)	2592 (8)	5062 (3)	2534 (4)	-625 (10)	4008 (5)	3115 (1)
C(1)	2163 (7)	4202 (3)	4944 (4)	2398 (7)	6190 (4)	3373 (1)
C(2)	1997 (6)	3720 (3)	6090 (4)	3624 (6)	7422 (3)	3526 (1)
C(3)	291 (6)	3869 (3)	7118 (4)	5288 (6)	7418 (4)	3890 (1)
C(4)	347 (7)	4809 (3)	7772 (4)	4197 (6)	6932 (4)	4300 (1)
C(5)	-1259 (10)	4898 (4)	8891 (5)	1872 (7)	7791 (4)	4416 (1)
C(6)	3947 (7)	4422 (3)	2917 (4)	-608 (8)	5197 (5)	2928 (1)
C(7)	5815 (10)	4086 (4)	2139 (5)	-2121 (8)	5582 (5)	2582 (1)
C(8)	2538 (6)	2532 (3)	7707 (4)	5400 (6)	9908 (4)	3561 (1)
C(9)	4770 (7)	2201 (3)	8845 (4)	4408 (8)	11585 (5)	3654 (1)
C(10)	665 (10)	1808 (4)	7049 (7)	7526 (7)	9976 (5)	3271 (1)
C(11)	-2064 (6)	6107 (3)	7311 (4)	1406 (6)	5063 (4)	4533 (1)
C(12)	-299 (11)	6896 (4)	7818 (8)	2153 (9)	4695 (5)	4963 (1)
C(13)	-4436 (7)	6407 (4)	6231 (6)	-259 (8)	3834 (5)	4339 (1)

Table 3. Anisotropic thermal parameters ($\times 10^4$) in the form:
 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Compound E	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
O(1)	493 (10)	46 (1)	139 (3)	37 (3)	149 (5)	13 (2)	4.4
O(2)	465 (10)	44 (1)	144 (4)	23 (3)	147 (5)	13 (2)	4.3
O(3)	516 (10)	47 (1)	135 (4)	35 (3)	147 (5)	14 (2)	4.5
O(4)	539 (10)	46 (1)	129 (3)	45 (3)	139 (5)	11 (2)	4.5
O(5)	802 (15)	71 (2)	210 (5)	105 (4)	278 (7)	33 (2)	6.7
O(6)	1257 (25)	110 (2)	227 (5)	215 (7)	341 (10)	86 (3)	9.6
C(1)	417 (14)	40 (2)	118 (5)	22 (4)	90 (7)	1 (2)	3.9
C(2)	351 (12)	40 (2)	110 (4)	5 (4)	71 (6)	-7 (2)	3.6
C(3)	343 (12)	46 (2)	112 (4)	9 (4)	76 (6)	9 (2)	3.7
C(4)	439 (14)	48 (2)	130 (5)	12 (4)	108 (7)	-3 (3)	4.3
C(5)	716 (23)	68 (3)	143 (6)	68 (7)	184 (10)	14 (3)	5.8
C(6)	555 (18)	56 (2)	112 (5)	27 (5)	109 (8)	7 (3)	4.8
C(7)	591 (20)	80 (3)	167 (7)	26 (7)	176 (10)	3 (4)	6.0
C(8)	494 (15)	37 (2)	148 (5)	10 (4)	150 (8)	9 (2)	4.2
C(9)	605 (17)	60 (2)	185 (6)	43 (5)	159 (8)	23 (3)	5.7
C(10)	597 (22)	52 (2)	287 (11)	-44 (6)	163 (12)	-11 (4)	6.6
C(11)	394 (13)	48 (2)	149 (5)	18 (4)	135 (7)	-2 (2)	4.2
C(12)	564 (21)	66 (3)	315 (12)	-8 (7)	106 (14)	-52 (5)	7.4
C(13)	410 (16)	66 (3)	235 (8)	16 (5)	109 (10)	18 (4)	5.9
Compound T	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
O(1)	521 (11)	185 (4)	11 (0)	-71 (6)	-23 (2)	1 (1)	5.4
O(2)	343 (8)	144 (4)	14 (0)	-34 (5)	-21 (1)	8 (1)	4.6
O(3)	438 (10)	219 (4)	13 (0)	-119 (6)	-27 (2)	5 (1)	5.7
O(4)	332 (8)	145 (4)	12 (0)	30 (5)	5 (1)	5 (1)	4.3
O(5)	316 (8)	202 (4)	24 (0)	34 (6)	19 (2)	12 (1)	6.5
O(6)	1546 (35)	339 (8)	36 (1)	-472 (16)	-134 (5)	35 (2)	14.5
C(1)	446 (14)	157 (5)	10 (0)	-13 (8)	-15 (2)	3 (1)	4.6
C(2)	287 (10)	121 (5)	10 (0)	2 (7)	-5 (2)	2 (1)	3.6
C(3)	262 (10)	148 (5)	11 (0)	5 (7)	-7 (2)	2 (1)	4.0
C(4)	297 (11)	173 (6)	10 (0)	3 (7)	-8 (2)	0 (1)	4.2
C(5)	350 (12)	167 (6)	13 (0)	6 (7)	3 (2)	-7 (1)	4.8
C(6)	621 (19)	177 (6)	14 (0)	-83 (11)	-20 (3)	-8 (1)	6.0
C(7)	578 (19)	344 (10)	13 (0)	-84 (12)	-21 (3)	-19 (2)	7.3
C(8)	286 (10)	144 (5)	12 (0)	-33 (7)	-12 (2)	0 (1)	4.2
C(9)	561 (19)	185 (7)	24 (1)	30 (11)	-4 (3)	-15 (2)	7.3
C(10)	401 (14)	250 (8)	19 (1)	-51 (11)	9 (2)	6 (2)	6.5
C(11)	323 (11)	148 (5)	12 (0)	29 (8)	5 (2)	4 (1)	4.4
C(12)	606 (19)	338 (10)	12 (0)	10 (14)	4 (3)	11 (2)	7.1
C(13)	437 (15)	281 (8)	16 (1)	-70 (11)	3 (3)	1 (2)	6.6

