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(2*S*,3*R*,5*S*)-3-Hydroxy-2-methyl-5-(1-methylethenyl)cyclohexanone 0.12-Diethyl Ether Solvate

MARTIN LUTZ AND ANTHONY L. SPEK

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands.
E-mail: m.lutz@chem.ruu.nl

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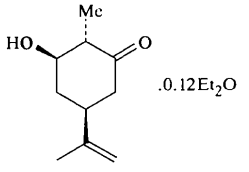
Abstract

The six-membered ring of the title compound, $C_{10}H_{16}O_2.0.12C_4H_{10}O$, exhibits a chair conformation with the hydroxy, methyl and isopropenyl groups in equatorial positions. In the crystal, hydrogen bonds join the molecules into one-dimensional co-operative chains, with the O atoms of the hydroxy groups acting as donors and acceptors. The empty space between these chains is occupied by disordered diethyl ether molecules from the solvent.

Comment

In connection with investigations into the stereoselective reduction of α,β-epoxyketones, we report here the crystal and molecular structure of (2*S*,3*R*,5*S*)-3-hydroxy-2-methyl-5-(1-methylethenyl)cyclohexanone, a diastereomer of the earlier published 2*S*,3*S*,5*S* compound (Spek *et al.*, 1990).



(I)

A molecular plot of the title compound, (I), with the atomic numbering scheme, is shown in Fig. 1. The different configuration of the hydroxy group in the two diastereomers has only a minor influence on the conformation of the cyclohexanone ring, which is in a chair conformation in both compounds. The 2*S*,3*R*,5*S* isomer has ring puckering parameters (Evans & Boeyens, 1989) Q = 0.570 (2) Å, θ = 6.0 (2)° and φ = 217.8 (16)°, while the 2*S*,3*S*,5*S* isomer has parameters Q = 0.543 (2) Å, θ = 7.9 (2)° and φ = 205 (2)°. The conformation of the isopropenyl group is also similar in the two compounds. The torsion angle C6—C5—C8—C10 is −131.46 (18)° in the title compound and −107.8 (3)° in the 2*S*,3*S*,5*S* isomer.

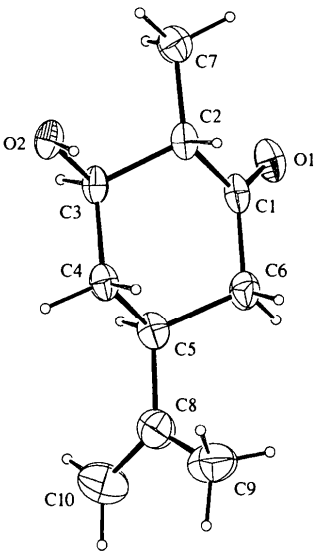


Fig. 1. Plot of the title molecule showing 50% probability displacement ellipsoids. The disordered solvent has been omitted.

The configuration of the hydroxy group has a major influence on the pattern of hydrogen bonding. While in the 2*S*,3*S*,5*S* isomer, the hydroxy group acts a hydrogen-bond donor and the keto group as an acceptor, in the 2*S*,3*R*,5*S* isomer, the hydroxy group acts both as donor and acceptor; the keto group is not involved in hydrogen bonding. The hydroxy–hydroxy hydrogen bond is nearly linear and much shorter than the hydroxy–keto hydrogen bond [O2···O1 = 2.892 (2) Å] of the 2*S*,3*S*,5*S* isomer.

The molecules join *via* hydroxy–hydroxy co-operative hydrogen bonds into an infinite chain around a 3_1 axis in the direction of the crystallographic *c* axis. These chains are not closest packed; there is empty space between them. This empty space forms infinite

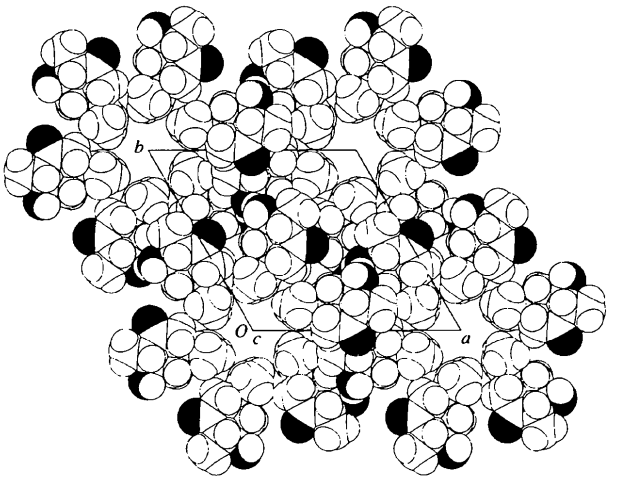


Fig. 2. Projection of a space-filling model of the structure onto the *ab* plane, illustrating the solvent channels down **c**. The solvent molecules are not shown.

