for support of this work. KMP is grateful to the Korea Research Foundation for his post-doctoral fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1001). Services for accessing these data are described at the back of the journal.

References

Autodesk (1993). *HyperChem Computational Chemistry Software*. Autodesk Inc., USA.

Bisson, A. P., Lynch, V. M., Monahan, M.-K. C. & Anslyn, E. V. (1997). *Angew. Chem.* **109**, 2435–2437; *Angew. Chem. Int. Ed. Engl.* **36**, 2340–2342.

Hartshorn, C. M. & Steel, P. J. (1997). *Chem. Commun.* pp. 541–542.

Hoskins, B. F., Robson, R. & Slizys, D. A. (1997). *Angew. Chem.* **109**, 2861–2863; *Angew. Chem. Int. Ed. Engl.* **36**, 2752–2755.

Hou, Z., Stack, T. D. P., Sunderland, C. J. & Raymond, K. N. (1997). *Inorg. Chim. Acta*, **263**, 341–355.

Iverson, D. J., Hunter, G., Blount, J. F., Damewood, J. R. & Mislow, K. (1981). *J. Am. Chem. Soc.* **103**, 6073–6083.

MacNicol, D. D. & Downing, G. A. (1996). *Comprehensive Supramolecular Chemistry*, Vol. 6, edited by D. D. MacNicol, F. Toda & R. Bishop, pp. 421–461. Oxford: Pergamon.

Metzger, A., Lynch, V. M. & Anslyn, E. V. (1997). *Angew. Chem.* **109**, 911–914; *Angew. Chem. Int. Ed. Engl.* **36**, 862–865.

Sheldrick, G. M. (1996). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stack, T. D. P., Hou, Z. & Raymond, K. N. (1993). *J. Am. Chem. Soc.* **115**, 6466–6467.

Walsdorff, C., Saak, W. & Pohl, S. (1996). *J. Chem. Res. (S)*, pp. 282–283; *J. Chem. Res. (M)*, pp. 1601–1618.

Walsdorff, C., Saak, W. & Pohl, S. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1857–1861.

Acta Cryst. (1999). C55, 110–112

2,2′-Biphenyl (cyclohexylamino)phosphonate: a hydrogen-bonded dimer

C. Muthiah and K. C. Kumara Swamy

School of Chemistry, University of Hyderabad, Hyderabad 500 046, AP, India. E-mail: kckssc@uohyd.ernet.in

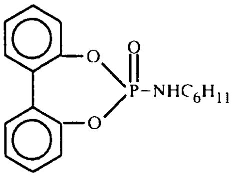
(*Received 2 April 1998; accepted 24 July 1998*)

Abstract

The structure of the title compound, $C_{18}H_{20}NO_3P$, reveals a hydrogen-bonding interaction between the NH group and the phosphoryl-O atom, resulting in a dimer; no interaction of the O atoms of the seven-membered 1,3,2-dioxaphosphepine ring with the NH proton is found.

Comment

We have recently described the structures of the amino phosphorus derivatives $(C_6H_{11}NH)P(OCH_2CMe_2CH_2O)$, (1), $(C_6H_{11}NH)P(OCH_2CMe_2CH_2O)(O_2C_6Cl_4)$, (2), $(C_6H_{11}NH)P[\{O\text{-}({}^tBu)_2C_6H_2\}_2CH_2]$, (3), and $(C_6H_{11}NH)P[\{O\text{-}({}^tBu)_2C_6H_2\}_2CH_2](O_2C_6H_4)$, (4) (Said *et al.*, 1997). Whereas the tricoordinated compounds, (1) and (3), showed hydrogen bonding involving $C_6H_{11}NH$ and an O atom of the six- or eight-membered ring, such a feature was absent in the pentacoordinated compounds, (2) and (4). In connection with this, we were interested in knowing the nature of the hydrogen bonding, if any, in cyclic phosphates bearing a primary amino group such as $C_6H_{11}NH$. Herein we report the results on one such phosphate, the title compound, $(C_6H_{11}NH)PO(2,2'\text{-}OC_6H_4\text{–}C_6H_4O)$, (5). Compound (5), with a tetracoordinated P atom, was also chosen in order to study any conformational changes in the seven-membered ring, compared with tri- or pentacoordinated phosphorus compounds (Said *et al.*, 1997).



