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Two phosphate–imidazole complexes with and without a hydrogen-bonded guest molecule

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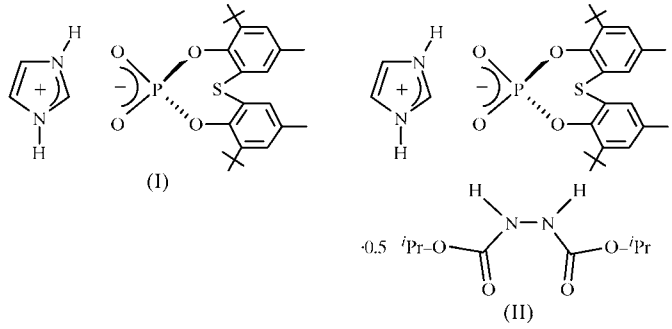
The molecular structures of the complexes imidazolium 6,6′-di-*tert*-butyl-4,4′-dimethyl-2,2′-thiodiphenyl phosphate, $C_3H_5N_2^+\cdot C_{22}H_{28}O_4PS^-$, (I), and imidazolium 6,6′-di-*tert*-butyl-4,4′-dimethyl-2,2′-thiodiphenyl phosphate diisopropyl hydrazodicarboxylate hemisolvate, $C_3H_5N_2^+\cdot C_{22}H_{28}O_4PS^-\cdot 0.5C_8H_{16}N_2O_4$, (II), have been determined. While (I) forms the expected hydrogen-bonded chain utilizing the two imidazole N-bound H atoms, in (II), the substituted hydrazine solvent molecule inserts itself between the chains. Compound (I) exhibits a strong N—H···O hydrogen bond, with an N···O distance of 2.603 (2) Å. The hydrazine solvent molecule in (II) lies about a twofold axis and the N-bound H atoms are involved in bifurcated hydrogen bonds with phosphate O atoms. A C-bound H atom of the imidazolium cation is involved in a C—H···O interaction with a carbonyl O atom of the hydrazine solvent molecule.

Comment

The imidazolium moiety of the hystidine residue plays an important role in the hydrolysis and cyclization of RNA-related biomolecules (Perreault & Anslyn, 1997). In previous reports of the imidazolium salts of diorganophosphates (Holmes *et al.*, 1992; Clark *et al.*, 1984; Blessing & McGandy, 1972), there were no additional guest molecules, except in the salt reported by Kumara Swamy *et al.* (2001). In the latter salt, a hydrogen-bonded methanol molecule, exhibiting C—H···O interactions with the imidazole CH group located between the two N atoms, was included as a guest. We report here the X-ray structures of two imidazolium compounds, *viz.* imidazolium 6,6′-di-*tert*-butyl-4,4′-dimethyl-2,2′-thiodiphenyl phosphate, {[S(6-^{t}Bu-4-Me-$C_6H_2O)_2$]P(O)(O)}($C_3N_2H_5$), (I), and imidazolium 6,6′-di-*tert*-butyl-4,4′-dimethyl-2,2′-thiodiphenyl phosphate diisopropyl hydrazodicarboxylate hemisolvate, {[S(6-^{t}Bu-4-Me-$C_6H_2O)_2$]P(O)(O)}($C_3N_2H_5$){[$(CH_3)_2$-CH]O(O)CN(H)—N(H)C(O)O[$CH(CH_3)_2$]}, (II), the latter containing the carboxylate-substituted hydrazine as a hydrogen-bonded guest. Compounds (I) and (II) were obtained in the reaction of [S(6-^{t}Bu-4-Me-$C_6H_2O)_2$]PCl–{NC(O)O[$CH(CH_3)_2$]N—CO[$CH(CH_3)_2$]O–} with imidazole in the presence of adventitious moisture. Compound (I) was also obtained by a direct route by treating the *in situ* prepared phosphate with imidazole.



