Fig. 2. The total energy as a function of the dihedral angle ϕ.

then found to be 0.6 kcal/mol and 103°, respectively. Compared with hydrogen disulfide the dihedral angle is increased from 90 to 102°, and the *anti* barrier reduced from 4.2 (calculated with same type of basis)[7] to 0.69 kcal/mol.

These reductions of the *anti* barrier and the very shallow minimum compared to hydrogen disulfide supply strong arguments for considerable delocalization in the planar form.

This conjugation is, however, not strong enough to give a planar equilibrium conformation, and with dihedral angle close to 90° the delocalization will not influence the S − S bond length to any extent.

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Crystal Structure of Methyl 2,3-*O*-Isopropylidene-β-D-allo-hept-6-ynofuranoside

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Methods for the synthesis and separation of epimeric uronic acids have been studied by Kjølberg *et al.*[1] One of the methods used for chain extention has been the ethynylation reaction described by Jones *et al.*[2] Reaction between methyl 2,3-*O*-isopropylidene-β-D-ribo-1,5-dialdopentofuranoside and ethynyl-magnesium bromide gave two isomers (C-5 epimers) in approximately equal amounts.[3] Since configurational assignments based on spectroscopic data were somewhat uncertain, an X-ray crystallographic investigation of the isomer which was supposed to be the methyl-2,3-*O*-isopropylidene-β-D-allo-hept-6-ynofuranoside has been carried out.

The crystals of $C_{11}O_5H_{16}$ are orthorhombic with cell dimensions $a = 5.855(2)$ Å, $b = 11.555(3)$ Å, $c = 18.174(3)$ Å and four molecules in the unit cell ($D_x = 1.23$ g/cm³). The space group is $P2_12_12_1$. The structure was solved by direct methods [4] and refined by full-matrix least squares technique *[5] to an R-value of 3.4 % ($R_w = 4.1$ %) for 971 reflections observed on an automatic four circle diffractometer at room temperature. Anisotropic temperature factors were introduced for oxygen and carbon atoms. The hydroxyl and methyl hydrogen atoms were found in the difference Fourier map. Positional parameters for the remaining hydrogen atoms were calculated. Weights for least squares refinement were obtained from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts and C_N the net count.

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. The principal axes of thermal vibration ellipsoids for carbon atoms were calculated from the temperature parameters of Table 1. Maximum r.m.s. amplitudes range from 0.220 to 0.331 Å (corresponding B-values 3.80 and 8.63 Å²).

Bond distances and angles are listed in Table 2. Fig. 1 is a schematic drawing of the molecule (viewed along [100]) which shows that it has the D-allo configuration.

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* All programs used (except those for phase determination) are included in this reference.

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. The expression for anisotropic vibration is $\exp(-2\pi^2(h^2a^{*2}U11 + \cdots + 2klb^*c^*U23))$. Hm is bonded to Cm, HMmn to CMm, and HO to O5.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O1	1.2680(6)	.2943(3)	.6921(2)	.0464(24)	.0575(23)	.0548(22)	.0021(21)	-.0054(19)	.0121(21)
O2	.7518(8)	.5382(3)	.6343(2)	.0694(27)	.0426(21)	.2680(22)	.0021(22)	-.0197(24)	-.0047(19)
O3	.5082(7)	.4407(3)	.5628(2)	.0569(25)	.0450(21)	.0002(22)	-.0002(22)	-.0171(23)	.0045(19)
O4	.6672(6)	.2944(3)	.6966(2)	.0473(24)	.0500(28)	.0366(17)	-.0058(20)	.0037(18)	.0005(18)
O5	.6469(8)	.1195(3)	.5288(2)	.0559(26)	.0669(25)	.0464(21)	.0004(26)	.0013(23)	-.0121(19)
C1	.8698(9)	.3619(5)	.6943(3)	.0479(34)	.0511(30)	.0406(29)	-.0033(33)	-.0037(34)	-.0053(28)
C2	.8603(11)	.4285(4)	.6229(3)	.0474(36)	.0417(30)	.0495(30)	-.0062(34)	-.0016(34)	.0036(25)
C3	.6924(9)	.3618(4)	.5753(3)	.0494(36)	.0463(29)	.0398(28)	.0091(31)	-.0087(27)	-.0049(26)
C4	.6127(10)	.2612(4)	.6229(3)	.0410(32)	.0460(30)	.0383(27)	.0034(31)	.0051(26)	.0085(22)
C5	.7266(11)	.1465(5)	.6014(3)	.0481(38)	.0479(32)	.0432(31)	-.0009(32)	.0010(24)	.0055(24)
C6	.6665(11)	.0534(5)	.6535(3)	.0646(43)	.0461(31)	.0574(31)	.0058(34)	.0040(32)	.0058(28)
C7	.6145(13)	-.0196(5)	.6949(4)	.0936(52)	.0503(35)	.0785(40)	.0053(39)	.2400(45)	.3111(35)
C8	.5899(11)	.5538(5)	.5775(3)	.0614(42)	.0434(31)	.0634(34)	.0016(34)	-.2117(34)	.3068(28)
CM1	1.1012(16)	.2222(7)	.7554(4)	.0623(59)	.0795(49)	.0723(43)	.2043(53)	-.0130(51)	.1278(39)
CM2	.7019(19)	.6042(8)	.5090(5)	.0936(68)	.0757(54)	.0802(52)	-.0066(54)	.0003(52)	.0301(44)
CM3	.3961(16)	.6256(7)	.6373(5)	.0760(58)	.0541(47)	.0921(55)	.0095(49)	-.0090(54)	.0044(45)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1	.870(8)	.409(3)	.738(2)	2.6(10)	H2	1.026(10)	.442(4)	.604(2)	3.4(11)
H3	.764(8)	.337(3)	.526(2)	2.3(8)	H4	.432(9)	.253(3)	.621(2)	2.9(9)
H5	.984(8)	-.160(3)	.600(2)	3.3(10)	H7	.543(9)	-.086(4)	.734(3)	7.2(15)
HM11	.977(17)	.159(7)	.758(4)	9.7(24)	HM12	1.019(10)	.241(5)	.799(2)	9.4(13)
HM13	1.261(9)	.181(4)	.763(2)	8.2(13)	HM21	.83M(13)	.559(5)	.440(2)	8.1(19)
HM22	.568(12)	.616(5)	.476(3)	5.4(19)	HM23	.759(15)	.679(6)	.528(3)	6.6(23)
HM31	.254(15)	.622(6)	.673(4)	8.2(22)	HM32	.448(13)	.699(5)	.613(3)	5.7(17)
HM33	.336(13)	.587(5)	.652(3)	7.3(21)	HO	.771(15)	.397(5)	.499(3)	7.7(19)

