

0.32 e Å<sup>-3</sup>. All calculations were performed on the Delft University Amdahl 470/V7B computer using XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic scattering factors are from XRAY72.

**Discussion.** Atomic coordinates are listed in Table 1\* and bond lengths and bond angles in Table 2. Fig. 1 shows the atomic numbering used in this report. The hydrazono group can adopt two configurations: the *Z* and *E* configuration. From the NMR spectra it remains questionable which part represents the *Z* or the *E* configuration. Fig. 1 shows the crystalline compound to be the *Z* isomer. NMR spectroscopy of this crystalline compound gives, now, unequivocally the data for the *Z* isomer.

The angle O(4)—C(14)—C(8)—O(1) is 75.6°. Thus, the position of the protons connected to C(14) and C(8), respectively, is *gauche*. In solution, a coupling constant for these two protons of 2 Hz was found. This value also points to a *gauche* conformation. Apparently, the average conformation in solution resembles the conformation in the crystalline state. The phenyl ring is nearly coplanar with the furanose ring of the sugar: the maximum deviations from the least-squares plane defined by 13 atoms

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55323 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0535]

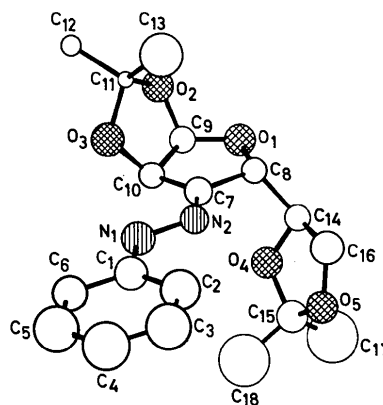


Fig. 1. View of the molecule showing the atomic numbering scheme. H atoms have been omitted for clarity.

[C(1), C(2),...C(10), N(1), N(2) and O(1)] is 0.07 Å [C(9)]. The two isopropylidene groups are at either side of the least-squares plane.

#### References

- BAKER, D. C., HORTON, D. & TINDALL, C. G. JR (1976). *Methods Carbohydr. Chem.* **7**, 3–6.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.  
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The XRAY72 system—version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.  
 WIT, D. DE, CUI YI QING, VAN RANTWIJK, F., MAAT, L. & KIEBOOM, A. P. G. (1992). *Bull. Soc. Chim. Belges*, **101**, 307–312.

*Acta Cryst.* (1992). **C48**, 1996–2000

## Structures of 4β-(Nitromethyl)-2α,6α-diphenyl-4α-piperidinol and 4β-(Nitromethyl)-2β,6β-diphenyl-4α-piperidinol

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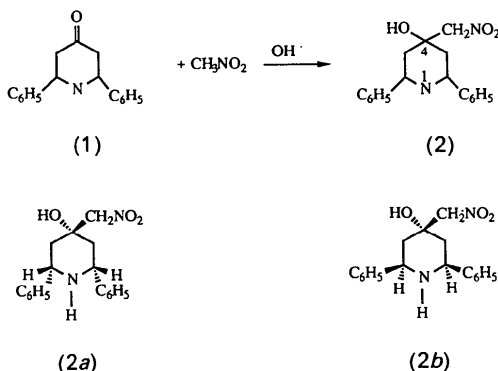
(Received 1 November 1990; accepted 25 March 1992)

**Abstract.** 4β-(Nitromethyl)-2α,6α-diphenyl-4α-piperidinol, isomer (2a), C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>, *M<sub>r</sub>* = 312.37, orthorhombic, *Ccm*2<sub>1</sub>, *a* = 10.548 (6), *b* = 19.590 (11), *c* = 7.729 (3) Å, *V* = 1597 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.30 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, μ = 0.8 cm<sup>-1</sup>, *F*(000) = 664, *T* = 298 K, *R* = 0.066 for 796 reflections with intensities ≥ 3σ(*I*). 4β-(Nitromethyl)-2β,6β-diphenyl-4α-piperidinol,

