al., 1988). La substitution par le chlore sur l'atome C(4) se traduit cependant par un renforcement de la liaison C(4)—C(5). Le cycle pyridazine est pratiquement plan; les atomes de chlore Cl(10) et d'hydrogène HC(5) sont proches du plan [0,038(1) et 0,03(3)Å respectivement]; par contre, les atomes de carbone des groupements chlorométhyl sont plus éloignés du plan moyen [0,151(4) et 0,079(4)Å pour C(7) et C(8) respectivement]. Enfin, la distance C aromatique—Cl(10) [1,722(4)Å] et très proche de la distance correspondante dans la dichloro-3,6 pyridazine déterminée à partir des résultats de diffraction électronique par Almenningen *et al.* (1977). Les deux distances C méthylique—Cl sont voisines des valeurs généralement calculées. La distance C aromatique—H vaut 0,93(4)Å alors que les distances C méthylique—H sont comprises entre 0.98(5) et 1,04(4)Å. La cohésion cristalline est assurée par contacts de van der Waals; la plus courte distance intermoléculaire vaut 3,186(3)A [entre N(2) et Cl(11)].

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Structures of Two Methyl β-D-Glucoseptanoside Derivatives

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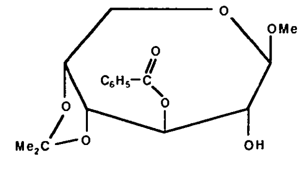
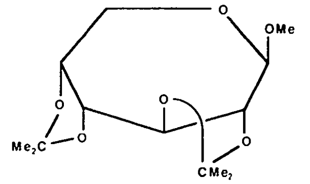
(*Received* 10 *February* 1988; *accepted* 13 *January* 1989)

Abstract. Methyl 3-*O*-benzoyl-4,5-*O*-isopropylidene-β-D-glucoseptanoside, (1), $C_{17}H_{22}O_7$, $M_r = 338{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}086\,(2)$, $b = 9{\cdot}514\,(3)$, $c = 29{\cdot}313\,(10)$ Å, $V = 1697{\cdot}3$ Å^3, $Z = 4$, $D_m = 1{\cdot}32\,(2)$ (by flotation in carbon tetrachloride/light petroleum), $D_x = 1{\cdot}324\,(3)$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha_1) = 1{\cdot}54056$ Å, $\mu = 0{\cdot}824$ mm^{-1}, $F(000) = 720$, $T = 293$ K, $R = 0{\cdot}031$ for 1376 observed reflexions $[I \geq 2{\cdot}58\sigma(I)]$. Methyl 2,3:4,5-di-*O*-isopropylidene-β-D-glucoseptanoside, (2), $C_{13}H_{22}O_6$, $M_r = 274{\cdot}3$, monoclinic, $P2_1$, $a = 9{\cdot}914\,(3)$, $b = 16{\cdot}852\,(3)$, $c = 9{\cdot}232\,(3)$ Å, $\beta = 108{\cdot}70\,(2)°$, $V = 1461{\cdot}0$ Å^3, $Z = 4$, $D_m = 1{\cdot}233$ (by flotation in aqueous solution of potassium iodide), $D_x = 1{\cdot}247$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha_1) = 1{\cdot}54056$ Å, $\mu = 0{\cdot}785$ mm^{-1}, $F(000) = 592$, $T = 293$ K, $R = 0{\cdot}034$ for 2306 observed reflexions $[I \geq 2{\cdot}58\sigma(I)]$. In both structures, the angles in the five-membered rings are significantly smaller than tetrahedral and the angles in the seven-membered rings are generally larger than tetrahedral. The five-membered rings all have envelope conformations and in both structures the septanoside ring has a twist-chair conformation, $^{5,6}TC_{3,4}$.

Introduction. Studies on the selective acid-catalysed hydrolysis of the *O*-isopropylidene acetal groups in compound (2) (Tran, 1979) and in the C(1) isomer of (2), methyl 2,3:4,5-di-*O*-isopropylidene-α-D-glucoseptanoside (3) (Stevens, 1975) showed that whereas the C(2), C(3) acetal in (3) could be removed selectively, in (2) it is the C(4), C(5) acetal group which is more readily removed. X-ray diffraction studies on



(1)



(2)

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(1) and (2) were carried out in order to determine whether the C(4), C(5) acetal rings show unusual strain.