(5)

The molecular structure of (5) is shown in Fig. 1. The P—N bond length in (5) [1.609 (2) Å] is shorter than those observed in the tricoordinated aminophosphites (1) (mean 1.656 Å) and (3) [1.635 (3) Å], but is close to that observed for the aminophosphoranes (2) [1.619 (2) Å] and (4) (1.629 Å). The seven-membered phosphepin ring has a ‘row-boat’ conformation similar to several other phosphorus derivatives with this ring (Said *et al.*, 1996, and references therein), with O2 at the prow of the boat. Atoms P1, O1, C7 and C12 form the basal

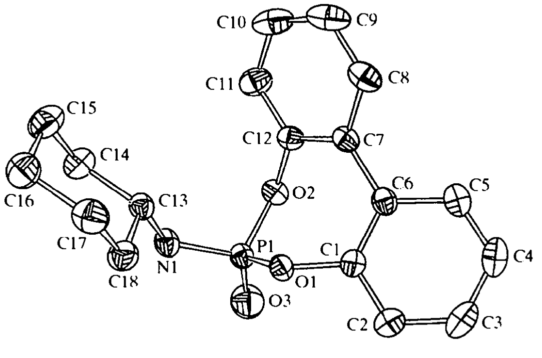


Fig. 1. The molecular structure of (5), with displacement ellipsoids plotted at the 25% probability level. For clarity, only non-H atoms are labelled.

plane, but this plane is more twisted (atoms C7 and C12 are above and below this plane, respectively, by *ca* 0.16 Å) than that in the pentacoordinated derivative, $(2,6\text{-Me}_2C_6H_3O)_3P(2,2'\text{-}OC_6H_4\text{-}C_6H_4O)$ (Burton *et al.*, 1990).

Hydrogen bonding is present in (5). However, instead of the ring-O atom [*cf.* compounds (1) and (3) (Said *et al.*, 1997)], it is the phosphoryl-O atom which is involved in hydrogen bonding, resulting in a dimer [Fig. 2; N1—H···O3(1 − *x*, −*y*, −*z*) 2.942 (3) Å]. This is perhaps logical, because the phosphoryl-O atom can be expected to have more *s*-character. Thus, although both (3) and (5) form dimers leading to the formation of an eight-membered ring (including H atoms) through hydrogen bonding, the types of participating atoms are different.

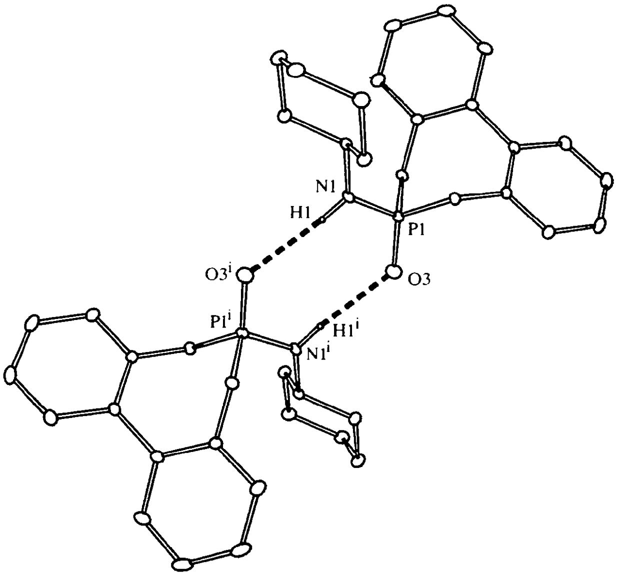


Fig. 2. The hydrogen-bonding interactions in (5) [symmetry code: (i) 1 − *x*, −*y*, −*z*].

Experimental

The title compound was obtained by air-oxidation of the phosphite $(C_6H_{11}NH)P(2,2'\text{-}OC_6H_4\text{-}C_6H_4O)$ (Said *et al.*, 1995). It was crystallized from a dichloromethane–hexane mixture (m.p. 432–434 K). IR: 3200 cm^{-1} [ν(NH)]; ^{1}H NMR (p.p.m.): 0.80–3.20 (*m*, 11H, cyclohexyl protons), 6.80–7.70 (*m*, 8H, aromatic protons); ^{31}P NMR: 11.1 p.p.m.; analysis calculated for $C_{18}H_{20}NO_3P$: C 65.65, H 6.07, N 4.25%; found: C 65.15, H 4.45, N 4.10%. The crystal used for analysis was inserted into a Lindemann capillary.