isomer (2b), C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>, *M<sub>r</sub>* = 312.37, triclinic, *P*1̄, *a* = 5.573 (2), *b* = 11.852 (6), *c* = 13.440 (7) Å, α = 68.42 (4), β = 89.46 (4), γ = 79.82 (3)°, *V* = 810.9 (6) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.28 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, μ = 0.8 cm<sup>-1</sup>, *F*(000) = 332, *T* = 298 K, *R* = 0.0604 for 2874 reflections with intensities ≥ 3σ(*I*). Both isomers were isolated from the same reaction mixture. They differ only in the orientation

of the axial and equatorial substituents at C-4 of the substituted piperidine ring. The major isomer, surprisingly, contains the bulkier substituent in axial orientation. There is an intramolecular hydrogen bond between the two substituents at C-4 in the minor isomer, (2*b*). The —NH H atom in either isomer does not participate in hydrogen bonding.

**Introduction.** Overberger and co-workers report that the base-catalyzed addition of nitromethane to 2,6-diphenyl-4-piperidone (1) leads, in 71% yield, to adduct (2) of unspecified configuration; the latter, after recrystallization, had m.p. 448–450 K (Overberger, Reichenthal & Anselme, 1970). Our repetition of the published procedure led to the following results. Filtration of the total crude product, in dichloromethane, through a small amount of silica gel, followed by crystallization from hot toluene, gave the major product (2*a*), m.p. 451–453 K, in agreement with the above workers. However, flash chromatography (Still, Kahn & Mitra, 1978) of the mother liquor residues provided a much smaller amount of a second product which, after crystallization from toluene, had m.p. 400–403 K. The latter was not mentioned by Overberger and co-workers. The structures of these two substances, determined by X-ray crystallography as described below, were found to differ only in the configuration at C-4 (2).



**Experimental.** For isomer (2*a*), a needle-shaped crystal measuring approximately  $0.63 \times 0.20 \times 0.10$  mm was mounted on a glass fiber and used for all X-ray measurements on a Nicolet R3m/ $\mu$  diffractometer equipped with a graphite monochromator. Cell dimensions were obtained from a least-squares refinement of the setting angles of 18 reflections with  $2\theta$  in the range 12–23°. The intensity data were collected to a maximum  $2\theta$  of 55° by the  $\omega$ -scan method at variable scan speeds between 3.9 and 29.3° min<sup>-1</sup> depending on intensity. 1281 unique reflections were measured, 796 of which with intensities  $I \geq 3\sigma(I)$  were considered observed; range in

$hkl$ :  $h$  0 to 15,  $k$  0 to 27 and  $l$  0 to 11. Stationary backgrounds were counted for half of the scan time on each side of a peak. Two standards (002 and 400), measured after every 48 reflections, showed no significant variation in intensity. Similarly, for isomer (2*b*): needle-shaped crystal ( $0.52 \times 0.15 \times 0.12$  mm), cell dimensions determined from 15 reflections with  $15 \leq 2\theta \leq 22^\circ$ ; intensity data collected to maximum  $2\theta = 55^\circ$  by the same method as for (2*a*); two standards measured (100 and 020); 3725 unique reflections measured, 2874 of which were observed [ $I \geq 3\sigma(I)$ ];  $R_{\text{int}} = 0.011$ ; range in  $hkl$ :  $h$  0 to 8,  $k$  -16 to 16,  $l$  -18 to 18.

