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received matching attention. As part of a detailed investigation (Mehta, Padma, Pattabhi, Pramanik & Chandrasekhar, 1990), we have studied the cycloaddition of several dienes to the novel dienophile tricyclo[6.2.1.0^{2,7}]undeca-2(7),4,9-triene-3,6-dione (1) (Cookson, Hill & Hudec, 1964; Mehta *et al.*, 1989), whose two faces are distinguishable by the presence of methano and etheno bridges, respectively. It was essential to establish unambiguously the stereochemistry of the cycloaddition products of (1); here we describe the molecular structure of the products (I) and (II), obtained by cycloadditions of tricyclo[5.2.1.0^{2,16}]deca-2,5,8-triene (2) and cyclooctatetraene (3), respectively.

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Cycloaddition Products of Tricyclo[6.2.1.0^{2,7}]undeca-2(7),4,9-triene-3,6-dione

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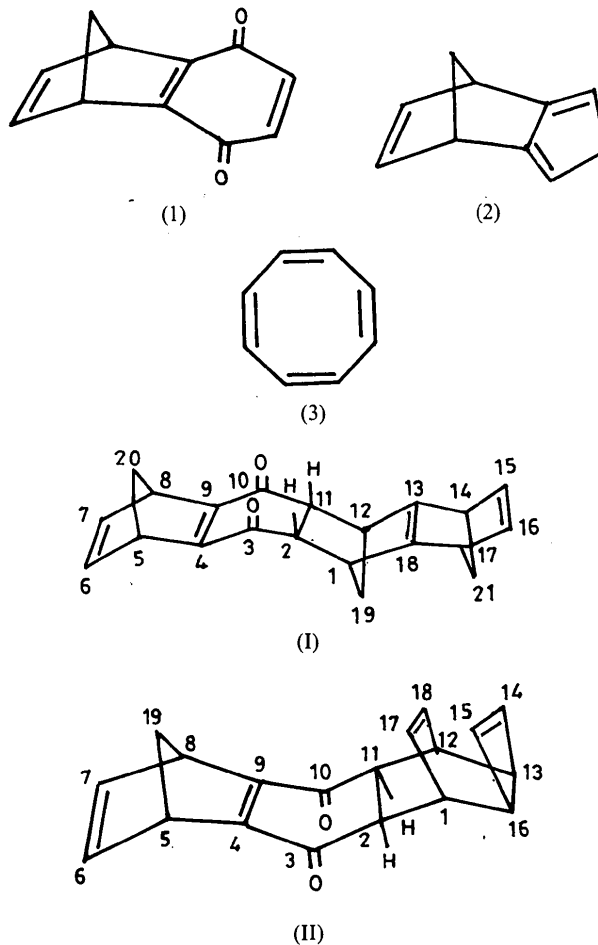
(Received 26 February 1993; accepted 22 July 1993)

Abstract

The crystal structures of *endo,anti,syn*-heptacyclo[10.6.1.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]henicosa-4(9),-6,13(18),15-tetraene-3,10-dione, C₂₁H₁₈O₂ (I), and *exo,syn,syn*-hexacyclo[10.4.2.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,16}]nonadeca-4(9),6,14,17-tetraene-3,10-dione, C₁₉H₁₆O₂ (II), are reported. The packing of the molecules in both structures is stabilized by van der Waal's forces.

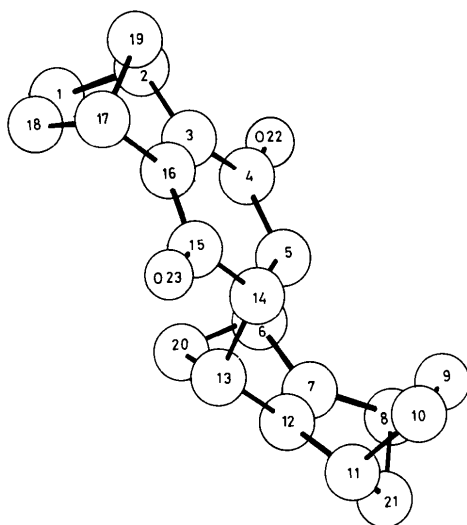
Comment

Stereoelectronic effects which influence the stereochemical outcome of the Diels–Alder reaction have been investigated extensively in recent years. In this context, facially perturbed diene or dienophile constituents are particularly incisive probes for evaluating the relative contributions of steric and electronic factors. While cycloadditions to facially perturbed dienes have been explored widely, the complementary response of facially perturbed dienophiles in Diels–Alder cycloadditions has not

