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Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2,3-diphenylazo-α-D-mannoside

BY GEORGE M. SHELDRICK

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

AND BRUCE E. DAVISON AND JILL TROTTER

Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB, England

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Abstract. $C_{26}H_{26}N_4O_4$, $M_r = 458{\cdot}5$, tetragonal, $I4$, $a = 22{\cdot}605\ (2)$, $c = 9{\cdot}859\ (3)$ Å, $U = 5037{\cdot}8$ Å^3, $Z = 8$, D_m (flotation) $= 1{\cdot}17$, $D_x = 1{\cdot}21$ g cm^{-3}. The structure confirms the indirect chemical evidence for the axial–equatorial (*a–e*) arrangement of the phenylazo groups. This arrangement is unexpected since an *e–e* disposition would be predicted on steric grounds.

Introduction. The title compound was prepared by reaction of periodate-oxidized methyl 4,6-*O*-benzylidene-α-D-glucopyranoside and fourfold excess of phenylhydrazine (Davison, Guthrie & Murphy, 1967): bright-yellow crystals were obtained from a large volume of methanol. Intensities were measured on a Philips PW 1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation and an ω–2θ scan. Cell dimensions were obtained by least-squares analysis from the setting angles of 25 reflections used to calculate the *UB* matrix. All independent reflections were measured in the range $3{\cdot}0 \le \theta \le 30{\cdot}0°$. The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 0{\cdot}5$ cm^{-1}), and 1694 unique reflections with $F > 3\sigma(F)$ were employed in the structure refinement. The systematic absences, hkl: $h + k + l = 2n + 1$, indicated possible space groups $I4$, $I\bar{4}$ and $I4/m$; since the compound is optically active (Davison *et al.*, 1967) $I4$ is uniquely determined.

The structure was solved by direct methods. The reflection subset with $l = 4n$ had a pseudocentrosymmetric E distribution, *i.e.* large mean $|E^2 - 1|$ even when $|E|^2$ was separately normalized to unity for the subset. Accordingly 40 $l = 4n$ reflections (13 $hk0$, 21 $hk4$ and 6 $hk8$), strongly linked by 122 triple-phase relations, were selected on the basis of a convergence map and solved by a novel multisolution technique assuming all their phase angles to be 0 or 180°. Four independent subset solutions were found which agreed with six strong Σ_1 indications. The multisolution tangent method was then employed to phase the full set of 352 reflections with $E \ge 1{\cdot}3$. One reflection with $l = 1$ was given a phase angle of zero to fix the origin in the z direction, and five other reflections with l odd were included in the starting set with magic-integer phases using the series 17, 25, 29, 31, 32 (White & Woolfson, 1975). The enantiomorph was defined by scanning only half of the magic-integer space. The E map with the best value of R_α (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) and the fourth best value of NQEST (De Titta, Edmonds, Langs & Hauptman, 1975)

Table 1. *Fractional atomic coordinates* (×10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U
O(1)	4094 (2)	2291 (2)	−4247 (8)	*
O(4)	4308 (2)	3227 (2)	−253 (7)	47 (1)
O(5)	4607 (2)	3172 (2)	−3886†	59 (1)
O(6)	3971 (2)	4100 (2)	−1238 (8)	57 (1)
N(1)	5574 (3)	2428 (3)	−2896 (9)	60 (2)
N(2)	5917 (3)	2017 (3)	−3169 (9)	57 (2)
N(3)	5004 (3)	2154 (3)	−463 (8)	56 (2)
N(4)	4724 (3)	1796 (3)	235 (9)	68 (2)
C(1)	4648 (3)	2556 (3)	−4088 (11)	64 (2)
C(2)	4946 (3)	2232 (3)	−2935 (9)	56 (2)
C(3)	4656 (3)	2399 (3)	−1576 (9)	49 (2)
C(4)	4628 (3)	3064 (3)	−1463 (9)	47 (2)
C(5)	4299 (3)	3312 (3)	−2654 (9)	52 (2)
C(6)	4246 (4)	3973 (3)	−2520 (9)	63 (2)
C(7)	3779 (5)	2477 (5)	−5438 (12)	*
C(8)	4291 (3)	3847 (3)	−149 (9)	49 (2)
C(9)	3978 (2)	4004 (2)	1155 (7)	*
C(10)	3380 (2)	4151 (2)	1243 (7)	*
C(11)	3126 (2)	4272 (2)	2503 (7)	*
C(12)	3471 (2)	4244 (2)	3675 (7)	*
C(13)	4069 (2)	4097 (2)	3587 (7)	*
C(14)	4322 (2)	3976 (2)	2327 (7)	*
C(15)	6527 (3)	2172 (2)	−3080 (8)	*
C(16)	6919 (3)	1799 (2)	−3760 (8)	*
C(17)	7526 (3)	1903 (2)	−3694 (8)	*
C(18)	7742 (3)	2381 (2)	−2948 (8)	*
C(19)	7351 (3)	2754 (2)	−2268 (8)	*
C(20)	6743 (3)	2650 (2)	−2334 (8)	*
C(21)	5048 (3)	1542 (3)	1308 (10)	*
C(22)	5665 (3)	1546 (3)	1390 (10)	*
C(23)	5947 (3)	1293 (3)	2507 (10)	*
C(24)	5613 (3)	1037 (3)	3542 (10)	*
C(25)	4997 (3)	1033 (3)	3460 (10)	*
C(26)	4715 (3)	1286 (3)	2344 (10)	*