Data sets for both isomers were corrected for background and Lorentz-polarization effects. Both structures were solved by direct methods and difference Fourier techniques and refined by blocked-cascade least squares to  $R = 0.066$  and  $wR = 0.065$  for (2*a*), and  $R = 0.060$  and  $wR = 0.048$  for (2*b*). Weights were assigned according to  $w = 1/[\sigma^2(F) + 0.0005F^2]$ ;  $\sigma$  values were based on counting statistics. Other parameters for (2*a*) and (2*b*), respectively, are: number of variables = 127 and 289; goodness of fit,  $S = 1.4$  and 1.7, maximum shift/ $\sigma = 0.04$  and 0.60; difference electron density excursions = 0.22, -0.24 and 0.24,  $-0.28 \text{ e \AA}^{-3}$ ; secondary-extinction coefficient =  $1.2(6) \times 10^{-6}$  and  $1.0(1) \times 10^{-5}$ . Non-H atoms were refined with anisotropic thermal displacement parameters. The H atoms of (2*a*), except as noted below, were placed in calculated positions with a C—H bond length of 0.96 Å and a  $U_{\text{iso}}$  value which was 1.2 times the  $U_{\text{eq}}$  value of the attached C atom. The exceptions were the N—H and O—H H atoms, which were located on the mirror plane from a difference Fourier map and refined isotropically. All the H atoms in (2*b*) were located from a difference Fourier map and refined isotropically. The —CH<sub>2</sub>NO<sub>2</sub> group in (2*a*) is disordered (see below).

Computations were performed on a Data General micro-Eclipse desktop computer with the program package *SHELXTL* (Sheldrick, 1985). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72–102).

**Discussion.** Fractional coordinates for both compounds, (2*a*) and (2*b*), are given in Table 1, their bond distances and angles in Table 2, and selected torsion angles in Table 3.\* Examination of the

\* Lists of anisotropic thermal parameters, H-atom coordinates and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55320 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0293]

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic or equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )For non-H atoms, equivalent isotropic  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Isomer (2a)	x	y	z	$U_{iso}/U_{eq}$
O(1)	4023 (6)	0	6172	123 (3)
O(2)	4083 (7)	-866 (4)	4159 (12)	100 (3)
N(1)	3837 (7)	-296 (4)	4655 (12)	65 (3)
C(1)	3322 (8)	0	3446 (11)	147 (6)
C(2)	1929 (5)	0	2949 (7)	49 (2)
O(3)	1277 (4)	0	4569 (6)	56 (1)
C(3)	1589 (4)	634 (2)	1918 (7)	52 (1)
C(4)	2053 (4)	617 (2)	45 (6)	50 (1)
N(2)	1521 (4)	0	-777 (6)	42 (1)
C(5)	1749 (4)	1260 (2)	-952 (6)	55 (1)
C(6)	647 (5)	1624 (3)	-713 (7)	67 (2)
C(7)	431 (6)	2226 (3)	-1615 (8)	84 (2)
C(8)	1289 (8)	2462 (3)	-2758 (10)	96 (3)
C(9)	2360 (7)	2103 (4)	-3072 (10)	99 (3)
C(10)	2616 (5)	1502 (3)	-2170 (7)	78 (2)
H(N2)	1752 (60)	0	-1907 (93)	73 (20)
H(O3)	519 (47)	0	4338 (88)	50 (18)

