| | | | |
|---|---|---|---|
| P—O7—C9 | 125.0 (5) | O4—C4—C5 | 126.3 (6) |
| Si—O2′—C2′ | 128.3 (4) | N3—C4—C5 | 113.0 (6) |
| C5′—O5′—C17 | 114.9 (5) | C4—C5—C6 | 121.1 (6) |
| C1′—N1—C2 | 118.9 (5) | N1—C6—C5 | 121.4 (5) |
| C1′—N1—C6 | 119.1 (5) | O5′—C5′—C4′ | 106.9 (5) |
| C2—N1—C6 | 121.7 (5) | O5′—C17—O8 | 123.0 (7) |
| C2—N3—C4 | 128.4 (5) | O5′—C17—C18 | 111.8 (6) |
| P—C3′—C2′ | 112.1 (4) | O8—C17—C18 | 125.3 (6) |
| P—C3′—C4′ | 115.1 (4) | C17—C18—C19 | 122.9 (6) |
| C2′—C3′—C4′ | 102.4 (4) | C17—C18—C23 | 118.6 (6) |
| O2′—C2′—C3′ | 110.5 (4) | C19—C18—C23 | 118.5 (6) |
| O2′—C2′—C1′ | 109.6 (4) | C18—C19—C20 | 120.9 (6) |
| C3′—C2′—C1′ | 103.7 (5) | C19—C20—C21 | 119.7 (7) |
| O4′—C1′—N1 | 108.2 (4) | C20—C21—C22 | 120.9 (8) |
| O4′—C1′—C2′ | 106.7 (4) | C21—C22—C23 | 120.1 (8) |
| N1—C1′—C2′ | 115.8 (5) | C18—C23—C22 | 119.9 (7) |
| O4′—C4′—C3′ | 105.0 (4) | | |
| C4′—O4′—C1′—C2′ | −35.1 (5) | C2′—C3′—C4′—O4′ | −32.7 (5) |
| C1′—O4′—C4′—C3′ | 42.7 (5) | C3′—C2′—C1′—O4′ | 13.3 (5) |
| C4′—C3′—C2′—C1′ | 11.2 (5) | | |

The diffraction analysis clearly demonstrates that the crystalline product is the 3′$\beta$-diethylphosphono isomer, indicating that H-atom transfer has occurred primarily to the less hindered $\alpha$ face in this product. The major product is formed with inversion of the C3′ stereochemistry. The structure was determined by direct methods. The absolute stereochemistry of the ribose moiety was known in advance so no attempt was made to determine the absolute configuration from X-ray diffraction data. The scattering factors $f'$ and $f''$ were included in the structure-factor calculations.

Data collection: Enraf–Nonius (1977) CAD-4 software. Cell refinement: Enraf–Nonius (1977) CAD-4 software. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SX1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# 1,3-Dicyclohexyl-2,4-bis(cyclohexylimino)-1,3-diazetidine: Dimer of Dicyclohexylcarbodiimide

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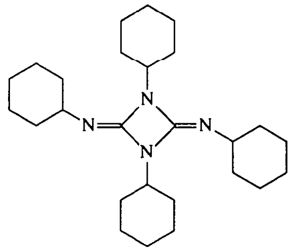
## Abstract

The title compound, $C_{26}H_{44}N_4$, was isolated as a by-product of an esterification reaction using dicyclohexylcarbodiimide as a dehydrating agent. The X-ray structure determination reveals a highly symmetrical molecule with a non-crystallographic inversion centre as a symmetry element. The substituents of the azetidine ring are cyclohexane rings with ideal chair conformation.

## Comment

During our attempts to determine the enantiomeric excess and the absolute configuration of several optically active fluorohydrins by derivatization with enantiopure carboxylic acids, we used the DCC method (DCC = dicyclohexylcarbodiimide) recommended for this type of esterification (Heumann & Faure, 1993). However, some of these reactions failed and we obtained the dimer of DCC. This compound, (I), had been found earlier as a major by-product in peptide synthesis with DCC and 1-hydroxybenzotriazole (Jakubke & Klessen, 1977) and can be synthesized by the reaction of DCC with $SO_2$ gas at 273 K for 21 h (Kaupp, Luebben & Sauerland, 1990).



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In our case the compound was isolated from the esterification mixture by column chromatography [silica gel (Merck), cyclohexane/ethyl acetate 5:1] and recrystallized from cyclohexane with traces of ethyl acetate. The X-ray crystallographic analysis (Fig. 1) shows the highly symmetric structure, with ideal chair conformation for all four cyclohexane rings. The core of the molecule, consisting of N1, N2, C3, C4, N5 and N6, is almost planar; the greatest deviation is 0.024 (1) Å for C3, with C11 0.908 (1) Å below and C21 0.925 (1) Å above this plane. The torsion angles [C4—N2—C3—N5 175.8 (1), C4—N1—C3—N5 −175.3 (2), C3—N2—C4—N6 177.2 (2), C3—N1—C4—N6 −177.6 (1), C11—N1—C3—N2 −130.6 (1), C11—N1—C4—N2 133.0 (1), C21—N2—C3—N1 −131.1 (1), C21—N2—C4—N1 129.7 (1)°] indicate the described geometry.