Experimental. Crystals of (1) (Tran, 1979), m.p. 414–417 K, obtained from a benzene solution; crystals of (2) (Stevens, 1975), m.p. 343–344 K, obtained from a light petroleum (b.p. 333–353 K) solution. Resolved Cu $K\alpha_1$ radiation was used for centring the cell determination reflexions. For the two structures, intensities of all symmetry-independent reflexions were measured on a Siemens automatic single-crystal diffractometer using Ni-filtered Cu $K\alpha_1$ radiation with θ–2θ scans (Arndt & Willis, 1966); standard reflexion measured every 21 reflexions with no significant variations; Lorentz, polarization, and absorption (Busing & Levy, 1957) corrections were applied using a local (Craig, 1968) absorption program. The structures were solved using *MULTAN*74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). All H atoms [except H″(C7*A*), H″(C10*A*), H″(C12*A*), H′(C7*B*), H′(C9*B*), H″(C12*B*) and H′(C13*B*) in (2)] were located in difference syntheses; positions of these seven were calculated using a C—H distance of 0·95 Å for peaks in electron distribution (Churchill, 1973); temperature parameters of H atoms were maintained throughout the refinements equal to those of the atoms to which they are bonded; structures refined by full-matrix least squares with a local version of *ORFLS* (Busing, Martin & Levy, 1962); all positional parameters, anisotropic temperature parameters for non-H atoms and an extinction parameter (Larson, 1970) were refined without constraint; scattering factors, including anomalous-dispersion corrections, were taken from *International Tables for X-ray Crystallography* (1974); the function minimized in the least-squares calculation was $\sum w(|F_o| - |F_c|)^2$ where $w = |\sigma(F_o)|^{-2}$ and $\sigma(I) = |N_P + N_B + (0{\cdot}04N_P)^2|^{1/2}$ where N_P, N_B are number of counts in peak and background respectively. A summary of data collection and structure refinement parameters is given in Table 1. At the time of these determinations, transmission factors were not included in the absorption correction output.

Table 1. *Summary of data collection and structure refinement parameters*

	(1)	(2)
Crystal size (mm)	0·4 × 0·4 × 0·1	0·5 × 0·15 × 0·1
Reflexions used for cell constants		
number	9	9
θ range(°)	45–50	45–50
Scan type	θ–2θ	θ–2θ
Range for data collection		
θ (°)	<65	<70
h	0/7	−12/11
k	0/11	0/20
l	0/34	0/11
Reflexions measured		
unique	1717	2872
observed $\lvert I \geq 2{\cdot}58\sigma(I)\rvert$	1376	2306
R, wR		
all reflexions	0·052, 0·040	0·051, 0·045
observed reflexions	0·031, 0·037	0·034, 0·043
Parameters refined	284	476
Maximum Δ/σ	1·09	0·69
Average Δ/σ, non-H, H	0·07, 0·15	0·08, 0·10
Final $\Delta\rho$ (absolute) (e Å^{-3})	0·15	0·17
Extinction parameter	$46 \pm 5 \times 10^{-5}$	$152 \pm 7 \times 10^{-5}$
Computer used	Cyber 171	Cyber 171

