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Mannose Phenylhydrazone, an Acyclic Monosaccharide Derivative

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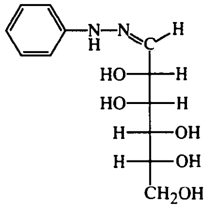
Abstract

In determining whether mannose phenylhydrazone ($C_{12}H_{18}N_2O_5$) is cyclic or acyclic, chemical and spectroscopic methods have yielded contradictory results. X-ray crystallography has now shown that this compound occurs in an acyclic form in the solid state. The conformation is closely similar to that assumed by mannose *p*-bromophenylhydrazone [Furberg & Solbakk (1969). *Acta Chem. Scand.* **23**, 3248–3256], and the hydrogen-bonding arrangements found in the two structures are identical.

Comment

Reaction of monosaccharides with phenylhydrazine and related compounds yields both cyclic and acyclic products (Staněk, Černý, Kocourek & Pacák, 1963). Crystal structure analyses of the *p*-bromophenylhydrazones of glucose (Bjamer, Dahm, Furberg & Petersen, 1963; Dukefos & Mostad, 1965) and arabinose (Furberg & Petersen, 1962) and the tosylhydrazones of glucose, galactose and arabinose (Ojala, Ojala & Gleason, 1996) have shown that these derivatives occur in ring form in the solid state, but the *p*-bromophenylhydrazones of ribose (Bjamer, Furberg & Petersen, 1964) and mannose (Furberg & Solbakk, 1969) have been found to occur in open-chain form. The structure of mannose phenylhydrazone is particularly interesting because the experimental evidence is ambiguous. The behavior of this compound in the formazan reaction (Mester & Major, 1955) suggests that in solution the molecule is acyclic, but the absence from the IR spectrum (Nujol) of an obvious C═N band suggests that the sugar assumes a ring structure and that the molecule is a phenylhydrazide and not a phenylhydrazone (Blair & Roberts, 1967). In our own investigation of the structures of monosaccharide derivatives, we have avoided relying on IR spectra for structure assignments because we have found that even such clear-cut hydrazones as cyclopentanone tosylhydrazone and cyclohexanone tosylhydrazone exhibit only very weak absorption bands in the C═N region (~1640 cm^{-1}). We have instead relied on X-ray crystallographic evidence. As part of this study we have determined the crystal structure of mannose phenylhydrazone, (1), and have found that this compound assumes an open-chain structure in the solid state.



(1)

The molecular conformation and atom-numbering scheme are shown in Fig. 1. The conformation of mannose phenylhydrazone is closely similar to that of mannose *p*-bromophenylhydrazone. Both molecules possess a planar, fully extended zigzag chain of C atoms. In both structures, the atoms N(2), N(1), C(1) and C(2) are coplanar within experimental error, and in both cases this plane assumes an angle of 124° with the plane of the sugar C atoms. The orientation of the phenyl group is similar in the two molecules with the least-squares plane through the phenyl C atoms assuming an angle

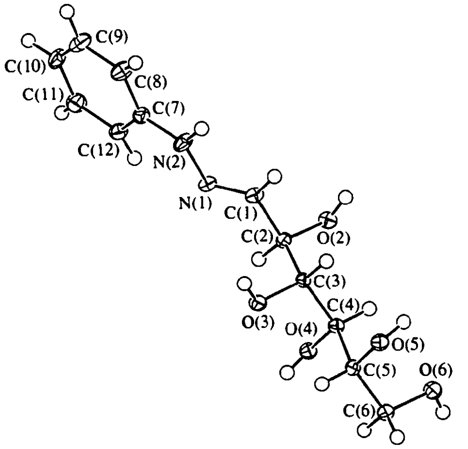


Fig. 1. *ORTEP*II (Johnson, 1976) view of (1), showing the atom numbering. For non-H atoms, 50% probability ellipsoids are shown.

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of 18.5° with the N(2)—N(1)—C(1)—C(2) plane in the phenylhydrazone and an angle of 21.3° in the *p*-bromophenylhydrazone.

The packing arrangement of mannose phenylhydrazone is shown in Fig. 2. Details of the hydrogen-bond geometry are given in Table 3. Every potential hydrogen-bond donor participates in hydrogen bonding. Of the potential acceptors, only N(2) does not participate, possibly as a result of delocalization of its lone electron pair into the aromatic ring as suggested by an N(1)—N(2)—C(7) bond angle close to 120°. Molecules are linked along the *a* and *c* axes by three hydrogen bonds in each of these directions, defining layers extending parallel to the *ac* plane. No hydrogen bonds link one layer to the next along the *b* axis. In spite of the difference in space-filling requirements posed by the Br atom, the hydrogen-bonding schemes assumed by the phenylhydrazone and *p*-bromophenylhydrazone are identical. With both compounds crystallizing in space group *P*1, the packing arrangements are similar. The preparation and structure solution of this heavy-atom derivative of mannose phenylhydrazone over 25 years ago yielded a faithful representation of the corresponding light-atom structure.

