

## Structure of Dimethyl 6-Hydroxy-8,9-bis(2-pyridyl)-1,3-diaza-5,7-adamantanedicarboxylate

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**Abstract.**  $C_{22}H_{24}N_4O_5$ ,  $M_r = 424.45$ , monoclinic,  $P2_1/a$ ,  $a = 14.976$  (4),  $b = 12.028$  (1),  $c = 12.154$  (3) Å,  $\beta = 107.49$  (2)°,  $V = 2088.1$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.350$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.091$  mm<sup>-1</sup>,  $F(000) = 896$ , room temperature,  $wR = 0.037$  for 1867 reflections [ $I > 2\sigma(I)$ ]. The pyridyl substituents are in equatorial positions, and the OH group is inclined towards the pyridyl-substituted part of the diazaadamantane skeleton as expected from geometric and electrostatic arguments. The molecules are interconnected by an O–H...N hydrogen bond (O...N 2.87 Å).

**Introduction.** Diazaadamantanes are of pharmacological interest, and are the subject of research owing to their potential central nervous system active properties. In this study, the structure of a substituted diazaadamantane was investigated to clarify the steric arrangement of the substituents and of the alcoholic OH group. Structures of diazaadamantanes with various substituents have been published by Biryukov, Unkovskii, Kornilov, Kuznetsov & Burdelev (1972) (6,6-dimethyl-5,7-dinitro-1,3-diazaadamantane), by Kurkutova, Goncharov, Zefirov & Palyulin (1976), Kurkutova, Goncharov, Ilyukhin & Belov (1977) (1-methyl-5,7-diphenyl-1,3-diaza-6-adamantanone iodide) and by Quast, Müller, Peters, Peters & von Schnering (1982) [8,9-bis(4-methylphenyl)-4,10-diphenyl-1,3-diaza-6-adamantanone and 2,4,8,9,10-pentakis(4-methylphenyl)-1,3-diaza-6-adamantanone]. The present paper presents the first example of a structure of a diazaadamantanol.

**Experimental.** The title compound was synthesized by reduction of a corresponding 1,3-diaza-6-adamantanone, which was produced by aminomethylation with paraformaldehyde and concentrated ammonia from dimethyl 4-oxo-2,6-bis(2-pyridyl)-1-aza-3,5-cyclohexanedicarboxylate. The reduction was performed in absolute methanol with sodium borohydride. Two epimeric alcohols were formed in this reduction in the

proportion 66:34. Their melting points are 510 and 535 K, respectively. The former product was used for the analysis described here. Its IR and NMR spectra are as follows. IR: 1720 cm<sup>-1</sup> (C=O ester). <sup>1</sup>H NMR: 7.1–8.5 (C<sub>5</sub>H<sub>4</sub>N), 5.43 s [H(8), H(9)], 4.34 [H(6)], 4.05 s (OH), 4.01 d [H(4), H(10)], 3.42 d [H(4'), H(10')],  $J_{gem}$  13.5 Hz, 3.72 s (ester), 3.34 s [H(2)].

Small single crystals were grown by slow cooling of saturated ethanolic solutions. Dimensions of the specimen used for the measurements: 0.35 × 0.13 × 0.30 mm. Diffractometer: Philips PW 1100,  $\theta$ - $2\theta$  scan. 56 reflections ( $3 < \theta < 22^\circ$ ) were used for lattice-parameter refinement. 3788 intensities were measured in the range  $2 < \theta < 25^\circ$  (index range  $-17 \leq h \leq 16$ ,  $0 \leq k \leq 14$ ,  $0 \leq l \leq 13$ ); 3612 unique reflections;  $R_{int} = 0.037$ ; three standard reflections ( $\bar{2}\bar{2}\bar{2}$ , 004,  $\bar{2}$ 30) monitored every 25 reflections showed no systematic decay, variation  $\pm 4\%$ , no absorption correction; scattering factors for neutral atoms from Cromer & Mann (1968); structure solved by direct methods; full-matrix least-squares refinement (based on  $F$ ) using 1867 reflections with  $I > 2\sigma(I)$  yielded  $wR = 0.037$  ( $R = 0.058$ ); anisotropic temperature factors for non-H, isotropic for H; weight  $\sim 1/\sigma^2$ ; isotropic extinction parameter  $g = 2.9(1) \times 10^{-7}$  [ $F' = F(1 - gF^2/\sin\theta)$ ]; max. final  $|A/\sigma| = 0.06$ ; residual electron density between  $-0.22$  and  $+0.22$  e Å<sup>-3</sup>; programs used: SHELX76 (Sheldrick, 1976), ORFFE (Busing, Martin & Levy, 1964), ORTEPII (Johnson, 1976).

Atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.\*

**Discussion.** The packing of the molecules in the unit cell is shown in a stereoscopic ORTEP plot in Fig. 1. H atoms have been omitted for clarity. In addition to van

\* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44077 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{\AA}^2 \times 10^4$ ) of non-H atoms

$U_{eq}$  is one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
N(1)	752 (2)	2325 (2)	4873 (2)	277 (8)
C(2)	1474 (2)	3135 (3)	4868 (3)	354 (12)
N(3)	2397 (2)	2653 (2)	4960 (2)	388 (9)
C(4)	2286 (3)	1899 (3)	3973 (4)	441 (14)
C(5)	1533 (2)	994 (2)	3908 (3)	339 (11)
C(6)	1892 (2)	328 (3)	5046 (3)	382 (13)
C(7)	1982 (2)	1104 (2)	6093 (3)	327 (11)
C(8)	1037 (2)	1674 (3)	5964 (3)	312 (11)
C(9)	601 (2)	1553 (3)	3876 (3)	317 (12)
C(10)	2706 (3)	2002 (3)	6038 (4)	438 (13)
O(11)	1306 (2)	9402 (2)	5068 (2)	407 (8)
C(12)	1487 (2)	209 (3)	2920 (3)	453 (13)
O(13)	2142 (2)	-6 (2)	2587 (2)	695 (11)
O(14)	641 (1)	-251 (2)	2508 (2)	509 (9)
C(15)	517 (5)	-962 (5)	1514 (5)	699 (22)
C(16)	2349 (3)	420 (3)	7187 (3)	469 (14)
O(17)	3164 (2)	244 (2)	7655 (2)	737 (11)
O(18)	1657 (1)	19 (2)	7548 (2)	480 (9)
C(19)	1939 (4)	-514 (5)	8673 (4)	727 (23)
C(31)	107 (2)	2186 (3)	2777 (3)	334 (11)
N(32)	464 (2)	2111 (2)	1903 (3)	459 (11)
C(33)	-2 (4)	2650 (4)	939 (4)	622 (18)
C(34)	-797 (4)	3259 (4)	801 (4)	648 (19)
C(35)	-1138 (3)	3347 (4)	1720 (4)	631 (17)
C(36)	-682 (3)	2794 (3)	2724 (3)	469 (14)
C(41)	1040 (2)	2435 (3)	6962 (3)	362 (11)
C(42)	310 (3)	3160 (3)	6863 (4)	504 (15)
C(43)	303 (3)	3838 (4)	7782 (4)	580 (17)
C(44)	1027 (3)	3755 (3)	8768 (4)	542 (17)
C(45)	1725 (3)	3010 (4)	8802 (4)	597 (16)
N(46)	1757 (2)	2353 (2)	7931 (3)	490 (11)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) within the diazaadamantanol skeleton

