# Very Strong C−H···O, N−H···O, and O−H···O Hydrogen Bonds Involving a Cyclic Phosphate

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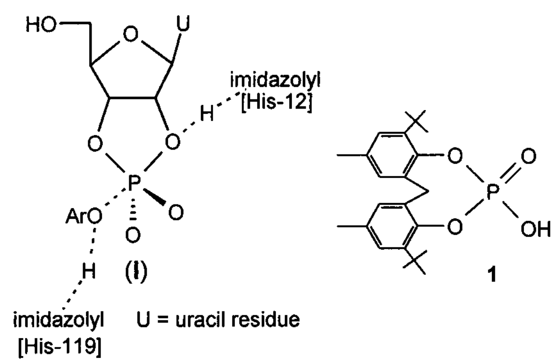
*Received March 19, 2001*

**Abstract:** Very short C−H···O, N−H···O, and O−H···O hydrogen bonds have been generated utilizing the cyclic phosphate [$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$]P(O)OH (**1**). X-ray structures of (i) **1** (unsolvated, two polymorphs), **1**·EtOH, and **1**·MeOH, (ii) [imidazolium]$^+$[$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2PO_2$]$^-$·MeOH [**2**], (iii) [$HNC_5H_4$−N═N−$C_5H_4NH$]$^{2+}$[{$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2PO_2$}$_2$]$^{2-}$.4$CH_3CN$·$H_2O$ [**3**], (v) [K, 18-crown-6]$^+$-[{$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(O)OH}{$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2PO_2$}]$^-$·2THF [**4**], (vi) **1**·cytosine·MeOH [**5**], (vii) **1**·adenine·$^1/_2$MeOH [**6**], and (viii) **1**·*S*-(−)-proline [**7**] have been determined. The phosphate **1** in both its forms is a hydrogen-bonded dimer with a short O−H···O distance of 2.481(2) [triclinic form] or 2.507(3) Å [monoclinic form]. Compound **2** has a helical structure with a very short C−H···O hydrogen bond involving an imidazolyl C−H and methanol in addition to N−H···O hydrogen bonds. A helical motif is also seen in **5**. In **3**, an extremely short N−H···O hydrogen bond [N···O 2.558(4) Å] is observed. Compounds **6** and **7** also exhibit short N−H···O hydrogen bonds. In **1**·EtOH, a 12-membered hydrogen-bonded ring motif, with one of the shortest known O−H···O hydrogen bonds [O···O 2.368(4) Å], is present. **1**·MeOH is a similar dimer with a very short O(−H)···O bond [2.429(3) Å]. In **4**, the deprotonated phosphate (anion) and the parent acid are held together by a hydrogen bond on one side and a coordinate/covalent bond to potassium on the other; the O−H···O bond is symmetrical and very strong [O···O 2.397(3) Å].

## Introduction

Hydrogen bonding in its various facets continues to be a topic of intense scrutiny in both chemistry and biology.[1,2] It has been observed that assistance by (i) charge, (ii) resonance, and (iii) $\sigma-\pi$ cooperation can lead to very short hydrogen bonds in organic systems.[3] Phosphates, by virtue of the strong acceptor as well as donor oxygen centers present in them, can exhibit strong hydrogen bonds;[4] it has been shown recently that the phosphoryl oxygen of triphenylphosphine oxide ($Ph_3P$═O) can also engage itself in or facilitate very short C−H···O hydrogen bonds.[5] Strong hydrogen bonds are also relevant in the context of proton-transfer reactions in chemical and biological systems,[1a] many of which involve a phosphate as a crucial component (e.g. species **I** in the bovine ribonuclease-A-catalyzed cyclization of aryl nucleotides).[2a,6] In the present study, we have chosen the cyclic phosphate $CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(O)OH (**1**) and studied the modes of hydrogen bonding by varying its hydrogen-bonding partners. Compound **1** has two desirable properties:




(i) ready solubility in a variety of solvents and (ii) stability to

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(3) (a) Vishweshwar, P.; Nangia, A.; Lynch, V. M. *Chem. Commun.* **2001**, 179. (b) Currie, M.; Speakman, J. C. *J. Chem. Soc. (A)* **1970**, 1923. (c) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909.

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10.1021/ja010713x CCC: $20.00 
Published on Web 11/21/2001

hydrolysis.[7] Herein we report the observation of very short (very strong) C−H···O, N−H···O, and O−H···O bonds in various types of complexes involving or assisted by the phosphate oxygens of **1**.[8] Specifically, the results include the X-ray structures of (i) [imidazolium]$^+$[$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$-$PO_2$]$^-$·MeOH [**2**], (ii) [4,4′-azopyridinium]$^{2+}$[{$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2PO_2$}$_2$]$^{2-}$·4$CH_3CN$·$H_2O$ [**3**], (iii) **1**·EtOH ,and (iv) [K, 18-crown-6]$^+$[{$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(O)OH}{$CH_2$-(6-*t*-Bu-4-Me-$C_6H_2O)_2PO_2$}]$^-$·2THF [**4**]. For purposes of comparison, we have included the X-ray structures of **1** (two polymorphs), **1**·MeOH, **1**·cytosine·MeOH [**5**], **1**·adenine·$^1/_2$MeOH [**6**], and **1**·*S*-(−)-proline [**7**].[9]

## Results and Discussion

**Synthesis and Spectra.** Compound **1** is prepared by treating the P(III) compound [$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$]PCl with $I_2/H_2O$. The triclinic form is obtained by recrystallization from toluene−heptane (1:1), whereas the monoclinic form is obtained from chloroform−acetonitrile (1:1); the ethanol solvate and the methanol solvate are crystallized from the respective solvents. The imidazole salt **2**, once it crystallizes out, has a very low solubility in common organic solvents. Compound **4** is prepared in a stepwise manner. The 1:1 complex obtained by reacting **1** with KF/18-crown-6 in tetrahydrofuran is treated with a second mole equivalent of **1** to give **4**. Formation of **4** takes place because the liberated HF is a weaker acid than **1**.

In the infrared spectrum of **1**, broad bands at ∼2650 and 2370 $cm^{-1}$ ascribable to the phosphate O−H are observed; upon salt formation as in **2**, in lieu of these bands, new bands appear at 2562 and 1942 $cm^{-1}$ (assignable to the N−H···O modes).[10] Additional bands at 3383 and 3155 $cm^{-1}$ are also observed for **2**; the former can be assigned to the methanolic O−H, since upon drying the crystal and recording the IR spectrum, this band disappeared.[11] The partial loss of solvent from **1**·EtOH, **1**·MeOH, **5**, and **6** hampered the analysis of their IR spectra. In **4**, a strong IR band at 1115 $cm^{-1}$ suggests a shift of the phosphoryl frequency by 87 $cm^{-1}$ from that of the phosphate **1** ($\nu$(PO) 1202 $cm^{-1}$).

**Structures.** Compound **2** [Figure 1, Table 1] exhibits a very strong C(26)−H···O(5) hydrogen bond and the C(26)···O(5) distance [3.090(4) Å] is in the range of exceptionally short C−H···O bonds [cf. Table 2].[1h,5,12] However, the following features distinguishing it from the previously reported examples need to be noted: (i) The acceptor site in **2** is the *methanolic* oxygen and not the *phosphoryl* oxygen and (ii) the donor site is an imidazolyl C−H and not an *acetylene*.[5] As regards the imidazolyl−phosphate structures reported earlier, there had been no mention of C−H···O interactions.[10,13] Hence we reexamined two of these, [$C_3N_2H_5$][$O_2P(OMe)_2$] (**II**)[13a] and [$C_3N_2H_5$][$O_2P$-$(OPh)_2$] (**III**)[10] (both these have a diorganophosphate moiety, as in **1**), for intermolecular contacts;[14] we find that in both **II** and **III**, the imidazolyl carbon that is situated between the two nitrogens is involved in weak but clearly discernible bifurcated C−H···O hydrogen bonding to two oxygens of the same phosphate [C···O (range) 3.231−3.454 Å]. Since **II** and **III** are unsolvated whereas our compound **2** is solvated, we ascribe the strong C−H···O interaction in **2** to the cooperative assistance by the hydrogen-bonded phosphoryl oxygen O(3) [cf. Figure 1b and the discussion on **1**·EtOH]. In conjunction with the recent