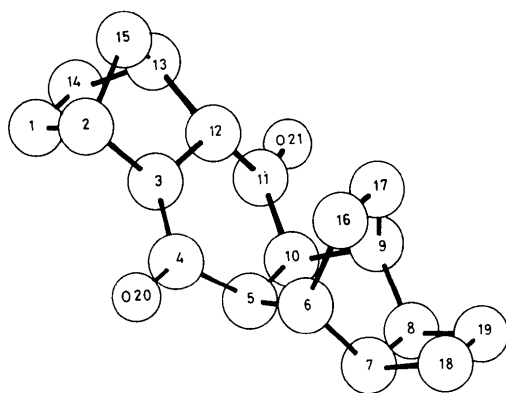


The average e.s.d.'s for the bond lengths and angles are 0.006 Å and 0.4°, respectively, in (I), and 0.003 Å and 0.2°, respectively, in (II). The bond lengths and angles in the two structures are comparable and normal. C(3)—C(4) and C(15)—C(16) in (I) and C(3)—C(4) and C(11)—C(12) in (II) exhibit partial double-bond character. The C(5)—C(6) bond in both compounds is significantly elongated, which may be due to overcrowding of the atoms at C(6).

† DCB contribution No. 821.



(I)



(II)

Fig. 1. View of the molecules of (I) and (II), showing the crystallographic numbering scheme.

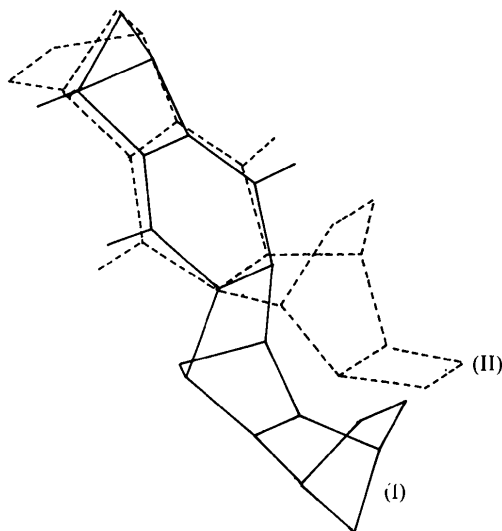


Fig. 2. Superposition of molecules of (I) and (II).

Experimental

Compound (I)

Crystal data

$C_{21}H_{18}O_2$
 $M_r = 302.37$
 Orthorhombic
 $P2_12_12_1$
 $a = 7.925 (1) \text{ \AA}$
 $b = 9.281 (2) \text{ \AA}$
 $c = 20.918 (3) \text{ \AA}$
 $V = 1538.6 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.31 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 20 - 30^\circ$
 $\mu = 0.62 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Rhombus
 $0.40 \times 0.40 \times 0.22 \text{ mm}$
 Greenish yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: empirical
 $T_{\min} = 0.73, T_{\max} = 0.96$
 1752 measured reflections
 1701 independent reflections
 1567 observed reflections
 $[I > 2.5\sigma(I)]$

$R_{\text{int}} = 0.03$
 $\theta_{\text{max}} = 70^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 11$
 $l = 0 \rightarrow 25$
 3 standard reflections
 frequency: 120 min
 intensity variation: <2.8%
 (linear correction factors 1.000–1.014)