The structures of (I) and (II) are shown in Figs. 1(*a*) and 2(*a*), respectively. The P—O bond distances in both compounds (Tables 1 and 3) are in the expected range (Kumara Swamy *et al.*, 2001; Kumaraswamy & Kumara Swamy, 2002). The eight-membered phosphocine ring has a boat–chair conformation. This situation is similar to that in the salts and methanol/ethanol solvates of {[CH_2(6-^{t}Bu-4-Me-$C_6H_2O)_2$]-P(O)(OH)} (Kumara Swamy *et al.*, 2001), but unlike the tub conformation observed by Holmes *et al.* (1992) for the phosphate salt [{S(6-^{t}Bu-4-Me-$C_6H_2O)_2$}P(O)(O)]{[HOC_6H_2-2,4-$(CH_3)_2$-6-CH_2]$_2$N(CH_3)H}, (III) (Chandrasekaran *et al.*, 1999). Perhaps as a consequence, the P···S distances of 3.584 (1) and 3.585 (1) Å in (I) and (II) is close to the sum of the van der Waals radii (3.65 Å), with essentially no P···S interaction. In (III), by contrast, the P···S distance is 3.281 (2) Å. This feature shows that the sulfur donor action in these phosphate salts is case sensitive and could depend on the nature of hydrogen-bonding interactions involving the cation.

In (I), hydrogen bonding (Fig. 1*b* and Table 2) leads to the formation of a chain utilizing the H atoms on the two imidazole N atoms and the two phosphate O atoms. This type of chain appears to be common for the imidazole salts of dior-

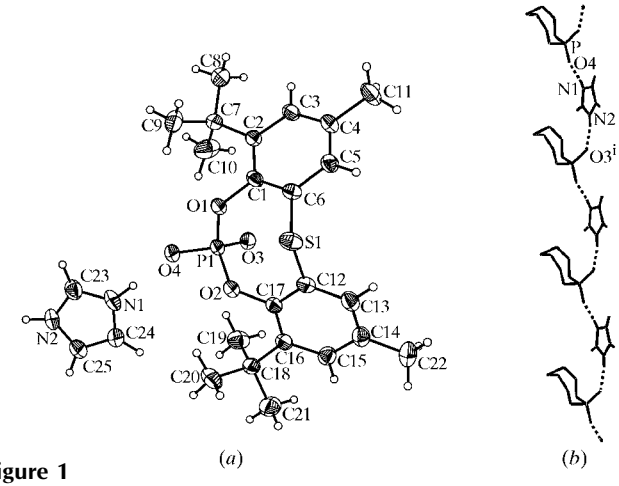


Figure 1
(*a*) The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 35% probability level. (*b*) The hydrogen-bonding scheme; not all the non-H atoms are shown in the chain. [Symmetry code: (i) $x+\frac{1}{2}, y-\frac{1}{2}, z$.]

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ganophosphates (Holmes *et al.*, 1992; Clark *et al.*, 1984; Blessing & McGandy, 1972; Kumara Swamy *et al.*, 2001). The same type of chain is also present in (II), but in addition, one of the phosphoryl O atoms is involved in 'bifurcated' hydrogen bonding, with additional interaction from the N-bound H atoms of the substituted hydrazine residue. These interactions (Table 4) lead to a 'ladder' type of structure, as shown in Fig. 2(*b*). The hydrogen-bond angles involving the phosphoryl O atom in the bifurcated hydrogen bonds in (II) are less linear than that at the corresponding O atom (O3) in (I), as expected. Accordingly, the O···N(imidazolyl) distance in (II) is also shorter than that in (I). We made an attempt to incorporate dimethyl maleate ($MeO_2CCH{=}CHCO_2Me$) in place of the substituted hydrazine, but no insertion took place.