* The anisotropic thermal parameters for these atoms have been deposited.

† The z coordinate of O(5) was fixed for origin definition.

revealed 26 of the 34 unique atoms. The missing atoms were subsequently found to possess high thermal parameters caused by phenyl-group libration.

Isotropic least-squares refinement (to $R = 0{\cdot}16$) followed by a difference synthesis showed 11 of the 26 H atoms. In subsequent refinement the atoms of the *trans*-fused decalin-type ring system and the N atoms were given isotropic temperature factors and the remaining atoms were refined anisotropically. Owing to the restricted amount of data the phenyl groups were treated as rigid hexagons with C—C 1·395 Å and C—C—C 120°. H atoms were inserted in calculated positions (C—H 1·08 Å), and refined subject to the constraint that the C—H vectors were constant in magnitude and direction but not position (*i.e.* a riding model was employed for H attached to C). A common H atom isotropic temperature factor refined to 0·076 (6) Å^2; the H atoms of the phenylazo groups were given a separate temperature factor [0·17 (1) Å^2]. In the final stages of refinement an accelerated full-matrix procedure was used to reduce computing time, the inverse matrix from cycle 1 being used for subsequent cycles. The refinement converged at R 0·118, R' 0·079 ($R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$) for 205 parameters; reflections were weighted as $w = 1/\sigma^2(F_o)$.

Final atomic coordinates and isotropic temperature factors are given in Table 1 and the molecular geometry is in Table 2.* The molecule is illustrated in Fig. 1. The mean origin shift of the refined structure was calculated as 0·016 Å along z from the final phases of the 40 $l = 4n$ subset reflections. After applying the origin shift this corresponds to a mean phase error of 10·3° for these 40 reflections.

A search of the Cambridge Crystallographic Data Centre files accessed *via The Crystal Structure Search Retrieval Program* (Elder & Machin, 1977) revealed only one other equal-atom structure in space group $I4$ solved by direct methods (Fletterick, Tsai & Hughes, 1971).

Table 2. *Molecular geometry*

(*a*) Bond lengths (Å)

C(1)—C(2)	1·512 (10)	C(5)—C(6)	1·505 (10)
C(2)—C(3)	1·540 (10)	C(1)—O(1)	1·398 (9)
C(3)—C(4)	1·509 (9)	O(1)—C(7)	1·436 (10)
C(4)—C(5)	1·499 (9)	C(2)—N(1)	1·487 (9)
C(5)—O(5)	1·435 (8)	N(1)—N(2)	1·240 (7)
O(5)—C(1)	1·409 (9)	N(2)—C(15)	1·425 (8)
C(4)—O(4)	1·443 (8)	C(3)—N(3)	1·459 (8)
O(4)—C(8)	1·405 (8)	N(3)—N(4)	1·237 (8)
C(8)—O(6)	1·415 (9)	N(4)—C(21)	1·410 (10)
O(6)—C(6)	1·438 (9)	C(8)—C(9)	1·509 (9)

