

Bis(cyclohexylammonium) 4-Nitrophenyl Phosphate Dihydrate,
 $2C_6H_{14}N^+ \cdot C_6H_4NO_6P^{2-} \cdot 2H_2O^*$

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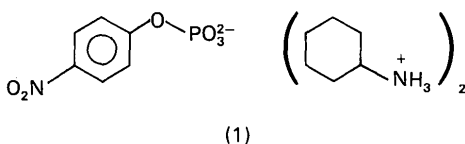
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Abstract. $M_r = 453.48$, triclinic, $P\bar{1}$, $a = 6.584$ (3), $b = 12.138$ (4), $c = 14.965$ (5) Å, $\alpha = 85.80$ (3), $\beta = 87.28$ (4), $\gamma = 81.45$ (3)°, $U = 1178.7$ Å³, $Z = 2$, $F(000) = 488$, $D_x = 1.28$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.16$ mm⁻¹, room temperature, $R = 0.078$, $R_w = 0.060$ for 1953 unique observed reflections. The P–OR bond length, 1.664 (5) Å, is appreciably greater than in alkyl phosphate dianions. A system of hydrogen bonds links the hydrophilic residues in bands parallel to **b** at $z = \frac{1}{2}$.

Introduction. For reasons set out in the previous paper (Jones, Sheldrick, Kirby & Abell, 1984), we are measuring P–O bond lengths in a series of phosphate monoester dianions, $RO-PO_3^{2-}$. This paper describes the structure determination for the 4-nitrophenyl phosphate dianion. The compound is available commercially as the disodium salt, but could not be crystallized satisfactorily in that form. It was therefore converted *via* the free acid to the bis(cyclohexylammonium) salt (1).



Colourless needles of (1) were obtained by evaporation of an aqueous solution.

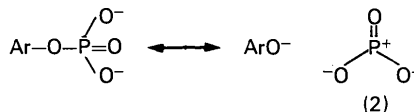
Experimental. D_m not determined. Stoe four-circle diffractometer (monochromated Mo $K\alpha$ radiation). No absorption correction. Crystal $0.6 \times 0.1 \times 0.05$ mm. 4786 profile-fitted intensities (Clegg, 1981) measured to $2\theta_{\max} 45^\circ$. Averaging equivalents gave 3049 unique reflections ($R_{\text{int}} 0.045$), 1953 of which with $F > 4\sigma(F)$ were used for all calculations. Cell constants refined from 2θ values of 32 reflections in the range $20^\circ <$

* Phosphate Ester Dianions. 2. Part I: Jones, Sheldrick, Kirby & Abell (1984).

$2\theta < 24^\circ$. Structure solved by routine direct methods and refined on F to $R 0.078$, $R_w 0.060$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.0003F^2$; all non-H atoms refined anisotropically, H attached to C or N using a riding model with $X-H 0.96$ Å, $H-X-H 109.5^\circ$, $U(H) = 1.2 U(X)$, water H with a common U subject to the restraint that all O–H bonds should be equal within e.s.d. of 0.04 Å]. One water H could not be reliably located. No correction for secondary extinction. Max. $\Delta/\sigma 0.1$. Max. features in a final $\Delta\rho$ map $+0.4$, -0.3 e Å⁻³. All calculations performed with the program system *SHELXTL* (Sheldrick, 1978).

Discussion. Final atomic coordinates are presented in Table 1,† with derived parameters in Table 2. Diagrams of the structure are given in Figs. 1 and 2.

The P–OR bond length [P–O(1) 1.664 (5) Å] in the 4-nitrophenyl phosphate dianion is significantly longer than the corresponding bond in the dianions of alkyl phosphates [mean 1.614 (4) Å] and in bis(cyclohexylammonium) propargyl phosphate (1.626 Å; Jones *et al.*, 1984). Furthermore, the three other P–O bonds show significant shortening [1.495, 1.498, 1.498 (5) Å] compared with 1.514, 1.519, 1.510 Å (mean values for 22 available alkyl phosphate dianion structures; Jones *et al.*, 1984). We take this to be evidence that the P–O bond in this series stretches with increasing electron withdrawal in the R group, as the metaphosphate/substituted phenoxide valence tautomer (2) makes an increasingly important contribution to the ground state.



† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and Table 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39046 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | x | y | z | U_{eq} |
|-------|-----------|----------|-----------|----------|
| OW(1) | 7199 (6) | 5069 (4) | 4199 (3) | 58 (2) |
| OW(2) | 2508 (8) | 2818 (5) | 4318 (4) | 65 (2) |
| P | 7301 (2) | 2230 (1) | 5664 (1) | 33 (1) |
| O(1) | 7639 (5) | 1948 (3) | 6757 (2) | 47 (2) |
| O(2) | 9446 (5) | 1915 (3) | 5294 (2) | 48 (2) |
| O(3) | 6503 (5) | 3452 (3) | 5561 (2) | 42 (1) |
| O(4) | 5804 (5) | 1512 (3) | 5396 (2) | 46 (2) |
| C(11) | 6144 (8) | 1975 (4) | 7424 (4) | 36 (2) |
| C(12) | 4081 (8) | 2374 (4) | 7306 (4) | 42 (2) |
| C(13) | 2710 (8) | 2357 (4) | 8022 (4) | 47 (3) |
| C(14) | 3369 (10) | 1930 (5) | 8840 (4) | 50 (2) |
| C(15) | 5407 (10) | 1532 (5) | 8973 (4) | 65 (3) |
| C(16) | 6773 (9) | 1552 (5) | 8265 (4) | 54 (3) |
| N(1) | 1904 (10) | 1852 (5) | 9607 (4) | 78 (3) |
| O(11) | 2481 (8) | 1335 (5) | 10288 (3) | 128 (3) |
| O(12) | 159 (8) | 2341 (5) | 9507 (3) | 100 (3) |
| C(21) | 7762 (8) | 164 (4) | 3292 (3) | 38 (2) |
| C(22) | 9467 (8) | 864 (5) | 3201 (4) | 50 (3) |
| C(23) | 9782 (9) | 1300 (5) | 2234 (4) | 69 (3) |
| C(24) | 7817 (10) | 1909 (5) | 1862 (4) | 65 (3) |
| C(25) | 6119 (11) | 1206 (6) | 1961 (5) | 77 (3) |
| C(26) | 5780 (8) | 792 (5) | 2930 (4) | 54 (3) |
| N(2) | 7434 (6) | -245 (4) | 4243 (3) | 39 (2) |
| C(31) | 1671 (7) | 5142 (5) | 2672 (3) | 41 (2) |
| C(32) | 3902 (8) | 4793 (5) | 2412 (4) | 54 (3) |
| C(33) | 4208 (9) | 4911 (6) | 1386 (4) | 73 (3) |
| C(34) | 2829 (10) | 4248 (6) | 941 (4) | 71 (3) |
| C(35) | 594 (9) | 4587 (6) | 1217 (4) | 73 (3) |
| C(36) | 279 (9) | 4492 (5) | 2241 (4) | 60 (3) |
| N(3) | 1358 (6) | 5032 (4) | 3670 (3) | 43 (2) |

Table 2. Bond lengths (\AA) and angles ($^\circ$)