Among the imidazolium salts of diorganophosphates, the N(—H)···O distances in (I) are the shortest; the N2···O3 distance of 2.603 (2) Å is at the lower end of the range for such hydrogen bonds (Kumara Swamy *et al.*, 2001) and hence comes under the category of very strong N—H···O hydrogen bonds. Since such strong hydrogen bonds were also observed by us in the salts of the analogous organophosphate, {[CH_2(6-^{t}Bu-4-Me-$C_6H_2O)_2$]P(O)(OH)} (Kumara Swamy *et al.*, 2001), we conclude that this feature is the result of the 1,3,2-dioxaphosphocine ring present in these compounds.

Although there is no significant interaction of the NCHN H atom with acceptor sites in (I), there is one such interaction in (II), involving the carbonyl O atom of the substituted hydrazine and the NCHN H atom. The C···O distance is short [2.980 (3) Å] and is comparable to that known for strong C—H···O hydrogen bonds (Kumara Swamy *et al.*, 2001; Kariuki *et al.*, 1997); the angle at the H atom, however, is quite far from linearity and the H···O distance is 2.30 Å. This 'non-innocent' behaviour of the imidazole NCHN H atom has been reported previously (Steiner, 1997; Kumara Swamy *et al.*, 2001). Such a feature may have some implications as regards the hydrolysis of RNA, where the hystidine residue comes close to the active phosphorus site, perhaps with the NCHN H atom interacting with the ribosolyl O atom, as pointed out previously by Kumara Swamy *et al.* (2001). This process could 'lock' the imidazole residue until the hydrolysis is complete. Substantiation of this hypothesis would require more structural studies, preferably involving hystidine itself.

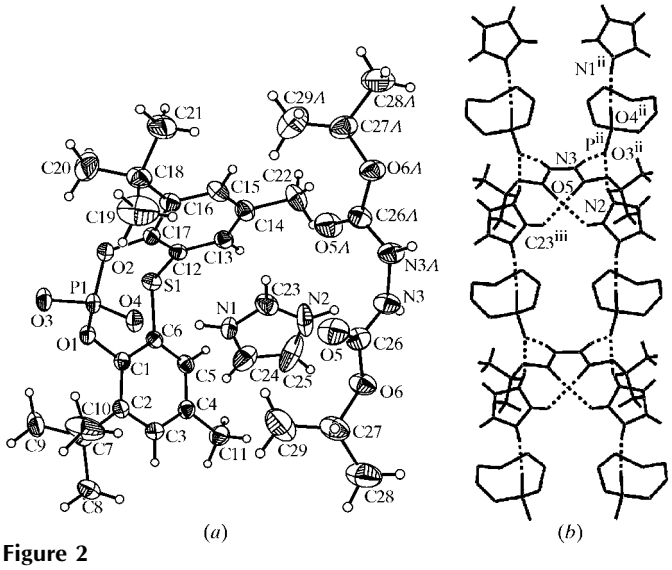

Figure 2
(*a*) The molecular structure of (II), showing the atom-numbering scheme and displacement ellipsoids at the 35% probability level. (*b*) The hydrogen-bonding scheme; not all the non-H atoms are shown in the chain. [Symmetry codes: (ii) $x, y+1, z$; (iii) $-x, y, -z+\frac{1}{2}$.]