Table 2. Bond distances and angles with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)	DISTANCE	(Å)
C1 – O1	1.399(6)	O1 – CM1	1.433(6)	C1 – O4	1.420(6)
C4 – O4	1.429(6)	C2 – O2	1.432(6)	C3 – O3	1.431(6)
C8 – O2	1.413(6)	C8 – O3	1.418(7)	C5 – O5	1.433(6)
C1 – C2	1.513(7)	C2 – C3	1.519(7)	C3 – C4	1.522(7)
C8 – CM2	1.521(9)	C8 – CM3	1.506(9)	C4 – C5	1.535(8)
C5 – C6	1.476(8)	C6 – C7	1.171(8)	O5 – O3	2.780(5)

ANGLE	(°)	ANGLE	(°)
C1 – O1 – CM1	114.5(5)	C1 – O4 – C4	107.8(4)
C2 – O2 – C8	107.8(4)	C3 – O3 – C8	107.6(4)
O1 – C1 – O4	112.8(4)	O1 – C1 – C2	106.9(4)
O4 – C1 – C2	105.9(4)	C1 – C2 – O2	110.1(4)
C1 – C2 – C3	104.7(4)	O2 – C2 – C3	104.2(5)
C2 – C3 – C4	105.2(4)	C2 – C3 – O3	104.8(4)
O3 – C3 – C4	110.2(4)	C3 – C4 – O4	105.0(4)
C5 – C4 – O4	111.9(4)	C3 – C4 – C5	112.4(4)
O2 – C8 – O3	104.3(4)	O3 – C8 – CM2	110.0(4)
O2 – C8 – CM2	111.1(6)	CM2 – C8 – CM3	113.9(6)
O3 – C8 – CM3	108.7(6)	O2 – C8 – CM3	108.3(5)
C4 – C5 – O5	106.3(5)	C4 – C5 – C6	111.3(4)
C6 – C5 – O5	110.7(4)	C5 – C6 – C7	178.6(7)
C5 – O5 – O3'	111.0(3)	O5 – O3' – C3'	120.6(3)
O5 – O3' – C8'	126.9(3)		

The bond distances and angles do not differ significantly from corresponding ones in methyl-α-D-galactofuranoside.[6] The two five-membered rings have the envelope form with O4 and C8 both 0.47 Å out of the planes (to within 0.01 Å) through C1, C2, C3, C4, and C2, C3, O2, O3, respectively. The angle between the planes is 63.9°. Apart from a hydrogen bond (of length 2.780 Å) between O5 and O3 in a symmetry related molecule, there are no short intermolecular contacts.

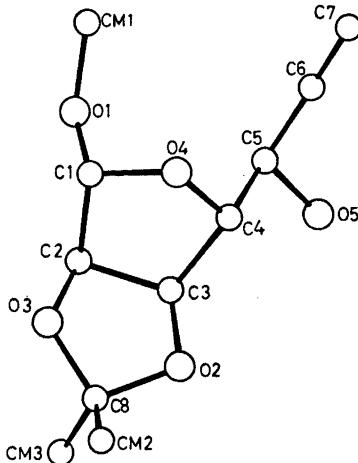A list of observed and calculated structure factors is available from the author.

Fig. 1. Schematic drawing of the molecule viewed along [100].

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