Isomer (2b)	x	y	z	$U_{iso}/U_{eq}$
O(1)	5824 (3)	3787 (1)	5870 (1)	77 (1)
O(2)	1998 (3)	3810 (2)	5990 (1)	83 (1)
N(1)	4002 (3)	3407 (1)	5771 (1)	51 (1)
C(1)	4239 (3)	2388 (2)	5354 (1)	43 (1)
C(2)	2393 (3)	2658 (1)	4423 (1)	36 (1)
O(3)	-11 (2)	2613 (1)	4789 (12)	48 (1)
C(3)	3018 (3)	1613 (1)	4009 (1)	38 (1)
C(4)	1452 (3)	1843 (1)	3000 (1)	38 (1)
N(2)	1785 (3)	3030 (1)	2190 (1)	40 (1)
C(5)	909 (3)	4064 (1)	2531 (1)	39 (1)
C(6)	2473 (3)	3893 (1)	3519 (1)	38 (1)
C(7)	2153 (3)	815 (1)	2587 (1)	36 (1)
C(8)	4183 (3)	755 (2)	1994 (1)	45 (1)
C(9)	4797 (4)	-185 (2)	1611 (2)	54 (1)
C(10)	3405 (4)	-1087 (2)	1820 (2)	56 (1)
C(11)	1415 (4)	-1051 (2)	2422 (2)	55 (1)
C(12)	791 (3)	-111 (2)	2805 (1)	45 (1)
C(13)	993 (3)	5282 (1)	1631 (1)	38 (1)
C(14)	-919 (4)	6266 (2)	1420 (2)	51 (1)
C(15)	-838 (4)	7388 (2)	613 (2)	62 (1)
C(16)	1121 (4)	7548 (2)	-2 (1)	55 (1)
C(17)	3041 (4)	6587 (2)	205 (2)	65 (1)
C(18)	2972 (4)	5461 (2)	1017 (2)	60 (1)
H(N2)	1002 (27)	3145 (13)	1597 (12)	40 (4)
H(O3)	-303 (36)	3148 (18)	5052 (16)	83 (6)

torsion angles in the piperidine ring shows that the ring assumes the chair conformation in both isomers. The major product, (2a), of the reaction has the  $-\text{CH}_2\text{NO}_2$  substituent oriented in the axial position, Fig. 1, and the minor product, (2b), in the equatorial position, Fig. 2. Our results are of interest in comparison with earlier studies by Trost and co-workers on the selectivity of addition to chair-form six-membered ketones (Trost, Florez & Jebaratnam, 1987). These authors found that the base-catalyzed addition of acetonitrile to 4-tert-butylcyclohexanone leads predominantly to axial attachment of the new carbon substituent, contrary to an earlier generalization, but in line with our present results.

The structure of (2a) is not determined as precisely as that of (2b) owing to rotational disorder of the  $-\text{CH}_2\text{NO}_2$  group around the C(1)—C(2) bond, Fig. 3, which puts the  $-\text{NO}_2$  N atom, N(1), 0.57 Å away from the crystallographic mirror plane passing through atoms O(1), C(1), C(2), N(2) and O(3).

Table 2. Bond lengths (Å) and bond angles (°)