channels along the 6_5 screw axes (Fig. 2). The solvent-accessible volume of these channels is 146 Å^3 per unit cell, which is occupied by heavily disordered diethyl ether molecules from the solvent of crystallization. These disordered ether molecules were not included in the refinement of the model, but their contribution to the intensities was handled with the *BYPASS* routine (van der Sluis & Spek, 1990) as described in the *Experimental*.

Experimental

The title compound was prepared by the selective reduction of the corresponding α,β-epoxyketone (Hanekamp, 1992) and crystallized from diethyl ether.

Crystal data

$C_{10}H_{16}O_2.0.12C_4H_{10}O$
M_r = 177.13
Hexagonal
$P6_5$
a = 16.9681 (10) Å
c = 6.5473 (6) Å
V = 1632.5 (2) Å^3
Z = 6
D_x = 1.081 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.24–19.55°
μ = 0.07 mm^{-1}
T = 100 (2) K
Hexagonal plate
0.35 × 0.30 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4908 measured reflections
1363 independent reflections
1284 reflections with $I > 2\sigma(I)$

R_{int} = 0.018
θ_{max} = 27.49°
$h = -22 \rightarrow 0$
$k = -19 \rightarrow 22$
$l = -8 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.084
S = 1.05
1363 reflections
137 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.0908P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.213 e Å^{-3}
$\Delta\rho_{min}$ = −0.132 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric and hydrogen-bonding parameters (Å, °)*

O1—C1	1.2140 (17)	C8—C10	1.364 (3)
O2—C3	1.4344 (16)	C8—C9	1.458 (3)
O1—C1—C6	122.10 (13)	C6—C1—C2	115.40 (11)
O1—C1—C2	122.50 (13)		
O1—C1—C2—C7	2.8 (2)	C3—C4—C5—C8	−175.43 (13)
C6—C1—C2—C7	−176.31 (13)	C3—C4—C5—C6	59.22 (15)
O1—C1—C2—C3	127.88 (14)	O1—C1—C6—C5	−124.13 (15)
C6—C1—C2—C3	−51.26 (16)	C2—C1—C6—C5	55.01 (16)
C7—C2—C3—O2	−59.28 (15)	C8—C5—C6—C1	178.65 (13)
C1—C2—C3—O2	175.21 (10)	C4—C5—C6—C1	−56.86 (16)
C7—C2—C3—C4	177.10 (12)	C4—C5—C8—C10	105.3 (2)
C1—C2—C3—C4	51.60 (15)	C6—C5—C8—C10	−131.56 (18)
O2—C3—C4—C5	179.71 (11)	C4—C5—C8—C9	−72.35 (19)
C2—C3—C4—C5	−57.65 (15)	C6—C5—C8—C9	50.82 (19)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···O2^{i}	0.81 (3)	1.80 (3)	2.6157 (9)	180 (2)

Symmetry code: (i) $-x + y, 1 - x, \frac{1}{3} + z$.

The contribution of the disordered solvent to the calculated structure factors was taken into account following the *BYPASS* algorithm (van der Sluis & Spek, 1990), implemented as the *SQUEEZE* option in *PLATON* (Spek, 1994). A total of 30 electrons per unit cell were detected in the channels, amounting to $\frac{3}{4}$ of a molecule of diethyl ether. The *BYPASS* routine takes the disordered molecules into account as diffuse electron density and adds this contribution to the F_c^2 values *via* back-Fourier transformation. The final F_o^2/F_c^2 data were calculated with the *FCF* routine of *PLATON* and include the disordered solvent contribution. A *SHELXL*97 (Sheldrick, 1997) estimation of the Flack x parameter (Flack, 1983) results in a value of 0.5 with an s.u. of 1.2. The absolute configuration could therefore not be determined reliably, but was chosen with respect to (*S*)-carvone, the starting material in the synthesis of the title compound. X-ray data were collected on a slightly larger than usual thin-plate crystal using a sufficiently large collimator tube to ensure a homogeneous X-ray beam at the crystal. The adaptation of the collimator to the crystal size is possible here in view of the use of a Zr β-filter as opposed to a graphite monochromator (Alexander & Smith, 1962).