N(1)—C(2)	1.457 (4)	C(8)—N(1)	1.487 (4)
C(2)—N(3)	1.472 (5)	N(3)—C(10)	1.477 (5)
N(3)—C(4)	1.473 (5)	C(10)—C(7)	1.545 (5)
C(4)—C(5)	1.552 (5)	N(1)—C(9)	1.489 (4)
C(5)—C(6)	1.548 (5)	C(9)—C(5)	1.540 (5)
C(6)—C(7)	1.551 (5)	C(6)—O(11)	1.423 (4)
C(7)—C(8)	1.539 (4)		
C(2)—N(1)—C(8)	109.9 (2)	C(6)—C(5)—C(9)	108.4 (3)
C(2)—N(1)—C(9)	110.2 (3)	C(5)—C(6)—C(7)	110.1 (3)
C(8)—N(1)—C(9)	109.2 (2)	C(5)—C(6)—O(11)	111.8 (2)
N(1)—C(2)—N(3)	114.7 (3)	C(7)—C(6)—O(11)	111.0 (3)
C(2)—N(3)—C(4)	107.8 (3)	C(6)—C(7)—C(8)	109.5 (2)
C(2)—N(3)—C(10)	108.2 (3)	C(6)—C(7)—C(10)	106.0 (3)
C(4)—N(3)—C(10)	109.0 (3)	C(8)—C(7)—C(10)	108.6 (3)
N(3)—C(4)—C(5)	112.1 (3)	N(1)—C(8)—C(7)	109.5 (3)
C(4)—C(5)—C(6)	105.4 (2)	N(1)—C(9)—C(5)	109.8 (2)
C(4)—C(5)—C(9)	109.5 (3)	N(3)—C(10)—C(7)	111.9 (3)

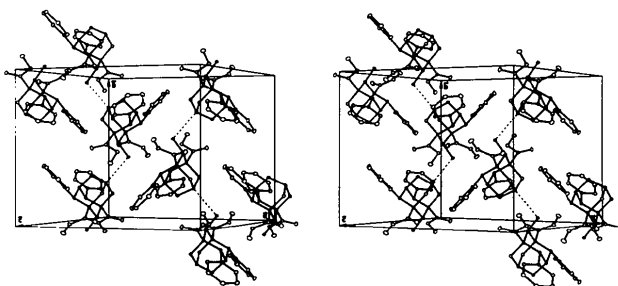


Fig. 1. Stereoscopic view of the unit cell [drawn by ORTEP (Johnson, 1976)].

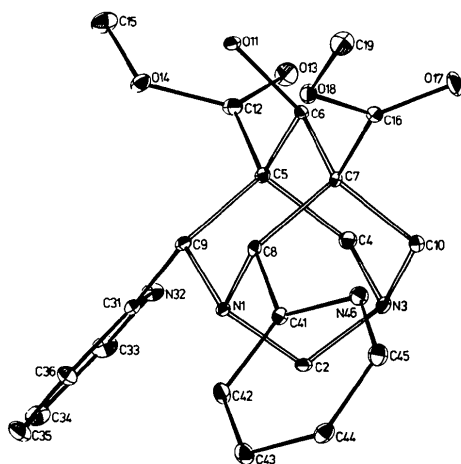


Fig. 2. Thermal-ellipsoid plot of the diazaadamantanol skeleton (H atoms omitted) [drawn by ORTEP (Johnson, 1976)].

der Waals interactions, the molecules are linked by an O—H...N hydrogen bond (dashed lines in Fig. 1) with the following geometry: O(11)...N(3) = 2.870 (4), O(11)—H(11) = 0.91 (3), N(3)...H(11) = 1.97 (3) Å; angle O(11)—H(11)...N(3) = 172 (3)°; fractional coordinates of H(11): 0.1680(22), -0.1196(27), 0.5076(31). The additional attraction by the hydrogen bond possibly accounts for the relatively high density of the present diazaadamantanol ( $D_x = 1.35 \text{ Mg m}^{-3}$ ) when compared with that of two diazaadamantanones reported by Quast *et al.* (1982) ( $D_x = 1.18$ ,  $1.19 \text{ Mg m}^{-3}$ ) and two related bicyclononanones reported by Küppers, Hesse, Ashauer-Holzgrabe, Haller & Boese (1987) ( $D_x = 1.25$ ,  $1.27 \text{ Mg m}^{-3}$ ).

