$S = 1.020$
2983 reflections
184 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.020$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: inferred from preparation

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.7576 (3)	0.6839 (3)	0.6587 (2)	0.0434 (5)
HO1	0.7910 (3)	0.7445 (3)	0.6171 (2)	
O2	0.9975 (3)	0.7165 (3)	0.4826 (2)	0.0374 (5)
C1	0.9081 (3)	0.4926 (3)	0.9822 (2)	0.0245 (4)
C2	0.9611 (3)	0.4671 (3)	1.1304 (2)	0.0270 (4)
C3	0.7945 (3)	0.4788 (3)	1.2138 (2)	0.0266 (4)
C4	0.6363 (3)	0.3930 (3)	1.1689 (2)	0.0203 (4)
C5	0.5933 (2)	0.4082 (3)	1.0141 (2)	0.0170 (3)
C6	0.4375 (3)	0.3259 (3)	0.9567 (2)	0.0231 (4)
C7	0.3778 (3)	0.3621 (3)	0.8121 (2)	0.0264 (5)
C8	0.5385 (3)	0.3681 (3)	0.7247 (2)	0.0237 (4)
C9	0.6885 (3)	0.4527 (3)	0.7816 (2)	0.0197 (4)
C10	0.7600 (2)	0.4044	0.9241 (2)	0.0174 (3)
C11	0.8373 (3)	0.4749 (3)	0.6874 (2)	0.0213 (4)
C12	0.8646 (3)	0.5851 (3)	0.6315 (2)	0.0224 (4)
C13	1.0032 (3)	0.6136 (3)	0.5339 (2)	0.0231 (4)
C16	1.1478 (3)	0.5228 (3)	0.5024 (2)	0.0274 (5)
C17	0.5465 (4)	0.3016 (3)	0.6135 (3)	0.0354 (6)
C18	0.4705 (3)	0.4353 (3)	1.2435 (2)	0.0275 (5)
C19	0.6801 (3)	0.2596 (3)	1.2123 (2)	0.0268 (4)
C20	0.8414 (3)	0.2745 (3)	0.9087 (2)	0.0235 (4)

Table 2. *Selected geometric parameters* (Å, °)

O1—C12	1.363 (3)	C6—C7	1.533 (3)
O2—C13	1.223 (3)	C7—C8	1.508 (3)
C1—C2	1.531 (3)	C8—C17	1.324 (3)
C1—C10	1.536 (3)	C8—C9	1.518 (3)
C2—C3	1.523 (3)	C9—C11	1.500 (3)
C3—C4	1.534 (3)	C9—C10	1.575 (3)
C4—C18	1.532 (3)	C10—C20	1.537 (3)
C4—C19	1.533 (3)	C11—C12	1.333 (3)
C4—C5	1.566 (3)	C12—C13	1.480 (3)
C5—C6	1.535 (3)	C13—C16	1.493 (3)
C5—C10	1.559 (3)		
C2—C1—C10	112.9 (2)	C11—C9—C8	113.7 (2)
C3—C2—C1	110.0 (2)	C11—C9—C10	113.5 (2)
C2—C3—C4	114.3 (2)	C8—C9—C10	109.6 (2)
C18—C4—C3	106.8 (2)	C20—C10—C1	109.4 (2)
C18—C4—C19	107.7 (2)	C20—C10—C5	113.9 (2)
C3—C4—C19	110.0 (2)	C1—C10—C5	109.3 (2)
C18—C4—C5	108.9 (2)	C20—C10—C9	109.0 (2)
C3—C4—C5	109.4 (2)	C1—C10—C9	109.1 (2)
C19—C4—C5	113.8 (2)	C5—C10—C9	105.96 (14)
C6—C5—C10	111.4 (2)	C12—C11—C9	122.4 (2)
C6—C5—C4	114.3 (2)	C11—C12—O1	120.9 (2)
C10—C5—C4	116.2 (2)	C11—C12—C13	125.8 (2)
C5—C6—C7	111.7 (2)	O1—C12—C13	113.2 (2)
C8—C7—C6	111.1 (2)	O2—C13—C12	117.1 (2)
C17—C8—C7	122.2 (2)	O2—C13—C16	121.2 (2)
C17—C8—C9	125.1 (2)	C12—C13—C16	121.7 (2)
C7—C8—C9	112.7 (2)		

The absolute stereochemistry of (1) could not be determined from the reflection data (Flack, 1983). The structure of the enantiomorph based on the stereochemistry of labda-8(17),14-dien-13-ol was refined and characterized. H atoms were placed in idealized positions and constrained to ride 0.96 Å from the appropriate C atom with fixed isotropic temperature factors.

