the presence of the aromatic ring. It is noteworthy that this paper reports the first type B photochemical conversion observed in solution for substituted tetrahydronaphthoquinols.

To summarize, reactions in solution, where molecular conformational equilibrium is facile, are governed chiefly by kinetics, whereas the solid-state reactions are topochemically controlled. The lowest-energy conformation (in which it is most likely to crystallize) is one which predisposes the molecules to a specific reaction in the solid state.

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Structure of Tetramethylammonium Dihydrogenorthophosphate Monohydrate

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Abstract. $N(CH_3)_4H_2PO_4.H_2O$, $M_r = 189.15$, monoclinic, $P2_1/c$, $a = 8.518$ (1), $b = 12.897$ (2), $c = 8.440$ (2) Å, $\beta = 99.05$ (1)°, $V = 915.6$ Å^3, $Z = 4$, $D_m = 1.36$ (1), $D_x = 1.372$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu(Mo\,K\alpha) = 0.2745$ mm^{-1}, $F(000) = 408$, $T = 296$ (1) K, final $R = 0.037$ for 2023 unique reflections. PO$_4$ tetrahedra are connected to each other along the c axis by H bonds [O$\cdots$O 2.543 (2) and 2.606 (2) Å, O—H$\cdots$O 171.1 (8) and 175.6 (8)°]; other H bonds [O$\cdots$O 2.809 (2) and 2.875 (2) Å, O—H$\cdots$O 167.7 (8) and 167.5 (8)°] between adjacent H$_2$PO$_4^-$ chains are formed with water molecules. Consequently a two-dimensional network of H bonds is constructed.

Introduction. In the crystal structures of alkali and ammonium dihydrogen orthophosphates, the type of hydrogen bonding between adjacent H$_2$PO$_4^-$ groups differs with varying ionic radii of cations: *i.e.* a three-dimensionally connected framework of H$_2$PO$_4^-$ groups for Rb or smaller cations (Haussühl, 1964;

Tenzer, Frazer & Pepinsky, 1958; Bacon & Pease, 1953; Choudhary, Nelmes & Rouse, 1981; Catti & Ivaldi, 1977), and a two-dimensional network for Cs or Tl ions (Nelmes & Choudhary, 1978, 1981).

We report here the crystal structure of tetramethylammonium dihydrogenorthophosphate monohydrate (hereafter abbreviated as TMADP.H$_2$O), which contains bulky univalent tetramethylammonium ions.

Experimental. Preparation of the crystal: A solution of orthophosphoric acid was added to a solution of tetramethylammonium hydroxide and pH adjusted to 4.5. The mixed solution was concentrated to grow polycrystals of TMADP.H$_2$O. Single crystals were grown in a refrigerator by slow evaporation of aqueous solutions of the polycrystals. D_m measured by flotation in $(C_2H_5)_2O/CHCl_3$. Colourless ellipsoidal crystal $0.43 \times 0.60 \times 0.61$ mm. X-ray measurements made with Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters and orientation matrix by least-squares

refinement for 23 reflections, $9.68 < \theta < 12.50°$. Total of 3051 reflections measured with ω–2θ scanning for θ 2 to 30°, up to $(\sin\theta/\lambda)_{max} = 0.7024$ Å^{-1} ($-11 \le h \le 11$, $0 \le k \le 18$, $0 \le l \le 11$); correction for Lorentz–polarization and no absorption correction; intensities of three standard reflections (322, 440, 015) monitored 37 times during data collection, intensity variation not significant; 2940 unique reflections ($R_{int} = 0.012$ with 766 reflections $[I < 3\sigma(I)]$ considered unobserved; systematic absences 0k0, k = odd and h0l, l = odd uniquely consistent with $P2_1/c$. Positions of PO$_4$ groups and N and C atoms obtained from Patterson synthesis and Fourier synthesis; H atoms from difference Fourier synthesis refined isotropically; final full-matrix least-squares refinement on F included positional parameters for all atoms, anisotropic thermal parameters for all non-H atoms and isotropic ones for all H atoms; fixed isotropic thermal parameters ($B_{iso} = 4.0$ Å^2) for H atoms in tetramethylammonium group; final refinement with 2023 reflections corresponding to $F_o > 3\sigma_F$; final $R = 0.037$, $wR = 0.037$ $\{w = 4F_o^2/[\sigma(F_o)^2]^2\}$, $S = 5.34$; $(\Delta/\sigma)_{max}$ in final least-squares cycle 0.03; final difference Fourier height maximum 0.237 and minimum 0.077 e Å^{-3}; refined secondary-extinction value $g = 5.2 \times 10^{-6}$.* Atomic

* $|F_c| = |F_o| (1 + gI_c)$ (Stout & Jensen, 1968).