Crystal data

$C_{18}H_{20}NO_3P$
$M_r = 329.32$
Monoclinic
$P2_1/c$
$a = 11.834\ (2)$ Å
$b = 12.159\ (4)$ Å
$c = 12.438\ (4)$ Å
$\beta = 112.77\ (2)°$
$V = 1650.4\ (8)$ Å^3
$Z = 4$
$D_x = 1.325$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 11–13°$
$\mu = 0.181$ mm^{-1}
$T = 293\ (2)$ K
Block
0.3 × 0.2 × 0.2 mm
White

Data collection

Enraf–Nonius MACH-3 diffractometer
ω scans
Absorption correction: none
3030 measured reflections
2890 independent reflections
2058 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.037$
$\theta_{\max} = 24.97°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 90 min
intensity decay: 2%

Refinement

Refinement on F^2
$R = 0.044$
$wR = 0.148$
$S = 1.08$
2890 reflections
212 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 0.684P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.641$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

P1—O3	1.422 (3)	O2—C12	1.401 (3)
P1—O1	1.602 (2)	C1—C6	1.388 (4)
P1—O2	1.605 (2)	C6—C7	1.476 (4)
P1—N1	1.609 (2)	C7—C12	1.393 (4)
O1—C1	1.413 (3)		
O3—P1—O1	118.9 (1)	C1—O1—P1	121.1 (2)
O3—P1—O2	107.9 (1)	C12—O2—P1	123.6 (2)
O1—P1—O2	101.1 (1)	C6—C1—O1	119.6 (2)
O3—P1—N1	116.2 (1)	C1—C6—C7	122.8 (2)
O1—P1—N1	100.7 (1)	C12—C7—C6	121.8 (2)
O2—P1—N1	111.0 (1)	C7—C12—O2	119.3 (2)

The structure was solved by conventional methods using *SHELXS*97 (Sheldrick, 1990) and refined by full-matrix least-squares methods (*SHELXL*97; Sheldrick, 1997). All non-H atoms were refined anisotropically. All H atoms except the amine-H atom were placed at idealized positions using a riding model; the amine-H atom was located from a difference map and refined isotropically.

Data reduction: *Xtal*3.4 (Hall *et al.*, 1995). Molecular graphics: *ORTEX5j* (McArdle, 1995).

We thank the Council of Scientific and Industrial Research (New Delhi) for funding. We also thank the Department of Science and Technology (New Delhi) for funding the Single Crystal X-ray Diffractometer Facility at the University of Hyderabad.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1092). Services for accessing these data are described at the back of the journal.

References

Burton, S. D., Kumara Swamy, K. C., Holmes, J. M., Day, R. O. & Holmes, R. R. (1990). *J. Am. Chem. Soc.* **112**, 6104–6115.
Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). Editors. *Xtal*3.4 *User's Manual*. University of Western Australia, Australia.
McArdle, P. (1995). *ORTEX5j*. UCG Crystallography Centre, University College Galway, Ireland.
Said, M. A., Kumara Swamy, K. C., Veith, M. & Huch, V. (1995). *J. Chem. Soc. Perkin Trans.* 1, pp. 2945–2951.
Said, M. A., Pülm, M., Herbst-Irmer, R. & Kumara Swamy, K. C. (1996). *J. Am. Chem. Soc.* **118**, 9841–9849.
Said, M. A., Pülm, M., Herbst-Irmer, R. & Kumara Swamy, K. C. (1997). *Inorg. Chem.* **36**, 2044–2051.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Acta Cryst. (1999). C**55**, 112–114

Scalarolide and scalarin, sesterterpenes from Cacospongia and Ircinia sponges

RICHARD C. CAMBIE, CLIFTON E. F. RICKARD, P. STEWART RUTLEDGE AND XIAO-SHUANG YANG

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: c.rickard@auckland.ac.nz

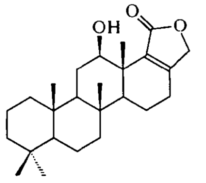
(*Received 2 April 1998; accepted 26 August 1998*)