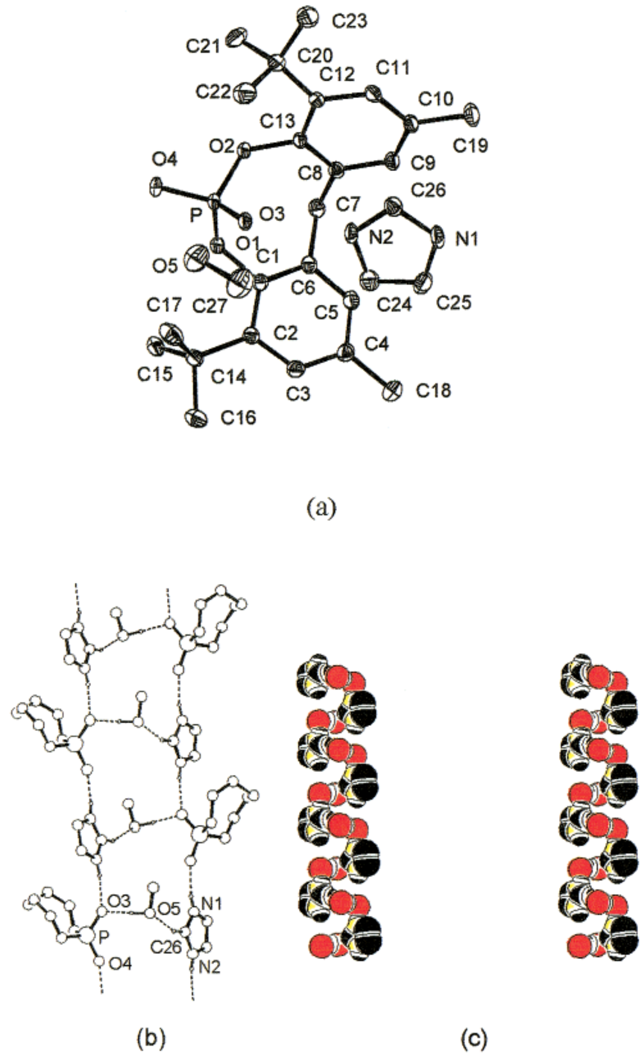


**Figure 1.** (a) An ORTEP drawing of **2** showing the numbering scheme, (b) hydrogen bonding scheme in **2** (only selected atoms shown), and (c) CPK model showing the helical structure in **2** [O(3), O(5), N(1), N(2), C(24)−C(26), and the hydrogen atoms on O(5), N(1), N(2), and C(26) are shown].

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(7) The stable 8-membered-ring system with the sterically protective *t*-Bu groups present in **1** has been utilized by us for synthesizing a variety of penta- and hexacoordinate compounds before: (a) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **1996**, *118*, 9841. (b) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *Inorg. Chem.* **1997**, *36*, 3044. (c) Kumaraswamy, S.; Muthiah, C.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **2000**, *122*, 964.

(8) Since the location of a hydrogen by X-ray diffraction is normally difficult to pinpoint accurately, in this study we prefer to take the C···O, N···O, and O···O distances as the criterion for the shortness of hydrogen bonds.

(9) In addition to these, it is observed that **1** can be obtained in other pseudopolymorphic forms by crystallizing it from $CH_2Cl_2$, DMSO, etc. Details are available with the authors.

(10) Holmes, R. R.; Day, R. O.; Yoshida, Y.; Holmes, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1771.

(11) Assignment of the P═O stretch in **2** could not be made with certainty. There are strong bands at 1228, 1080, and 891 $cm^{-1}$ in **2**, whereas in the phosphate **1**, strong bands at 1202, 1020, and 985 $cm^{-1}$ are observed. In **6**, strong bands at 1206 and 1078 $cm^{-1}$ are observed. The unique imidazolium proton N−C*H*−N in **2** has a $^1$H NMR chemical shift value (8.31 ppm) close to that observed for a 0.108 M (DMSO-$d_6$) solution of [$C_3N_3H_5$][PhP(OH)$O_2$].[10] The very low solubility of **2** did not permit a detailed assessment of the involvement of this C−*H* in C−H···O interactions.

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(14) Atomic coordinates taken from CCDC updated version, April 2001.

**Table 1.** Hydrogen Bond Parameters in **1**−**7**, **1**·MeOH, and **1**·EtOH

| D−H···A | D−H• (Å) | H···A (Å) | D···A (Å) | D−H···A (deg) |
|---|---|---|---|---|
| compd **1** (triclinic form) | | | | |
| O(4)−H(O4)−O(3)[a] | 0.94(3) | 1.54(3) | 2.481(2) | 175(3) |
| compd **1** (monoclinic form) | | | | |
| O(4)−H(O4)−O(3)[a] | 1.20(8) | 1.32(8) | 2.507(3) | 171(7) |
| compd **1**·EtOH | | | | |
| O(4)−H(O4)−O(10) | 1.14(8) | 1.24(7) | 2.368(4) | 167(6) |
| O(7)−H(O7)−O(9) | 1.12(6) | 1.36(6) | 2.467(3) | 169(5) |
| O(9)−H(O9)−O(3) | 0.98(5) | 1.57(5) | 2.541(3) | 170(4) |
| O(8)−H(O8)−O(10) | 1.16(8) | 1.33(8) | 2.484(4) | 171(6) |
| compd **1**·MeOH | | | | |
| O(5)−H(5B)−O(3)[b] | 1.19(4) | 1.32(4) | 2.505(3) | 177(4) |
| O(5)−H(5A)−O(4)[b] | 1.21(4) | 1.22(4) | 2.429(3) | 176(3) |
| O(3)−H(O3)−O(5)[c] | 0.82 | 1.71) | 2.514(3) | 164.8 |
| O(5)−H(O5)−O(4)[c] | 0.82 | 1.97 | 2.433(3) | 115.4 |
| compd **2** | | | | |
| N(2)−H(N2)−O(3) | 0.84(3) | 1.87(3) | 2.679(2) | 161(3) |
| O(5)−H(O5)−O(3) | 1.06(6) | 1.72(6) | 2.778(3) | 177(5) |
| N(1)−H(N1)−O(4) | 0.83(3) | 1.81(3) | 2.633(3) | 169(3) |
| C(26)−H(26)−O(5) | 0.97(3) | 2.17(3) | 3.090(4) | 157(2) |
| compd **3** | | | | |
| N(1)−H(N1)−O(4) | 1.04(5) | 1.52(5) | 2.558(3) | 173(4) |
| C(31)−H(31B)−O(3) | 0.96 | 2.09 | 3.040(8) | 172.2 |
| O(5)−H(O5)−N(4) | 1.10(4) | 1.99(5) | 3.07(2) | 167(3) |
| C(29)−H(29B)−O(3) | 0.96 | 2.33 | 3.263(6) | 164.2 |
| compd **4** | | | | |
| O(8)−H(8)−O(4) | 1.26(8) | 1.14(8) | 2.397(4) | 173(6) |