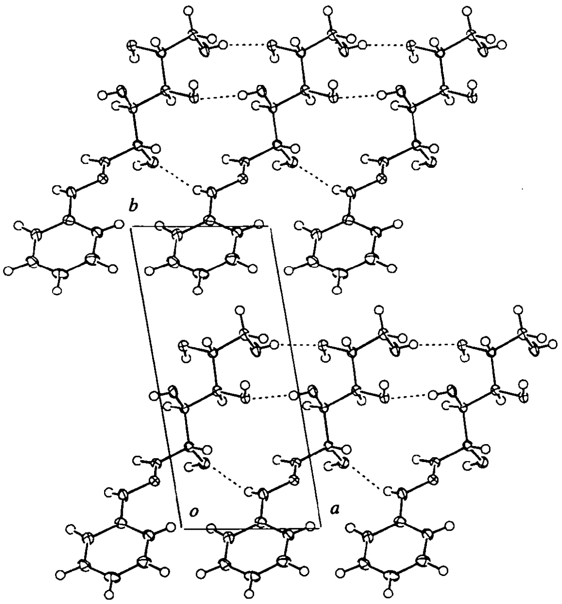

Fig. 2. View of the packing arrangement down the *c* axis. Hydrogen bonds that link the molecules along the *a* axis are indicated by dashed lines.

Experimental

The title compound was prepared by standard methods and melted at 471–473 K, in agreement with the literature value (Blair & Roberts, 1967).

Crystal data

$C_{12}H_{18}N_2O_5$
$M_r = 270.28$
Triclinic
$P1$
$a = 5.655\,(1)$ Å
$b = 12.248\,(2)$ Å
$c = 4.736\,(1)$ Å
$\alpha = 99.54\,(1)°$
$\beta = 106.34\,(1)°$
$\gamma = 96.27\,(1)°$
$V = 306.2\,(1)$ Å^3
$Z = 1$
$D_x = 1.466$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 24$–$25°$
$\mu = 0.920$ mm^{-1}
$T = 173$ K
Plate
0.48 × 0.30 × 0.03 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical, ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.813$, $T_{\max} = 1.000$
2237 measured reflections
2237 independent reflections

2163 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 70°$
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -5 \rightarrow 5$
3 standard reflections monitored every 150 reflections intensity decay: <1% (no correction applied)

Refinement

Refinement on F
$R = 0.027$
$wR = 0.033$
$S = 2.46$
2163 reflections
224 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
Extinction coefficient: 0.235×10^{-4}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
O(2)	0.2359	0.2138	−0.1529	0.0191 (3)
O(3)	0.1008 (4)	0.4485 (2)	0.3366 (4)	0.0190 (4)
O(4)	0.6104 (4)	0.4288 (2)	0.3327 (5)	0.0179 (4)
O(5)	0.2338 (4)	0.5997 (2)	−0.1347 (5)	0.0182 (4)
O(6)	0.7409 (4)	0.5869 (2)	−0.1504 (5)	0.0238 (4)
N(1)	−0.1397 (4)	0.1584 (2)	0.2548 (5)	0.0172 (4)
N(2)	−0.3796 (4)	0.1118 (2)	0.2172 (5)	0.0220 (5)
C(1)	−0.1055 (4)	0.2141 (2)	0.0603 (6)	0.0174 (5)
C(2)	0.1528 (5)	0.2688 (2)	0.0842 (6)	0.0158 (5)
C(3)	0.1612 (5)	0.3939 (2)	0.0804 (6)	0.0141 (5)
C(4)	0.4172 (5)	0.4506 (2)	0.0895 (6)	0.0156 (5)
C(5)	0.4300 (5)	0.5775 (2)	0.1057 (6)	0.0157 (5)
C(6)	0.6825 (5)	0.6359 (2)	0.1111 (6)	0.0182 (5)
C(7)	−0.4291 (5)	0.0212 (2)	0.3483 (6)	0.0190 (5)
C(8)	−0.6779 (5)	−0.0286 (2)	0.2786 (6)	0.0257 (6)
C(9)	−0.7390 (5)	−0.1184 (2)	0.4024 (6)	0.0285 (6)
C(10)	−0.5558 (5)	−0.1585 (2)	0.5999 (6)	0.0261 (6)
C(11)	−0.3098 (5)	−0.1090 (2)	0.6687 (6)	0.0268 (6)
C(12)	−0.2445 (5)	−0.0200 (2)	0.5442 (6)	0.0207 (5)