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

We thank Professor W. T. Robinson (University of Canterbury) for data collection and the University of Otago for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N,*N*-Dimethyl-1*H*-pyrrole-2-carboxamide

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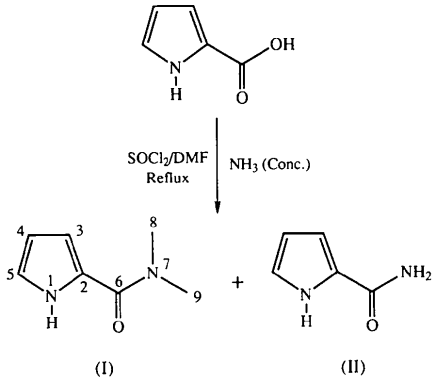
Abstract

The low-temperature X-ray crystal structure of *N*,*N*-dimethyl-1*H*-pyrrole-2-carboxamide, $C_7H_{10}N_2O$, was determined. The molecular geometry indicates that the carbonyl π system interacts preferentially with the lone-pair electrons of the amide N atom rather than with the π system of the pyrrole ring. Intermolecular hydrogen bonds link the molecules into centrosymmetric dimers.

Comment

In attempts to synthesize 1*H*-pyrrole-2-carboxamide, (II), as well as some other natural products, *N*,*N*-dimethyl-1*H*-pyrrole-2-carboxamide, (I), was consistently produced as the major product from refluxing 1*H*-pyrrole-2-carboxylic acid with $SOCl_2$ and dimethylformamide.



(I) (II)

A view of compound (I) showing the displacement ellipsoids and the atomic numbering is given in Fig. 1. The pyrrole ring is planar (χ^2 = 17.1), with a maximum deviation of 0.006 (3) Å from the least-squares plane defined by the five ring atoms. The six atoms of the amide group are also coplanar (χ^2 = 174), with a maximum deviation of 0.023 (3) Å from the least-squares plane. The environment around atom C(2) is slightly distorted from planarity, with atom C(6) lying 0.078 (3) Å out of the pyrrole ring plane.

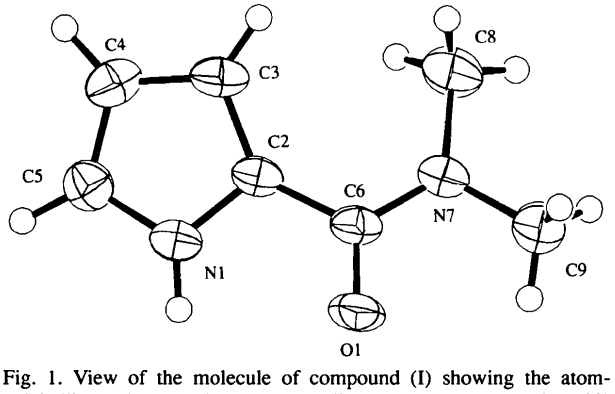


Fig. 1. View of the molecule of compound (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

The pyrrole ring possesses approximate C_{2v} symmetry and the bond lengths within the ring correspond closely to the typical bond lengths of such rings listed by Allen *et al.* (1992). This is in contrast with the distortions observed in the pyrrole rings of the closely related compounds 2-benzoyl-1*H*-pyrrole, 2-(4-chlorobenzoyl)-1*H*-pyrrole and 2-(4-methoxybenzoyl)-1*H*-pyrrole (English, McGillivray & Smal, 1980). In these compounds, there is a slight shortening of the N(1)—C(5) bond and a lengthening of the N(1)—C(2) bond with a corresponding shortening of the C(2)—C(6) bond. These distortions were explained as being due to a contribution to the normal electronic pyrrole ring configuration from a canonical form resulting from the overlap of the carbonyl π system with that of the pyrrole ring. This hypothesis was supported by the coplanarity of the carbonyl and pyrrole groups of these compounds. Similar observations have been made by Bonnett, Hursthouse & Neidle (1972) and Cullen, Meyer, Eivazi & Smith (1978). In compound (I), the N(1)—C bonds are almost symmetrical about the N atom and the C(2)—C(6) bond length is 0.2–0.3 Å longer than the corresponding bond in the 2-benzoylpyrrole compounds. This indicates that there is less overlap of the pyrrole and carbonyl π systems, which is also supported by the significant twist of 25.2° between the amide plane and the pyrrole ring plane.