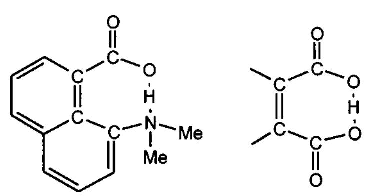
| D−H···A | D−H• (Å) | H···A (Å) | D···A (Å) | D−H···A (deg) |
|---|---|---|---|---|
| compd **5**[c] | | | | |
| N(1)−H(N1)−O(4) | 1.09(9) | 1.64(9) | 2.683(7) | 157(7) |
| N(2)−H(N2)−O(6) | 0.92(6) | 1.87(7) | 2.703(7) | 151(6) |
| N(3)−H(3B)−O(3) | 0.86 | 1.86 | 2.684(8) | 159.8 |
| N(3)−H(3A)−O(5) | 0.86 | 2.02 | 2.845(8) | 160.9 |
| O(6)−H(O6)−O(4)[d] | 0.62(7) | 2.14(2) | 2.742(6) | 167(9) |
| O(6)−H(O6)−O(5)[d] | 0.62(7) | 2.81(7) | 3.054(9) | 108(7) |
| compd **6**[e] | | | | |
| N(1)−H(N1A)−O(5) | 1.11(5) | 1.72(5) | 2.817(6) | 170(3) |
| N(1)−H(N1B)−N(8) (too weak?) | 0.69(5) | 3.04(5) | 3.358(7) | 111(5) |
| N(2)−H(N2)−O(6) | 0.92(6) | 1.70(5) | 2.594(6) | 165(4) |
| N(4)−H(N4)−O(2) | 0.84(4) | 1.86(5) | 2.698(6) | 176(5) |
| N(6)−H(N6B)−O(2) | 0.71(5) | 2.14(5) | 2.849(7) | 172(5) |
| N(6)−H(N6A)−N(3) (too weak?) | 0.75(4) | 2.73(5) | 3.258(7) | 129(5) |
| N(7)−H(N7)−O(3) | 0.80(5) | 1.81(5) | 2.611(6) | 178(5) |
| N(9)−H(N9)−O(5) | 0.84(4) | 1.81(4) | 2.643(6) | 171(4) |
| O(3)−H(O3)−O(7) | 0.82 | 2.03 | 2.691(8) | 137.5 |
| compd **7**[f] | | | | |
| O(11)−H(O11)−O(8) | 1.01(10) | 1.48(10) | 2.488(6) | 179(8) |
| O(9)−H(O9)−O(4) | 1.05(9) | 1.45(9) | 2.483(6) | 165(7) |
| N(1)−H(1AN)−O(10) | 0.80(5) | 2.18(6) | 2.633(7) | 116(5) |
| N(1)−H(1BN)−O(3) | 1.04(6) | 1.60(7) | 2.597(6) | 159(5) |
| N(2)−H(2AN)−O(12) | 1.13(7) | 2.12(7) | 2.656(6) | 106(4) |
| N(2)−H(2BN)−O(7) | 1.04(7) | 1.60(7) | 2.631(6) | 170(5) |

[a] Diagram showing hydrogen bonding in the triclinic form is shown in Figure 6a; labels on the carbon atoms of the eight-membered ring are the same as those for **2** shown in Figure 1. For the monoclinic form also the same labeling is used. [b] Hydrogen-bonded hydrogens located by difference map; H(5A) and H(5B) are assigned only half occupancy each. For labels see Figure 6b. [c] Hydrogen-bonded hydrogens fixed by geometry. For labels see Figure 6c. [d] H(O6) coordinates only refined; the angle O(6)−H(O6)−O(5) of 108° could suggest a forced contact. For labels see Figure 6d. [e] For labels see Figure 6g. [f] For labels see Figure 6h.

**Table 2.** Selected Data from Literature for Some Very Short X−H···O [X = O, N, C] Hydrogen Bonds[a]

| Sl. No. | compound | D−H···A | D−H (Å) | H···A (Å) | D···A (Å) | D−H···A (deg) | ref |
|---|---|---|---|---|---|---|---|
| 1 | [1,8-$C_{10}H_6(NMe_2)H]^+$[1,2-dichlorohydrogen maleate]$^-$(neutron) | O−H···O | 1.149(7) | 1.235(7) | 2.383(4) | 178.5(6) | 20 |
| 2 | $[(H_2N)_2COH]^+$ $[H_2PO_4]^-$ (neutron) | O−H···O | 1.223(6) | 1.207(6) | 2.421(3) | 169.9(4) | 21a |
| | $[(H_2N)_2COH]^+$ $[H_2PO_4]^-$ (X-ray) | O−H···O | 1.25(4) | 1.18(4) | 2.424(2) | 173(4) | 21b |
| 3 | 1,8-$C_{10}H_6(NHMe_2)^+(COO)^-$ (intramolecular)[b] | N−H···O | 1.153 | 1.305 | 2.451 | 171.5 | 18 |
| 4 | 1,2-$C_6H_4(NH)_2C-C_6H_4N-O]^+[H_2PO_4]^-\cdot H_2O$ | N−H···O | 0.87(3) | 1.69(3) | 2.555(2) | 168(3) | 17d |
| 5 | $[HNC_6H_4-C_6H_4N]^+[C_4(O)_2(OH)(O^-)]$ (neutron)[c] | N−H···O | 1.098(45) | 1.509(45) | 2.580(4) | 162.9 | 19a |
| 6 | $[(O_2N)_3CH]_2.O(CH_2CH_2)_2O$ | C−H···O | 0.900 | 2.148 | 2.937(2) | 145.7 | 12c |
| 7 | [1,4-$C_6H_4(C{\equiv}CH)_2$][$OPPh_3$]($H_2O$) | C−H···O | 1.083 | 1.948 | 3.018 | 169.1 | 5a |
| 8 | [$Ph_3SiC{\equiv}CH$][$OPPh_3$] | C−H···O | 1.08 | 1.99−2.05 | 3.02−3.09 | 155−176 | 5b |

[a] Esd's are given at places where this information is available. It should be noted that this table is only representative, but not exhaustive. [b] It is important to note the analogy between this and the maleate system; whereas the maleate system has been talked about at many places, the amino acid zwitterion does not figure in the discussions:




1-dimethylamino-naphthalene -8-carboxylic acid (zwitterion)    hydrogen maleate anion

[c] Triclinic form.

recognition that $C^{\epsilon}$ of the histidine imidazolyl ring is well-suited for hydrogen-bonding interactions,[2i] our finding about the C(26)−H···O(5) interaction in **2** suggests that $C^{\epsilon}$−H···O interactions involving water/alcohol may play at least a supportive role in enzymatic processes [cf. structure **I** also]; in the general base catalysis of RNA or its analogues, similar $C^{\epsilon}$−H···O interactions involving water (or the ribosyl hydroxy group) may be involved [cf. Scheme 1].[15]

An additional point of interest in the structure of **2** is the helical motif directed by hydrogen bonding [Figure 1c].[16] We believe that the presence of doubly hydrogen bonded methanol is responsible for no observation of the alternative zigzag chain. Given the current interest in self-assembled hydrogen-bonded

(15) (a) Perreault, D. M.; Anslyn, E. V. *Angew. Chem., Int. Ed. Engl.* **1998**, *36*, 432. (b) Eftink, M. R.; Biltonen, R. L. *Biochemistry* **1983**, *22*, 5134.

(16) Some leading references in this context: (a) Hirschberg, J. H. K. K.; Brunsveld, L.; Ramzi, A.; Vekemans, J. A. J. M.; Sijbesma, R. P.; Meijer, E. W. *Nature* **2000**, *407*, 168. (b) Norsten, T. B.; McDonald, R.; Branda, N. R. *Chem. Commun.* **1999**, 719. (c) Geib, S. T.; Vicent, C.; Fan, E.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119.

