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5,7-Dihydroxy-6,6-dimethyl-6,7-dihydrodibenzo[*d*,*f*][1,3]diazepine

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Abstract. $C_{15}H_{16}N_2O_2$, monoclinic, $P2_1/n$, a = 18·80 (2), b = 15·57 (2), c = 10·07 (1) Å, β = 114·18 (7)°, V = 2689 Å^3, Z = 8, d_c = 1·276 g cm^{-3}, $F(000)$ = 1088, μ(Mo $K\alpha$) = 0·92 cm^{-1}. The structure was refined to R = 0·103 for 2343 observed reflexions. The two independent molecules are identical and correspond to the name given in the title. The benzene rings in the biphenyl part form an angle of 43°, held in position by the diazepine ring formation. The molecules have approximate twofold axes and are linked into chains along **c** by hydrogen bonds involving all the N and O atoms.

Introduction. The title compound was prepared by electrolytic reduction of 2,2′-dinitrobiphenyl and reaction of the resulting 2,2′-dihydroxyaminobiphenyl with acetone (Becher & Iversen, 1974). X-ray data for a hemisphere of reflexions with $\sin\theta/\lambda < 0{\cdot}7$ Å^{-1} were collected on a diffractometer of the Arndt & Phillips (1961) type with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter with pulse-height discrimination. About 500 reflexions near the rotation axis (c) were replaced by data measured on a Picker FACS1 diffractometer. The number of accessible reflexions was 4544; 2343 of these had $I > 2\sigma I$ and were used in the refinement. Systematically absent were: $h0l$: $h \neq 2n$, $l \neq 2n$; $0k0$: $k \neq 2n$, giving the possible space groups $P2_1/a$, $P2_1/n$ and $P2_1/c$. It was noticeable that $h1l$, $h \neq 2n$ were very weak and $h2l$, $h \neq 2n$ weak, so initially the space group $P2_1/c$ was assumed (Becher & Iversen, 1974). The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971).

When information about the presence of benzene rings was used in the normalization of the reflexions a solution was obtained in $P2_1/c$ which showed one molecule and two molecules displaced from each other in the y direction and of half weight. In space group $P2_1/n$ the correct solution was that selected by *MULTAN*. Refinement by least squares with *LINUS* (Coppens & Hamilton, 1970) included positional and anisotropic thermal parameters of the non-hydrogen atoms. Finally, the H atoms of the phenyl rings were included at calculated positions and those of the OH groups inserted in positions so that they formed linear hydrogen bonds to N atoms in neighbouring molecules.

Table 1. *Fractional coordinates* (×10^4) *for the non-hydrogen atoms*

The numbering is as in Fig. 1 with chemically equivalent atoms next to one another; the coordinates of molecule *A* (Fig. 2) are given first.

	x	*y*	*z*
C(1)	2376 (4)	6530 (4)	1382 (7)
	3221 (4)	6368 (4)	1901 (7)
	7404 (4)	6042 (4)	1367 (7)
	8257 (4)	5905 (4)	1902 (7)
C(2)	2131 (4)	7338 (4)	1547 (7)
	3716 (4)	6951 (4)	1665 (7)
	8113 (4)	6831 (4)	1519 (7)
	8703 (4)	6544 (4)	1651 (7)
C(3)	1338 (5)	7524 (5)	1084 (8)
	4506 (4)	6811 (5)	2182 (8)
	6316 (5)	6984 (6)	1062 (9)
	9501 (4)	6452 (5)	2190 (8)
C(4)	808 (5)	6879 (6)	448 (9)
	4816 (5)	6064 (6)	2950 (8)
	5817 (5)	6306 (7)	412 (9)
	9854 (5)	5740 (6)	2921 (10)
C(5)	1022 (5)	6094 (6)	260 (9)
	4339 (5)	5465 (6)	3158 (9)
	6094 (6)	5503 (7)	265 (10)
	9436 (5)	5104 (6)	3147 (9)
C(6)	1815 (5)	5891 (5)	744 (8)
	3559 (5)	5616 (5)	2656 (8)
	6882 (5)	5396 (6)	740 (9)
	8633 (5)	5184 (5)	2650 (8)
N	2729 (3)	7955 (3)	2343 (5)
	3316 (3)	7670 (3)	733 (6)
	7694 (3)	7484 (3)	2310 (6)
	8294 (3)	7247 (3)	728 (6)
O	2409 (3)	8613 (3)	2937 (5)
	3831 (3)	8042 (3)	140 (5)
	7351 (3)	8135 (3)	2895 (5)
	8785 (3)	7633 (3)	108 (5)
C(7)	3088 (4)	8404 (4)	1446 (7)
	8032 (4)	7972 (4)	1415 (8)
C(8)	3793 (4)	8919 (5)	2493 (8)
	2496 (5)	8950 (4)	222 (8)
	8724 (5)	8501 (5)	2433 (9)
	7428 (5)	8503 (5)	188 (8)

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* Deceased.