The bond lengths within the amide group have typical values for *N*,*N*-disubstituted amides (Allen *et al.*, 1992). In amides, the C=O bond is usually slightly longer than that found in unconjugated carbonyl groups and the C(6)—N(7) bond is quite short. This is due to some contribution to the structure from the tautomeric form of the amide. In compound (I), there is apparently a greater preference for an interaction of the lone electron pair on the amide N atom with the carbonyl π system than for an interaction between the carbonyl π system and that of the pyrrole ring. This would explain the absence of any distortion of the pyrrole ring geometry. In the substituted 2-benzoylpyrroles (English, McGillivray & Smal, 1980), the carbonyl π system overlaps with that of the pyrrole ring rather than with the π system of the adjacent phenyl ring. Although in these pyrroles the

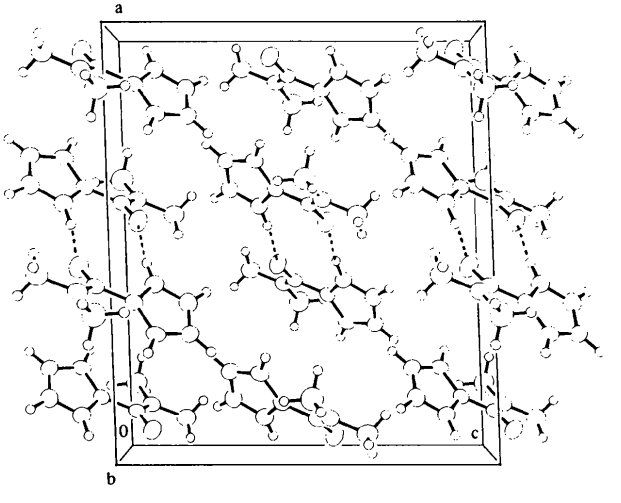


Fig. 2. The packing of compound (I) in the unit cell viewed down the *b* axis. Dashed lines indicate the hydrogen-bonding interactions.

phenyl ring is unable to lie coplanar with the pyrrole ring because of H···H steric interactions, the absence of a compensating torsional twist about the C(2)—C(6) bond confirms this preference.

The pyrrole NH group forms an intermolecular hydrogen bond with the amide O atom. These interactions link the molecules into centrosymmetric dimers as shown in Fig. 2. It is worth noting that the three substituted 2-benzoylpyrroles reported by English, McGillivray & Smal (1980) also form centrosymmetric hydrogen-bonded dimers in the same manner. Related ^1H and ^{13}C NMR data for compound (I) are given in Table 3.

Experimental

Crystal data

$C_7H_{10}N_2O$
M_r = 138.17
Monoclinic
$C2/c$
a = 15.620 (2) Å
b = 6.887 (2) Å
c = 13.616 (2) Å
β = 91.82 (1)°
V = 1463.9 (5) Å^3
Z = 8
D_x = 1.254 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 19 reflections
θ = 15–18.5°
μ = 0.0809 mm^{-1}
T = 173 (1) K
Prism
0.35 × 0.20 × 0.13 mm
Colourless
Crystal source: aqueous solution

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2375 measured reflections
2135 independent reflections
890 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.040
θ_{max} = 30°
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 9$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 150 reflections
intensity decay: insignificant