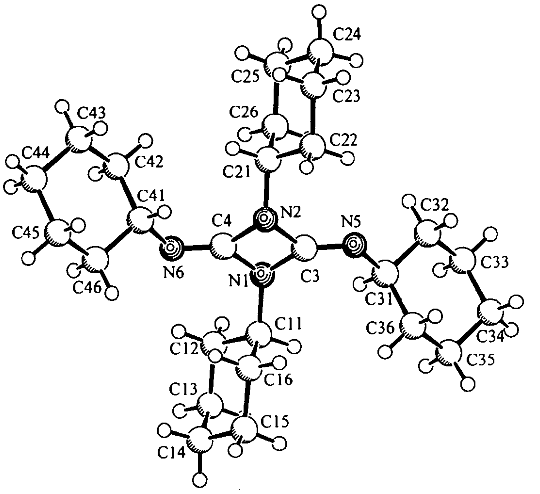

Fig. 1. *SCHAKAL*92 (Keller, 1992) plot of the dimer with atomic numbering scheme.

The distances in the four-membered ring are almost equal [C—N 1.422 (2)–1.433 (2) Å], while the bonds from the ring to the exocyclic N atoms are, at 1.253 (2) Å, in the expected range for C=N double bonds.

The packing of the molecules shows no unusual features; there are no contacts shorter than typical van der Waals distances.

## Experimental

The title compound was isolated as described in the *Comment*.

*Crystal data*

$C_{26}H_{44}N_4$
$M_r = 412.65$
Monoclinic
$P2_1/c$
$a = 10.166$ (1) Å
$b = 12.206$ (1) Å
$c = 20.873$ (2) Å
$\beta = 102.20$ (1)°
$V = 2531.6$ (4) Å$^3$
$Z = 4$
$D_x = 1.083$ Mg m$^{-3}$

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40.04$–$46.85°$
$\mu = 0.483$ mm$^{-1}$
$T = 223$ (2) K
Irregular
0.5 × 0.5 × 0.3 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: $\psi$ scan (*MolEN*; Fair, 1990)
$T_{min} = 0.941$, $T_{max} = 0.999$
5307 measured reflections
5159 independent reflections

4117 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0172$
$\theta_{max} = 74.31°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 15$
$l = -26 \rightarrow 0$
3 standard reflections monitored every 250 reflections intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.0505$
$wR(F^2) = 0.1557$
$S = 1.057$
5159 reflections
272 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0904P)^2 + 0.4437P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.315$ e Å$^{-3}$
$\Delta\rho_{min} = -0.205$ e Å$^{-3}$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0020 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.27951 (10) | 0.19663 (9) | 0.23047 (5) | 0.0281 (2) |
| N2 | 0.23014 (10) | 0.04595 (9) | 0.26220 (5) | 0.0275 (2) |
| C3 | 0.34158 (12) | 0.11906 (10) | 0.27872 (6) | 0.0269 (3) |
| C4 | 0.16792 (12) | 0.12412 (10) | 0.21402 (6) | 0.0273 (3) |
| N5 | 0.44586 (10) | 0.11237 (9) | 0.32302 (5) | 0.0305 (3) |
| N6 | 0.06243 (10) | 0.13226 (9) | 0.17059 (5) | 0.0309 (3) |
| C11 | 0.34254 (12) | 0.24940 (10) | 0.18091 (6) | 0.0279 (3) |
| C12 | 0.25304 (14) | 0.34185 (11) | 0.14762 (6) | 0.0320 (3) |
| C13 | 0.3170 (2) | 0.39825 (12) | 0.09669 (7) | 0.0393 (3) |
| C14 | 0.3468 (2) | 0.31686 (14) | 0.04623 (7) | 0.0471 (4) |
| C15 | 0.4350 (2) | 0.22364 (13) | 0.07906 (8) | 0.0430 (4) |
| C16 | 0.37280 (14) | 0.16704 (11) | 0.13074 (7) | 0.0352 (3) |
| C21 | 0.16449 (12) | −0.00404 (10) | 0.31171 (6) | 0.0273 (3) |
| C22 | 0.25152 (13) | −0.09506 (11) | 0.34811 (6) | 0.0318 (3) |
| C23 | 0.1809 (2) | −0.14924 (12) | 0.39742 (7) | 0.0406 (3) |
| C24 | 0.1470 (2) | −0.06549 (15) | 0.44508 (7) | 0.0529 (4) |
| C25 | 0.0628 (2) | 0.02768 (14) | 0.40973 (8) | 0.0504 (4) |
| C26 | 0.13089 (15) | 0.08125 (12) | 0.35924 (7) | 0.0375 (3) |
| C31 | 0.53801 (12) | 0.20613 (10) | 0.33556 (6) | 0.0282 (3) |
| C32 | 0.57522 (14) | 0.22415 (12) | 0.40960 (6) | 0.0350 (3) |
| C33 | 0.6749 (2) | 0.31771 (14) | 0.42726 (7) | 0.0494 (4) |
| C34 | 0.8001 (2) | 0.2971 (2) | 0.40069 (9) | 0.0570 (5) |
| C35 | 0.7651 (2) | 0.27850 (14) | 0.32681 (8) | 0.0475 (4) |
| C36 | 0.66373 (13) | 0.18567 (12) | 0.30864 (7) | 0.0370 (3) |
| C41 | −0.03189 (12) | 0.04019 (11) | 0.15737 (6) | 0.0294 (3) |
| C42 | −0.15321 (13) | 0.05882 (12) | 0.18831 (7) | 0.0363 (3) |
| C43 | −0.2580 (2) | −0.03158 (15) | 0.16925 (9) | 0.0498 (4) |
| C44 | −0.3015 (2) | −0.0411 (2) | 0.09482 (9) | 0.0590 (5) |
| C45 | −0.1815 (2) | −0.05974 (14) | 0.06364 (8) | 0.0518 (4) |
| C46 | −0.07674 (14) | 0.03011 (12) | 0.08300 (6) | 0.0358 (3) |