Isomer (2a)		Isomer (2b)	
O(1)—N(1)	1.323 (9)	O(1)—N(1)	1.209 (2)
N(1)—C(1)	1.226 (12)	N(1)—C(1)	1.494 (3)
C(2)—O(3)	1.429 (7)	C(2)—O(3)	1.426 (2)
C(3)—C(4)	1.528 (7)	C(2)—C(6)	1.528 (2)
C(4)—C(5)	1.511 (6)	C(4)—N(2)	1.469 (2)
C(5)—C(10)	1.395 (7)	N(2)—C(5)	1.466 (2)
C(7)—C(8)	1.347 (10)	C(5)—C(13)	1.512 (2)
C(9)—C(10)	1.396 (9)	C(7)—C(12)	1.385 (3)
O(1)—N(1)—O(2)	130.8 (9)	C(9)—C(10)	1.375 (3)
O(2)—N(1)—C(1)	106.9 (8)	C(11)—C(12)	1.381 (3)
C(1)—C(2)—O(3)	104.1 (5)	C(13)—C(18)	1.371 (3)
O(3)—C(2)—C(3)	110.2 (3)	C(15)—C(16)	1.360 (3)
C(3)—C(2)—C(4)	113.8 (4)	C(17)—C(18)	1.386 (3)
C(3)—C(4)—C(5)	113.4 (4)	O(1)—N(1)—O(2)	123.5 (2)
C(4)—N(2)—C(4')	109.9 (4)	O(2)—N(1)—C(1)	118.5 (2)
C(4)—C(5)—C(10)	119.2 (4)	C(1)—C(2)—O(3)	110.8 (1)
C(5)—C(6)—C(7)	120.7 (5)	O(3)—C(2)—C(3)	105.7 (1)
C(7)—C(8)—C(9)	120.1 (6)	C(3)—C(2)—C(6)	110.9 (1)
C(5)—C(10)—C(9)	119.8 (5)	C(2)—C(3)—C(4)	112.3 (1)
O(1)—N(1)—C(1)	122.3 (7)	C(3)—C(4)—C(7)	111.3 (1)
N(1)—C(1)—C(2)	128.4 (7)	C(4)—N(2)—C(5)	112.0 (1)
C(1)—C(2)—C(3)	111.2 (3)	N(2)—C(5)—C(13)	110.6 (1)
C(3)—C(2)—C(3')	109.8 (5)	C(2)—C(6)—C(5)	111.4 (2)
C(3)—C(4)—N(2)	107.7 (4)	C(4)—C(7)—C(12)	120.7 (2)
N(2)—C(4)—C(5)	112.5 (4)	C(7)—C(8)—C(9)	120.9 (2)
C(4)—C(5)—C(6)	122.8 (4)	C(9)—C(10)—C(11)	119.3 (2)
C(6)—C(5)—C(10)	118.0 (4)	C(7)—C(12)—C(11)	120.9 (2)
C(6)—C(7)—C(8)	120.7 (6)	C(5)—C(13)—C(18)	121.8 (1)
C(8)—C(9)—C(10)	120.7 (7)	C(13)—C(14)—C(15)	120.8 (2)
O(2)—N(1)	1.213 (2)	C(15)—C(16)—C(17)	119.0 (2)
C(1)—C(1)	1.529 (2)	C(13)—C(18)—C(17)	121.3 (2)
C(2)—C(3)	1.523 (3)	O(1)—N(1)—C(1)	118.0 (2)
C(3)—C(4)	1.530 (3)	N(1)—C(1)—C(2)	113.1 (1)
C(4)—C(7)	1.507 (3)	C(1)—C(2)—C(3)	107.3 (1)
C(5)—C(6)	1.525 (3)	C(1)—C(2)—C(6)	112.0 (2)
C(7)—C(8)	1.385 (3)	C(3)—C(2)—C(6)	109.9 (1)
C(8)—C(9)	1.381 (3)	C(3)—C(4)—N(2)	107.8 (1)
C(10)—C(11)	1.370 (3)	N(2)—C(4)—C(7)	110.8 (1)
C(13)—C(14)	1.378 (2)	N(2)—C(5)—C(6)	108.3 (1)
C(14)—C(15)	1.381 (2)	C(6)—C(5)—C(13)	111.7 (2)
C(16)—C(17)	1.364 (3)	C(4)—C(7)—C(8)	121.3 (2)
		C(8)—C(7)—C(12)	118.0 (2)
		C(8)—C(9)—C(10)	120.4 (2)
		C(10)—C(11)—C(12)	120.5 (2)
		C(5)—C(13)—C(14)	120.4 (2)
		C(14)—C(13)—C(18)	117.7 (1)
		C(14)—C(15)—C(16)	120.9 (2)
		C(16)—C(17)—C(18)	120.3 (2)

Atoms O(1) and C(1) are also disordered but have been refined as non-disordered with anisotropic thermal displacement parameters which results in their thermal ellipsoids being elongated normal to the mirror plane, Fig. 3.\* In (2b), where there is no disorder and where it is not constrained by symmetry, N(1) is even farther away (1.227 Å) from the mean plane of C(1), C(2), N(2) and O(3). In (2a), the plane of the  $-\text{NO}_2$  group is tilted at an angle of 26.6° from the mean plane of the piperidine ring,

\* At the suggestion of a referee we have collected a monoclinic data set ( $hkl$  and  $h\bar{k}l$ ) and refined the structure in space group  $Cc$ . The  $-\text{CH}_2\text{NO}_2$  group is still disordered, the two halves of C(1) being further apart from each other than those of O(1), which is consistent with the shape of the anisotropic thermal displacement ellipsoids, Fig. 3. There is, however, no violation of the orthorhombic symmetry in the intensity data;  $R_{int} = 0.010$  when  $F(hkl)$  and  $F(h\bar{k}l)$  are averaged. The space group as reported is, therefore, correct.