Refinement

Refinement on F
 $R = 0.068$
 $wR = 0.099$
 $S = 3.25$
 1567 reflections
 280 parameters
 All H-atom parameters refined
 $w = 4(F_o^2)/\sigma^2(F_o^2)$
 where $\sigma(F_o^2) = [\sigma^2(I) + (0.05I)^2]^{1/2}/Lp$
 $(\Delta/\sigma)_{\text{max}} = 0.03$

$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: Zachariasen (1963)
 Extinction coefficient: 1.35×10^{-5}
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O22	0.9009 (4)	0.5150 (4)	0.5348 (2)	6.83 (7)
O23	0.4831 (5)	0.3618 (4)	0.7280 (1)	6.55 (7)
C1	0.4120 (6)	0.6259 (5)	0.5362 (2)	5.56 (9)
C2	0.5775 (6)	0.6829 (4)	0.5634 (2)	4.93 (8)
C3	0.6589 (5)	0.5545 (4)	0.5963 (2)	3.88 (6)
C4	0.8086 (5)	0.4740 (4)	0.5782 (2)	4.27 (7)
C5	0.8509 (4)	0.3379 (4)	0.6161 (2)	3.69 (6)
C6	0.8392 (6)	0.2039 (4)	0.5701 (2)	4.55 (8)
C7	0.9212 (5)	0.0816 (4)	0.6051 (2)	4.15 (7)
C8	1.0967 (6)	0.0285 (5)	0.6212 (2)	5.06 (8)
C9	1.1530 (6)	0.1120 (6)	0.6817 (3)	6.1 (1)
C10	1.0539 (6)	0.0756 (5)	0.7287 (2)	5.60 (9)
C11	0.9248 (6)	-0.0351 (4)	0.7027 (2)	4.50 (8)
C12	0.8206 (5)	0.0448 (4)	0.6539 (2)	3.91 (7)
C13	0.6669 (5)	0.1403 (4)	0.6523 (2)	4.03 (7)
C14	0.7333 (4)	0.2945 (4)	0.6715 (2)	3.33 (6)
C15	0.5838 (5)	0.3917 (4)	0.6863 (2)	3.74 (6)
C16	0.5594 (4)	0.5190 (4)	0.6462 (2)	3.44 (6)
C17	0.4116 (5)	0.6240 (4)	0.6464 (2)	4.16 (7)
C18	0.3129 (6)	0.5936 (5)	0.5852 (3)	5.55 (9)

C19	0.5070 (6)	0.7605 (4)	0.6244 (2)	4.86 (8)
C20	0.6515 (6)	0.1620 (5)	0.5795 (2)	5.14 (8)
C21	1.0450 (6)	-0.1146 (5)	0.6546 (2)	5.20 (9)

Table 2. Selected geometric parameters (Å, °) for (I)