Experimental

For the preparation of (I), the phosphate S[(6-^{t}Bu-4-Me-$C_6H_2O)_2$]P(O)OH (m.p. > 523 K; Chandrasekaran *et al.*, 1999) was prepared by a procedure similar to that used to prepare CH_2[(6-^{t}Bu-4-Me-$C_6H_2O)_2$]P(O)OH (Kumara Swamy *et al.*, 2001). The phosphate (0.2 g, 0.4 mmol) was dissolved in chloroform (5 ml) and a solution of imidazole (0.032 g, 0.4 mmol) in chloroform (2 ml) was added slowly, leading to the formation of a clear solution followed by (immediate) crystallization of (I). A small amount (*ca* 5%) of the same compound also crystallized along with (II) (m.p. > 543 K). IR (Nujol mull, cm^{-1}): 3158 (sharp), 1460, 1253. ^{1}H NMR (400 MHz, DMSO-d_6, p.p.m.): 1.35 (*s*, 18H, ^{t}Bu H), 2.19 (*s*, 6H, Ar–CH_3), 7.08, 7.29, 7.46 (*s* each, 6H, Ar–H + imidazole H), 8.71 (*s*, 1H, imidazole H). The signals for imidazole N-bound H atoms were very broad. The solubility was too low for recording a satisfactory ^{13}C NMR spectrum. ^{31}P NMR (160 MHz, DMSO-d_6, p.p.m.): −10.6. For the preparation of (II), diisopropyl azodicarboxylate (0.45 g, 2.2 mmol) was added dropwise at 195 K to a stirred solution of S[(6-^{t}Bu-4-Me-$C_6H_2O)_2$]PCl (0.92 g, 2.2 mmol) in toluene and the contents were stirred overnight. Imidazole (0.15 g, 2.2 mmol) and triethylamine (0.22 g, 2.2 mmol) in toluene (5 ml) were then added. The mixture was stirred for a further 12 h and then filtered, and the solvent was evaporated *in vacuo*. Upon crystallization of the residue from dichloromethane–hexane in air, compound (II) was obtained [0.3 g, 21.4%; a small quantity of (I) also crystallized, which could be separated by hand] [m.p. 464–466 K (charring)]. IR (Nujol mull, cm^{-1}): 3223 (*br*), 3152, 1732, 1711, 1464, 1256. ^{1}H NMR (400 MHz, DMSO-d_6, p.p.m.): 1.15 {*d*, ^3J(HH) = 5.2 Hz, 12H, [$CH(CH_3)_2$]}, 1.34 (*s*, 18H, ^{t}Bu H), 2.18 (*s*, 6H, Ar–CH_3), 2.48 (*s*, 2H, N–H), 4.74 [*m*, 2H, $CH(CH_3)_2$], 7.07 and 7.45 (*s* each, 5H, Ar–H + imidazole H), 8.65 and 8.84 (*s* each, 2H, imidazole H). The signals for imidazole N-bound H atoms were very broad. The solubility was too low for recording a satisfactory ^{13}C NMR spectrum. ^{31}P NMR (160 MHz, DMSO-d_6, p.p.m.): −10.5.

Compound (I)

Crystal data

$C_3H_5N_2^+\cdot C_{22}H_{28}O_4PS^-$
M_r = 488.56
Monoclinic, *Cc*
a = 7.6466 (6) Å
b = 17.0714 (12) Å
c = 19.7596 (14) Å
β = 98.060 (1)°
V = 2553.9 (3) Å^3
Z = 4
D_x = 1.271 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3061 reflections
θ = 2.5–24.6°
μ = 0.22 mm^{-1}
T = 295 (2) K
Needle, colourless
0.44 × 0.30 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.762, T_{max} = 0.953
14692 measured reflections
5940 independent reflections
4683 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 28.3°
$h = -10 \rightarrow 10$
$k = -21 \rightarrow 21$
$l = -26 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.087$
$S = 0.93$
5940 reflections
306 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.032$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), 2760 Friedel pairs
Flack parameter: 0.00 (5)

Table 1
Selected geometric parameters (Å, °) for (I).

P1—O3	1.4687 (16)	P1—O1	1.6077 (15)
P1—O4	1.4688 (15)	P1—O2	1.6112 (16)
O3—P1—O4	120.85 (10)	O3—P1—O2	109.24 (9)
O3—P1—O1	109.38 (9)	O4—P1—O2	105.53 (9)
O4—P1—O1	104.82 (9)	O1—P1—O2	106.03 (9)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O4	0.86	1.77	2.628 (2)	174
N2—H2N···O3^{i}	0.86	1.76	2.603 (2)	167

Symmetry code: (i) $x+\frac{1}{2}, y-\frac{1}{2}, z$.