(*b*) Selected bond angles (°)

C(1)—O(5)—C(5)	111·6 (6)	O(6)—C(8)—C(9)	108·2 (5)
O(5)—C(1)—C(2)	113·7 (7)	O(6)—C(8)—O(4)	111·2 (6)
O(5)—C(1)—O(1)	112·4 (6)	O(4)—C(8)—C(9)	108·0 (5)
O(1)—C(1)—C(2)	106·0 (7)	C(8)—O(4)—C(4)	109·2 (5)
C(1)—C(2)—C(3)	110·2 (6)	C(1)—O(1)—C(7)	114·2 (7)
C(1)—C(2)—N(1)	107·5 (6)	C(2)—N(1)—N(2)	111·7 (6)
N(1)—C(2)—C(3)	108·1 (7)	N(1)—N(2)—C(15)	114·1 (5)
C(2)—C(3)—C(4)	109·1 (6)	N(2)—C(15)—C(16)	115·8 (3)*
C(2)—C(3)—N(3)	109·3 (6)	N(2)—C(15)—C(20)	124·2 (3)*
N(3)—C(3)—C(4)	110·2 (6)	C(3)—N(3)—N(4)	113·0 (6)
C(3)—C(4)—C(5)	109·6 (6)	N(3)—N(4)—C(21)	114·7 (6)
C(3)—C(4)—O(4)	109·7 (6)	N(4)—C(21)—C(22)	124·1 (4)*
O(4)—C(4)—C(5)	107·7 (5)	N(4)—C(21)—C(26)	115·9 (4)*
C(4)—C(5)—O(5)	109·9 (5)	C(8)—C(9)—C(10)	124·3 (3)*
C(4)—C(5)—C(6)	110·0 (6)	C(8)—C(9)—C(14)	115·7 (3)*
O(5)—C(5)—C(6)	109·3 (6)		
C(5)—C(6)—O(6)	108·0 (6)		
C(6)—O(6)—C(8)	111·5 (5)		

* Angle at pivot atom of rigid group.

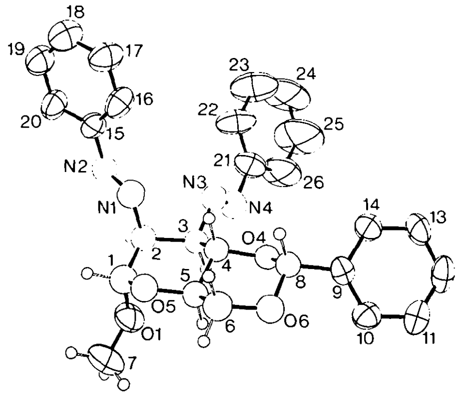

Fig. 1. A view of the molecule showing the atom numbering. H atoms are given the number of the C atom to which they are attached. The phenyl H atoms have been omitted for clarity. Thermal ellipsoids are at the 50% probability level; H atoms have arbitrary radii.

Discussion. The structure determination confirms the *a–e* arrangement of the phenylazo groups: this was deduced indirectly from the signal in the NMR spectrum due to H(1) and from the reduction of the title compound to the known diamine (Davison *et al.*, 1967). By analogy with previous work (Guthrie & Johnson, 1961; Chittenden, Guthrie & McCarthy, 1965) the reduction was assumed to occur without configurational change although the possibility of a different mechanism when two phenylazo groups were present could not be excluded; the present result eliminates the possibility of any isomerization during the reaction. The *a–e* disposition of the phenylazo groups is surprising since similar cyclizations of bis(phenylhydrazones) (Bellamy & Guthrie, 1966) give rise to diequatorial products, and α,ω-dialdehydes react with one molecule of phenylhydrazine to give

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* Lists of structure factors, H atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33257 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

diequatorial hydroxyphenylazo compounds (Guthrie & Honeyman, 1959). The unusual *a–e* arrangement may arise from the stereochemical requirement of the electrocyclization (Davison *et al.*, 1967).