O22—C4	1.226 (5)	C8—C9	1.550 (7)
O23—C15	1.216 (5)	C8—C21	1.556 (6)
C1—C2	1.524 (7)	C9—C10	1.303 (7)
C1—C18	1.325 (7)	C10—C11	1.549 (6)
C2—C3	1.520 (5)	C11—C12	1.508 (6)
C2—C19	1.568 (6)	C11—C21	1.569 (6)
C3—C4	1.452 (5)	C12—C13	1.507 (5)
C3—C16	1.350 (5)	C13—C14	1.577 (5)
C4—C5	1.528 (5)	C13—C20	1.540 (6)
C5—C6	1.575 (5)	C14—C15	1.521 (5)
C5—C14	1.542 (5)	C15—C16	1.461 (5)
C6—C7	1.499 (5)	C16—C17	1.524 (5)
C6—C20	1.550 (6)	C17—C18	1.526 (6)
C7—C8	1.514 (6)	C17—C19	1.546 (6)
C7—C12	1.338 (5)		
C2—C1—C18	107.5 (4)	C10—C11—C21	97.8 (3)
C1—C2—C3	105.2 (3)	C12—C11—C21	97.4 (3)
C1—C2—C19	99.0 (3)	C7—C12—C11	108.4 (3)
C3—C2—C19	98.2 (3)	C7—C12—C13	108.3 (3)
C2—C3—C4	129.2 (3)	C11—C12—C13	138.3 (3)
C2—C3—C16	107.1 (3)	C12—C13—C14	105.0 (3)
C4—C3—C16	123.6 (3)	C12—C13—C20	99.4 (3)
O22—C4—C3	121.4 (4)	C14—C13—C20	99.2 (3)
O22—C4—C5	120.6 (3)	C5—C14—C13	104.3 (3)
C3—C4—C5	118.0 (3)	C5—C14—C15	118.0 (3)
C4—C5—C6	108.9 (3)	C13—C14—C15	109.2 (3)
C4—C5—C14	118.3 (3)	O23—C15—C14	121.5 (3)
C6—C5—C14	102.6 (3)	O23—C15—C16	120.6 (4)
C5—C6—C7	105.9 (3)	C14—C15—C16	117.8 (3)
C5—C6—C20	100.2 (3)	C3—C16—C15	124.3 (3)
C7—C6—C20	99.4 (3)	C3—C16—C17	107.1 (3)
C6—C7—C8	138.8 (4)	C15—C16—C17	128.1 (3)
C6—C7—C12	107.9 (3)	C16—C17—C18	105.9 (3)
C8—C7—C12	107.2 (3)	C16—C17—C19	98.5 (3)
C7—C8—C9	106.4 (3)	C18—C17—C19	98.8 (3)
C7—C8—C21	97.8 (3)	C1—C18—C17	107.6 (4)
C9—C8—C21	97.7 (4)	C2—C19—C17	92.3 (3)
C8—C9—C10	108.3 (4)	C6—C20—C13	94.7 (3)
C9—C10—C11	107.8 (4)	C8—C21—C11	92.7 (3)
C10—C11—C12	105.9 (3)		

Refinement

Refinement on F $R = 0.064$ $wR = 0.063$ $S = 2.6$

2143 reflections

254 parameters

All H-atom parameters refined

$$w = 4(F_o^2)/\sigma^2(F_o^2)$$

$$\text{where } \sigma(F_o^2) = [\sigma^2(I) + (0.05I)^2]^{1/2}/Lp$$

 $(\Delta/\sigma)_{\max} = 0.07$ $\Delta\rho_{\max} = 0.32 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O20	0.1458 (3)	0.18518 (5)	1.3004 (2)	5.48 (3)
O21	0.1707 (3)	0.05488 (5)	0.8013 (2)	4.88 (2)
C1	0.4871 (3)	0.06798 (8)	1.3701 (2)	4.64 (3)
C2	0.2560 (3)	0.08224 (7)	1.3847 (2)	4.22 (3)
C3	0.1815 (2)	0.10670 (5)	1.2164 (2)	3.27 (2)
C4	0.1320 (2)	0.15619 (5)	1.1853 (2)	3.32 (2)
C5	0.0558 (2)	0.17075 (4)	1.0034 (2)	2.90 (2)
C6	-0.1822 (2)	0.18766 (5)	0.9991 (2)	3.41 (2)
C7	-0.2243 (3)	0.21464 (5)	0.8296 (2)	3.78 (2)
C8	-0.1964 (3)	0.18056 (6)	0.6773 (2)	4.16 (3)
C9	-0.1426 (3)	0.13068 (6)	0.7472 (2)	3.74 (2)
C10	0.0742 (2)	0.13413 (5)	0.8581 (1)	2.85 (2)
C11	0.1443 (2)	0.08447 (5)	0.9092 (1)	3.03 (2)
C12	0.1843 (2)	0.07378 (4)	1.0911 (2)	2.98 (2)
C13	0.2562 (3)	0.02743 (5)	1.1751 (2)	4.08 (3)
C14	0.4882 (3)	0.03537 (7)	1.2483 (3)	4.53 (3)
C15	0.1468 (4)	0.03338 (8)	1.3432 (3)	5.11 (3)
C16	-0.3237 (3)	0.14488 (6)	0.9955 (2)	4.22 (2)
C17	-0.3051 (3)	0.11579 (5)	0.8653 (3)	4.32 (3)
C18	-0.4503 (3)	0.22127 (6)	0.7488 (3)	4.62 (3)
C19	-0.4254 (3)	0.19272 (7)	0.6190 (3)	4.93 (3)