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 2.* The atomic numbering scheme used for (1) is given in Fig. 1 and for (2) in Fig. 2. Bond lengths, angles and torsional angles are given in Tables 3 and 4. The seven-membered rings in both (1) and (2) adopt the twist-chair conformation $^{5,6}TC_{3,4}$ (Stoddart, 1971) in the solid state. Similar conformations have been found for the *S*-ethyl analogue of (2), ethyl 2,3:4,5-di-*O*-isopropylidene-1-thio-*β*-D-glucoseptanoside (4) (Beale, Stephenson & Stevens, 1972), methyl 2,3,4,5-tetra-*O*-acetyl-*β*-D-glucoseptanoside (5) (Beale, Stephenson & Stevens, 1971), methyl 2,3,4,5-tetra-*O*-acetyl-*β*-D-alloseptanoside (6) (James & Stevens, 1982*a*), methyl 2,3,4,5-tetra-*O*-acetyl-*α*-L-idoseptanoside (7) (James & Stevens, 1982*b*), and methyl *α*-L-idoseptanoside (8) (Grainger, Rukvichai & Stevens, 1982). This conformation, in which the pseudo axis of symmetry passes through C(1), corresponds to a member of one (the twist-chair *C*) of two low-energy groups of conformations of the parent heterocycle, oxepane (Bocian & Strauss, 1977) and there is generally good agreement between observed ring torsional angles of (1) and (2) and those of oxepane. A comparison of the ring torsional angles in (1) and (2) shows that in (1), in which there is no conformation-restraining fused five-membered ring at C(2), C(3), the seven-membered-ring torsional angle C(3)—C(4)—C(5)—C(6) is the same as that found in (2), suggesting that acid lability of the 4,5-*O*isopropylidene group in (2) is not due primarily to inherent torsional strain. We note, however, that, in oxepane, the corresponding torsional angle is −50·8° (Bocian & Strauss, 1977): presence of the *cis*-fused five-membered ring in (1) and (2) has resulted in a general flattening of the seven-membered ring in the region C(4), C(5). Although there are no obvious features of the C(4), C(5) acetal ring in (2) which could readily acount for its greater lability towards aqueous acids, we note that the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51860 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates with e.s.d.'s and equivalent isotropic temperature parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} or B_{iso}
Compound (1)				
C(1)	0·7114 (5)	0·5732 (3)	0·4931 (1)	3·48
C(2)	0·8167 (5)	0·6539 (3)	0·4537 (1)	3·35
C(3)	0·7814 (5)	0·5725 (3)	0·4088 (1)	3·34
C(4)	0·9625 (5)	0·4676 (3)	0·3987 (1)	3·62
C(5)	0·9967 (6)	0·3483 (3)	0·4326 (1)	4·13
C(6)	0·9549 (6)	0·3773 (4)	0·4825 (1)	4·42
C(7)	0·7074 (7)	0·5622 (4)	0·5738 (1)	4·73
C(8)	0·8279 (6)	0·2571 (3)	0·3691 (1)	4·45
C(9)	0·5856 (8)	0·2470 (5)	0·3564 (2)	6·38
C(10)	0·9642 (8)	0·1486 (4)	0·3446 (1)	5·37
C(31)	0·6054 (5)	0·7110 (3)	0·3519 (1)	3·35
C(32)	0·6456 (5)	0·8022 (3)	0·3110 (1)	3·50
C(33)	0·4757 (6)	0·8844 (4)	0·2951 (1)	5·06
C(34)	0·5076 (8)	0·9696 (5)	0·2573 (1)	6·60
C(35)	0·7056 (8)	0·9695 (5)	0·2352 (1)	6·20
C(36)	0·8745 (7)	0·8883 (4)	0·2506 (1)	5.44
C(37)	0·8478 (6)	0·8037 (3)	0·2889 (1)	4·34
O(1)	0·8010 (3)	0·6257 (2)	0·5338 (1)	4·12
O(2)	0·7372 (4)	0·7934 (2)	0·4526 (1)	4·23
O(31)	0·7929 (3)	0·6705 (2)	0·3711 (1)	3·80
O(32)	0·4260 (4)	0·6776 (2)	0·3651 (1)	4·80
O(4)	0·9122 (4)	0·3934 (2)	0·3577 (1)	4·65
O(5)	0·8460 (4)	0·2446 (2)	0·4169 (1)	5·07
O(6)	0·7351 (3)	0·4264 (2)	0·4895 (1)	3·87
H(C1)	0·537 (6)	0·586 (3)	0·493 (1)	3·48
H(C2)	0·965 (6)	0·658 (4)	0·457 (1)	3·34
H(C3)	0·634 (6)	0·528 (4)	0·409 (1)	3·35
H(C4)	1·103 (6)	0·516 (4)	0·396 (1)	3·62
H(C5)	1·147 (7)	0·319 (4)	0·429 (1)	4·13
H(C6)	0·959 (7)	0·287 (4)	0·499 (1)	4·42
H′(C6)	1·073 (7)	0·447 (4)	0·497 (1)	4·42
H(O2)	0·599 (7)	0·793 (4)	0·452 (1)	4·23
Compound (2)				
C(1*A*)	0·6609 (3)	−0·1576	0·6796 (3)	4·08
C(2*A*)	0·6835 (3)	−0·0749 (2)	0·6279 (3)	4·08
C(3*A*)	0·8384 (3)	−0·0552 (2)	0·6555 (3)	3·78
C(4*A*)	0·9112 (3)	−0·0175 (2)	0·8097 (3)	4·06
C(5*A*)	0·9159 (3)	−0·0677 (2)	0·9496 (3)	4·39
C(6*A*)	0·7962 (4)	−0·1252 (2)	0·9397 (3)	4·61
C(7*A*)	0·4899 (5)	−0·2387 (3)	0·7285 (6)	6·90
C(8*A*)	0·6991 (3)	−0·0090 (2)	0·4164 (3)	4·51
C(9*A*)	0·6215 (4)	0·0693 (2)	0·3937 (5)	5·92
C(10*A*)	0·7259 (6)	−0·0371 (3)	0·2733 (5)	6·48
C(11*A*)	1·1438 (3)	−0·0590 (2)	0·9407 (3)	4·86
C(12*A*)	1·2301 (5)	−0·0114 (3)	1·0785 (5)	6·84
C(13*A*)	1·2325 (5)	−0·1072 (3)	0·8685 (5)	6·88
O(1*A*)	0·5279 (2)	−0·1600 (1)	0·6995 (2)	5·20
O(2*A*)	0·6240 (2)	−0·0695 (1)	0·4662 (2)	5·24
O(3*A*)	0·8322 (2)	0·0003 (1)	0·5369 (2)	5·02
O(4*A*)	1·0582 (2)	−0·0042 (1)	0·8301 (2)	5·29
O(5*A*)	1·0466 (2)	−0·1101 (1)	0·9777 (2)	4·84
O(6*A*)	0·7713 (2)	−0·1791 (2)	0·8142 (2)	4·32
C(1*B*)	−0·0528 (3)	0·6935 (2)	0·6655 (3)	4·58
C(2*B*)	−0·0039 (3)	0·6965 (2)	0·5267 (3)	4·46
C(3*B*)	−0·1234 (3)	0·7224 (2)	0·3834 (3)	4·39
C(4*B*)	−0·1982 (3)	0·6518 (2)	0·2910 (3)	4·83
C(5*B*)	−0·2759 (4)	0·6009 (2)	0·3746 (4)	5·58
C(6*B*)	−0·2150 (5)	0·5888 (2)	0·5449 (4)	6·06
C(7*B*)	0·0370 (6)	0·6686 (3)	0·9285 (4)	7·00
C(8*B*)	0·0897 (3)	0·7849 (2)	0·3973 (3)	5·32
C(9*B*)	0·1890 (6)	0·7410 (5)	0·3335 (5)	9·30
C(10*B*)	0·1133 (6)	0·8727 (3)	0·4092 (6)	7·87
C(11*B*)	−0·4420 (3)	0·6689 (3)	0·1876 (4)	5·98
C(12*B*)	−0·5368 (6)	0·6115 (5)	0·0740 (6)	9·10
C(13*B*)	−0·5046 (6)	0·7515 (5)	0·1825 (6)	8·69
O(1*B*)	0·0474 (3)	0·6513 (1)	0·7810 (2)	5·86
O(2*B*)	0·0997 (2)	0·7566 (2)	0·5464 (2)	5·47
O(3*B*)	−0·0526 (2)	0·7695 (2)	0·3024 (2)	6·32
O(4*B*)	−0·3106 (2)	0·6759 (2)	0·1578 (2)	5·80
O(5*B*)	−0·4097 (2)	0·6396 (2)	0·3381 (3)	6·48
O(6*B*)	−0·1905 (2)	0·6608 (1)	0·6304 (2)	5·25
H(C1*A*)	0·668 (4)	−0·202 (2)	0·603 (4)	4·08
H(C2*A*)	0·638 (4)	−0·036 (2)	0·667 (4)	4·08
H(C3*A*)	0·895 (4)	−0·105 (2)	0·640 (4)	3·78
H(C4*A*)	0·858 (3)	0·035 (2)	0·803 (4)	4·06
H(C5*A*)	0·922 (4)	−0·033 (2)	1·032 (5)	4·39
H(C6*A*)	0·823 (4)	−0·157 (2)	1·032 (4)	4·61
H′(C6*A*)	0·705 (4)	−0·098 (2)	0·934 (4)	4·61
H(C1*B*)	−0·064 (4)	0·745 (3)	0·694 (4)	4·58