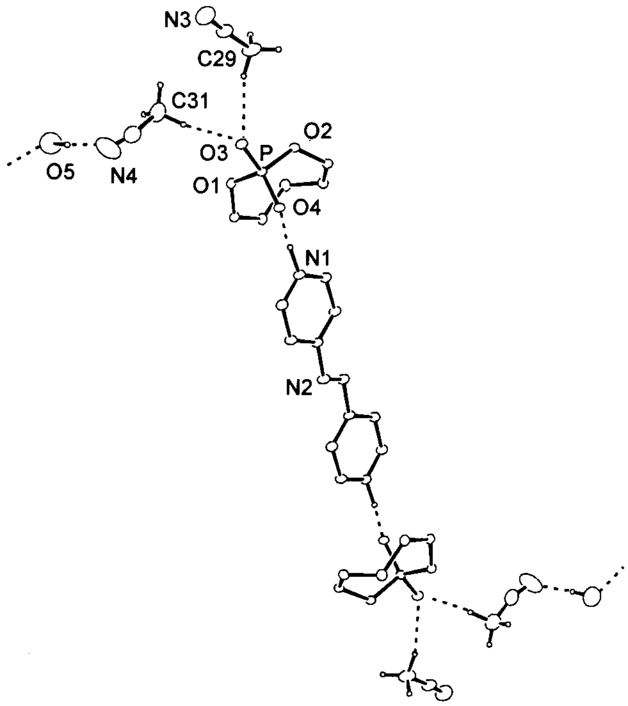
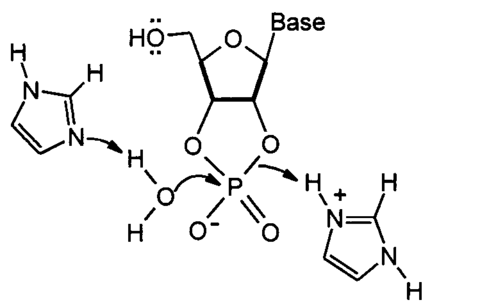



**Figure 2.** Hydrogen bonding scheme in **3** (only selected atoms shown); the phosphate ring is the same as shown in Figure 1a. C(29) and C(31) are methyl carbons of the solvent $CH_3CN$; O(5) is oxygen of the water molecule. N(1) and N(2) are nitrogens of azopyridine. Only one-half of the molecule is labeled.

**Scheme 1**




**Eftink's picture of the bifunctional hydrolysis of an RNA cyclic phosphodiester (modified from ref. 15(a))**

helical structures,[16] it will be worthwhile to carry out a more detailed study on the structural motifs responsible for helicity in **2**, perhaps by varying the phosphate and alcohol.

An extremely short N−H···O (P) hydrogen bond is revealed in the structure of **3** [Figure 2, Table 1]. The N···O distance is *much shorter than that in Emsley's compound* $[C_6H_{11}N_3H_2]^+$-$[H_2PO_4]^-$ [N···O 2.611, 2.661 Å].[4a,17−19] An examination of the structures available in the Cambridge database showed that the N(−H)···O (P) distance in **3** is at the lower end for such hydrogen bonds (cf. Figure 3). These observations are significant

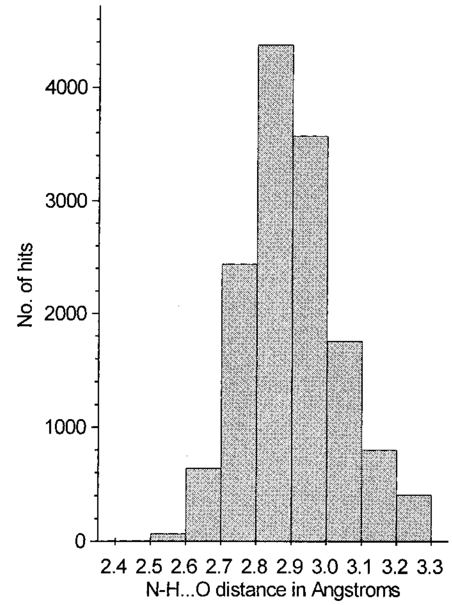



**Figure 3.** A diagram showing the distribution of N(−H)···O distances using the Cambridge database (April 2001). Restrictions imposed: (a) $R < 10\%$, (b) N−H···O angle 150−180°, (c) only organic structures, (d) error-free, and (e) both intra- and intermolecular distances included. Because of these restrictions, this diagram is to be taken only as a guideline to know the general trends.

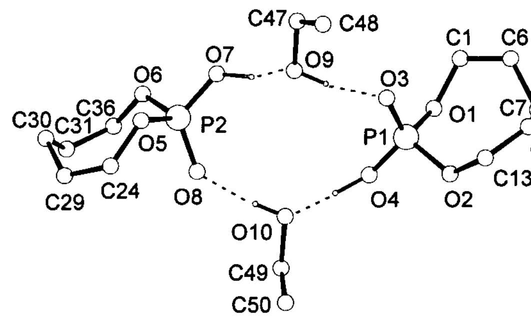



**Figure 4.** Hydrogen bonding scheme in **1**·EtOH (only selected atoms shown); the phosphate rings are the same as shown in Figure 1a.

because (i) Jeffrey and Saenger in their book on hydrogen bonding[1c] note that "unlike the O−H···O bonds, there are no examples of strong N−H···O hydrogen bonds", and (ii) Corbridge's book[4c] gives the observed ranges of N−H···O hydrogen bond lengths as (approximately) 2.60−3.20 Å.

As noted by Emsley et al.,[4a] the formal positive charge on the N−H bond is influential in producing short N−H···O bonds; in addition, the presence of an aromatic residue may further enhance the acceptor capacity of the phosphoryl oxygen in **3**.

Interestingly, the remaining phosphoryl oxygen on each phosphate engages itself in strong bifurcated acceptor[1b] C−H···O hydrogen bonds involving *methyl* hydrogens of the solvent methyl cyanide (cf. Table 1). This feature suggests that even less acidic $C(sp^3)$−H donors can participate in strong C−H···O interactions.

A 12-membered hydrogen-bonded ring motif is present in **1**·EtOH [Figure 4]. The O(4)···O(10) distance of 2.368(4) Å is one of the *shortest* O−H···O *bonds known* [cf. Table 2].[3c,20,21]

(17) Apart from **3**, **6**, and **7** reported in this paper, a short N−H···O (P) hydrogen bond (N···O < 2.600 Å) is present in a few other cases also: (a) Sundaralingam, M.; Haromey, T. P.; Prusiner, P. *Acta Crystallogr. B* **1982**, *38*, 1536. (b) Hoffman, F.; Griehl, C. *J. Mol. Struct.* **1998**, *440*, 113. (c) Ferguson, G.; Glidewell, D. C.; Gregson, R. M.; Meehan, P. R. *Acta Crystallogr. B* **1998**, *54*, 129. (d) Zhang, B.-G.; Liu, Y.-J.; Gou, S.-H.; Duan, C.-Y.; You, X.-Z. *Acta Crystallogr. C* **1999**, *55*, 1929

(18) A short N−H···O hydrogen bond is observed in 8-(*N*,*N*-dimethylamino)naphthalene-1-carboxylic acid; however, it is intramolecular and does not involve a phosphate (cf. Table 2): Schweizer, W. B.; Procter, G.; Kaftory, M.; Dunitz, J. D. *Helv. Chim. Acta* **1978**, *61*, 2783.

(19) In salts containing a protonated 4,4′-bipyridyl unit as the cation and a squarate anion, short N−H···O (C) hydrogen bonds (N···O < 2.600 Å) can be observed. See, for example: (a) Reetz, M.; Höger, S.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 181. (b) MacLean, E. J.; Wheatley, P. S.; Ferguson, G.; Glidewell, C. *Acta Crystallogr. C* **1999**, *55*, 1892.

(20) Mallinson, P. R.; Wozniak, K.; Smith, G. T.; McCormack, K. L. *J. Am. Chem. Soc.* **1997**, *119*, 11502.

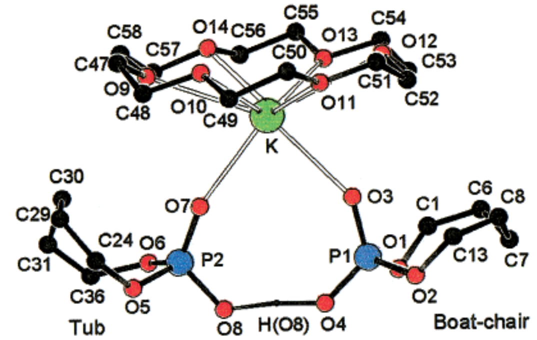



**Figure 5.** A PLATON drawing of **4** showing the overall structure and hydrogen bonding (only selected atoms shown); the phosphate rings are the same as shown in Figure 1a. Selected distances: K−O(3) 2.760(3), K−O(7) 2.673(3), K−O(9) 2.958(4), K−O(10) 3.045(5), K−O(11) 2.894(4), K−O(12) 3.045(4), K−O(13) 2.937(4), K−O(14) 3.157(5), P(1)−O(1) 1.616(3), P(1)−O(2) 1.616(3), P(1)−O(3) 1.473(3), P(1)−O(4) 1.482(3), P(2)−O(5) 1.581(3), P(2)−O(6) 1.593(3), P(2)−O(7) 1.448(3), P(2)−O(8) 1.520(3) Å.

