

Cyclohexylammonium 2'-hydroxy-2-biphenyl phosphonate

K. C. Kumara Swamy* and Musa A. Said

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

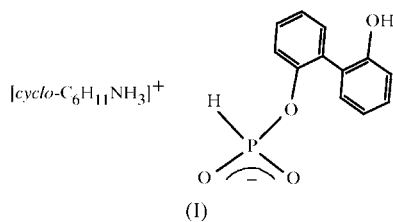
Received 22 November 2000

Accepted 16 January 2001

In the molecular structure of the title compound, $C_6H_{14}N^+ \cdot C_{12}H_{10}O_4P^-$, three O atoms are bonded to phosphorus. The oxygen connected to the biphenoxy residue is not involved in hydrogen bonding; of the other two, one oxygen is involved in intermolecular hydrogen bonding to an N—H group as well as the O—H group of the biphenoxy residue, while the second oxygen is involved in hydrogen bonding to two N—H groups.

Comment

We have been interested in hydrolytic pathways of cyclic phosphites, phosphates and phosphoranes (Said *et al.*, 1995, 1997; Vijjulatha *et al.*, 1998; Kumara Swamy *et al.*, 1998). In cyclic phosphites of the type $(O-R-O)P(NHR')$ (R as part of a ring), hydrolysis can lead to the cleavage of either the P—N or P—O bond leading to different sets of products. Double hydrolysis can also take place resulting in the cleavage of both the P—N bond and a P—O bond of the ring containing phosphorus. The resulting compound, in this case, will be a phosphonic acid with a P(O)—H moiety formed by the tautomerization of the P—OH bond. The amine liberated during the hydrolysis will form a salt and the present compound, (I) (Fig. 1), is one such compound, prepared by the hydrolysis of the aminophosphite $(2,2'-OC_6H_4-C_6H_4O)P(NHC_6H_{11})$.



The P—O bond distances are normal (Holmes *et al.*, 1992) and the one with the oxygen connected to the 2,2'-biphenoxy residue is the longest, as expected. The P—H distance [1.31 (5) Å] is also in the previously observed range (Vijjulatha *et al.*, 1999; Thompson *et al.*, 1982), but is longer than that observed in compounds with a P(S)H moiety [1.20 (4) Å]

(Potrzebowski *et al.*, 1995). Obviously hydrogen-bonding interactions are present in (I) (Fig. 2). Both O1 and O2, which are bonded to phosphorus, exhibit intermolecular hydrogen-bonding interactions to two H atoms each. Atom O1 is hydrogen bonded to O4 and an NH proton, while O2 is hydrogen bonded to two N—H H atoms from different amino residues. It can be noted that in the pyridinium salt $[C_5H_5NH]^+[PhPO_2(1,2-OC_6H_4OH)]^- \cdot 1,2-C_6H_4(OH)_2$ also,

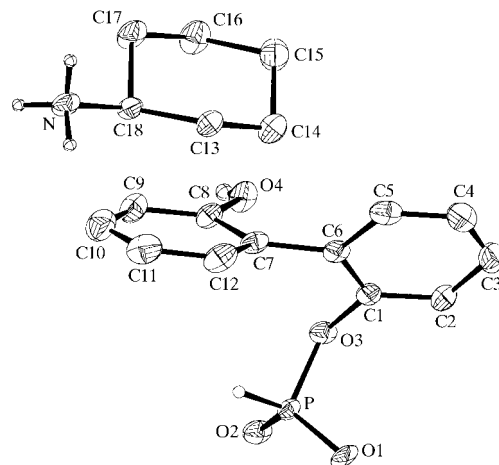


Figure 1

The molecular structure of (I) showing the atom-numbering scheme. All non-H atoms are represented by 25% probability displacement ellipsoids.

both the phosphoryl O atoms are each hydrogen bonded to two other H atoms (Poutasse *et al.*, 1986). The O1...O4 distance [2.717 (7) Å] is close to that found in $(OCH_2-CMe_2CH_2O)P(O)(2,2'-OC_6H_4-C_6H_4OH)$, (II) [2.702 (2) Å; Kumara Swamy *et al.*, 1998]. Another point about the hydrogen bond is related to the angle subtended at O1 and O2

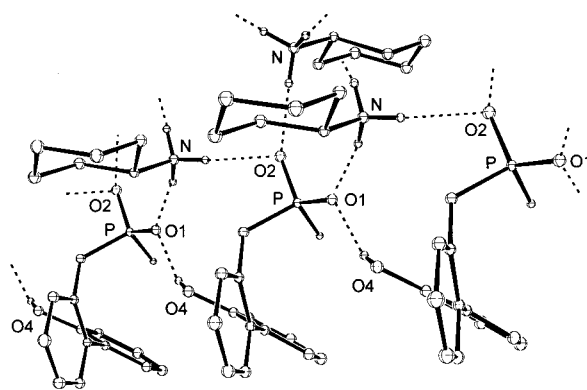


Figure 2

Hydrogen-bonding scheme in (I). For clarity, phosphonate units with symmetry $(x, y, z - 1)$, (x, y, z) and $(x, y, z + 1)$ and cyclohexyl ammonium moieties with symmetry $(\frac{1}{2} - x, y - 1, z - \frac{1}{2})$, $(\frac{1}{2} - x, y - 1, z + \frac{1}{2})$ and $(x - \frac{1}{2}, y - 1, z)$ only are shown.

with the two hydrogen-bonded partners $[N \cdots O1 \cdots O4$ 80 and $N \cdots O2 \cdots N$ 100.2°], which shows a difference of nearly 20°. Such a feature might be of some interest in connection with the charge-density distribution at the acceptor atoms.