Table 2 (*cont.*)

	x	y	z	B_{iso}
H(C2*B*)	0·028 (4)	0·642 (2)	0·506 (5)	4·46
H(C3*B*)	−0·186 (4)	0·757 (2)	0·417 (4)	4·39
H(C4*B*)	−0·130 (4)	0·626 (2)	0·254 (4)	4·83
H(C5*B*)	−0·287 (4)	0·553 (3)	0·327 (5)	5·58
H(C6*B*)	−0·287 (5)	0·558 (3)	0·583 (5)	6·06
H′(C6*B*)	−0·132 (5)	0·557 (3)	0·569 (5)	6·06

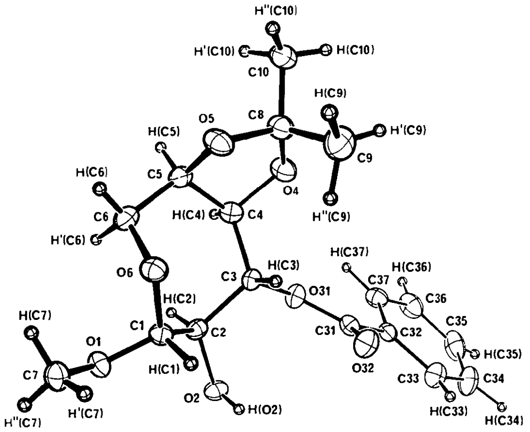


Fig. 1. An *ORTEP* plot (Johnson, 1965) of one molecule of compound (1) showing atom numbering. Non-H atoms are represented by 50% probability ellipsoids and H atoms by spheres of radius 0·1 Å.