Table 3. Selected torsion angles ( $^{\circ}$ ) in isomers (2a) and (2b)

	Isomer (2a)	Isomer (2b)
O(2)—N(1)—C(1)—C(2)	86.0 (9)	50.4 (2)
N(1)—C(1)—C(2)—O(3)	37.1 (7)	-70.9 (2)
C(1)—C(2)—O(3)—H(O3)	180.0	60 (1)
C(1)—C(2)—C(3)—C(4)	75.3 (5)*	-174.3 (1)*
C(2)—C(3)—C(4)—C(5)[C(7)]†	-178.1 (4)	178.5 (1)
C(2)—C(3)—C(4)—N(2)	56.9 (4)	56.7 (2)
C(3)—C(4)—N(2)—C(4')[C(5)]	-65.5 (4)	-63.2 (2)
C(4)—N(2)—C(4')[C(5)]—C(3')[C(6)]	65.5 (4)	64.1 (2)
N(2)—C(4)[C(5)]—C(3)[C(6)]—C(2)	-56.9 (4)	-57.6 (2)
C(4)[C(5)]—C(3)[C(6)]—C(2)—C(3)	48.1 (4)	52.4 (2)
C(3)[C(6)]—C(2)—C(3)—C(4)	-48.1 (4)	-52.3 (2)
C(3)—C(4)—N(2)—H(N2)	177 (4)	175 (1)
O(3)—C(2)—C(3)—C(4)	-169.7 (5)	67.5 (2)
N(2)—C(4)—C(5)[C(7)]—C(6)[C(8)]	86.6 (5)	40.6 (2)
N(2)—C(5)—C(13)—C(14)	-	137.0 (2)

\* Indicates that C(1) is axial in (2a) and equatorial in (2b).

† Atom symbols in square brackets refer to the corresponding atoms in (2b).

whereas in (2b) it is almost perpendicular to it (dihedral angle =  $97.7^{\circ}$ ). The two benzene rings in both isomers are oriented *cis* to each other, as they are in the parent ketone, 2,6-diphenyl-4-piperidone (Singh, Levine & Kasdorf, 1990), and are rotated out of the mean plane of the piperidine ring, the dihedral angles being  $62.0^{\circ}$  in (2a), and  $72.8$  and  $75.8^{\circ}$  for the two independent benzene rings containing atoms C(7) through C(12), and C(13) through C(18), respectively, in (2b).

In (2a) there are O(3)—H $\cdots$ N(2) hydrogen bonds linking molecules running parallel to the *c* axis near the origin and near  $(\frac{1}{2}, \frac{1}{2}, 0)$ . The hydrogen-bonding parameters are: O(3)—H = 0.82, H $\cdots$ N(2) = 2.15, O(3) $\cdots$ N(2) = 2.963 Å and O(3)—H $\cdots$ N(2) =  $170^{\circ}$ . In (2b) there is an intramolecular hydrogen bond O(3)—H $\cdots$ O(2) between the axial and equatorial substituents on C(2): O(3)—H = 0.83, H $\cdots$ O(2) = 2.24, O(3) $\cdots$ O(2) = 2.855 Å, O(3)—H $\cdots$ O(2) =  $132^{\circ}$ . There is no such intramolecular hydrogen bond in (2a) because the orientation of the —NO<sub>2</sub> group is different from that in (2b) (see above); O(3) $\cdots$ O(1) = 3.15 and H(O3) $\cdots$ O(1) = 3.96 Å. The —NH H atom does not participate in hydrogen bonding in either isomer. This is also true in the starting material, 2,6-diphenyl-4-piperidone (1) (Singh, Levine & Kasdorf, 1990). The non-participation of —NH H atoms in hydrogen bonding in these compounds may be a result of steric crowding by the flanking phenyl groups.