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The parameters for the latter H atoms were allowed to vary but did not move far from where they were inserted. The final $R = (\sum ||F_o| - |F_c||/\sum |F_o|)$ was 0·103.* A difference map at this point showed as its only significant feature positive regions near the methyl groups which could be attributed to H atoms with large temperature movements or possibly to some of the methyl groups being disordered with two main orientations. Final coordinates are given in Table 1.

Discussion. The analysis confirms the structural formula suggested by Becher & Iversen (1974) on the basis of chemical and spectroscopic evidence (^{13}C NMR, ^{1}H NMR, IR, UV and ESR). The two molecules in the asymmetric unit are similar within experimental error. Table 2 contains individual bond lengths and angles. Fig. 1 shows a molecule with the numbering of atoms and with the average values of bond lengths and angles. The two benzene rings of a molecule are twisted by 43° with respect to one other which is similar to the 42° in several *para*-substituted biphenyls (Casalone, Mariani, Mugnoli & Simonetta, 1969; Kronebusch, Gleason & Britton, 1976*a*,*b*). We may therefore conclude that no strain is introduced in this part of the molecule by the formation of the seven-membered ring.

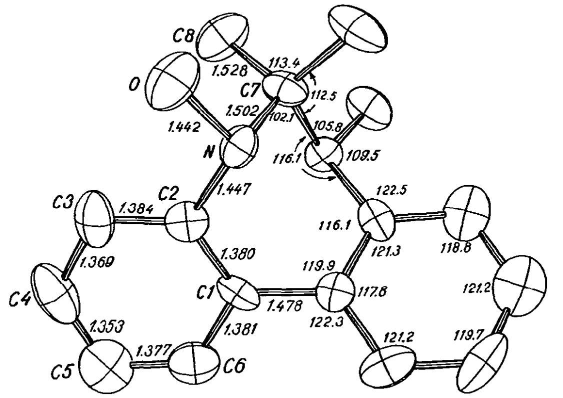

Fig. 1. Drawing of a molecule showing the numbering of the atoms and the average values of bond lengths (Å) and angles (°).

In two other compounds where biphenyl is bridged by three atoms, 2,2′-biphenyldicarboximide (Caillet & Le Marouille, 1978) and benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene (Hazell, 1978), the angle is smaller, 33 and 30°, but in both all ring atoms are sp^2 hybridized tending towards planarity.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

A prime denotes the chemically equivalent atom in the other half of the molecule. The sequence is as in Table 1.

C(1)–C(2)	1·371 (8)	1·386 (9)	1·375 (9)	1·386 (9)
C(2)–C(3)	1·394 (9)	1·372 (9)	1·393 (10)	1·376 (9)
C(3)–C(4)	1·372 (10)	1·381 (10)	1·382 (11)	1·341 (10)
C(4)–C(5)	1·322 (11)	1·366 (11)	1·382 (12)	1·340 (12)
C(5)–C(6)	1·399 (11)	1·359 (10)	1·366 (11)	1·384 (11)
C(6)–C(1)	1·395 (9)	1·395 (9)	1·362 (9)	1·371 (9)
C(1)–C(1)′	1·474 (9)		1·481 (9)	
C(2)–N	1·442 (8)	1·452 (8)	1·462 (8)	1·432 (8)
N–C(7)	1·501 (8)	1·499 (8)	1·501 (8)	1·505 (8)
N–O	1·434 (6)	1·448 (6)	1·447 (7)	1·440 (7)
C(7)–C(8)	1·533 (9)	1·529 (9)	1·522 (10)	1·527 (10)
C(2)–C(1)–C(6)	118·6 (7)	116·9 (7)	117·7 (8)	118·1 (9)
C(1)–C(2)–C(3)	121·0 (7)	121·9 (7)	122·5 (7)	119·7 (7)
C(2)–C(3)–C(4)	118·3 (8)	119·1 (8)	116·9 (9)	120·9 (8)
C(3)–C(4)–C(5)	122·3 (9)	120·3 (8)	121·7 (9)	120·6 (9)
C(4)–C(5)–C(6)	120·1 (8)	120·1 (8)	118·4 (9)	120·0 (9)
C(5)–C(6)–C(1)	119·6 (8)	121·7 (8)	122·7 (9)	120·6 (8)
C(1)′–C(1)–C(2)	118·7 (6)	122·0 (6)	120·5 (6)	118·4 (6)
C(1)′–C(1)–C(6)	122·8 (7)	121·2 (6)	121·8 (7)	123·5 (7)
C(1)–C(2)–N	116·9 (6)	114·0 (6)	115·9 (6)	117·4 (6)
C(3)–C(2)–N	121·8 (6)	123·9 (6)	121·4 (7)	122·7 (6)
C(2)–N–O	109·9 (5)	108·4 (5)	110·3 (5)	109·2 (5)
C(2)–N–C(7)	114·6 (5)	116·8 (5)	115·5 (5)	117·6 (5)
O–N–C(7)	106·7 (5)	105·3 (5)	105·0 (5)	106·0 (5)
N–C(7)–N′	102·8 (5)		101·3 (5)	
N–C(7)–C(8)	107·8 (6)	107·1 (6)	109·0 (6)	108·0 (6)
N–C(7)–C(8)′	112·4 (6)	112·8 (6)	113·5 (6)	111·1 (6)
C(8)–C(7)–C(8)′	113·5 (6)		113·3 (7)	