Table 4. Selected geometric parameters (Å, °) for (II)

O20—C4	1.219 (2)	C7—C8	1.561 (2)
O21—C11	1.214 (2)	C7—C18	1.514 (3)
C1—C2	1.524 (3)	C8—C9	1.543 (2)
C1—C14	1.331 (3)	C8—C19	1.511 (3)
C2—C3	1.528 (2)	C9—C10	1.553 (2)
C2—C15	1.567 (3)	C9—C17	1.503 (2)
C3—C4	1.453 (2)	C10—C11	1.518 (2)
C3—C12	1.358 (2)	C11—C12	1.460 (2)
C4—C5	1.523 (2)	C12—C13	1.520 (2)
C5—C6	1.571 (2)	C13—C14	1.536 (3)
C5—C10	1.555 (2)	C13—C15	1.554 (3)
C6—C7	1.537 (2)	C16—C17	1.328 (3)
C6—C16	1.503 (2)	C18—C19	1.322 (3)
C2—C1—C14	107.8 (2)	C8—C9—C10	107.1 (1)
C1—C2—C3	105.9 (1)	C8—C9—C17	109.8 (1)
C1—C2—C15	98.8 (2)	C10—C9—C17	106.5 (1)
C3—C2—C15	97.3 (1)	C5—C10—C9	109.4 (1)
C2—C3—C4	128.9 (1)	C5—C10—C11	117.70 (9)
C2—C3—C12	107.0 (1)	C9—C10—C11	108.0 (1)
C4—C3—C12	124.0 (1)	O21—C11—C10	120.8 (1)
O20—C4—C3	121.8 (1)	O21—C11—C12	121.1 (1)
O20—C4—C5	120.5 (1)	C10—C11—C12	118.1 (1)
C3—C4—C5	117.6 (1)	C3—C12—C11	123.7 (1)
C4—C5—C6	108.7 (1)	C3—C12—C13	107.6 (1)
C4—C5—C10	118.0 (1)	C11—C12—C13	128.4 (1)
C6—C5—C10	108.9 (1)	C12—C13—C14	105.7 (1)
C5—C6—C7	105.0 (1)	C12—C13—C15	97.9 (1)
C5—C6—C16	108.4 (1)	C14—C13—C15	98.4 (1)
C7—C6—C16	109.3 (1)	C1—C14—C13	107.7 (2)
C6—C7—C8	109.5 (1)	C2—C15—C13	93.0 (1)
C6—C7—C18	120.3 (1)	C6—C16—C17	114.9 (1)
C8—C7—C18	85.6 (1)	C9—C17—C16	114.5 (1)

Compound (II)

Crystal data

C₁₉H₁₆O₂ $M_r = 276.34$

Monoclinic

 $P2_1/c$ $a = 6.293 (1) \text{ Å}$ $b = 28.348 (1) \text{ Å}$ $c = 7.856 (1) \text{ Å}$ $\beta = 95.29 (1)^\circ$ $V = 1395.5 (4) \text{ Å}^3$ $Z = 4$ $D_x = 1.31 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius diffractometer

 ω - 2θ scans

Absorption correction:

none

3038 measured reflections

2406 independent reflections

2143 observed reflections

 $[I > 2.5\sigma(I)]$ Cu $K\alpha$ radiation $\lambda = 1.5418 \text{ Å}$

Cell parameters from 25

reflections

 $\theta = 11-34^\circ$ $\mu = 0.63 \text{ mm}^{-1}$ $T = 295 \text{ K}$

Parallelepiped

 $0.32 \times 0.20 \times 0.20 \text{ mm}$

Pale green

 $R_{\text{int}} = 0.01$ $\theta_{\text{max}} = 70^\circ$ $h = 0 \rightarrow 8$ $k = 0 \rightarrow 32$ $l = -10 \rightarrow 10$