Compound (II)

Crystal data

$C_3H_5N_2^+\cdot C_{22}H_{28}O_4PS^-\cdot 0.5C_8H_{16}N_2O_4$
$M_r = 590.68$
Monoclinic, $C2/c$
$a = 29.333$ (2) Å
$b = 9.9415$ (7) Å
$c = 23.3483$ (17) Å
$\beta = 112.542$ (1)°
$V = 6288.5$ (8) Å^3
$Z = 8$
$D_x = 1.248$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7692 reflections
$\theta = 2.5$–24.6°
$\mu = 0.20$ mm^{-1}
$T = 295$ (2) K
Needle, colourless
0.44 × 0.30 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.796$, $T_{max} = 0.958$
35617 measured reflections
7424 independent reflections
4746 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 28.3$°
$h = -37 \rightarrow 37$
$k = -13 \rightarrow 13$
$l = -31 \rightarrow 31$

Table 3
Selected geometric parameters (Å, °) for (II).

P1—O3	1.4741 (13)	P1—O2	1.6095 (14)
P1—O4	1.4759 (13)	P1—O1	1.6125 (14)
O3—P1—O4	121.15 (8)	O3—P1—O1	104.86 (7)
O3—P1—O2	105.42 (8)	O4—P1—O1	109.97 (8)
O4—P1—O2	109.41 (7)	O2—P1—O1	104.79 (7)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.135$
$S = 0.95$
7424 reflections
375 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0778P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O4	0.86	1.79	2.630 (2)	166
N2—H2N···O3^{ii}	0.86	1.94	2.753 (2)	158
N3—H3N···O3^{ii}	0.86 (2)	2.01 (2)	2.830 (2)	159 (2)
C23—H23···O5^{iii}	0.93	2.30	2.980 (3)	130

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

The N-bound H atom of the hydrazine residue in (II) was located in a difference Fourier map and refined isotropically. All other H atoms were placed geometrically and refined using a riding model, with C—H distances constrained to 0.98 (methine), 0.96 (CH_3) and 0.93 Å (aromatic), N—H distances constrained to 0.86 Å (imidazole), and U_{iso}(H) values of $1.5U_{eq}$(C) for methyl groups and $1.2U_{eq}$(C,N) otherwise. Compound (I) is not chiral but crystallized in a non-centrosymmetric space group, and hence the absolute configuration for this structure is not relevant.

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL-NT*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1869). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. & McGandy, E. L. (1972). *J. Am. Chem. Soc.* **94**, 4034–4035.
Bruker (2000). *SMART* and *SAINT*. Version 6.22. Bruker AXS Inc., Madison, Wisconsin, USA.
Chandrasekaran, A., Sood, P., Day, R. O. & Holmes, R. R. (1999). *Inorg. Chem.* **38**, 3952–3953.
Clark, J. H., Green, M., Madden, R., Reynolds, C. D. & Dauter, Z. (1984). *J. Am. Chem. Soc.* **106**, 4056–4057.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Holmes, R. R., Day, R. O., Yoshida, Y. & Holmes, J. M. (1992). *J. Am. Chem. Soc.* **114**, 1771–1778.
Kariuki, B. M., Harris, K. D. M., Philp, D. & Robinson, J. M. A. (1997). *J. Am. Chem. Soc.* **119**, 12679–12680.
Kumara Swamy, K. C., Kumaraswamy, S. & Kommana, P. (2001). *J. Am. Chem. Soc.* **123**, 12642–12649.
Kumaraswamy, S. & Kumara Swamy, K. C. (2002). *Polyhedron*, **21**, 1155–1161.
Perreault, D. M. & Anslyn, E. V. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 432–450.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1999). *SHELXTL-NT*. Version 5.10. Bruker AXS Inc., Wisconsin, USA.
Steiner, T. (1997). *Chem. Commun.* pp. 727–734.