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.

Acta Cryst. (1978). B**34**, 1389–1391

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

(*Received* 23 *December* 1977; *accepted* 20 *January* 1978)

Abstract. $C_{23}H_{29}NO_3$; monoclinic, $P2_1/c$; $a = 18\cdot716\,(5)$, $b = 6\cdot522\,(5)$, $c = 17\cdot198\,(5)$ Å, $\beta = 102\cdot64\,(5)°$, $D_m = 1\cdot16$, $D_c = 1\cdot17$ 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 $K\bar{\alpha}$, $\lambda = 1\cdot54178$ Å
Scan: ω–2θ
Graphite monochromator
Confidence level: $2\cdot5\sigma$, with $\sigma^2(I) = S + B + (0\cdot03S)^2$
(S being the scan and B the background count)
$2\cdot0 \le \theta \le 70\cdot0°$
$\Delta\theta = 0\cdot8 + 0\cdot3 \tan\theta$ (°)
Aperture: $2\cdot0 + 0\cdot5 \tan\theta$ (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 $R = 0\cdot045$ (for observed

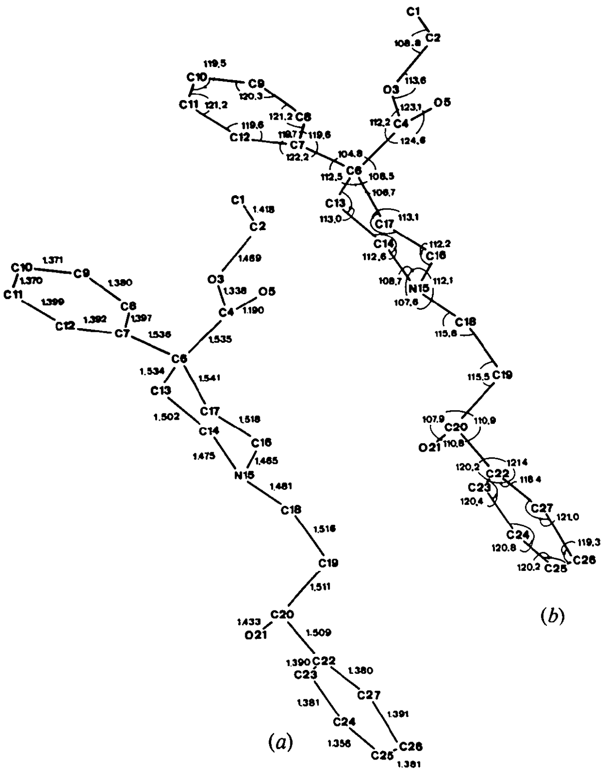

Fig. 1. (*a*) Bond distances (Å) and (*b*) angles (°). The maximum e.s.d.'s are 0·008 Å for the lengths and 0·4° for angles. [The angle C(8)–C(7)–C(12) (shown incorrectly as 119·7°) is 118·2°.]

reflexions). The final positional parameters are given in Table 2.*

Discussion. The atomic numbering, bond distances and angles are given in Fig. 1. A stereoview of the molecule is shown in Fig. 2. The main torsion angles required to describe the structure are listed in Table 3.

Table 2. *Final positional* ($\times 10^4$) *parameters with e.s.d.'s in parentheses*

	x	*y*	*z*
C(1)	14458 (3)	12905 (10)	4300 (4)
C(2)	14123 (3)	10957 (8)	4138 (3)
O(3)	13622 (1)	10629 (4)	4675 (2)
C(4)	13242 (2)	8880 (6)	4538 (2)
O(5)	13295 (2)	7720 (5)	4019 (2)
C(6)	12766 (2)	8512 (6)	5147 (2)
C(7)	13278 (2)	7465 (6)	5856 (2)
C(8)	13543 (2)	5497 (9)	5764 (2)
C(9)	14016 (2)	4526 (7)	6383 (3)
C(10)	14230 (2)	5475 (9)	7108 (3)
C(11)	13974 (2)	7399 (9)	7213 (2)
C(12)	13496 (2)	8417 (7)	6594 (2)
C(13)	12427 (2)	10491 (6)	5388 (2)
C(14)	11870 (2)	11419 (6)	4719 (2)
N(15)	11264 (2)	10001 (5)	4396 (2)
C(16)	11567 (2)	8145 (6)	4112 (2)
C(17)	12124 (2)	7102 (6)	4767 (2)
C(18)	10752 (2)	11083 (7)	3747 (2)
C(19)	10077 (2)	9887 (7)	3346 (2)
C(20)	9577 (2)	9242 (6)	3883 (2)
O(21)	9363 (1)	11050 (4)	4247 (1)
C(22)	8915 (2)	8121 (6)	3417 (2)
C(23)	8806 (2)	6067 (6)	3571 (2)
C(24)	8186 (3)	5059 (8)	3170 (3)
C(25)	7674 (2)	6051 (9)	2618 (3)
C(26)	7772 (2)	8084 (9)	2442 (2)
C(27)	8397 (2)	9104 (8)	2845 (2)

Table 3. *Torsion angles* (°)