Refinement

Refinement on F
R = 0.0442
wR = 0.0353
S = 1.611
890 reflections
126 parameters
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
$(\Delta/\sigma)_{max}$ = 0.0006
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O(1)	0.0520 (1)	0.3418 (3)	0.0712 (1)	0.0553 (7)
N(1)	0.0914 (1)	0.4312 (3)	−0.1168 (2)	0.0404 (7)
C(2)	0.1297 (1)	0.2770 (3)	−0.0694 (2)	0.0347 (8)
C(3)	0.1992 (2)	0.2248 (4)	−0.1237 (2)	0.0426 (9)
C(4)	0.2015 (2)	0.3487 (4)	−0.2053 (2)	0.048 (1)
C(5)	0.1337 (2)	0.4750 (4)	−0.2000 (2)	0.045 (1)
C(6)	0.0935 (2)	0.2198 (4)	0.0248 (2)	0.0389 (8)
N(7)	0.1036 (1)	0.0378 (3)	0.0592 (1)	0.0404 (7)
C(8)	0.1521 (2)	−0.1157 (5)	0.0131 (3)	0.058 (1)
C(9)	0.0686 (2)	−0.0088 (4)	0.1550 (2)	0.054 (1)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(6)	1.246 (3)	C(3)—C(4)	1.402 (4)
N(1)—C(2)	1.371 (3)	C(4)—C(5)	1.373 (4)
N(1)—C(5)	1.363 (3)	C(6)—N(7)	1.346 (3)
C(2)—C(3)	1.381 (3)	N(7)—C(8)	1.454 (3)
C(2)—C(6)	1.472 (3)	N(7)—C(9)	1.465 (3)
C(2)—N(1)—C(5)	110.3 (2)	O(1)—C(6)—N(7)	120.6 (2)
N(1)—C(2)—C(3)	106.8 (2)	O(1)—C(6)—C(2)	118.8 (2)
N(1)—C(2)—C(6)	116.3 (2)	C(2)—C(6)—N(7)	120.6 (2)
C(3)—C(2)—C(6)	136.7 (2)	C(6)—N(7)—C(8)	125.7 (2)
C(2)—C(3)—C(4)	107.8 (2)	C(6)—N(7)—C(9)	118.1 (2)
C(3)—C(4)—C(5)	107.7 (2)	C(8)—N(7)—C(9)	116.1 (2)
N(1)—C(5)—C(4)	107.4 (2)		
O(1)—C(6)—N(7)—C(8)	−178.6 (3)	C(3)—C(2)—C(6)—N(7)	−30.0 (4)
O(1)—C(6)—N(7)—C(9)	−3.3 (3)	C(2)—C(6)—N(7)—C(8)	2.8 (4)
O(1)—C(6)—C(2)—N(1)	−22.6 (3)	C(2)—C(6)—N(7)—C(9)	178.1 (2)
O(1)—C(6)—C(2)—C(3)	151.4 (3)	C(4)—C(3)—C(2)—C(6)	−175.1 (3)
N(1)—C(2)—C(6)—N(7)	156.0 (2)	C(5)—N(1)—C(2)—C(6)	176.8 (2)

D—H···A	D—H	H···A	D···A	D—H···A
N(1)—H(1)···O(1^i)	0.92 (2)	1.91 (2)	2.816 (3)	171 (2)

Symmetry code: (i) $-x, 1-y, -z$.

Table 3. ^1H *NMR and* ^{13}C *NMR data for compound* (I) *measured in* d_6*-acetone*

	δ ^1H (p.p.m.; 300 MHz)	δ ^{13}C (p.p.m.; 75.5 MHz)
N(1)	10.80 (*br*)	
C(2)		126.0 (*s*)*
C(3)	6.59 (*ddd*, *J* 1.4, 2.6, 3.8) †	113.4 (*d*)
C(4)	6.17 (*ddd*, *J* 2.6, 2.6, 3.8)	109.7 (*d*)
C(5)	6.95 (*ddd*, *J* 1.4, 2.6, 2.6)	121.8 (*d*)
C(6)		163.2 (*s*)
C(8)	3.19 (*br*)	37.7 (*br*, *q*)
C(9)	3.19 (*br*)	37.7 (*br*, *q*)

* Multiplicity by DEPT (distortionless enhanced polarization transfer).

† Coupling constants in Hz.