Experimental

Water (3 ml) was added directly to (OC₆H₄-C₆H₄O)P(NHC₆H₁₁) (1.30 g, 4.15 mmol) to give the title compound. Needle-shaped crystals grew over a period of 3 d from the aqueous solution [yield 1.35 g (93%), m.p. 453 K]. Analysis calculated for C₁₈H₂₄NO₄P: C 61.89, H 6.88, N 4.01%; found: C 62.18, H 7.05, N 4.09%. IR (cm⁻¹): 2391 (P-H). ¹H NMR (DMSO-*d*₆): 1.00–2.00 (*m*, 10H, cyclohexyl-CH₂), 2.85 (*m*, NCH), 3.10–4.20 (*br*, 1H, OH), 6.82 [*d*, ¹J(P-H) = 606 Hz, PH], 6.70–7.40 (*m*, 8H, Ar-H), 8.10 (*s*, 3H, cyclohexyl-NH₃⁺) p.p.m. ¹³C NMR: 23.8, 24.6, 30.2, 49.1, 115.8, 116.9, 118.6, 121.2, 122.2, 125.9, 127.8, 128.0, 128.2, 131.1, 131.4, 137.6, 154.5, 154.8 p.p.m. ³¹P NMR: 2.98 p.p.m.

Crystal data

C₆H₁₄N⁺·C₁₂H₁₀O₄P⁻
M_r = 349.35
 Orthorhombic, *Pca*2₁
a = 30.992 (7) Å
b = 8.613 (4) Å
c = 6.721 (7) Å
V = 1794 (2) Å³
Z = 4
D_x = 1.293 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 9.5–12.0°
 μ = 0.174 mm⁻¹
T = 293 (2) K
 Needles, colourless
 0.30 × 0.20 × 0.20 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 Profile data from ω scans
 1706 measured reflections
 1705 independent reflections
 1309 reflections with *I* > 2 σ (*I*)
R_{int} = 0.006

θ_{\max} = 25.01°
h = 0 → 36
k = 0 → 10
l = 0 → 7
 3 standard reflections
 frequency: 90 min
 intensity decay: none

Table 1

Selected geometric parameters (Å, °).

P–O1	1.482 (5)	P–O3	1.592 (5)
P–O2	1.473 (5)		
O2–P–O1	119.9 (3)	O1–P–O3	110.5 (3)
O2–P–O3	103.9 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N–HC...O1 ⁱ	0.89	1.94	2.811 (8)	167
N–HB...O2 ⁱⁱ	0.89	2.03	2.920 (8)	175
N–HA...O2 ⁱⁱⁱ	0.89	1.89	2.775 (7)	176
O4–HO4...O1 ^{iv}	0.74 (13)	1.98 (13)	2.717 (7)	175 (15)

Symmetry codes: (i) $\frac{1}{2} - x, 1 + y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, 1 + y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, 1 - y, z$; (iv) *x, y, z* - 1.

Refinement

Refinement on *F*²
R(*F*) = 0.054
wR(*F*²) = 0.177
S = 1.137
 1705 reflections
 226 parameters
 H atoms: see text

$w = 1/[\sigma^2(F_o^2) + (0.0925P)^2 + 1.9000P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

H atoms were placed geometrically and refined using a riding model, with C–H and N–H constrained to 0.93 and 0.89 Å and *U*_{iso}(H) values of 1.2*U*_{eq}(C) and 1.5*U*_{eq}(N), respectively. The H atoms connected to the P and O4 atoms were picked up by a difference map and were refined isotropically.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *Structure Determination Package* (Frenz, 1985); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX6a* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

Funding for this work was provided by the Council of Scientific and Industrial Research, New Delhi, India.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1128). Services for accessing these data are described at the back of the journal.

References

- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Frenz, B. A. (1985). *Structure Determination Package*. Texas A & M University, College Station, Texas, and Enraf-Nonius, Delft, The Netherlands.
- Holmes, R. R., Day, R. O., Yoshida, Y. & Holmes, J. M. (1992). *J. Am. Chem. Soc.* **114**, 1771–1778.
- Kumara Swamy, K. C., Said, M. A., Kumara Swamy, S., Herbst-Irmer, R. & Puelm, M. (1998). *Polyhedron*, **17**, 3643–3648.
- McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
- Potrzebowski, M., Vereshchagina, J., Michalski, J., Wiczorek, M. W. & Majzner, W. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3683–3690.
- Poutasse, C. A., Day, R. O. & Holmes, R. R. (1986). *J. Am. Chem. Soc.* **106**, 3814–3820.
- Said, M. A., Kumara Swamy, K. C., Veith, M. & Huch, V. (1995). *J. Chem. Soc. Perkin Trans. 1*, pp. 2945–2951.
- Said, M. A., Puelm, M., Herbst-Irmer, R. & Kumara Swamy, K. C. (1997). *Inorg. Chem.* **36**, 2044–2051.
- Sheldrick, G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Thompson, M. L., Haltiwanger, R. C., Tarassoli, A., Coons, D. E. & Norman, A. D. (1982). *Inorg. Chem.* **21**, 1287–1292.
- Vijjulatha, M., Kumara Swamy, K. C., Vittal, J. J. & Koh, L. L. (1999). *Polyhedron*, **18**, 2249–2254.
- Vijjulatha, M., Praveen Kumar, K., Kumara Swamy, K. C. & Vittal, J. J. (1998). *Tetrahedron Lett.* **39**, 1819–1822.