3 standard reflections

frequency: 120 min

intensity variation: <5%

C7—C8—C9	109.3 (1)	C7—C18—C19	94.2 (2)
C7—C8—C19	85.4 (1)	C8—C19—C18	94.8 (2)
C9—C8—C19	119.2 (2)		

Structure solution and refinement were performed using the *SDP* (Frenz, 1978) program package on a VAXII/730 computer. Molecular structures were plotted using the *PLUTO* program (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71521 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1052]

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Acta Cryst. (1994). **C50**, 597–601

2,2'-Di-*O*-acetyl-3,6;3',6'-dianhydro-4,4'-dideoxy- α,α -trehalose

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Abstract

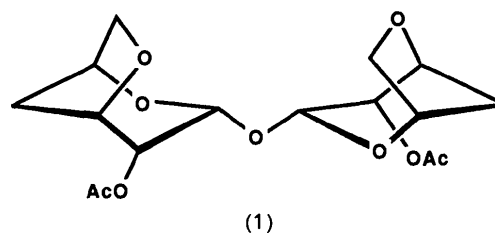
The structure of 2,2'-di-*O*-acetyl-3,6;3',6'-dianhydro-4,4'-dideoxy- α,α -trehalose (2-*O*-acetyl-3,6-anhydro-4-deoxy- α -D-xylo-hexopyranosyl 2-*O*-acetyl-3,6-anhydro-4-deoxy- α -D-xylo-hexopyranoside), C₁₆H₂₂O₉, is described. The molecule has approximate two-fold symmetry through O(1). Both pyranoid rings have distorted ¹C₄ chair conformations and the five-membered anhydro rings have distorted ⁴E conformations. The structure of the compound appears to show the absence of a sweet AH,B gluco-

phore, which would explain the absence of sweetness in the unsubstituted derivative.

Comment

The Shallenberger AH,B theory of sweetness (Shallenberger & Acree, 1967) suggests that the fundamental unit of sweetness is an AH,B system, where A and B are electronegative atoms in suitable geometric proximity. The Kier extension to the AH,B concept (Kier, 1972) is that a third hydrophilic (γ) binding site, if present, will increase the intensity of the sweet taste. The ideal molecule for taste studies in sugars is probably α,α -trehalose. It contains two chemically equivalent glucopyranose residues in the most stable ⁴C₁ conformation, linked glycosidically through their reducing (anomeric) C atoms. Stability is high in the sugar and its derivatives because all the hydroxyl substituents are equatorially disposed. Because the interatomic distances are of great importance in determining sweetness, we have undertaken the X-ray crystal diffraction study of α,α -trehalose derivatives.

A *SHELXTL-Plus* (Sheldrick, 1990) *XP* plot of 2,2'-di-*O*-acetyl-3,6;3',6'-dianhydro-4,4'-dideoxy- α,α -trehalose (Birch, Lee & Richardson, 1974) (1) with the atomic numbering scheme is shown in Fig. 1, and the molecular packing in the crystal is shown in Fig. 2. Like α,α -trehalose, the two glucopyranosyl residues of (1) have approximate C₂ symmetry but the structural differences between the two residues are much smaller. Differences are found in the torsion angles about the glycosidic O atom, especially those involving C(2) and C(2') (Table 3), and in the conformation of the C(2) and C(2') acetyl groups.



Bond lengths, bond angles and selected torsion angles are given in Tables 2 and 3. Bond lengths and angles agree well with those of methyl 3,6-anhydro- α -D-hexopyranosides (Lindberg, Lindberg & Svensson, 1973; Campbell & Harding, 1972), and most other pyranose sugars (Berman, Chu & Jeffrey, 1967). The O(1)—C(1) and O(1)—C(1') bond lengths show systematic trends similar to those observed in other α -pyranose sugars (Berman, Chu & Jeffrey, 1967) but are shorter than those in α,α -trehalose (Brown, Rohrer, Berking, Beevers, Gould & Simpson, 1972; Taga, Senma & Osaki, 1972; Jeffrey & Nanni, 1985) and its 3,3-dideoxy derivative (Lee &