Since there is no charge assistance here, it is possible that in this case a cooperative phenomenon involving the two phosphates and ethanol is operative, resulting in a very short hydrogen bond. It can be noted that the O−H···O distance in **1**·EtOH is ca. 0.12 Å shorter than that in both the polymorphs of unsolvated **1** (Table 1). That a cooperative interaction does exist is also shown by the structure of **1**·MeOH [cf. Table 1 and Figure 6b below], in which again a very short O−H···O distance of 2.429(3) Å is observed.

In compound **4**, the deprotonated phosphate (anion) and the parent acid are held together by a hydrogen bond on one side and a coordinate/covalent bond to potassium on the other [Figure 5]; thus an analogy could be made to monodeprotonated dibasic acids.[1a,c,3c] Based on the P−O distances, we can ascertain that the phosphate at P(1) is deprotonated. The O(8)···O(4) distance [2.397(4) Å] is again among the shortest O−H···O hydrogen bonds known [cf. Table 2].

The eight-membered 1,3,2-dioxaphosphocin ring in unsolvated **1** and in the nondeprotonated phosphate of **4** [the one corresponding to P(2)] has a *tub* conformation whereas the same ring in **1**·MeOH, **1**·EtOH, **2**, **3** and the deprotonated phosphate [the one corresponding to P(1)] in **4** has a *boat-chair* conformation. In the *tub* conformation, one of the Ar−$CH_2$−Ar hydrogens is pretty close to the phosphoryl oxygen of the same ring, suggesting perhaps a weak C−H···O(=P) interaction.[22]

**Brief Comments on the Structures of 5−7.** Diagrams showing the hydrogen bonding in **1**, **1**·MeOH, and **5**−**7** are shown in Figure 6; the structures of **1** and **1**·MeOH have been commented upon above. In **5**, the cytosine base exists as the cytosinium cation with the N(2) site protonated [Figure 6d]. Although the hydrogen-bonded rings are quite different from that in cytosine·$H_3PO_4$,[23] the distances are normal. The most interesting feature is the helical structure mediated by methanol [Figure 6e,f]. As regards the adenine complex **6**, between the two types of phosphates, only one is hydrogen bonded to methanol. Protonation at the adenine occurs at N(2) [and N(7)] of the six-membered ring, which is similar to that in adeninium phosphate, $[C_5H_6N_5]^+[H_2PO_4]^-$.[24] The main point of interest here is the very short N−H···O bonds involving N(2) [or N(7)] of the adenine residue and O(6) [or O(3)] of the phosphate [cf. Table 1]. In the *S*-(−)-proline−phosphate complex **6**, the amino group is protonated by the phosphate and the carboxylic group retains its proton as expected.[25] The O−H···O hydrogen bonds between the carboxylic acid and the phosphate are short, and comparable to that in **1**. The N(1)−H(1BN)···O(3) hydrogen bond involving the phosphate is again in the range of very short hydrogen bonds of this type.

## Summary

We have demonstrated the utility of the phosphate **1** in generating very strong hydrogen bonds, be it N−H···O, O−H···O, or C−H···O; the D(H)···A distances are in the range of the shortest known hydrogen bonds in their respective classes. Additionally, the phosphate assisted strong C−H···O interaction observed in **2** could have ramifications in analyzing biological proton-transfer processes involving histidine residues such as those suggested in structure **I**. Finally, the helical motif shown by **2** (and **5**)[9] as well as polymorphism/pseudopolymorphism exhibited by **1**[9,26] should make the cyclic phosphate **1** a promising substrate for further investigations in hydrogen bonding.

## Experimental Section

Chemicals were procured from Aldrich or from local manufacturers. Solvents were purified according to standard procedures.[27] NMR spectra were recorded on a Bruker 200 MHz spectrometer; chemical shifts are referenced with respect to TMS ($^1$H) or ext. 85% $H_3PO_4$ ($^{31}$P). IR spectra were recorded on a JASCO FT IR-5300 spectrophotometer. Elemental analysis was performed on a Perkin-Elmer 240C CHN analyzer.

**$CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(O)OH (1).** To a stirred solution of $CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2$PCl [mp 157−158 °C (lit.[28] mp 145−147 °C); $^1$H NMR ($CDCl_3$) 1.41 (s, 18 H, *t*-Bu-*H*), 2.32 (s, 6 H, Ar−C*H*$_3$), 3.71 (d, $^2J$ ∼ 15. 0 Hz, 1 H, ArC$H_AH_B$), 4.02 (d, $^2J$ ∼ 15. 0 Hz, 1 H, ArC$H_AH_B$), 7.06, 7.12 (two s, 4 H, Ar−*H*); $^{31}$P NMR ($CDCl_3$) 153.7] (5.0 g, 12.4 mmol) in dichloromethane (20 mL) was added iodine (3.15 g, 12.4 mmol) in small portions and the mixture was stirred at room temperature for 72 h. The solution was washed with 10% aqueous $Na_2S_2O_3$ until the organic layer was colorless. After dichloromethane was removed, the resulting solid (3.75 g) was crystallized from the appropriate solvent [toluene−heptane, $CHCl_3$−acetonitrile, methanol, ethanol, etc.] to afford solvated or unsolvated **1**. Mp (unsolvated **1**) 300 °C dec. IR (KBr, cm$^{-1}$) 2955, ∼2650 (br), 2370 (br), 1439, 1202, 1020, 985. $^1$H NMR 1.40 (s, 18 H, *t*-Bu-*H*), 2.26 (s, 6 H, Ar−C*H*$_3$), 4.04 (br, 2 H, ArC*H*$_2$), 6.96, 7.10 (two s, 4 H, Ar−*H*), 9.40 (br, ca. 1 H, O*H*). $^{31}$P NMR −10.3. Anal. Calcd for $C_{23}H_{31}O_4P$: C, 68.64; H, 7.76. Found: C, 68.56; H, 7.69.

**$[C_3N_2H_5]^+[CH_2$(6-*t*-Bu-4-Me-$C_6H_2O)_2PO_2]^-$·MeOH [2].** To a solution of **1** (0.100 g, 0.25 mmol) in methanol (15 mL) was added imidazole (0.017 g, 0.25 mmol). After effecting dissolution, the solution was left aside for 2 days whereupon **2** (0.073 g) crystallized. Mp 292 °C dec. IR (KBr, cm$^{-1}$): (a) without drying 3383, 3156, 2959, 2562, 1942, 1595, 1447, 1228, 1080; (b) after powdering and drying in vacuo 3148, 2955, 1954, 1593, 1467, 1252, 1082. $^1$H NMR ($CD_3OD$ + $D_2O$): 1.40 (s, 18 H, *t*-Bu-*H*), 2.22 (s, 6 H, Ar−C*H*$_3$), 3.89 (br s, 2 H,

(21) (a) Kostansek, E. C.; Busing, W. R. *Acta Crystallogr. B* **1972**, *28*, 2454. (b) Mootz, D.; Albrand, K.-R. *Acta Crystallogr. B* **1972**, *28*, 2459.

(22) Relevant D−H···A parameters: (a) **1** (triclinic): C(7)−H(7A)···O(3) 0.97, 2.45, 3.235 (3) Å, 138°. (b) **1** (monoclinic): C(7)−H(7B)···O(3) 0.97, 2.32, 3.128 (5) Å, 140°. (c) **4**: C(30)−H(30B)···O(7) 0.97, 2.45, 3.235(6) Å, 137.9°.

(23) Bagieu-Beucher, M. *Acta Crystallogr. C* **1990**, *46*, 238.

(24) Langer, V.; Huml, K.; Zachova, J. *Acta Crystallogr. B* **1979**, *35*, 1148.

(25) (a) Pouchot, M. T. A.; Durif, A.; Guitel, J. C. *Acta Crystallogr. C* **1988**, *44*, 1968. (b) ten Hoeve, W.; Wynberg, H. *J. Org. Chem.* **1985**, *50*, 4508.