Table 1. *Final atomic coordinates and equivalent isotropic or isotropic thermal parameters (Å^2) with e.s.d.'s in parentheses*

	x	y	z	B_{eq} or B_{iso}*
P	0.16769 (5)	0.27867 (3)	0.55145 (5)	2.579 (7)
O(1)	0.2460 (2)	0.3440 (1)	0.6883 (1)	3.39 (2)
O(2)	0.0740 (2)	0.3356 (1)	0.4134 (1)	3.74 (3)
O(3)	0.2987 (2)	0.2122 (1)	0.4886 (2)	4.69 (3)
O(4)	0.0525 (2)	0.2001 (1)	0.6145 (2)	4.83 (3)
O(5)	0.2228 (2)	0.5649 (1)	0.6453 (2)	4.41 (3)
N	0.2898 (2)	0.5815 (1)	0.2056 (2)	2.88 (3)
C(1)	0.1196 (2)	0.5608 (2)	0.2148 (2)	3.94 (4)
C(2)	0.3874 (3)	0.4954 (2)	0.2858 (3)	4.82 (5)
C(3)	0.3120 (3)	0.5867 (2)	0.0349 (3)	5.41 (5)
C(4)	0.3373 (3)	0.6799 (2)	0.2890 (4)	6.47 (6)
H(1)	0.281 (3)	0.199 (2)	0.399 (3)	5.4 (5)
H(2)	0.069 (3)	0.190 (2)	0.709 (3)	5.7 (6)
H(3)	0.133 (2)	0.585 (2)	0.623 (2)	4.3 (5)
H(4)	0.215 (3)	0.512 (2)	0.658 (3)	6.0 (6)
H(5)	0.110 (2)	0.556 (2)	0.327 (2)	4.0
H(6)	0.061 (2)	0.611 (2)	0.164 (2)	4.0
H(7)	0.096 (2)	0.499 (2)	0.157 (2)	4.0
H(8)	0.490 (2)	0.509 (2)	0.281 (2)	4.0
H(9)	0.370 (2)	0.492 (2)	0.393 (2)	4.0
H(10)	0.363 (2)	0.435 (2)	0.220 (2)	4.0
H(11)	0.418 (2)	0.606 (2)	0.040 (2)	4.0
H(12)	0.240 (2)	0.636 (2)	−0.020 (2)	4.0
H(13)	0.285 (2)	0.521 (2)	−0.008 (2)	4.0
H(14)	0.449 (2)	0.686 (2)	0.290 (2)	4.0
H(15)	0.274 (2)	0.732 (2)	0.223 (2)	4.0
H(16)	0.315 (2)	0.672 (2)	0.406 (2)	4.0

* $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$. B_{iso}'s are fixed for H atoms in a tetramethylammonium group ($B_{iso} = 4.0$ Å^2).

scattering factors and f',f'' values from *International Tables for X-ray Crystallography* (1974). Computer programs: Enraf–Nonius *SDP-Plus* program package (Enraf–Nonius, 1985) and *ORTEP*II (Johnson, 1976) for all calculations.

Discussion. The final atomic coordinates, B_{eq} values for non-hydrogen atoms and B_{iso} for H atoms are listed in Table 1, and bond lengths and angles in Table 2. Bond lengths and angles in the hydrogen-bond scheme are given in Table 3.*

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43639 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

P–O(1)	1.499 (1)	C(1)–H(5)	0.963 (9)
P–O(2)	1.497 (1)	C(1)–H(6)	0.891 (10)
P–O(3)	1.565 (1)	C(1)–H(7)	0.938 (10)
P–O(4)	1.561 (1)	C(2)–H(8)	0.899 (11)
O(3)–H(1)	0.770 (11)	C(2)–H(9)	0.939 (9)
O(4)–H(2)	0.795 (11)	C(2)–H(10)	0.961 (10)
O(5)–H(3)	0.800 (12)	C(3)–H(11)	0.932 (9)
O(5)–H(4)	0.701 (13)	C(3)–H(12)	0.956 (10)
N–C(1)	1.488 (1)	C(3)–H(13)	0.933 (9)
N–C(2)	1.485 (1)	C(4)–H(14)	0.957 (10)
N–C(3)	1.484 (1)	C(4)–H(15)	0.977 (9)
N–C(4)	1.476 (1)	C(4)–H(16)	1.039 (9)