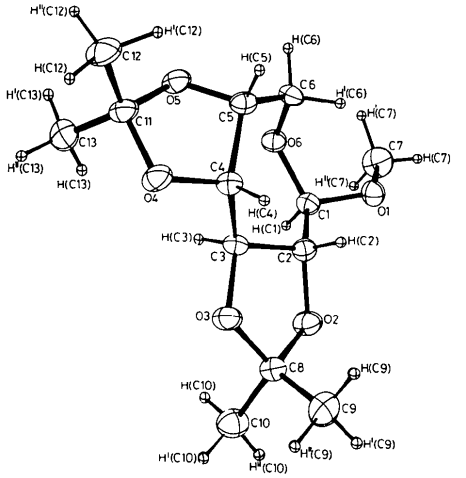


Fig. 2. An *ORTEP* plot (Johnson, 1965) of one molecule of compound (2) showing atom numbering. Non-H atoms are represented by 20% probability ellipsoids and H atoms by spheres of radius 0·1 Å.

C(4)—C(5)—C(6) ring angle (average 120°) is larger than any of the angles observed in the five septanoside structures (2), (5), (6), (7) and (8), in which the seven-membered ring adopts the twist-chair conformation found for (2).

The conformation in the region C(7), O(1), C(1), O(6) is similar in the two structures. The distances

Table 3. *Interatomic distances and standard deviations* (Å)

Compound (1)

C(1)—C(2)	1·528 (4)	O(1)—C(1)	1·403 (3)
C(2)—C(3)	1·544 (4)	O(1)—C(7)	1·436 (4)
C(3)—C(4)	1·516 (4)	O(2)—C(2)	1·413 (3)
C(4)—C(5)	1·523 (4)	O(31)—C(3)	1·448 (3)
C(5)—C(6)	1·512 (4)	O(31)—C(31)	1·330 (4)
C(8)—C(9)	1·524 (6)	O(32)—C(31)	1·201 (4)
C(8)—C(10)	1·506 (5)	O(4)—C(4)	1·425 (3)
C(31)—C(32)	1·500 (4)	O(4)—C(8)	1·434 (4)
C(32)—C(33)	1·378 (5)	O(5)—C(5)	1·423 (4)
C(33)—C(34)	1·386 (5)	O(5)—C(8)	1·410 (4)
C(34)—C(35)	1·368 (6)	O(6)—C(1)	1·407 (3)
C(35)—C(36)	1·363 (6)	O(6)—C(6)	1·432 (4)
C(36)—C(37)	1·391 (5)		
C(37)—C(32)	1·391 (5)		

Compound (2)

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
C(1)—C(2)	1·513 (3)	1·510 (4)	O(2)—C(2)	1·421 (3)	1·412 (4)
C(2)—C(3)	1·511 (4)	1·529 (4)	O(2)—C(8)	1·423 (4)	1·430 (4)
C(3)—C(4)	1·514 (4)	1·513 (5)	O(3)—C(3)	1·425 (3)	1·421 (4)
C(4)—C(5)	1·531 (4)	1·519 (5)	O(3)—C(8)	1·436 (3)	1·426 (4)
C(5)—C(6)	1·512 (4)	1·506 (5)	O(4)—C(4)	1·426 (3)	1·428 (4)
C(8)—C(9)	1·508 (5)	1·496 (6)	O(4)—C(11)	1·435 (4)	1·420 (4)
C(8)—C(10)	1·505 (5)	1·495 (6)	O(5)—C(5)	1·428 (4)	1·418 (4)
C(11)—C(12)	1·517 (5)	1·512 (7)	O(5)—C(11)	1·414 (4)	1·412 (4)
C(11)—C(13)	1·501 (6)	1·519 (7)	O(6)—C(6)	1·430 (4)	1·426 (4)
O(1)—C(1)	1·390 (3)	1·396 (4)	O(6)—C(1)	1·414 (3)	1·410 (4)
O(1)—C(7)	1·427 (5)	1·429 (4)			