There are two short intermolecular distances in (2a) [the sum of the van der Waals radii is given in parentheses (Pauling, 1960)]: H(1B) $\cdots$ O(1)<sub>1-x, -y, -1/2+z</sub> = 2.55 (2.60) and H(9) $\cdots$ C(7)<sub>1/2-x, 1/2-y, -1/2+z</sub> = 2.87 (2.90) Å; and three in (2b): H3(O) $\cdots$ O(1)<sub>-1+x, y, z</sub> = 2.53, H(1A) $\cdots$ O(3)<sub>1+x, y, z</sub> = 2.36 and HN(2) $\cdots$ C(16)<sub>-x, 1-y, -z</sub> = 2.89 Å.

The bond distances and angles in the two isomers, Tables 1 and 2, are in excellent agreement with each

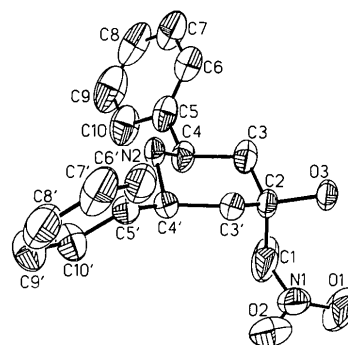


Fig. 1. An ORTEP (Johnson, 1965) plot (50% probability ellipsoids) of isomer (2a) showing the numbering system and the axial orientation of the —CH<sub>2</sub>NO<sub>2</sub> moiety on the piperidine ring. The H atoms and the disordered half of the —NO<sub>2</sub> group are omitted for clarity.

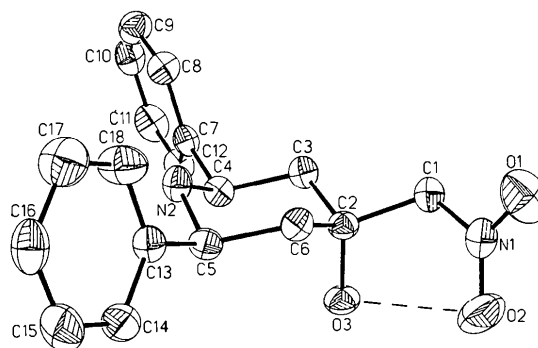


Fig. 2. An ORTEP (Johnson, 1965) plot (50% probability ellipsoids) of isomer (2b) showing the numbering system and the equatorial orientation of the —CH<sub>2</sub>NO<sub>2</sub> moiety. H atoms are omitted for clarity. The dashed line indicates an intramolecular hydrogen bond.

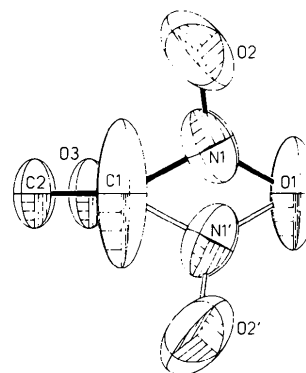


Fig. 3. A plot of the two substituents, the —OH and the —CH<sub>2</sub>NO<sub>2</sub>, on C(2) of the piperidine ring of (2a), viewed along the crystallographic mirror plane, showing the disorder of —CH<sub>2</sub>NO<sub>2</sub>. C(1) and O(1) are refined as single ordered atoms lying on the mirror plane with high thermal displacement parameters normal to the plane. H atoms are not shown.

other except for those in the —CH<sub>2</sub>NO<sub>2</sub> moiety which, as mentioned earlier, is disordered in (2a) but not in (2b).