Fig. 2 shows the diazaadamantanol molecule (H atoms omitted) which confirms the configuration expected from NMR spectroscopic measurements. Both pyridine rings are in equatorial positions, and the OH group and the methyl groups of the esters are inclined toward the pyridyl-substituted part of the diazaadamantanol skeleton. The configuration of the OH group seems plausible from the steric conditions during the reduction of the C=O group of the educt, which was carried out with  $\text{NaBH}_4$  in absolute methanol. In water-free solvents the sodium borohydride reduction preferentially yields an epimeric alcohol with an axial OH position referred to the ring containing the two aryl groups. This can be seen in reductions of piperidones as well as of diazabicyclononanones containing ester groups. The reason for this reduction course has been explained by geometrical and electrostatic interactions (Haller, 1965; Haller & Unholzer, 1971). Therefore, the result for the oxidiazadamantanedicarboxylate reduction from this study is in good agreement with the results of the reduction of corresponding heterocycles from earlier studies.

Distances and angles within the diazaadamantanol skeleton are given in Table 2. Distances and angles within the pyridyl groups are in the usual range.

The molecule shows an approximate mirror symmetry with the mirror plane defined by atoms N(1),

C(2), N(3) and C(6). The mean planes through the pyridine rings C(31) to C(36) and C(41) to N(46) form angles of 54.7 (2) and 47.4 (2)°, respectively, with the plane defined by atoms C(9), N(1) and C(8). The direction of this rotation is such that the rings tend to be parallel with the bonds C(9)—C(5) and C(8)—C(7). This orientation of the rings is quite different (approximately perpendicular) to that of the phenyl rings in the comparable chair-chair bicyclononanone (Küppers *et al.*, 1987). Whereas in several similar bicyclononanones the mean planes through the carboxylic groups [C(5), C(12), O(13), O(14) and C(7), C(16), O(17), O(18)] are nearly coplanar with the planes C(5), C(4), N(3) and C(7), C(10), N(3), respectively, (Küppers *et al.*, 1987), in the molecule in this study the planes of the carboxylic groups are tilted by 29.7 (3) and 30.3 (3)°, respectively, from these planes. This is a consequence of the reduction of the carbonyl group to an alcohol and the resulting inclination towards the pyridyl-substituted part of the molecule and the consequential spatial requirements (*cf.* Fig. 2). The distances O(11)···O(14) and O(11)···O(18) are 2.997 (3) and 2.994 (4) Å, respectively.

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## Structure of *trans*-1,4,5,8-Tetrathiadecalin (Hexahydro-1,4-dithiino-[2,3-*b*]-1,4-dithiin)

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**Abstract.** C<sub>6</sub>H<sub>10</sub>S<sub>4</sub>, *M<sub>r</sub>* = 210.4, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 8.587 (2), *b* = 11.813 (2), *c* = 4.519 (1) Å, *α* = 97.65°, *V* = 454.3 (3) Å<sup>3</sup>, *D<sub>x</sub>* = 1.538 g cm<sup>-3</sup>, *Z* = 2, *λ*(Mo *Kα*) = 0.71069 Å, *μ*(Mo *Kα*) = 9.31 cm<sup>-1</sup>, *F*(000) = 220, *T* = 288 K, *R* = 0.034 for 819 observed reflections. Both six-membered rings are in a chair conformation, with ring dihedral angles of 66.4 (1) (central) and 68.1 (1)° (peripheral). The bond distances and angles are normal. An attractive non-bonded interaction between sulfur atoms in an S—C—S system is suggested by a short S—S distance (2.82 Å) and by a small value of the S—C—S angle (101.4°).

**Introduction.** 1,4,5,8-Tetraheterodecalins (1)–(3) have attracted the interest of synthetic and structural chemists, since they offer the opportunity of testing the

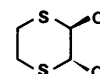
importance and geometrical consequences of anomeric effects.



- (1) *x* = O  
 (2) *x* = NH  
 (3) *x* = S



(5)



(6)