| | | | |
|-------------------|------------|-------------------|------------|
| O(1)—P | 1.664 (5) | O(2)—P | 1.498 (4) |
| O(3)—P | 1.498 (5) | O(4)—P | 1.495 (5) |
| C(11)—O(1) | 1.368 (7) | C(11)—C(12) | 1.388 (8) |
| C(11)—C(16) | 1.381 (9) | C(12)—C(13) | 1.369 (9) |
| C(13)—C(14) | 1.358 (9) | C(14)—C(15) | 1.376 (10) |
| C(14)—N(1) | 1.471 (10) | C(15)—C(16) | 1.359 (10) |
| N(1)—O(11) | 1.204 (8) | N(1)—O(12) | 1.222 (9) |
| C(21)—C(22) | 1.501 (9) | C(21)—C(26) | 1.513 (8) |
| C(21)—N(2) | 1.489 (8) | C(22)—C(23) | 1.520 (9) |
| C(23)—C(24) | 1.502 (9) | C(24)—C(25) | 1.499 (11) |
| C(25)—C(26) | 1.517 (10) | C(31)—C(32) | 1.508 (8) |
| C(31)—C(36) | 1.492 (10) | C(31)—N(3) | 1.497 (8) |
| C(32)—C(33) | 1.538 (9) | C(33)—C(34) | 1.506 (11) |
| C(34)—C(35) | 1.514 (10) | C(35)—C(36) | 1.535 (9) |
| O(1)—P—O(2) | 100.9 (3) | O(1)—P—O(3) | 105.4 (3) |
| O(2)—P—O(3) | 114.6 (3) | O(1)—P—O(4) | 107.1 (3) |
| O(2)—P—O(4) | 114.2 (3) | O(3)—P—O(4) | 113.1 (3) |
| P—O(1)—C(11) | 126.9 (4) | O(1)—C(11)—C(12) | 124.6 (6) |
| O(1)—C(11)—C(16) | 116.3 (6) | C(12)—C(11)—C(16) | 119.1 (6) |
| C(11)—C(12)—C(13) | 119.8 (6) | C(12)—C(1)—C(14) | 119.9 (6) |
| C(13)—C(14)—C(15) | 121.4 (7) | C(13)—C(14)—N(1) | 120.7 (7) |
| C(15)—C(14)—N(1) | 117.9 (6) | C(14)—C(15)—C(16) | 118.8 (7) |
| C(11)—C(16)—C(15) | 121.0 (6) | C(14)—N(1)—O(11) | 119.1 (7) |
| C(14)—N(1)—O(12) | 116.7 (6) | O(11)—N(1)—O(12) | 124.2 (7) |
| C(22)—C(21)—C(26) | 111.8 (6) | C(22)—C(21)—N(2) | 110.9 (5) |
| C(26)—C(21)—N(2) | 110.2 (5) | C(21)—C(22)—C(23) | 111.1 (6) |
| C(22)—C(23)—C(24) | 111.4 (6) | C(23)—C(24)—C(25) | 111.8 (6) |
| C(24)—C(25)—C(26) | 111.4 (7) | C(21)—C(26)—C(25) | 110.1 (6) |
| C(32)—C(31)—C(36) | 112.5 (6) | C(32)—C(31)—N(3) | 110.2 (5) |
| C(36)—C(31)—N(3) | 110.1 (5) | C(31)—C(32)—C(33) | 109.8 (5) |
| C(32)—C(33)—C(34) | 110.8 (6) | C(33)—C(34)—C(35) | 111.5 (7) |
| C(34)—C(35)—C(36) | 111.0 (6) | C(31)—C(36)—C(35) | 110.7 (6) |

Table 3 shows P—O bond lengths in the five simple monoester dianions so far measured, listed in order of increasing electronegativity of the ester O atom (as measured by the pK_a of ROH). (No sugar derivatives are included in the table because pK_a 's are not generally available for sugar OH. These will generally fall between those of ethanol and propargyl alcohol; the mean P—OR bond length of 1.614 \AA quoted above for 22 compounds, 20 of them sugar phosphates, also lies between the values for ethyl and propargyl phosphates.) There is a monotonic increase in the length of the P—OR bond with increasing electron withdrawal in the R group. These data fall on or close to a straight line (r 0.929) when the P—OR bond length is plotted against the pK_a of ROH (Jones & Kirby, 1979), but the precision of some of the points is not high, and the fit can be improved greatly by omitting single data points. We are therefore investigating other phosphate ester dianions to explore this relationship further.

The bond-length changes are accompanied by smaller changes in bond angles. The mean CO—P—O angle in (1) is 114.0 $^\circ$, compared with 112.8 $^\circ$ (mean value) for the 22 alkyl phosphates. This is also an expected consequence of an increasing contribution

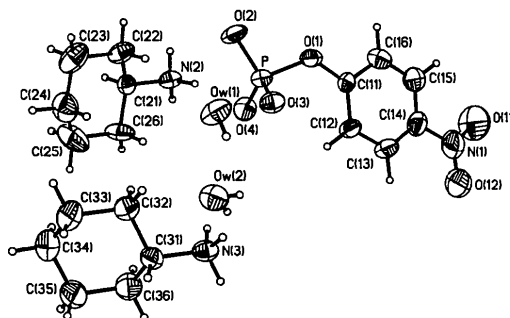


Fig. 1. Thermal-ellipsoid plot of the asymmetric unit, showing the atom-numbering scheme.

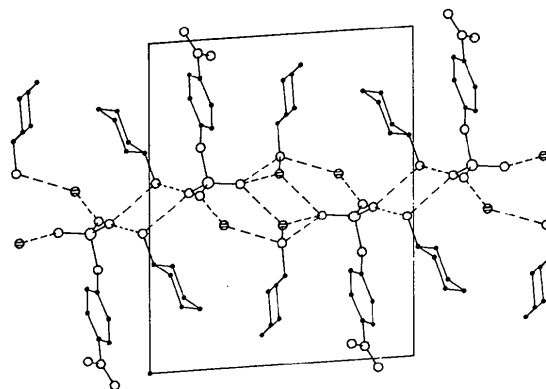
Fig. 2. Projection of the structure along a , showing the hydrophilic and hydrophobic regions around $z = \frac{1}{2}$, 0 respectively. Hydrogen bonds are shown by dashed lines. Shaded circles, water O; open circles, P, N, and other O; filled circles, C. H atoms omitted for clarity.