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1051). Services for accessing these data are described at the back of the journal.

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trans-2,6-Bis(ethylamino)-2,4,4,6,8,8-hexamorpholinocyclo-2λ^5, 4λ^5, 6λ^5, 8λ^5-tetraphosphazatetraene

TUNCER HÖKELEK,[a]* EMİNE KILIÇ[b] AND ZEYNEL KILIÇ[b]

[a]*Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and* [b]*Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr*

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Abstract

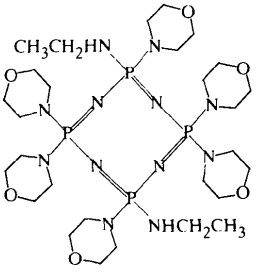
The title compound, $C_{28}H_{60}N_{12}O_6P_4$, consists of a chair-shaped cyclic tetrameric phosphazene ring with six bulky morpholino and two ethylamino side groups. The two ethylamino side groups are in *trans* positions. The bulky substituents are effective in determining the eight-membered-ring conformation. The endocyclic N—P—N angles around the P atoms having different substituents are not the same as the P—N—P angles of the macrocyclic ring.

Comment

Cyclophosphazenes ($N_3P_3Cl_6$ and $N_4P_4Cl_8$) have potential use in the synthesis of new high polymeric phosphazenes with inorganic backbones, which have many different uses (Allcock, 1985; Hökelek & Kılıç, 1990; Hökelek *et al.*, 1996). The small-molecule organo–cyclophosphazenes are also small-molecule models for the corresponding linear organo–polyphosphazenes (Allcock, 1985). Some of the aminophosphazenes are thought to be useful as cancer chemotherapeutic agents (Chernov *et al.*, 1959; van der Huizen, 1984). A relationship is observed between the structures of the cyclophosphazenes and cytostatic activity (van der Huizen, 1984), and for effective tumour growth inhibition, electron-donating groups (*e.g.* aziridine, pyrrolidine and morpholine) in the P–N ring skeleton appear to be essential.

There are two crystal modifications, *K* and *T* forms, of $N_4P_4Cl_8$, which is known as a standard compound for tetrameric phosphazenes (Hazekamp *et al.*, 1962; Wagner & Vos, 1968). The crystal structures of some $N_4P_4Cl_8$ derivatives, such as *β-trans*-$N_4P_4(NHMe)_4Ph_4$ (Bullen & Mallinson, 1972), $N_4P_4Cl_4(NEt_2)_4$ (Hökelek & Kılıç, 1990), $N_4P_4(NMe_2)_8$ (Bullen, 1962) and $N_4P_4Cl_7(OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)$ (Hökelek *et al.*, 1996), have been determined.

A structure analysis of the title compound, (I), was undertaken to determine the influences of the relatively hindered side groups, and also of steric and electronic factors, on the macrocyclic tetraphosphazene ring. The title compound is illustrated in Fig. 1. Its structure consists of a cyclic tetrameric phosphazene ring in a chair conformation with two ethylamino (in 2,6-*trans* positions) and six bulky morpholino side groups. The four P atoms are coplanar and the four N atoms are displaced above (+) and below (−) their plane by equal amounts [N1 −0.380 (5) and N2 0.555 (4) Å]. The conformation of the macrocyclic phosphazene ring is indicated by the torsion angles of the ring bonds in



(I)

which the symmetry operation reverses the sign of a torsion angle (shown in Fig. 2). From the distribution of the endocyclic torsion angles, it appears that in the central ring there are two local pseudo-mirrors, one running along the midpoints of the N1—P1 and N1′—P1′ bonds, the other along the midpoints of the P2—N2′ and P2′—N2 bonds.

The P—N—P bond angles are in the range 127.3 (2)–134.4 (2)° [average 130.9 (2)°]. Similar spreads of P—N—P angles were observed in *β-trans*-$N_4P_4Cl_4(NMe_2)$ (Hökelek & Kılıç, 1990) and $N_4P_4Cl_7(OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)$ (Hökelek *et al.*, 1996), and it was reported that such large angles appear to be characteristic of molecules containing chlorine or fluorine (George *et al.*, 1972). Although, the title compound contains neither chlorine nor fluorine, large P—N—P angles appear to be due to the different substituents on the P atoms. The variation in the endocyclic N—P—N bond angles are in the range 117.4 (2)–121.5 (2)° [average 119.5 (2)°]. In $N_3P_3Cl_6$ derivatives, it has been observed that endocyclic (N—P—N) angles about P decrease