Table 4. Hydrogen-atom coordinates ($\times 10^3$)

Compound E	x	y	z	x	y	z
H(1)	125 (6)	468 (2)	467 (3)	255 (5)	511 (3)	350 (1)
H(3)	-143 (6)	371 (2)	674 (3)	682 (5)	685 (3)	383 (1)
H(4)	216 (6)	501 (2)	816 (3)	544 (5)	704 (3)	453 (1)
H(5a)	-47 (7)	485 (3)	987 (4)	125 (5)	840 (3)	419 (1)
H(5b)	-268 (7)	448 (3)	859 (4)	204 (5)	858 (3)	467 (1)
H(7a)	743 (8)	398 (3)	257 (4)	-310 (7)	490 (4)	250 (1)
H(7b)	522 (7)	349 (3)	174 (4)	-314 (6)	655 (4)	264 (1)
H(7c)	567 (7)	427 (3)	113 (4)	-132 (6)	572 (4)	233 (1)
H(9a)	427 (6)	197 (2)	947 (3)	345 (7)	1146 (4)	385 (1)
H(9b)	559 (5)	175 (2)	853 (3)	591 (7)	1229 (4)	382 (1)
H(9c)	606 (5)	279 (2)	935 (3)	405 (7)	1221 (4)	340 (1)
H(10a)	-67 (8)	208 (3)	625 (5)	876 (6)	1053 (4)	340 (1)
H(10b)	171 (8)	127 (3)	675 (4)	698 (6)	1043 (4)	302 (1)
H(10c)	-14 (8)	160 (3)	759 (5)	819 (6)	907 (4)	316 (1)
H(12a)	141 (8)	666 (3)	836 (5)	303 (7)	375 (4)	495 (1)
H(12b)	-22 (8)	721 (3)	680 (5)	108 (7)	448 (4)	513 (1)
H(12c)	-80 (8)	732 (3)	840 (5)	356 (7)	513 (4)	512 (1)
H(13a)	-392 (6)	658 (3)	524 (4)	-164 (6)	397 (4)	447 (1)
H(13b)	-541 (6)	593 (3)	604 (4)	-50 (7)	411 (4)	404 (1)
H(13c)	-538 (7)	693 (3)	682 (4)	72 (6)	272 (4)	439 (1)
Compound T	x	y	z			

