

Diethylsilanediol, C₄H₁₂O₂Si, a Redetermination

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(Received 24 October 1984; accepted 18 February 1985)

Abstract. $M_r = 120.22$, monoclinic, $P2_1/n$, $a = 14.656$ (5), $b = 4.945$ (1), $c = 10.432$ (3) Å, $\beta = 111.27$ (3)°, $V = 704.55$ Å³, $Z = 4$, $D_x = 1.13$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 2.12$ mm⁻¹, $F(000) = 264$, $T = 293$ K, $R = 0.062$ for 944 unique observed reflections. The full three-dimensional structure, first described by Kakudo & Watase [*Technol. Rep. Osaka Univ.* (1952). 5, 247-250], has been redetermined, using the space group $P2_1/n$ not $P2_1/a$, and the positions of the hydrogen atoms determined from difference Fourier maps. The hydroxyl hydrogen atoms occur in two alternative arrangements with hydrogen bonds of normal type, O...O distances 2.679 (6)-2.727 (6) Å.

Introduction. The structure of the title compound was first determined by Kakudo & Watase (1952) from a restricted data set, assuming the space group to be $P2_1/a$. However, the relationships $c^* = 4a^*\cos\beta$ and $F(hkl) = F[h, k, (-\frac{1}{2}+l)]$ indicate the possibility of a centred orthorhombic cell and an additional unusual feature is a postulated 'opposed dipole' hydrogen-bonding arrangement with an O-H...O angle of about 90°.

Experimental. Material prepared by Dr R. Bushby (hydrolysis of dichlorodiethylsilane). Tabular crystal 0.31 × 0.26 × 0.15 mm. Enraf-Nonius CAD-4 diffractometer, moving-crystal/moving-counter technique, Ni-filtered Cu $K\alpha$ radiation, $2\theta < 140^\circ$, lattice parameters from θ measurements on 71 reflections, no absorption corrections, reflection $\bar{6}02$ as intensity standard, average count 681 with σ (calculated from distribution of the measurements) = 61.4, 2965 reflections measured ($\pm h k \pm l$) and merged, using *SHELX76* (Sheldrick, 1976), to give 1070 unique reflections, merging $R_{\text{int}} = 0.066$; of these, 126 excluded during refinement [$F_o < 3\sigma(F_o)$], index range of data used in analysis: $h \pm 16$, $k 0/6$, $l 0/12$. Structure solved using *MULTAN80* (Main *et al.*, 1980); H atoms from subsequent difference syntheses; least-squares refinement on F ; H atoms with fixed isotropic temperature factors, other atoms anisotropic; final $R = 0.062$,

$wR = 0.079$; $w = 1/[\sigma^2(F) + 0.0017F^2]$. In final cycle max. LS shift/errors 0.090 (non-H) and 0.141 (H), average shift/error 0.027. Final difference Fourier synthesis showed max. and min. values of 0.46 and -0.25 e Å⁻³ respectively. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1† gives the atom parameters and Table 2 has the intramolecular bond distances and angles, and details of the hydrogen bonding. Fig. 1 shows the molecule and numbering scheme. Fig. 2 the packing in the unit cell.

‡ Lists of structure factors, anisotropic thermal parameters, hydrogen-atom parameters and the weighted a^*c^* reciprocal-lattice projection indexed according to Kakudo & Watase (1952) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42066 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å² × 10⁴)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Si(1)	883 (1)	2548 (2)	7331 (1)	470
O(1)	757 (2)	77 (6)	6234 (3)	562
O(2)	1503 (2)	5024 (6)	6995 (3)	574
C(1)	-337 (4)	3893 (10)	7127 (6)	633
C(2)	-1038 (5)	1873 (13)	7364 (8)	909
C(3)	1582 (4)	1179 (10)	9063 (5)	622
C(4)	1786 (6)	3197 (13)	10218 (6)	890