(26) (a) Bilton, C.; Howard, J. A. K.; Madhavi, N. N. L.; Nangia, A.; Desiraju, G. R.; Allen, F. H.; Wilson, C. C. *Chem. Commun.* **1999**, 1675. (b) Threlfall, T. L. *Analyst* **1995**, *120*, 2435.

(27) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Organic Chemicals*; Pergamaon, Oxford, 1986.

(28) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 5082.

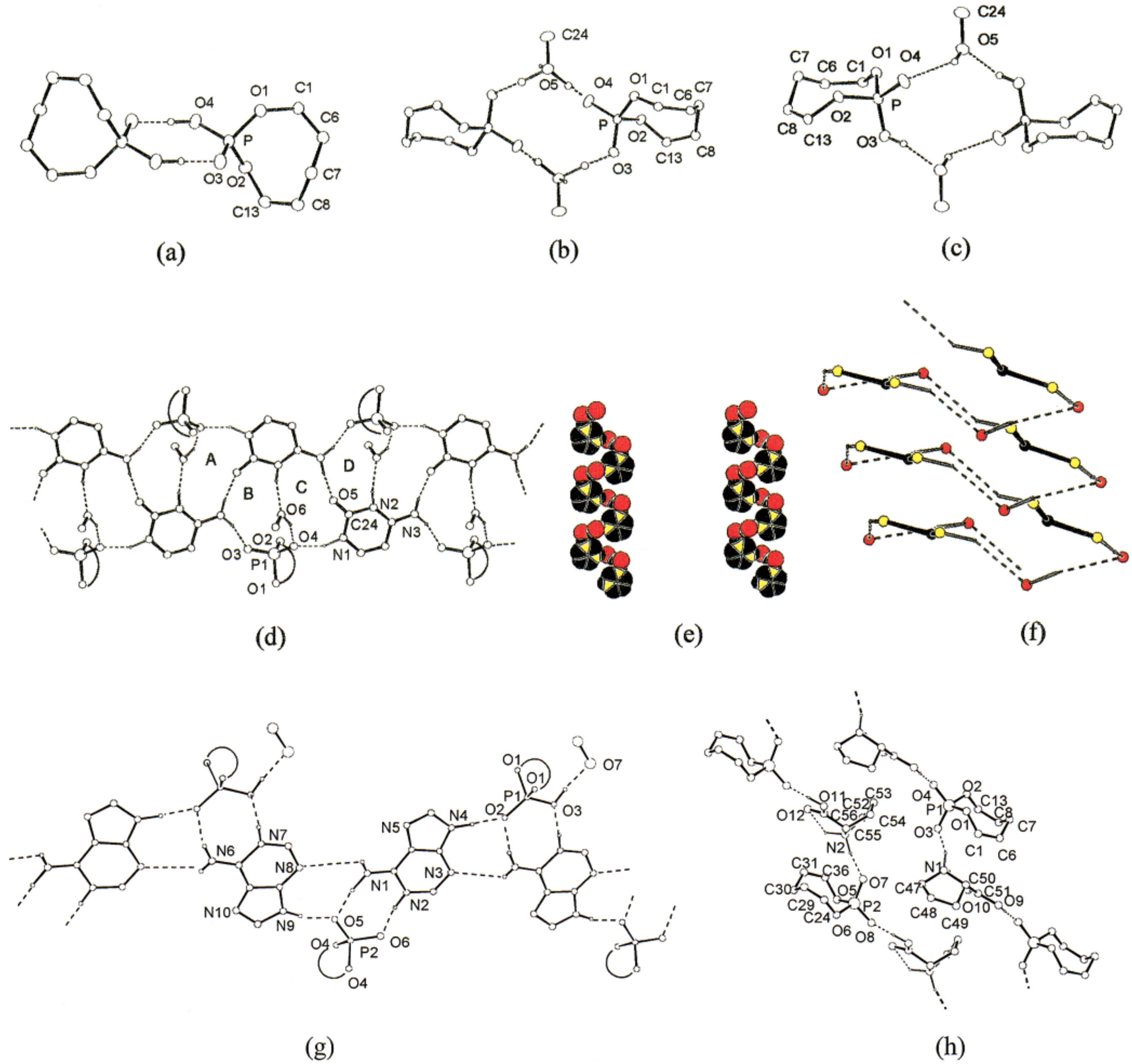



**Figure 6.** Diagrams showing (a) hydrogen bonding in **1** (triclinic form; in the monoclinic form the numbering is the same), (b) hydrogen bonding in **1**·MeOH [hydrogen-bonded hydrogens by difference Fourier], and (c) hydrogen bonding in **1**·MeOH [hydrogen-bonded hydrogens by geometry]. (d) Hydrogen bonding in **5** [O(6)−H···O(5) contact is not shown; the arc represents the eight-membered phosphate ring]. (e and f) Diagrams showing the helical nature in **5**. For clarity only selected atoms that include O(4) of phosphate, O(6) of methanol, and cytosinium ring atoms are shown in part e, whereas atoms O(4), O(6), C(24), N(1), and N(2) are shown in part f. (g) Hydrogen bonding in **6** [the arc represents the eight-membered phosphate ring] and (h) **7**.

ArC*H*$_2$), 6.98, 7.04 (two s, 4 H, Ar−*H*), 7.32 (br s, 2 H, imidazolyl-*H*), 8.31 (br s, 1 H, imidazolyl-*H*). The solubility was too low for recording a satisfactory $^{31}$P NMR spectrum. Anal. Calcd for $C_{26}H_{35}N_2O_4P$ (after drying in vacuo for 2 h): C, 66.37; H, 7.50; N, 5.95. Found: C, 66.42; H, 7.52; N, 5.89.

**[HNC$_5$H$_4$−N═N−C$_5$H$_4$NH]$^{2+}$[{CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$PO$_2$}$_2$]$^{2-}$·4CH$_3$CN·H$_2$O** [**3**]. A mixture of **1** (0.105 g, 0.261 mmol) and 4,4′-azopyridine (0.025 g, 0.136 mmol) in acetonitrile (8 mL) was heated at 50 °C for 10 min in open air and left aside. Dark red crystals (0.090 g) of **3** appeared after 12 h. Even when a higher stoichiometry of azopyridine was used, the same salt was obtained. Mp 220−222 °C dec. IR (KBr, cm$^{-1}$): 3399 (br), 3081, 2957, 2421 (br), 2249, 1900−2000 (br), 1630, 1260, 1063. $^1$H NMR (CDCl$_3$): 1.41 (s, 36 H, *t*-Bu-*H*), 1.98 (s, ca. 12 H, C*H*$_3$CN), 2.25 (s, 12 H, Ar−C*H*$_3$), 4.02 (br s, 4 H, Ar−C*H*$_2$), 6.97, 7.00 (two s, total 8 H, Ar−*H*), 7.89 (d, $J \sim 8.5$ Hz, 4 H, pyridyl-*H*), 8.72 (d, $J \sim 8.5$ Hz, 4 H, pyridyl-*H*), 13.05 (br, ca. 2 H, N*H*$^+$). $^1$H NMR (after powdering and drying in vacuo, CDCl$_3$): 1.45 (s, 36 H, *t*-Bu-*H*), 2.25 (br, 12 H, Ar−C*H*$_3$), 4.00 (br s, 4 H, Ar−C*H*$_2$), 6.90, 7.00 (two s, total 8 H, Ar−*H*), 7.85 (d, $J \sim 8.5$ Hz, 4 H, pyridyl-*H*), 8.70 (br, ca. 2 H, N*H*$^+$), 8.82 (d, $J \sim 8.5$ Hz, 4 H, pyridyl-*H*). $^{31}$P NMR (CDCl$_3$): −11.6. Anal. Calcd for $C_{56}H_{70}N_4O_8P_2$ (after powdering and drying in vacuo): C, 68.00; H, 7.13; N, 5.66. Found: C, 67.93; H, 7.15; N, 5.59.