Table 4. *Bond and torsion angles* (°)

Compound (1)

O(6)—C(1)—C(2)	113.5 (2)	O(31)—C(31)—C(32)	111·5 (2)
C(1)—C(2)—C(3)	109·5 (2)	O(31)—C(31)—O(32)	124·6 (2)
C(2)—C(3)—C(4)	113·4 (2)	O(32)—C(31)—C(32)	123·9 (3)
C(3)—C(4)—C(5)	117·5 (2)	C(31)—C(32)—C(33)	118·5 (3)
C(4)—C(5)—C(6)	118·2 (3)	C(31)—C(32)—C(37)	121·5 (3)
C(5)—C(6)—O(6)	110·8 (3)	C(33)—C(32)—C(37)	120·0 (3)
C(6)—O(6)—C(1)	115·5 (2)	C(32)—C(33)—C(34)	119·8 (4)
O(6)—C(1)—O(1)	112·2 (2)	C(33)—C(34)—C(35)	120·1 (4)
O(1)—C(1)—C(2)	107·5 (2)	C(34)—C(35)—C(36)	120·5 (3)
C(1)—C(2)—O(2)	110·2 (2)	C(35)—C(36)—C(37)	120·5 (4)
O(2)—C(2)—C(3)	113·8 (2)	C(36)—C(37)—C(32)	119·0 (3)
C(2)—C(3)—O(31)	108·7 (2)	C(4)—O(4)—C(8)	109·2 (2)
O(31)—C(3)—C(4)	103·9 (2)	O(4)—C(8)—O(5)	106·2 (2)
C(3)—C(4)—O(4)	109·6 (2)	O(4)—C(8)—C(9)	110·3 (3)
O(4)—C(4)—C(5)	102·1 (2)	O(4)—C(8)—C(10)	108·2 (3)
C(4)—C(5)—O(5)	102·6 (2)	C(5)—O(5)—C(8)	108·2 (2)
O(5)—C(5)—C(6)	109·3 (3)	O(5)—C(8)—C(9)	108·2 (3)
C(1)—O(1)—C(7)	112·9 (2)	O(5)—C(8)—C(10)	111·9 (3)
C(3)—O(31)—C(31)	117·9 (2)	C(9)—C(8)—C(10)	111·9 (3)
O(6)—C(1)—C(2)—C(3)	38·0 (3)	C(2)—C(3)—O(31)—C(31)	−102·8 (3)
C(1)—C(2)—C(3)—C(4)	−89·3 (3)	C(3)—O(31)—C(31)—O(32)	4·0 (4)
C(2)—C(3)—C(4)—C(5)	61·8 (3)	O(31)—C(31)—C(32)—C(37)	19·0 (4)
C(3)—C(4)—C(5)—C(6)	−33·6 (4)	O(32)—C(31)—C(32)—C(33)	19·0 (4)
C(4)—C(5)—C(6)—O(6)	57·2 (4)	O(4)—C(4)—C(5)—O(5)	−33·1 (3)
C(5)—C(6)—O(6)—C(1)	−98·1 (3)	C(4)—C(5)—O(5)—C(8)	31·6 (3)
C(6)—O(6)—C(1)—C(2)	52·2 (3)	C(5)—O(5)—C(8)—O(4)	−17·5 (3)
C(7)—O(1)—C(1)—C(2)	177·4 (3)	O(5)—C(8)—O(4)—C(4)	−5·1 (3)
C(7)—O(1)—C(1)—O(6)	−57·2 (3)	C(8)—O(4)—C(4)—C(5)	23·6 (3)
O(1)—C(1)—O(6)—C(6)	−69·8 (3)	O(2)—C(2)—C(3)—O(31)	31·8 (3)

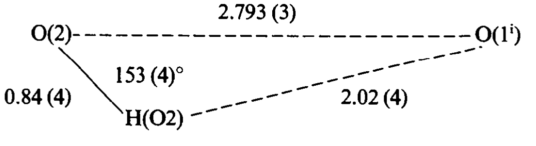
Compound (2)