Description of the structure

Three-dimensional views of the two molecules, with the numbering and short intramolecular contacts, are illustrated in Fig. 1. The bond lengths and valency angles are given in Tables 5 and 6. Comparison of the two sets shows good agreement. In both structures the average C—H bond length is 0.96 Å. The two structures present common features:

- The stereochemistry about the double bond is Z (Blackwood, Gladys, Loening, Petrarca & Rush, 1968).
- The atoms O(3) and O(4) are in antiparallel disposition.
- Short intramolecular contacts are identical. Thus, despite the difference of configuration at C(3), the two molecules have the same compact shape.

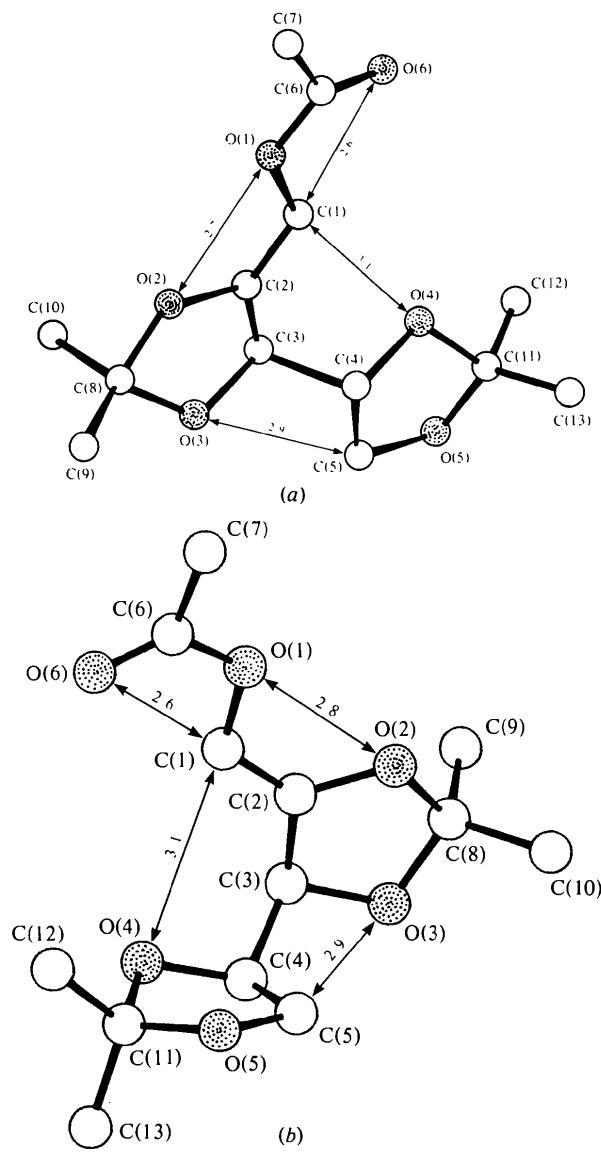


Fig. 1. (a) Compound E, (b) compound T.

The carbon chain

As compound E is obtained from an *arabino* configuration (with a planar carbon chain), we may expect an approximately planar zigzag carbon chain. The planarity of (E) is distorted by the presence of the double bond between C(1) and C(2). C(1) is displaced 0.7 Å out of the best mean plane defined by the other four C atoms (Table 7). Compared with corresponding deviations (from X-ray data) in related compounds (Table 8), this deviation is intermediate between planar and non-planar carbon chains, as in acyclic sugars substituted at C(1) (Ducruix & Pascard-Billy, 1975a).

Compound T, obtained from a *xylo* configuration (with bent conformation), is non-planar (Table 7).

The Newman projections along the C—C bonds of the carbon chain are represented in Fig. 2.