Table 3. P—O bond lengths (Å) in some simple phosphate monoester dianions ROPO_3^{2-}

| R | Cation | P—OR | Others | Reference |
|---------------|--|-----------|---------------------------------|--------------------------------------|
| Ethyl | K^+ | 1.56 (2) | 1.54 (2), 1.48 (2), 1.55 (2) | McDonald & Cruickshank (1971) |
| Methyl | NH_4^+ | 1.597 (6) | 1.500 (7), 1.525 (7), 1.495 (6) | Garbassi, Giarda & Fagherazzi (1972) |
| Propargyl | $\text{C}_6\text{H}_{11}\text{NH}_3^+$ | 1.626 (4) | 1.510 (4), 1.503 (4), 1.501 (5) | Jones <i>et al.</i> (1984) |
| Phenyl | K^+ | 1.64 (2) | 1.53 (2), 1.51 (2), 1.53 (2) | Caughlan & Mazhar-ul-Haque (1967) |
| 4-Nitrophenyl | $\text{C}_6\text{H}_{11}\text{NH}_3^+$ | 1.664 (5) | 1.498 (4), 1.498 (5), 1.495 (5) | This work |

from (2), since the metaphosphate fragment is likely to be trigonal at P. [Similar coupled bond-length/angle changes have been noted previously in PO_4^{3-} tetrahedra (Murray-Rust, Bürgi & Dunitz (1978, and references therein).] The fact that the three P—O⁻ bond lengths are equal is presumably the result of a symmetrical pattern of hydrogen bonding, though the lengths of the shorter P—O bonds of (1) are expected to be less sensitive to environment than those of alkyl phosphate dianions. Details of the hydrogen-bonding network, which links hydrophilic residues in bands parallel to **b**, are given in Table 4 (deposited) and Fig. 2.

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Gas–Crystal Photoreaction: the Structures of 4,4'-Dimethoxy(thiobenzophenone) (I), $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$, and 4,4'-Bis(dimethylamino)thiobenzophenone (II), $\text{C}_{17}\text{H}_{20}\text{N}_2\text{S}$

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Abstract. (I): $M_r = 258.34$, triclinic, $P\bar{1}$, $a = 9.810$ (3), $b = 9.635$ (3), $c = 15.015$ (4) Å, $\alpha = 79.11$ (2), $\beta = 102.38$ (3), $\gamma = 107.76$ (3)°, $V = 1308.5$ Å³, $Z = 4$, $D_m = 1.318$ (3) (by flotation in KI solution), $D_x = 1.311$ g cm⁻³, $\text{Cu } K\alpha$, $\lambda = 1.5418$ Å, $\mu = 20.05$ cm⁻¹, $F(000) = 544$, $T = 293$ K, $R = 0.074$ for 2663 reflections. (II): $M_r = 284.43$, monoclinic, $P2_1/c$, $a = 17.029$ (5), $b = 6.706$ (5), $c = 14.629$ (4), $\beta = 113.55$ (2)°, $V = 1531.4$ Å³, $Z = 4$, $D_m = 1.230$ (5) (by flotation in KI solution), $D_x = 1.234$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.7107$ Å, $\mu = 1.63$ cm⁻¹, $F(000) = 608$, $T = 293$ K, $R = 0.062$ for 855 reflections. The orientation of the C=S chromophores in the crystal lattice and their reactivity in the crystalline state are discussed. The C=S bonds are much shorter than the normal bond length [1.605 (4) (I), 1.665 (8) Å (II) *cf.* 1.71 Å].

Introduction. The basic difference between solution and solid-state reactivity is that, while the former is crucially dependent on the electronic properties of the reactants, reactivity in crystals depends to a large extent on the packing factors. Thioketones in general are readily oxidized in solution to the corresponding S oxides and/or ketones (Ramnath, Ramesh & Ramamurthy, 1983) and the rate and product distribution of oxidation are controlled by their inherent electronic and steric properties. However, among a large number of diaryl thioketones investigated for their reactivity in the crystalline state only a few underwent photo-oxidation (Arjunan, Ramamurthy & Venkatesan, 1984). It is therefore of interest to examine the molecular packing of these compounds and explore the factors that control their reactivity in the crystalline media. X-ray results