Table 2. *Geometric parameters (Å, °)*

O(2)—C(2)	1.432 (3)	C(3)—C(4)	1.521 (4)
O(3)—C(3)	1.432 (4)	C(4)—C(5)	1.536 (4)
O(4)—C(4)	1.431 (3)	C(5)—C(6)	1.517 (4)
O(5)—C(5)	1.435 (3)	C(7)—C(8)	1.394 (4)
O(6)—C(6)	1.425 (4)	C(7)—C(12)	1.389 (4)
N(1)—N(2)	1.364 (3)	C(8)—C(9)	1.385 (4)
N(1)—C(1)	1.277 (4)	C(9)—C(10)	1.381 (4)
N(2)—C(7)	1.398 (4)	C(10)—C(11)	1.380 (4)
C(1)—C(2)	1.505 (4)	C(11)—C(12)	1.386 (4)
C(2)—C(3)	1.532 (4)		
N(2)—N(1)—C(1)	116.8 (2)	O(5)—C(5)—C(4)	110.7 (1)
N(1)—N(2)—C(7)	120.6 (2)	O(5)—C(5)—C(6)	110.9 (2)
N(1)—C(1)—C(2)	120.4 (2)	C(4)—C(5)—C(6)	113.3 (2)
O(2)—C(2)—C(1)	110.8 (2)	O(6)—C(6)—C(5)	109.6 (2)
O(2)—C(2)—C(3)	110.4 (2)	N(2)—C(7)—C(8)	117.4 (2)
C(1)—C(2)—C(3)	111.0 (2)	N(2)—C(7)—C(12)	123.3 (2)
O(3)—C(3)—C(2)	109.1 (2)	C(8)—C(7)—C(12)	119.2 (2)
O(3)—C(3)—C(4)	108.5 (2)	C(7)—C(8)—C(9)	120.2 (2)
C(2)—C(3)—C(4)	112.3 (2)	C(8)—C(9)—C(10)	120.6 (2)
O(4)—C(4)—C(3)	111.4 (2)	C(9)—C(10)—C(11)	119.1 (2)
O(4)—C(4)—C(5)	110.5 (2)	C(10)—C(11)—C(12)	121.2 (2)
C(3)—C(4)—C(5)	112.2 (1)	C(7)—C(12)—C(11)	119.7 (2)
C(1)—N(1)—N(2)—C(7)	158.4 (2)		
C(4)—C(5)—C(6)—O(6)	58.1 (3)		
N(1)—N(2)—C(7)—C(8)	−174.4 (2)		
N(1)—C(1)—C(2)—C(3)	−126.2 (3)		
N(2)—N(1)—C(1)—C(2)	179.9 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O(2)—H(2O)$\cdots$N(1^{i})	2.10 (2)	2.923 (2)	173 (3)
O(3)—H(3O)$\cdots$O(4^{ii})	1.99 (3)	2.752 (3)	169 (2)
O(4)—H(4O)$\cdots$O(6^{iii})	1.95 (2)	2.718 (3)	164 (3)
O(5)—H(5O)$\cdots$O(3^{i})	1.92 (2)	2.714 (3)	156 (3)
O(6)—H(6O)$\cdots$O(5^{iv})	2.02 (3)	2.754 (3)	161 (3)
N(2)—H(2N)$\cdots$O(2^{ii})	2.21 (3)	2.922 (2)	151 (3)

Symmetry codes: (i) $x, y, z-1$; (ii) $x-1, y, z$; (iii) $x, y, 1+z$; (iv) $1+x, y, z$.

Non-H atoms were refined anisotropically and H atoms were refined with isotropic displacement parameters fixed at approximately 1.2 times the isotropic equivalent of the attached atom [C—H distances 0.88 (3)–1.03 (2), N—H 0.79 (3), O—H 0.77 (3)–0.85 (3) Å].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1257). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-1,11-Dimethyl-3,9-dinitro-5,7-dihydrodibenz[*c*,*e*]oxepine

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Abstract

Racemic crystals of the atropisomeric title compound, $C_{16}H_{14}N_2O_5$, are composed of independent molecules separated by normal van der Waals distances. The molecule, as well as its central seven-membered ring, has an approximate C_2 symmetry. The nitro groups are twisted from coplanarity with the phenyl rings by 11.5 (3) and 15.6 (3)°.

Comment

Optically active inherently chiral biphenyls such as 1,11-dimethyl-3,9-dinitro-5,7-dihydrodibenz[*c*,*e*]oxepine, (I), are known to induce a twisted cholesteric phase when doped into a nematic liquid crystal (Gottarelli *et al.*, 1983). The propensity of this dopant to induce a

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