Abstract

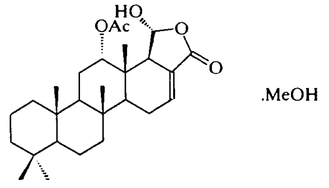
The structures of scalarolide (12β-hydroxyscalar-17-en-24,25-olide) [alternative name (5α,12β)-17a,17-lactone-12-hydroxy-17-(hydroxymethyl)-4,4,8-trimethyl-D-homoandrost-17-ene-17a-carboxylic acid], $C_{25}H_{38}O_3$, from a Cacospongia sponge and scalarin (12α-acetoxy-25α-hydroxyscalar-16-en-25,24-olide) methanol solvate {alternative name [5α,12α,17aβ(*R*)]-γ-lactone-12-(acetyloxy)-17a-(dihydroxymethyl)-4,4,8-trimethyl-D-homoandrost-16-ene-17-carboxylic acid methanol solvate}, $C_{27}H_{40}O_5\cdot CH_4O$, from an Ircinia sponge have been verified.

Comment

Tetracyclic sesterterpenes with a scalarane skeleton occur frequently as metabolites of sponges of the family Thorectidae (order dictyoceratida) (Faulkner, 1997) which includes the genera Cacospongia and Ircinia. Such compounds have biological importance (Rueda *et al.*, 1997) and their investigation has attracted much interest. During an investigation of the dictyoceratida sponges we have examined the constituents of two unnamed sponges of the genera Cacospongia and Ircinia which have yielded the known scalarane sesterpenes scalarolide (Walker *et al.*, 1980) and scalarin (Fattorusso *et al.*, 1972), respectively. The structures and relative stereochemistry of the title compounds (I) and (II) have been verified by X-ray crystallography.



(I)



(II)

Compounds with a scalarane-type skeleton which have been examined by this method previously include the homoscalarane 22-acetoxy-24-methyl-12,24-dioxoscalar-16-en-25-al (Kazlauskas *et al.*, 1980), the bishomoscalaranes (20*S*,24*S*)-20-acetoxy-12β-hydroxy-20,24-dimethyl-25-norscalar-17-ene-18,24-carbolactone (Croft *et al.*, 1983), methyl 12α-acetoxy-20,24-dimethyl-16,24-dioxoscalara-14,17-dien-25-oate (Declercq *et al.*, 1985) and 24-*O*-methyl scalardysin-B (16β-acetoxy-24α-methoxy-20,24-dimethyl-12-oxoscalar-24,25-oxide) (Kitagawa *et al.*, 1989), heteronemin (16β,25α-diacetoxy-12β-hydroxyscalar-17(24)-en-24,25-oxide) (Patil *et al.*, 1991), 12-deacetoxyscalaradial, (scalar-16-en-24,25-dicarboxaldehyde) (De Rosa *et al.*, 1994), scalaradial (Puliti *et al.*, 1995) and 3β,25α-dihydroxy-20,24-dimethylscalar-16-en-24,25-oxide (Jaspers *et al.*, 1997).

The structure determinations verify the chemical composition and relative stereochemistry. The figures show the same absolute stereochemistry as scalarane (Kazlauskas *et al.*, 1980). Both molecules show a skeletal distortion similar to that observed for (20*S*,24*S*)-20-acetoxy-12β-hydroxy-20,24-dimethyl-25-norscalar-17-ene-18,24-carbolactone (Croft *et al.*, 1983) in that the distances between atoms in the sequence C4, C5, C10, C9, C8, C14, C13, C18 tend to be longer than expected (see Tables 1 and 2). In addition, the angles around C5, C9 and C14 tend to be larger than the tetrahedral value. This has been rationalized in terms of non-bonded hydrogen contacts (Croft *et al.*, 1983). Both molecules also show the bend in the molecular skeleton as found for scalaradial which has been ascribed to interactions between the axial methyl groups (Puliti *et al.*, 1995). An indication of the degree of bending is given by the angle between the mean planes of the *A* and *C* rings, 26.4 (2) and 30.4 (1)° for scalarolide (I) and scalarin (II), respectively.