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

Si(1)-O(1)	1.638 (3)	Si(1)-C(3)	1.852 (5)	
Si(1)-O(2)	1.636 (3)	C(1)-C(2)	1.515 (7)	
Si(1)-C(1)	1.847 (5)	C(3)-C(4)	1.508 (7)	
O(1)-Si(1)-O(2)	109.8 (2)	O(2)-Si(1)-C(3)	109.2 (2)	
O(1)-Si(1)-C(1)	109.2 (2)	C(1)-Si(1)-C(3)	114.4 (2)	
O(1)-Si(1)-C(3)	106.9 (2)	Si(1)-C(1)-C(2)	115.4 (4)	
O(2)-Si(1)-C(1)	107.2 (2)	Si(1)-C(3)-C(4)	114.6 (4)	
Hydrogen bond	O...O	O-H	-H...O	Equivalent position
O(1)-H(011)...O(1)'	2.724 (6)	0.72 (7)	2.01 (7)	-x, -y, 1-z
O(2)-H(021)...O(2)'	2.724 (6)	0.68 (8)	2.05 (8)	$\frac{1}{2}-x, y, \frac{1}{2}-z$
O(1)-H(012)...O(2)'	2.727 (6)	0.73 (6)	2.00 (6)	x, y-1, z
O(2)-H(022)...O(1)	2.679 (6)	0.75 (6)	1.99 (6)	x, y, z

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* Shown on Fig. 2.

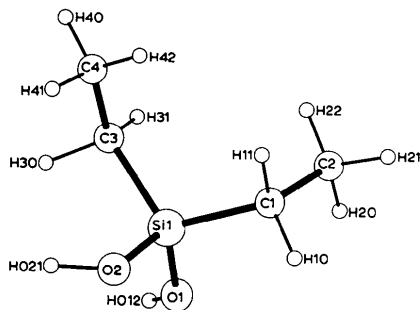


Fig. 1. Diagram of the molecule showing numbering scheme.

The structure differs from that deduced by Kakudo & Watase (1952) (in which the space group was assumed to be $P2_1/a$). Their suggested unusual 'opposed dipole' arrangement of OH groups does not occur and the hydrogen bonds have normal lengths (2.679 to 2.727 Å). There are two equally populated schemes of hydrogen bonding as listed in Table 2. In addition, although the *ac* projection may be described in terms of a centred orthorhombic cell, the quoted relationship between structure factors is only valid when $k = 0$.*

It has been suggested that other silanediol structures were analogous to that of the title compound and therefore contained an unusual type of hydrogen bonding. It now appears that these assumptions are unnecessary.

* See deposition footnote.

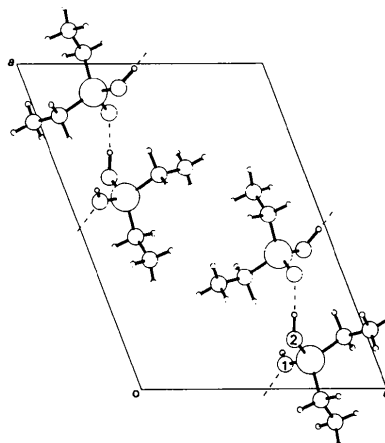


Fig. 2. *b*-axis-projection packing diagram (*PLUTO*78, Motherwell & Clegg, 1978).

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Acta Cryst. (1985). **C41**, 942–944

Structure of a Carbocyclic Analogue of Penicillin

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(Received 4 December 1984; accepted 21 February 1985)

Abstract. Methyl 4-(6-*endo*-hydroxybicyclo[3.2.0]-hept-2-en-7-*endo*-ylamino)-4-oxobutyrate (6*R**,7*S**), $C_{12}H_{17}NO_4$, $M_r = 239.27$, monoclinic, $P2_1/c$, $a = 11.594(1)$, $b = 6.138(1)$, $c = 17.512(1)$ Å, $\beta = 102.35(1)^\circ$, $V = 1217.3$ Å³, $Z = 4$, $D_x = 1.31$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.725$ mm⁻¹, $F(000) = 512$, $T = 293$ K, $R = 0.077$ for 1714 unique observed reflections. The cyclobutanone and cyclopentene rings of the bicyclohept-2-en-6-one moiety make an angle of $116.5(6)^\circ$, the bond lengths and

angles are normal. Both the NH and OH groups form hydrogen bonds with lengths of 3.35(1) and 2.74(1) Å respectively, linking molecules in the *b*-axis direction.

Introduction. This determination forms one of a series of structure determinations of carbocyclic analogues of penicillin in which the β -lactam ring is replaced by a cyclobutanone. One structure of such a carbocyclic analogue of penicillin has been published (Sheldrick, Akrigg, Page & Agathocleous, 1984).