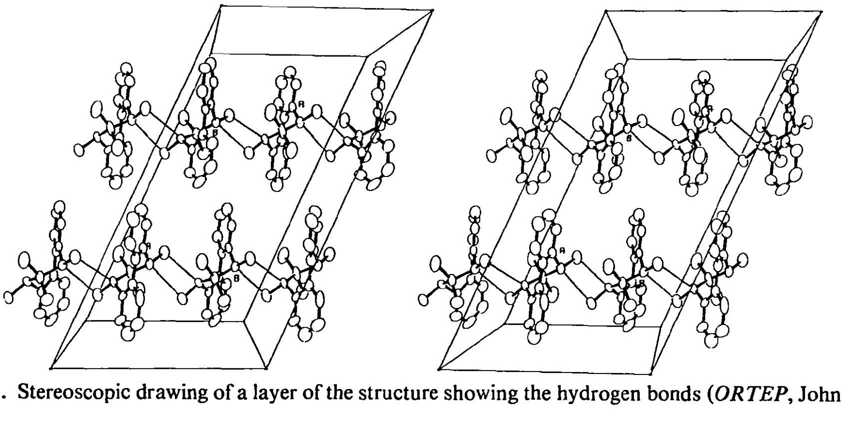

Fig. 2. Stereoscopic drawing of a layer of the structure showing the hydrogen bonds (*ORTEP*, Johnson, 1965)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33767 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The plane through the three extra atoms (NCN) that complete the seven-membered ring forms an angle of 70° with the axis of the biphenyl part. The N atoms are sp^3 hybridized in spite of being next to a benzene ring. Often N atoms next to double bonds or aromatic systems are sp^2 hybridized in the same plane as the π system, but here the lone pair is instead engaged in hydrogen bonding. Fig. 2 shows how all N and O atoms take part in the double hydrogen bonds that link the molecules into chains along **c**. The hydrogen bonds are in the range 2·83–2·95 Å, and are probably not quite linear because that would not give the best angles at O and N.

The bond lengths are all in the expected range, especially when thermal motion is taken into account. An analysis of the thermal motion in terms of a rigid body for each molecule (Schomaker & Trueblood, 1968) shows a not too good agreement but the corrections brought the lengths of the outer bonds in the benzene rings up to 1·39–1·40 Å.

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Methyl Benzylpenillonate: A Penicillin Rearrangement Product

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Abstract. $C_{17}H_{20}N_2O_4S$, monoclinic, $P2_1$, a = 12·435 (3), b = 6·211 (1), c = 12·834 (3) Å, β = 118·31 (2)°, Z = 2, D_o = 1·32, D_c = 1·326 g cm^{-3}. An envelope thiazolidine ring is fused to a planar NCNCC ring. The ring junction at C(5) is *trans* to the carboxymethyl side chain.

Introduction. Crystals suitable for X-ray diffraction were obtained by recrystallization from benzene. Precession photographs (Mo $K\alpha$ radiation) provided initial cell dimensions, and the space group $P2_1$ was indicated by systematic absences (0k0 for odd k) and the optical activity of the compound.

A well-formed plate crystal (~0·6 × 0·6 × 0·2 mm) was mounted in a Lindemann-glass tube on a Hilger & Watts Y290 four-circle diffractometer with **a** a few degrees from the φ axis. Cell parameters and the orientation matrix were refined by a least-squares procedure from 12 reflexions ($2\theta > 40°$, Mo $K\alpha$ radiation, λ = 0·71069 Å, Zr filter, room temperature). Intensities were collected for all independent reflexions with $2\theta \leq 55°$ (θ–2θ step scan: 2 s count at each of 50 steps of 0·02° in θ, 25 s background count at each end). Calibrated attenuators were inserted into the beam for very intense reflexions. Three periodically monitored standard reflexions showed no significant intensity variation. Absorption corrections were not applied (μ = 2·10 cm^{-1}).

All 2037 independent reflexions with measured $I > 0$ were used for structure solution and refinement.

Attempts to solve the structure by direct methods failed: it was subsequently found that several atoms had y coordinates very close to that of the S atom (totalling about 25% of the scattering power). x and z coordinates for the S atom were obtained from a Patterson synthesis; y was fixed at 0 to define the cell origin. Other non-hydrogen atoms were located by Fourier syntheses. Refinement of coordinates and anisotropic thermal parameters was by full-matrix least-squares methods, to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F)$ based on counting statistics]. H atoms (clearly revealed in a difference synthesis after refinement of the other atoms had converged) were placed in geometrically calculated

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