#### References

- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- OVERBERGER, C. G., REICHENTHAL, J. & ANSELME, J.-P. (1970). *J. Org. Chem.* **35**, 128–141.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 360. Ithaca: Cornell Univ. Press.
- SHELDRIK, G. M. (1985). *SHELXTL User's Manual*. Revision 5.1. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.
- SINGH, P., LEVINE, S. G. & KASDORF, K. (1990). *Acta Cryst.* **C46**, 2469–2470.
- STILL, W. C., KAHN, M. & MITRA, A. (1978). *J. Org. Chem.* **43**, 2923–2925.
- TROST, B., FLOREZ, J. & JEBARATNAM, D. J. (1987). *J. Am. Chem. Soc.* **109**, 613–615.

*Acta Cryst.* (1992). **C48**, 2000–2002

## Structure of Wigandol\*

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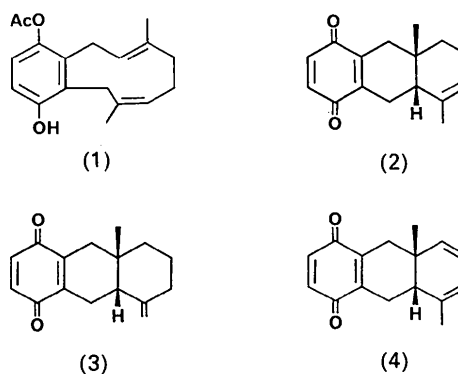
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(Received 11 October 1991; accepted 9 March 1992)

**Abstract.** (*Z,E*)-5,8,9,12-Tetrahydro-4-hydroxy-6,10-dimethylbenzocyclodecen-1-yl acetate, C<sub>18</sub>H<sub>22</sub>O<sub>3</sub>, *M<sub>r</sub>* = 286.4, monoclinic, *C2/c*, *a* = 20.828 (5), *b* = 8.364 (2), *c* = 21.508 (4) Å, β = 122.39 (2)°, *V* = 3164 (1) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.20 Mg m<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å, μ = 6.09 cm<sup>-1</sup>, *F*(000) = 1232, *T* = 292 K, final *R* = 0.049 for 1697 unique observed reflections [*F<sub>o</sub>* > 3σ(*F<sub>o</sub>*)]. Wigandol is characterized by a *cis,trans*-cyclodeca-1,5-diene with the methyl groups *anti*-related. The cyclodecadiene ring adopts a chair-half-chair conformation. The acetate group lies nearly perpendicular to the planar phenyl ring. In the crystal the molecules are held together by hydrogen bonds involving the phenolic group and the carbonyl O atom in the acetate group of a symmetry-related molecule, forming endless zigzag chains along the *b* axis.

**Introduction.** Wigandol (1), isolated from *Wigandia kunthii Choisy* (Gómez, Quijano, Calderón & Ríos, 1980), is the monoacetate derivative of the hypothetical precursor in the biogenetic route to the cordiachromes (Manners & Jurd, 1977; Manners, 1983). The putative precursor was proposed as a *trans,trans*-cyclodeca-1,5-diene, which in a boat conformation could undergo acid-catalyzed cyclization to cordiachromes A and B (2 and 3) with *cis* ring junction, while Cope rearrangement would give

cordiachrome C (4), a *cis*-1,2-divinylcyclohexane derivative (Moir & Thompson, 1973).



Although, in a few cases, Cope rearrangement has already been observed proceeding via a boat conformation (Wiberg, Matturro & Adams, 1981; Shea & Phillips, 1980), it is also true that the structures had been 1,5-diene systems with a high degree of rigidity. On the other hand, although it is well known (Takeda & Horibe, 1975) that *trans,trans*-cyclodeca-1,5-dienes undergo Cope rearrangement to give *trans*-1,2-divinylcyclohexane derivatives (contrary to cordiachrome C) whereas the *cis,trans*-cyclodeca-1,5-diene system gives a *cis*-1,2-divinyl derivative, two compounds (neolinderolactone and sericene: *cis,trans*- and *trans,cis*-cyclodeca-1,5-dienes) with structures closely related to wigandol, failed to follow this path (Takeda, Horibe & Minato, 1970).

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