Dioxolane rings

In compound E, ring A is a half-chair with C(8) +0.2 Å and O(3) -0.3 Å from the plane. With the convention of Altona, Geise & Romers (1968), this is defined by $\Delta = 5.82^\circ$ and $\varphi_m = 33.60^\circ$. Ring B is an envelope with O(4) 0.4 Å out of the best mean plane defined by the other four atoms ($\Delta = 26.08^\circ$, $\varphi_m = 29.76^\circ$).

In compound T, ring A is an envelope with C(8) 0.3 Å out of the plane ($\Delta = 22.27^\circ$, $\varphi_m = 11.35^\circ$), whereas ring B is a half-chair with O(4) +0.3 Å and C(11) -0.2 Å from the plane ($\Delta = 4.57^\circ$, $\varphi_m = 30.90^\circ$).

For compound E, rings A and B are roughly centrosymmetrically related. The deviation from ideal symmetry is 0.06 Å.

For compound T, an approximate twofold axis relates the two dioxolane rings, the deviation from ideal symmetry being 0.1 Å.

Table 5. Bond lengths (Å)

	Compound E	Compound T
O(1)—C(1)	1.406 (4)	1.393 (4)
O(1)—C(6)	1.329 (4)	1.347 (5)
O(2)—C(2)	1.372 (5)	1.367 (4)
O(2)—C(8)	1.452 (4)	1.450 (4)
O(3)—C(3)	1.430 (5)	1.433 (4)
O(3)—C(8)	1.430 (5)	1.404 (4)
O(4)—C(4)	1.429 (5)	1.448 (4)
O(4)—C(11)	1.423 (5)	1.426 (4)
O(5)—C(5)	1.371 (6)	1.384 (4)
O(5)—C(11)	1.409 (5)	1.424 (4)
O(6)—C(6)	1.195 (6)	1.151 (6)
C(1)—C(2)	1.305 (5)	1.319 (4)
C(2)—C(3)	1.504 (5)	1.495 (4)
C(3)—C(4)	1.507 (6)	1.510 (5)
C(5)—C(5)	1.521 (6)	1.517 (5)
C(6)—C(7)	1.471 (7)	1.435 (6)
C(8)—C(9)	1.485 (5)	1.517 (5)
C(8)—C(10)	1.497 (7)	1.506 (5)
C(11)—C(12)	1.505 (7)	1.481 (5)
C(11)—C(13)	1.496 (6)	1.507 (5)

Table 6. Valency angles ($^{\circ}$)

	Compound E	Compound T
C(1)–O(1)–C(6)	118.3 (3)	117.9 (3)
C(2)–O(2)–C(8)	107.6 (3)	107.8 (2)
C(3)–O(3)–C(8)	107.7 (3)	109.1 (2)
C(4)–O(4)–C(11)	107.3 (3)	106.9 (2)
C(5)–O(5)–C(11)	110.3 (3)	109.5 (3)
O(1)–C(1)–C(2)	119.5 (3)	120.3 (3)
O(2)–C(2)–C(1)	122.7 (3)	123.3 (3)
O(2)–C(2)–C(3)	108.9 (3)	108.9 (3)
C(1)–C(2)–C(3)	128.3 (3)	127.8 (3)
O(3)–C(3)–C(2)	101.8 (3)	103.2 (2)
O(3)–C(3)–C(4)	107.2 (3)	106.3 (3)
C(2)–C(3)–C(4)	115.9 (3)	116.3 (3)
O(4)–C(4)–C(3)	108.8 (3)	108.3 (3)
O(4)–C(4)–C(5)	102.6 (3)	103.0 (3)
C(3)–C(4)–C(5)	113.5 (3)	115.7 (3)
O(5)–C(5)–C(4)	106.4 (4)	106.8 (3)
O(1)–C(6)–O(6)	122.1 (4)	120.5 (4)
O(1)–C(6)–C(7)	113.5 (4)	113.1 (4)
O(6)–C(6)–C(7)	124.4 (4)	126.4 (4)
O(2)–C(8)–O(3)	103.4 (3)	105.3 (3)
O(2)–C(8)–C(9)	107.7 (3)	108.2 (3)
O(2)–C(8)–C(10)	109.6 (3)	108.9 (3)
O(3)–C(8)–C(9)	109.4 (3)	110.4 (3)
O(3)–C(8)–C(10)	111.6 (4)	111.9 (3)
C(9)–C(8)–C(10)	114.5 (4)	111.9 (3)
O(4)–C(11)–O(5)	105.2 (3)	104.8 (3)
O(4)–C(11)–C(12)	110.7 (4)	110.5 (3)
O(4)–C(11)–C(13)	108.8 (3)	108.5 (3)
O(5)–C(11)–C(12)	110.8 (4)	109.9 (3)
O(5)–C(11)–C(13)	109.9 (3)	107.4 (3)
C(12)–C(11)–C(13)	111.3 (4)	115.1 (3)