The H atoms of the C(9) methyl group are disordered with two distinct sets of positions being observed in a difference electron density map. These H atoms were subsequently fixed at ideal positions with their orientation based on the difference map positions and their isotropic displacement parameters were refined. The relative site occupation factors of the two orientations were refined while constraining the total occupation to unity. The occupancy of the major component of the disorder was 0.59 (8). The positions and isotropic displacement parameters of all other H atoms were refined.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Structure solution: by direct methods using *SHELXS*86 (Sheldrick, 1990). Structure refinement: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Miss I. Klingenfuss is thanked for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and N···O contact distances, have been deposited with the IUCr (Reference: PA1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 747–751

3-*O*-Benzoyl-4,6;4′,6′-di-*O*-benzylidene-2,2′-dideoxy-α,α-*ribo*-trehalose†

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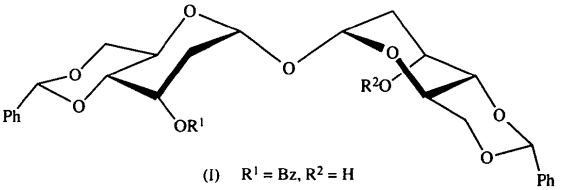
Abstract

The low-temperature X-ray structure of an asymmetrically substituted derivative of α,α-trehalose, 3-*O*-benzoyl-4,6;4′,6′-di-*O*-benzylidene-2,2′-dideoxy-α,α-*ribo*-trehalose (3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranosyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside, $C_{33}H_{34}O_{10}$), is reported. The hexopyranosyl rings and the 1,3-dioxane rings have normal $^4C_1$ chair conformations, so that each half of the molecule has a double-chair conformation, resembling a *trans*-decalin ring system. Each benzylidene acetal group takes the form of the thermodynamically more stable (*R*)-diastereomer with its phenyl group attached to the 1,3-dioxane ring in an equatorial orientation. The conformations about the glycosidic linkages are stabilized by the anomeric effect and by an intramolecular hydrogen bond between the lone hydroxy group and the glycosidic O atom.

Comment

α,α-Trehalose (α-D-glucopyranosyl α-D-glucopyranoside) is widely distributed in nature (Birch, 1963; Elbein, 1974; Lee, 1980). Chemical modification of the disaccharide is relatively facile and generally results in symmetrical modification of both glycosyl moieties, because of the twofold symmetry about the bridging O atom. However, most symmetrical derivatives show no trehalase activity, suggesting that one intact α-D-glucopyranosyl ring, or a close modification thereof, is a prerequisite for enzymatic recognition (Labat-Robert, 1982). Significantly, a number of such asymmetrically substituted derivatives, particularly monoaminated ones, occur naturally as antibiotically active metabolites (Arcamone & Bizioli, 1957; Umezawa, Tasuta & Muto, 1967; Uramoto, Otaka & Yonehara, 1967; Naganawa, Usui, Hamada, Maeda & Umezawa, 1974), but the selective synthetic modification of only one of the two glucosyl rings to give non-symmetrical analogues is generally difficult (Guilloux, Percheron & Defaye, 1969; Richardson & Tarelli, 1971; Hanessian & Lavallée, 1973; Defaye, Driguez, Henrissat, Gelas & Bar-Guilloux, 1978; Defaye & Horton, 1978; Dolak, Castle & Laborde, 1980). Here we report the synthesis and X-ray structure of an asymmetrically substituted derivative of α,α-trehalose: 3-*O*-benzoyl-4,6;4′,6′-di-*O*-benzylidene-2,2′-dideoxy-α,α-*ribo*-trehalose (I).



(I) R^1 = Bz, R^2 = H
(II) R^1 = R^2 = Bz
(III) R^1 = R^2 = H

It has been observed that several years storage of 3,3′-di-*O*-benzoyl-4,6;4′,6′-di-*O*-benzylidene-2,2′-dideoxy-α,α-*ribo*-trehalose, (II) (Hough, Richardson & Tarelli, 1971), resulted in the loss of one of the C-3,3′ benzoate substituents to yield (I). The synthesis of (I) can also be achieved by selective benzoylation of 4,6;4′,6′-di-*O*-benzylidene-2,2′-dideoxy-α,α-*ribo*-trehalose, (III), using *N*-benzoylimidazole in chloroform. The structure of (I) is consistent with the ^{1}H and ^{13}C NMR data.

A view of (I), showing the displacement ellipsoids and the atomic numbering, is given in Fig. 1. The figure

† Crystal Structures of Trehalose Derivatives, Part 8. For Part 7, see Lee & Linden (1994).