H-atom positions could be found from difference Fourier maps, but refinement resulted in slightly deformed arrangements. Thus, for final refinement, H atoms were set at calculated positions and included as riding atoms in refinement.

Data collection: *CAD*-4 *EXPRESS* (Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*-92 (Keller, 1992). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# 8-(4-Methylphenoxy)-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*][1,3,2]dioxaphosphocine 8-Sulfide

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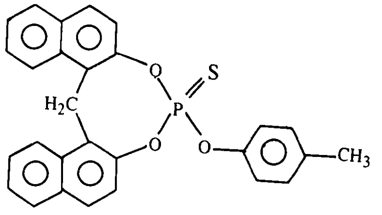
## Abstract

The eight-membered dioxaphosphocine ring in $C_{28}H_{21}O_3PS$ adopts a distorted boat conformation with the phosphoryl S atom axial and the phenoxy group equatorial. The phenyl ring takes a perpendicular orientation with respect to the two naphthalene ring systems; the dihedral angle between the naphthalene planes is 64.78 (7)°. The structure is stabilized by van der Waals interactions.

## Comment

The crystal structures and conformations of organophosphorus compounds have become the subject of intense study due to their involvement in many biological processes (Corbridge, 1977; Emsley & Hall, 1976; Sankara Reddy & Devendranath Reddy, 1995). The proven toxic effects of phosphoric acid esters on pests and their possible application as lubricant additives prompted the synthesis of a new class of organophosphorus heterocyclic esters (1,3,2-dioxaphosphocine derivatives) (Reddy, 1988). To our knowledge, there have been few reports of structural studies of eight-membered heterocyclic organophosphorus compounds, which prompted us to undertake the crystal structure determination of 1,3,2-dioxaphosphocin derivatives (Mani Naidu, 1990). The present work on the title compound, (I), forms part of our studies of the structure and conformation of 1,3,2-dioxaphosphocine derivatives. A perspective view of the molecule with the atomic numbering scheme is shown in Fig. 1.



(I)

The bond lengths and angles in this structure have normal values. The P═S bond length of 1.894 (1) Å agrees well with the reported value of 1.894 (1) Å for 6-(4-chlorophenoxy)dibenzo[*d*,*f*][1,3,2]dioxaphosphocine 6-sulfide (Sivakumar, Subramanian, Natarajan, Krishnaiah & Ramamurthy, 1989). The dioxaphosphocine ring adopts a distorted boat conformation. Atoms O(1), C(1), C(12) and C(21) are puckered to the same side of the least-squares plane through the atoms P, O(2), C(10) and C(11) with varying magnitudes. The deviations are 0.896 (2) [O(1)], 0.436 (3) [C(1)], 1.102 (3) [C(12)] and 1.081 (3) Å [C(21)]. The conformation of the dioxaphosphocine ring has been found in all the naphtho-substituted structures reported so far. For example, a similar conformation was observed for 8-(2,3-dimethylphenyl)-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*][1,3,2]dioxaphosphocine 8-oxide (Reddy, 1988). The substitution of sulfur for the phosphoryl oxygen does not appear to have any effect on the molecular conformation. This dioxaphophocine ring with naphtho fusion was not found in any of the canonical conformations described by Evans & Boeyens (1988) for eight-membered ring systems. The sulfur substituent is axial and the phenoxy group is equatorial.