The asterisks refer to atoms not included in the least-squares procedure. A, B, C and D are the parameters defining the equation $Ax + By + Cz + D = 0$.

Table 7. Mean planes

	(E)	(E)	(T)	(T)	(T)
C(1)	0.13	0.75*	-0.43	1.28*	0.14
C(2)	-0.19	-0.02	0.40	0.09	-0.23
C(3)	0.16	0.02	0.08	-0.22	0.20
C(4)	-0.17	0.02	-0.45	0.24	-0.08
C(5)	0.11	-0.04	0.35	-0.13	-1.51*
A	-0.7938	-0.5915	-0.1309	-0.2621	0.6573
B	-0.0472	0.2748	0.9777	-0.9629	-0.7397
C	-0.6064	-0.7580	-0.1645	-0.0648	-0.1444
D	3.1713	2.4748	-3.4455	7.2493	4.6177

Table 8. A comparison of the different types of carbon chain

	Ref.	Atom out of plane	D*	D†
Arabinitol	1	planar	—	0.01
6-Mercaptourine-D-arabinose				
Molecule I	2	C(1)	0.4	0.02
Molecule II	2	C(1)	0.5	0.03
Compound E	3	C(1)	0.7	0.03
Xylitol	4	C(5)	1.4	0.02
Diphenyl-dithioacetal-D-xylose	5	C(1)	1.3	0.02
Compound T	3	C(1)	1.3	0.17
Compound T	3	C(5)	1.5	0.17

References: (1) Hunter & Rosenstein, 1968. (2) Ducruix & Pascard-Billy, 1975. (3) This work. (4) Kim & Jeffrey, 1969. (5) Ducruix & Pascard-Billy, 1977.

* Distance of the atom out of the best mean plane defined by the other C atoms of the chain.

† Mean deviations for the atoms in the plane.

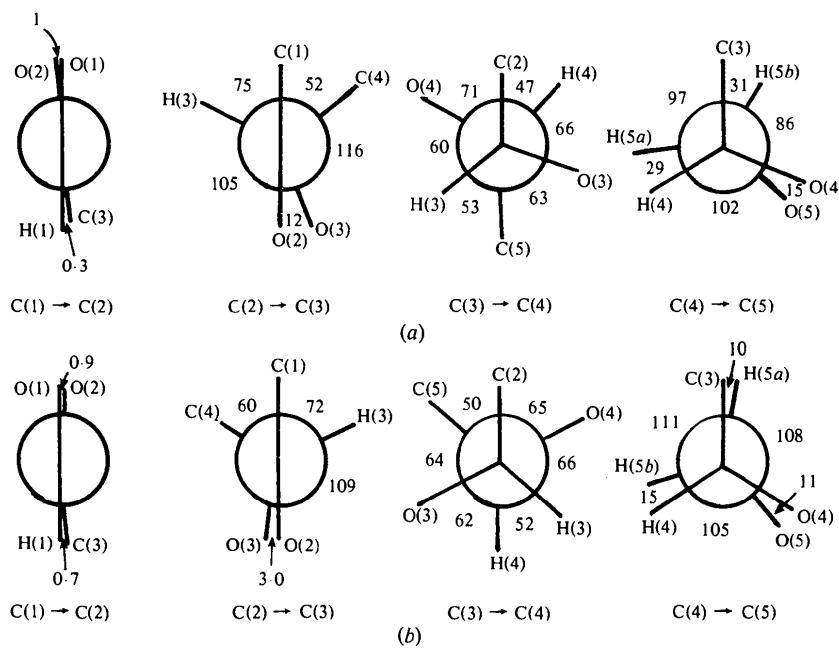


Fig. 2. Newman projections along the carbon chain: (a) molecule E, (b) molecule T.