The dihedral angle of the diphenylazo substituents on C(2) and C(3) [N(1)–C(2)–C(3)–N(3) 54·7°] deviates significantly from the theoretical value of 60°. This may be due to either conformational interactions or to packing constraints, although it might be expected that angles greater than 60° would be preferred with large substituents. A literature search (as above) revealed no other crystal structures of carbohydrates having two phenylazo groups so no comparisons can be made with the geometry of the present structure. Correlation of the H(1) signal coupling in the PMR spectrum ($J_{1,2}$) indicates that the dihedral angle H(1)–C(1)–C(2)–H(2) of 72·6° [H(1) and H(2) in calculated positions] persists in solution.

The molecular packing in the structure is governed by van der Waals interactions and there are no intermolecular contacts significantly shorter than the sum of the appropriate van der Waals radii.

References

BELLAMY, A. J. & GUTHRIE, R. D. (1966). *J. Chem. Soc. C*, pp. 1989–1993.

CHITTENDEN, G. J. F., GUTHRIE, R. D. & MCCARTHY, J. F. (1965). *Carbohydr. Res.* **1**, 196–207.

DAVISON, B. E., GUTHRIE, R. D. & MURPHY, D. (1967). *Carbohydr. Res.* **5**, 449–452.

DE TITTA, G. T., EDMONDS, J. W., LANGS, D. A. & HAUPTMAN, H. (1975). *Acta Cryst.* A**31**, 472–479.

ELDER, M. & MACHIN, P. (1977). *The Crystal Structure Search Retrieval Program.* Daresbury Laboratory, Science Research Council, Daresbury, Warrington WA4 4AD, England.

FLETTERICK, R. J., TSAI, C. & HUGHES, R. E. (1971). *J. Phys. Chem.* **75**, 918–922.

GUTHRIE, R. D. & HONEYMAN, J. (1959). *J. Chem. Soc.* pp. 2441–2448.

GUTHRIE, R. D. & JOHNSON, L. F. (1961). *J. Chem. Soc.* pp. 4166–4172.

ROBERTS, P. J., PETTERSEN, R. C., SHELDRICK, G. M., ISAACS, N. W. & KENNARD, O. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 1978–1984.

WHITE, P. S. & WOOLFSON, M. M. (1975). *Acta Cryst.* A**31**, 53–56.

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DL-4-Phenyl-4-ethoxycarbonyl-1-(3-hydroxy-3-phenylpropyl)piperidine: DL-Phenoperidine

BY C. HUMBLET, G. EVRARD AND F. DURANT

Laboratoire de Chimie Moléculaire Structurale, Groupe de Chimie-Physique, Facultés Universitaires Notre-Dame de la Paix, 61 *rue de Bruxelles, B*-5000 *Namur, Belgium*

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Abstract. $C_{23}H_{29}NO_3$; monoclinic, $P2_1/c$; a = 18·716 (5), b = 6·522 (5), c = 17·198 (5) Å, β = 102·64 (5)°, $D_m = 1{\cdot}16$, $D_c = 1{\cdot}17$ g cm^{-3}, $Z = 4$. The molecular packing is essentially a result of hydrogen bonds.

Introduction. The present study was undertaken as part of an investigation of the structure–activity relationship in narcotic analgesics. The title compound is 30 times more potent than morphine.

Colourless prismatic crystals were obtained from ether at ~4 °C. The space group was determined from photographs. Cell dimensions and intensities were measured on a Nonius CAD-4 diffractometer with the experimental conditions given in Table 1.

Table 1. *Experimental conditions*

Source: Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54178$ Å
Scan: ω–2θ
Graphite monochromator
Confidence level: 2·5σ, with $\sigma^2(I) = S + B + (0{\cdot}03S)^2$
 (S being the scan and B the background count)
$2{\cdot}0 \leq \theta \leq 70{\cdot}0°$
$\Delta\theta = 0{\cdot}8 + 0{\cdot}3 \tan\theta$ (°)
Aperture: $2{\cdot}0 + 0{\cdot}5 \tan\theta$ (mm)
Number of independent reflexions: 3351
Number observed: 2225

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The 22nd set obtained from the tangent formula contained the whole molecule, except for one atom which was located by Fourier series with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Application of the tangent method to the *MULTAN* hypothesis was necessary before full-matrix least-squares refinement with anisotropic temperature factors for the O, N and C atoms, and with isotropic temperature factors for H, could converge at $R = 0{\cdot}045$ (for observed