**1·EtOH** (loses solvent). **1**·EtOH was obtained by crystallization of **1** from ethanol. Mp 300 °C dec (same as **1**). IR (KBr, cm$^{-1}$): 3200 (br), 1600 (br), 1439, 1261, 1215, 1017. $^1$H NMR (CDCl$_3$): 1.25 (t, variable intensity depending on the amount of EtOH lost, OCH$_2$C*H*$_3$), 1.40 (s, 18 H, *t*-Bu-*H*), 2.30 (s, 6 H, Ar−C*H*$_3$), 3.70 (q, variable intensity depending on the amount of EtOH lost, OC*H*$_2$CH$_3$), 4.05 (br, 2 H, Ar−C*H*$_2$), 6.95, 7.05 (two s, 4 H, Ar−*H*), 7.40 (br, ca. 1 H, O*H*). $^{31}$P NMR (CDCl$_3$): −10.8. Anal. Calcd for $C_{23}H_{31}O_4P$ (after powdering and drying in vacuo): C, 68.64; H, 7.76. Found: C, 68.61; H, 7.75.

The compound **1**·MeOH was similarly obtained by crystallization from methanol; the physical data were analogous to **1**·EtOH.

**[K, 18-crown-6]+[{CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$P(O)OH}{CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$ PO$_2$}]$^-$·2THF** [**4**]. To a mixture of 18-crown-6 (0.140 g, 0.53 mmol) and KF (0.042 g, 0.72 mmol) in THF was added **1** (0.200 g, 0.50 mmol). The mixture was stirred overnight, filtered, and left aside. The crystalline mass obtained [0.185 g; phosphate to 18-crown-6 ratio 1:1 by $^1$H NMR; $^{31}$P NMR −10.6] was further treated with **1** (0.106 g, 0.26 mmol) in THF (5 mL) to get a clear solution. Slow evaporation of the solvent gave **4** as rectangular plates (0.186 g). Mp 222 °C. IR (KBr, cm$^{-1}$): 2955, 2890, 1441, 1290, 1115. $^1$H NMR (after powdering and drying in vacuo; CDCl$_3$): 1.47 (s, 36 H, *t*-Bu-*H*), 2.24 (s, 12 H, Ar−C*H*$_3$), 3.21 (s, 24 H, crown-OC*H*$_2$), 4.01 (br s, 4 H, Ar−C*H*$_2$), 6.95 (s, 8 H, Ar−*H*). The presence of THF in the crystals was confirmed separately by $^1$H NMR [multiplets at $\delta$ 1.85 and 3.75]. $^{31}$P NMR: −11.9. Anal. Calcd for $C_{58}H_{85}O_{14}P_2K$ (after powdering and drying in vacuo): C, 62.91; H, 7.74. Found: C, 62.70; H, 7.68.

**1·Cytosine·MeOH** [**5**, loses solvent]. Cytosine (0.028 g, 0.25 mmol) was dissolved in methanol (15 mL) by heating. The solution was cooled to room temperature and **1** (0.100 g, 0.25 mmol) was added. The mixture was swirled without heating to effect dissolution and then left to crystallize. From this, **5** (0.089 g) was obtained. Mp 230 °C dec. IR (KBr, cm$^{-1}$): 3277, 2949, 2800−2900 (br), 1736, 1682, 1650, 1221, 1078. $^1$H NMR (after crushing, DMSO-*d*$_6$): 1.34 (s, 18 H, *t*-Bu-*H*), 2.23 (s, 6 H, Ar−C*H*$_3$), 3.11−3.59 (br, variable intensity, remaining O*H* protons + MeO*H*), 3.87 (s, 2 H, Ar−C*H*$_2$,), 5.82 (d, $^3J$ = 8.0 Hz, 1 H, cytosine−*H*), 6.90, 7.04 (2 s, 4 H, Ar−*H*), 7.59 (s 1 H, $^3J$ = 8.0 Hz, 1 H, cytosine−*H*), 9.00 and 9.30 (two br s, 1 +1 H, N*H*$_2$ (?)). $^{31}$P NMR (DMSO-*d*$_6$): −10.6. Anal. Calcd for $C_{27}H_{36}N_3O_5P$ (after drying in vacuo for 2 h): C, 63.15; H, 7.07; N, 8.18. Found: C, 63.05; H, 6.95; N, 8.08.

**1·Adenine·$^1/_2$MeOH** [**6**, loses solvent]. A procedure similar to that for **5** with 0.25 mmol each of adenine and **1** was used. Yield 0.091 g. Mp 312−320 °C dec. IR (KBr, cm$^{-1}$): 3472, 2400−2800 (br), 1906 (br), 1672, 1186, 1076. $^1$H NMR (after crushing, DMSO-*d*$_6$): 1.34 (s, 18 H, *t*-Bu−*H*), 2.23 (s, 6 H, Ar−C*H*$_3$), 3.90 (s, 2 H, Ar−C*H*$_2$,), 6.94, 7.09 (2 s, 4 H, Ar−*H*), 8.24, 8.28 (2 s, 2 H, purine ring−*H*), 8.53 (br s, 2 H, N*H*$_2$ (?)). There was also a broad peak at 3.00−5.00, probably due to the remaining O*H* and N*H* protons. $^{31}$P NMR (DMSO-*d*$_6$): −10.8. Anal. Calcd for $C_{28}H_{36}N_5O_4P$ (after drying in vacuo for 2 h): C, 62.56; H, 6.75; N, 13.03. Found: C, 62.43; H, 6.67; N, 12.96.

**1·*S*-(−)-Proline** [**7**]. A procedure similar to that for **5** with 0.25 mmol each of *S*-(−)-proline and **1** was used. Yield 0.092 g (71%). Mp 290−292 °C. IR (KBr, cm$^{-1}$): 3181, 2955, 2351 (br), 1923 (br), 1699 (br), 1456, 1206, 1078. $^1$H NMR (DMSO-*d*$_6$): 1.36 (s, 18 H, *t*-Bu-*H*), 1.50−1.96 (m, 4 H, C*H*$_2$), 2.22 (s, 6 H, Ar−C*H*$_3$), 2.54−2.69 (m, 1 H, NC*H*$_A$H$_B$), 2.87−3.02 (m, 1 H, NCH$_A$*H*$_B$), 3.48 (t, $^3J \sim$ 7.0 Hz, 1 H, N−C*H*), 3.82 (br, 2 H, ArC*H*$_2$), 3.80−4.20 (br, O*H* (?)), 3.87 (s, 2 H, Ar−C*H*$_2$,), 6.92, 7.06 (2 s, 4 H, Ar−*H*). $^{31}$P NMR (DMSO-*d*$_6$): −10.7. Anal. Calcd for $C_{28}H_{40}NO_6P$: C, 64.97; H, 7.79; N, 2.71. Found: C, 64.86; H, 7.67; N, 2.38.

X-ray data were collected on an Enraf-Nonius-MACH3 diffractometer at 293 K with Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation; while **1** and **7** were mounted on a glass fiber, others were mounted inside Lindemann capillaries during data collection. Structures were solved and refined with standard methods.[29] In general, non-hydrogen atoms were refined anisotropically; hydrogen atoms were either fixed by geometry by using a riding model or located by difference Fourier maps and refined isotropically. The solvent and some of the *tert*-butyl carbons had relatively higher thermals, as expected. In the case of **1**·MeOH, for the hydrogen-bonded hydrogens, located by a difference map, the best fit was found when they were assigned only half occupancy. Refinement after fixing them by geometry was also done, but it led to a higher *R* value and the O−H···O angle was much less than 180° [cf. Table 1]. For **4**, the disordered THF molecules as well as the high thermals of the crown ether atoms have led to a slightly higher *R* value. In the case of the adenine complex **6**, the six-membered ring of one of the adenine moieties [corresponding to C(30)] is slightly disordered and a residual density of 0.75 e Å$^{-3}$ is observed close to it. The asymmetric unit has two phosphate and two adenine residues in addition to the methanol; non-hydrogen atoms of the two adenines and methanol, the two phosphorus atoms with their phosphoryl oxygens, and the Ar−*C*−Ar carbon lie in a mirror plane. Only the coordinates and not the thermals of the hydrogen-bonded hydrogen atoms were refined. For **7**, attempts were made to solve the structure in the higher symmetry space groups $P2_1/m$ and $P2_1/n$; in the former the structure could not be solved and in the latter the number of systematic absence violations were too many (69) and the refinement could not be done satisfactorily. Only the chiral space group $P2_1$ used here gave satisfactory results; two molecules each of the phosphate and the amino acid are present in the asymmetric unit.