	Molecule *A*	Molecule *B*
O(6)—C(1)—C(2)	111·2 (3)	111·7 (2)
C(1)—C(2)—C(3)	113·2 (2)	111·9 (2)
C(2)—C(3)—C(4)	113·8 (2)	111·5 (3)
C(3)—C(4)—C(5)	116·0 (2)	113·2 (3)
C(4)—C(5)—C(6)	119·5 (2)	120·5 (3)
C(5)—C(6)—O(6)	112·5 (2)	113·8 (3)
C(1)—O(6)—C(6)	115·7 (2)	116·1 (3)
O(1)—C(1)—C(2)	108·2 (2)	108·8 (3)
O(1)—C(1)—O(6)	112·1 (2)	112·1 (2)
C(1)—C(2)—O(2)	109·7 (2)	109·4 (2)
O(2)—C(2)—C(3)	102·7 (2)	103·7 (2)
C(2)—C(3)—O(3)	102·9 (2)	103·8 (2)
O(3)—C(3)—C(4)	109·7 (2)	112·2 (2)
C(3)—C(4)—O(4)	110·4 (2)	111·6 (3)
O(4)—C(4)—C(5)	102·8 (2)	102·4 (3)
C(4)—C(5)—O(5)	102·2 (2)	102·0 (3)
O(5)—C(5)—C(6)	109·8 (3)	110·0 (3)
C(9)—C(8)—C(10)	112·3 (3)	114·3 (5)
C(9)—C(8)—O(3)	108·3 (3)	108·3 (4)

Table 4 (*cont.*)

	Molecule *A*	Molecule *B*
C(9)—C(8)—O(2)	112·1 (3)	111·2 (3)
C(10)—C(8)—O(2)	108·4 (3)	107·4 (3)
C(10)—C(8)—O(3)	109·7 (3)	109·0 (3)
O(2)—C(8)—O(3)	105·9 (2)	106·3 (2)
C(12)—C(11)—C(13)	114·0 (3)	114·1 (4)
C(12)—C(11)—O(4)	107·6 (3)	108·9 (3)
C(12)—C(11)—O(5)	111·4 (3)	110·7 (4)
C(13)—C(11)—O(4)	109·3 (3)	108·0 (4)
C(13)—C(11)—O(5)	108·6 (3)	108·2 (3)
O(4)—C(11)—O(5)	105·7 (2)	106·7 (2)
C(1)—O(1)—C(7)	111·8 (2)	111·9 (3)
C(2)—O(2)—C(8)	107·5 (2)	107·0 (2)
C(3)—O(3)—C(8)	109·0 (2)	109·7 (2)
C(4)—O(4)—C(11)	109·8 (2)	108·8 (2)
C(5)—O(5)—C(11)	107·5 (2)	107·1 (2)
O(6)—C(1)—C(2)—C(3)	36·0 (3)	41·1 (4)
C(1)—C(2)—C(3)—C(4)	−90·3 (3)	−95·5 (3)
C(2)—C(3)—C(4)—C(5)	60·9 (3)	64·6 (3)
C(3)—C(4)—C(5)—C(6)	−31·3 (4)	−35·8 (5)
C(4)—C(5)—C(6)—O(6)	54·1 (4)	57·2 (5)
C(5)—C(6)—O(6)—C(1)	−96·5 (3)	−93·1 (4)
C(6)—O(6)—C(1)—C(2)	54·3 (3)	47·9 (3)
C(3)—C(2)—O(2)—C(8)	−33·2 (3)	−31·5 (3)
C(2)—O(2)—C(8)—O(3)	20·7 (3)	25·7 (3)
O(2)—C(8)—O(3)—C(3)	1·4 (3)	−8·5 (4)
C(8)—O(3)—C(3)—C(2)	−21·2 (3)	−10·4 (3)
O(3)—C(3)—C(2)—O(2)	32·9 (3)	25·6 (3)
C(5)—C(4)—O(4)—C(11)	16·1 (3)	21·5 (4)
C(4)—O(4)—C(11)—O(5)	4·8 (3)	−0·8 (4)
O(4)—C(11)—O(5)—C(5)	−25·7 (3)	−22·4 (4)
C(11)—O(5)—C(5)—C(4)	34·9 (3)	34·8 (4)
O(5)—C(5)—C(4)—O(4)	−30·5 (3)	−34·0 (3)
C(7)—O(1)—C(1)—C(2)	172·2 (3)	159·6 (3)
C(7)—O(1)—C(1)—O(6)	−64·8 (3)	−76·4 (4)
O(1)—C(1)—O(6)—C(6)	−67·0 (2)	−74·5 (3)
O(1)—C(1)—C(2)—O(2)	−86·4 (3)	−80·3 (3)
O(3)—C(3)—C(4)—O(4)	−68·1 (3)	−64·5 (3)

and angles in these acetal portions of the structures compare well with the corresponding values for *α*-aldopyranosides and with the values obtained from a theoretical study on dimethoxymethane (Jeffrey, Pople, Binkley & Vishveshwara, 1978). In common with other ester groups (*e.g.* for acetate esters, see Choong, McConnell, Stephenson & Stevens, 1980), the ester C=O group in (1) eclipses the C(3)—O(31) group. The conformations of the five-membered rings are close to envelopes in which the out-of-plane atoms are C(5) for (1) and C(2) and C(5) for (2). For (1), a weak hydrogen bond (Brown, 1976) occurs between the hydroxyl group on C(2) and O(1) in a neighbouring molecule:



(i) $-1/2+x, 3/2-y, 1-z$

Although the two independent molecules in (2) are very similar, they are not identical. Using an accepted criterion (Cruickshank & Robertson, 1953) for a significant difference, several bond lengths [*e.g.* C(2)—C(3), O(4)—C(11)], bond angles [*e.g.* C(1)—C(2)—C(3), C(2)—C(3)—C(4), C(3)—C(4)—C(5)] and many torsional angles [*e.g.* O(1)—C(1)—

C(2)—C(3), C(6)—O(6)—C(1)—C(2)] fall within this category, the torsional-angle differences being the most pronounced.

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Structures of Two Conducting Salts of Pyrazinoethylenedithiotetrathiafulvalene (PEDTTTF): $(PEDTTTF)_2PF_6$ and $(PEDTTTF)_2BF_4.(CH_2Cl_2)_{0.5}$

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(*Received* 8 *November* 1988; *accepted* 16 *January* 1989)

Abstract. (I): Bis{2-(dithiolo[4,5-*b*]dithiin-2-ylidene)-dithiolo[4,5-*b*]pyrazinium} hexafluorophosphate, $(C_{10}H_6N_2S_6)_2PF_6$, $M_r = 838{\cdot}07$, triclinic, $P\bar{1}$, $a = 5{\cdot}573\,(2)$, $b = 8{\cdot}173\,(1)$, $c = 16{\cdot}332\,(2)$ Å, $\alpha = 94{\cdot}70\,(1)$, $\beta = 89{\cdot}39\,(1)$, $\gamma = 75{\cdot}74\,(1)°$, $V = 718{\cdot}2\,(2)$ Å^3, $Z = 1$, $D_m = 1{\cdot}97$, $D_x = 1{\cdot}938$ Mg m^{-3}, Cu $K\bar{\alpha}$ ($\lambda = 1{\cdot}54178$ Å), $\mu = 9{\cdot}292$ mm^{-1}, $F(000) = 421{\cdot}0$, $T = 296\,(2)$ K. (II): Bis{2-(dithiolo[4,5-*b*]-dithiin-2-ylidene)dithiolo[4,5-*b*]pyrazinium} tetrafluoroborate dichloromethane solvate, $(C_{10}H_6N_2S_6)_2BF_4.(CH_2Cl_2)_{1/2}$. $M_r = 822{\cdot}38$, monoclinic, $C2/c$, $a = 34{\cdot}655\,(7)$, $b = 12{\cdot}122\,(3)$, $c = 14{\cdot}212\,(1)$ Å, $\beta = 97{\cdot}13\,(1)°$, $V = 5925\,(2)$ Å^3, $Z = 8$, $D_m = 1{\cdot}75$, $D_x = 1{\cdot}843$ Mg m^{-3}, Cu $K\bar{\alpha}$ ($\lambda = 1{\cdot}54178$ Å), $\mu = 9{\cdot}211$ mm^{-1}, $F(000) = 3312{\cdot}00$, $T = 296\,(2)$ K. Final R values 0·0393 (I) and 0·0396 (II) for 2626 (all reflections) (I) and 3570 observed reflections with $F_o \geq 5{\cdot}0\sigma(F_o)$ (II). The salts show metallic behavior down to 280 K (I) and 180 K (II). Below these temperatures they undergo metal-to-semiconductor (I) and metal-to-insulator (II) transition. Cations in both structures pack side by side, in a planar arrangement, through strong S···S and weak S···N contacts, the shortest of which are S···S = 3·456, S···N = 3·336 Å (I) and S···S = 3·467, S···N = 3·344 Å (II).

Introduction. Following a systematic study of the crystal structures of $(PEDTTTF)_2X$ salts (Terzis, Hountas & Papavassiliou, 1986; Psycharis, Hountas, Terzis & Papavassiliou, 1988; Terzis, Psycharis, Hountas & Papavassiliou, 1988) we present here two more salts, where $X = PF_6$ (I) and BF_4 (II). PEDTTTF (Fig. 1) is a modification of ET, and it

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0108-2701/89/091333-04$03.00