C(1)–C(2)–O(3)–C(4)	176·12
C(2)–O(3)–C(4)–O(5)	358·59
C(2)–O(3)–C(4)–C(6)	175·88
O(3)–C(4)–C(6)–C(7)	274·70
C(4)–C(6)–C(7)–C(12)	112·86
C(4)–C(6)–C(7)–C(8)	296·87
O(3)–C(4)–C(6)–C(13)	37·48
O(3)–C(4)–C(6)–C(17)	155·52
C(14)–N(15)–C(18)–C(19)	181·26
C(16)–N(15)–C(18)–C(19)	61·70
N(15)–C(18)–C(19)–C(20)	60·87
C(18)–C(19)–C(20)–O(21)	56·81
C(18)–C(19)–C(20)–C(22)	178·35
C(19)–C(20)–C(22)–C(23)	115·05
C(19)–C(20)–C(22)–C(27)	293·54

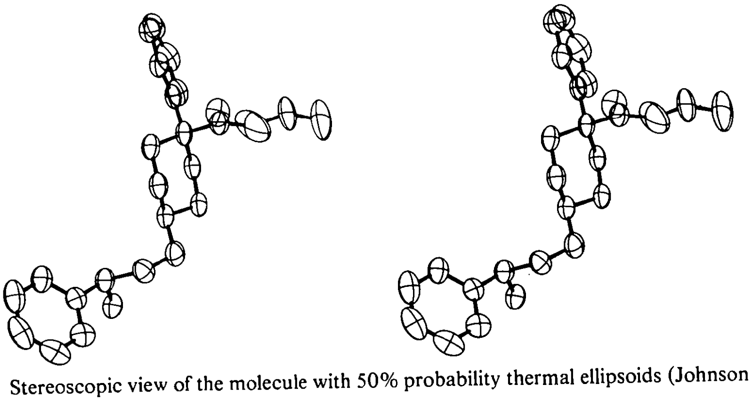

Fig. 2. Stereoscopic view of the molecule with 50% probability thermal ellipsoids (Johnson, 1965).

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33344 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

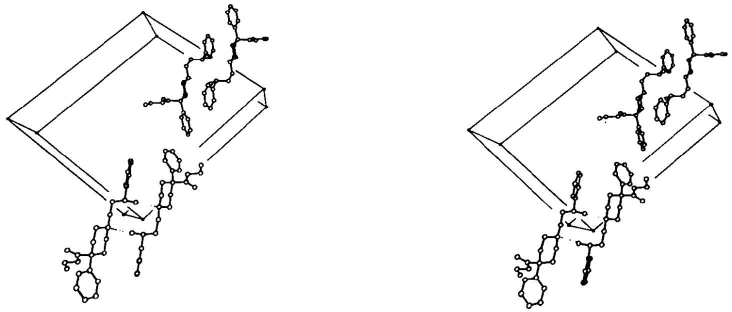

Fig. 3. Stereoscopic view of the molecular packing.

Fig. 3 shows that the molecular packing is essentially due to hydrogen bonds which arise between the piperidine N of one molecule and the alcohol O atom of the one opposite, in order to form a dimeric association.

We thank Dr P. A. J. Janssen (Janssen Pharmaceutica, B-2340 Beerse, Belgium) for providing the sample, and l'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (IRSIA) for the award of a doctoral fellowship to CH.

References

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A27, 368–376.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1978). B**34**, 1391–1393

1-Phenyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]-3,3′-dione

By A. Valentina Rivera and George M. Sheldrick

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

(*Received* 9 *January* 1978; *accepted* 21 *January* 1978)

Abstract. $C_6H_5P(C_7H_4O_2)_2$, monoclinic, $C2/c$, a = 25·252 (6), b = 8·549 (9), c = 15·252 (6) Å, β = 97·15 (9)°, Z = 8, U = 3267 Å^3, D_x = 1·416 g cm^{-3}, μ(Cu $K\alpha$) = 15·8 cm^{-1}. The structure was solved by direct methods and refined to an R of 0·036 for 2047 unique diffractometer data. The coordination at P is close to ideal trigonal bipyramidal, with axial O atoms. The mean P–O and P–C lengths are 1·781 (2) and 1·801 (2) Å respectively.

Introduction. Segall, Granoth, Kalir & Bergmann (1975) have reported the synthesis of stable spiro bicyclic acyloxyphosphoranes by the spontaneous acid-catalysed intramolecular dehydration of bis(*o*-carboxyphenyl)phosphine oxides. Structural elucidation of these phosphoranes was based mainly on ^{31}P NMR data. In view of the isolation of the corresponding *P*-hydroxyphosphorane by Segall & Granoth (1977) crystallographic structural confirmation was desirable, and is reported here for the *P*-phenyl phosphorane.

Intensities were measured with a Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation, and a crystal 0·15 × 0·23 × 0·50 mm. No corrections were applied for absorption. Equivalent reflexions were averaged, reducing the 3364 measured data to 2047 unique reflexions with $F > 4\sigma(F)$ based on counting statistics. Cell dimensions were obtained from the diffractometer settings for 15 strong reflexions. Intensity statistics indicated the space group $C2/c$ rather than Cc; $C2/c$ was confirmed by the successful structure refinement. All the non-hydrogen atoms were located from the best E map obtained by multisolution Σ_2 sign expansion; a subsequent difference synthesis revealed the H atoms. The structure was refined by blocked-matrix least squares, with complex neutral-atom scattering factors and the weighting scheme $w = [\sigma^2(F) + 0{\cdot}00037F^2]^{-1}$, to $R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}F_o$ = 0·040 and R = 0·036. The H atoms were allowed to refine freely, with individual isotropic temperature factors; the remaining atoms were anisotropic. An