**1** (triclinic form): $C_{23}H_{31}O_4P$, fw 402.45, triclinic, space group $P\bar{1}$, $a$ = 9.345(3) Å, $b$ = 10.092(2) Å, $c$ = 12.695(2) Å, $\alpha$ = 88.11(2)°, $\beta$ = 69.93(2)°, $\gamma$ = 83.13(3)°, $V$ = 1116.4(5) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.197 Mg m$^{-3}$, $\mu$ = 0.148 mm$^{-1}$, $F$(000) = 432, data/restraints/ parameters 3901/0/265. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0403; $wR2$ (all) = 0.1054; GOF = 1.015; max/min residual electron density 0.216/−0.293 eÅ$^{-3}$.

**1** (monoclinic form): $C_{23}H_{31}O_4P$, fw 402.45, monoclinic, space group $P2_1/c$, $a$ = 15.271(3) Å, $b$ = 9.390(2) Å, $c$ = 17.055(3) Å, $\beta$ = 112.80(2)°, $V$ = 2254.6(8) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.186 Mg m$^{-3}$, $\mu$ = 0.146 mm$^{-1}$, $F$(000) = 864, Data/restraints/parameters 3943/0/265. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0571; $wR2$ (all) = 0.1104; GOF = 1.018; max/min residual electron density 0.250/−0.269 eÅ$^{-3}$.

**2**: $C_{27}H_{39}N_2O_5P$, fw 502.57, monoclinic, space group $P2_1/n$, $a$ = 13.323(3) Å, $b$ = 9.806(2) Å, $c$ = 21.147(3) Å, $\beta$ = 92.19(2)°, $V$ = 2760.6(10) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.209 Mg m$^{-3}$, $\mu$ = 0.137 mm$^{-1}$, $F$(000) = 1080; data/restraints/ parameters 4847/0/341. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0419; $wR2$ (all) = 0.1257; GOF = 1.061; max/min residual electron density 0.295/−0.286 eÅ$^{-3}$.

**3**: $C_{32}H_{42}N_4O_{4.5}P$, fw 585.67, monoclinic, space group $C2/c$, $a$ = 23.6647(19) Å, $b$ = 12.624(2) Å, $c$ = 22.149(5) Å, $\beta$ = 95.301(14)°, $V$ = 6588(2) Å$^3$, $Z$ = 8, $\rho_{calcd}$ = 1.181 Mg m$^{-3}$, $\mu$ = 0.125 mm$^{-1}$, $F$(000) = 2504; data/restraints/ parameters 5776/3/398. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0561; $wR2$ (all) = 0.1783; GOF = 1.042; ext. coeff. 0.00101(19); max/min residual electron density 0.298/−0.303eÅ$^{-3}$.

**1**·EtOH: $C_{50}H_{74}O_{10}P_2$, fw 897.03, monoclinic, space group $P2_1/n$, $a$ = 9.617(2) Å, $b$ = 22.944(2) Å, $c$ = 23.369(4), $\beta$ = 99.24(2)°, $V$ = 5089.7(15) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.171 Mg m$^{-3}$, $\mu$ = 0.139 mm$^{-1}$, $F$(000) = 1936; data/restraints/parameters 8959/0/593. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0506; $wR2$ (all) = 0.1518; GOF = 1.034; ext. coeff. 0.00101(19); max/min residual electron density 0.432/−0.382 eÅ$^{-3}$.

**1**·MeOH (hydrogen-bonded hydrogens by difference map): $C_{24}H_{35}O_5P$, fw 434.49, triclinic, space group $P\bar{1}$, $a$ = 8.601(3) Å, $b$ = 12.744(2) Å, $c$ = 13.149(2) Å, $\alpha$ = 107.95(2)°, $\beta$ = 107.20(2)°, $\gamma$ = 103.49(3)°, $V$ = 1223.6(5) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.179 Mg m$^{-3}$, $\mu$ = 0.142 mm$^{-1}$, $F$(000) = 468; data/restraints/parameters 4292/0/292. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0420; $wR2$ (all) = 0.1140; GOF = 1.094; max/min residual electron density 0.277/−0.299 eÅ$^{-3}$.

**4**: $C_{66}H_{101}KO_{16}P_2$, fw 1251.51, monoclinic, space group $P2_1/n$; $a$ = 16.9360(12) Å, $b$ = 19.447(6) Å, $c$ = 22.983(3) Å, $\beta$ = 111.093(9)°, $V$ = 7062(2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.177 Mg m$^{-3}$, $\mu$ = 0.182 mm$^{-1}$, $F$(000) = 2696; data/restraints/parameters: 12400/10/787. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0633; $wR2$ (all) = 0.2030; GOF = 1.012; ext. coeff. 0.00054(15); max/min residual electron density 0.371/−0.346 eÅ$^{-3}$.

**5**: $C_{28}H_{40}N_3O_6P$, fw 545.60, monoclinic, space group $P2_1$, $a$ = 12.219(3) Å, $b$ = 10.395(2) Å, $c$ = 12.940(5) Å, $\beta$ = 109.26(2)°, $V$ = 1551.6(7) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.168 Mg m$^{-3}$, $\mu$ = 0.130 mm$^{-1}$, $F$(000) = 584; data/restraints/parameters 3392/1/364. $R$ indices ($I > 2\sigma$(I)): $R1$ = 0.0592; $wR2$ (all) = 0.1898; GOF = 1.045; absolute structure parameter 0.2(2); ext. coeff. 0.012(7); max/min residual electron density 0.364/−0.217 eÅ$^{-3}$.

**6**: $C_{28.5}H_{38}N_5O_{4.5}P$, fw 553.61, monoclinic, space group $P2_1/m$, $a$ = 13.312(3) Å, $b$ = 14.871(3) Å, $c$ = 14.950(9) Å, $\beta$ = 97.66(3)°, $V$ = 2933(2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.254 Mg m$^{-3}$, $\mu$ = 0.137 mm$^{-1}$, $F$(000) = 1180; data/restraints/parameters 6283/0/423. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0621; $wR2$ (all) = 0.2200; GOF = 1.004; max/min residual electron density 0.753/−0.285 eÅ$^{-3}$.

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**7**: $C_{56}H_{80}N_2O_{12}P_2$, fw 1035.16, monoclinic, space group $P2_1$, $a$ = 14.647(3) Å, $b$ = 10.056(2) Å, $c$ = 19.454(3) Å, $\beta$ = 96.998(10)°, $V$ = 2844.1(10) $Å^3$, $Z$ = 2, $\rho_{calcd}$ = 1.209 Mg $m^{-3}$, $\mu$ = 0.137 $mm^{-1}$, $F(000)$ = 1112; data restraints/parameters 5306/1/689. $R$ indices ($I > 2\sigma(I)$): $R1$ = 0.0434; $wR2$ (all) = 0.1104; GOF = 1.070; absolute structure parameter 0.02(16); max/min residual electron density 0.232/−0.261 $eÅ^{-3}$.

**Acknowledgment.** This work was supported by the Council of Scientific and Industrial Research (CSIR), New Delhi. The National Single Crystal Diffractometer Facility at the University of Hyderabad funded by the Department of Science and Technology (DST), New Delhi, is gratefully acknowledged. Thanks are also due to UGC, India (COSIST and Special Assistance Program) for other instrumental facilities. P.K. thanks CSIR for a fellowship. We thank Ms. G. Padmaja for performing some preliminary experiments.

**Supporting Information Available:** X-ray structure determination and crystal data for **1**, **1**·MeOH, **1**·EtOH and **2**−**7** as CIF files. ORTEP diagrams for **1**, **1**·MeOH, **1**·EtOH, **3**−**7**, and the revised hydrogen bonding scheme in **II** and **III** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA010713X