Crystal packing

There are no short intermolecular contacts less than the sum of the van der Waals radii.

The programs used are: *DEVIN* (Riche, 1972); *ORTEP* (Johnson, 1965); the *NRC* series (Ahmed, Hall, Pippy & Huber, 1966); and *ORFLS* (Busing, Martin & Levy, 1962).

The authors wish to thank Dr Eitelman for supplying the crystals and Professor Horton for helpful discussions.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *NRC* programs. *World List of Crystallographic Computer Programs*. 2nd ed., p. 52. Utrecht: Oosthoek.
- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
- BLACKWOOD, J. E., GLADYS, C. L., LOENING, K. L., PETRARCA, A. E. & RUSH, J. E. (1968). *J. Amer. Chem. Soc.* **90**, 509–510.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- DUCRUIX, A. & PASCARD-BILLY, C. (1974). *Acta Cryst.* **B30**, 1056–1063.
- DUCRUIX, A. & PASCARD-BILLY, C. (1975a). *Acta Cryst.* **B31**, 2250–2256.
- DUCRUIX, A. & PASCARD-BILLY, C. (1975b). *Acta Cryst.* **A31**, S108.
- DUCRUIX, A. & PASCARD-BILLY, C. (1977). To be published.
- HUNTER, F. D. & ROSENSTEIN, R. D. (1968). *Acta Cryst.* **B24**, 1652–1660.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KIM, H. S. & JEFFREY, G. A. (1969). *Acta Cryst.* **B25**, 2607–2613.
- RICHE, C. (1972). *DEVIN*. Institut de Chimie des Substances Naturelles Rapport n° 1.
- RICHE, C. (1973). *Acta Cryst.* **A29**, 133–137.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1977). **B33**, 1389–1396

On the Crystal Structure of LiTe_3 *

BY DIANE Y. VALENTINE,[†] O. BURL CAVIN[‡] AND HARRY L. YAKEL[‡]

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

(Received 2 July 1976; accepted 20 October 1976)

The crystal structure of LiTe_3 has been analyzed from X-ray and neutron powder diffraction data, and from photographically recorded X-ray single-crystal data. The proposed structure is based on harmonically related positional displacements of Te atoms from a reference structure that has six Te atoms at the centers of faces and edges of a cubic unit cell. The rhombohedrally centered hexagonal cell corresponding to the diffraction symmetry has $|\mathbf{A}| = 8.7144(3)$ and $|\mathbf{C}| = 5.3363(2)$ Å. Displacements are in basal-plane directions of this hexagonal cell; the wave vector of the harmonic function describing them is parallel to \mathbf{C} and has a period of $4|\mathbf{C}|$ from -103 to 150°C . The unique axial ratio ($\equiv \sqrt{\frac{3}{8}}$) of the hexagonal cell of the reference structure is also maintained over this temperature range. While the actual structure must be classified as a superstructure, the symmetry relationships developed for modulated three-dimensional structure (MS_3) groups are applicable to its derivation. The proposed displacements produce sections normal to \mathbf{C} in which segments of Te-like chains can be distinguished. These sections are separated by metal-like layers that occur as the displacements become small. Li atoms are regularly distributed in channels parallel to \mathbf{C} .

Introduction

Lithium tritelluride is the only phase of unknown structure in the Li–Te system. We prepared LiTe_3 in an in-

vestigation of materials that might be produced in a molten-salt breeder reactor. This compound, first reported by Foster, Johnson, Davis, Peck & Schablaske (1969), then confirmed by Cunningham, Johnson & Cairns (1973), melts congruently at 460°C and forms simple eutectics with Te at 423°C and with Li_2Te (fluorite structure, Zintl, Harder & Dauth, 1934) at 449°C . Cunningham *et al.* (1973) stated that X-ray powder patterns of LiTe_3 were consistent with a body-

* Research sponsored by the Energy Research and Development Administration under contract with the Union Carbide Corporation.

[†] Chemistry Division.

[‡] Metals and Ceramics Division.