O(1)–P–O(2)	116.25 (3)	H(6)–C(1)–H(7)	108.1 (8)
O(1)–P–O(3)	108.33 (4)	N–C(2)–H(8)	108.4 (6)
O(1)–P–O(4)	109.23 (3)	N–C(2)–H(9)	108.5 (6)
O(2)–P–O(3)	109.03 (3)	N–C(2)–H(10)	106.6 (6)
O(2)–P–O(4)	107.29 (4)	H(8)–C(2)–H(9)	110.7 (8)
O(3)–P–O(4)	106.26 (4)	H(8)–C(2)–H(10)	104.3 (8)
P–O(3)–H(1)	114.9 (8)	H(9)–C(2)–H(10)	117.8 (8)
P–O(4)–H(2)	115.1 (8)	N–C(3)–H(11)	104.0 (6)
H(3)–O(5)–H(4)	104. (1)	N–C(3)–H(12)	109.5 (6)
C(1)–N–C(2)	108.77 (7)	N–C(3)–H(13)	105.8 (6)
C(1)–N–C(3)	109.41 (8)	H(11)–C(3)–H(12)	112.9 (8)
C(1)–N–C(4)	109.01 (8)	H(11)–C(3)–H(13)	115.6 (9)
C(2)–N–C(3)	109.18 (8)	H(12)–C(3)–H(13)	108.6 (8)
C(2)–N–C(4)	109.53 (9)	N–C(4)–H(14)	105.5 (6)
C(3)–N–C(4)	110.9 (1)	N–C(4)–H(15)	103.5 (6)
N–C(1)–H(5)	107.2 (5)	N–C(4)–H(16)	106.9 (5)
N–C(1)–H(6)	108.7 (6)	H(14)–C(4)–H(15)	114.4 (8)
N–C(1)–H(7)	104.8 (6)	H(14)–C(4)–H(16)	109.5 (8)
H(5)–C(1)–H(6)	113.0 (8)	H(15)–C(4)–H(16)	116.0 (8)
H(5)–C(1)–H(7)	114.5 (8)		

Table 3. *Bond lengths (Å) and angles (°) in the hydrogen-bond scheme*

	O–H	H···O	O–O	O–H···O
O(3)–H(1)···O(1^i)	0.770 (11)	1.838 (11)	2.606 (2)	175.6 (8)
O(4^i)–H(2^i)···O(2)	0.795 (11)	1.754 (11)	2.543 (2)	171.1 (8)
O(5)–H(4)···O(1)	0.701 (13)	2.186 (13)	2.875 (2)	167.5 (8)
O(5^{ii})–H(3^{ii})···O(2)	0.800 (13)	2.022 (13)	2.809 (2)	167.7 (8)

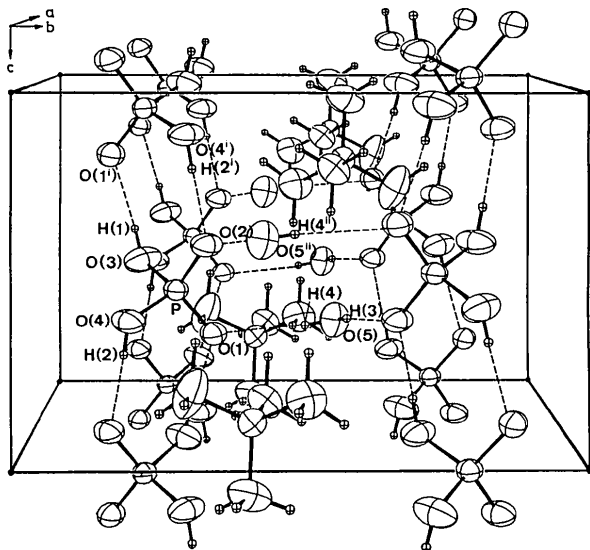Equivalent positions: (i) x, $\frac{1}{2}-y$, $z-\frac{1}{2}$; (ii) $-x$, $1-y$, $1-z$.

Fig. 1. Crystal structure of TMADP.H₂O. Hydrogen bonds are drawn as broken lines (Johnson, 1976).

The structure shown in Fig. 1 can be described as follows: $H_2PO_4^-$ chains along the c axis are formed with PO_4 tetrahedra connected to each other by two H bonds $[O(3)-H(1)\cdots O(1^i)$ and $O(4^i)-H(2^i)\cdots O(2)]$; two other H bonds $[O(5)-H(4)\cdots O(1)$ and $O(5^{ii})-H(3^{ii})\cdots O(2)]$ between adjacent $H_2PO_4^-$ chains are also formed with water molecules. Consequently a two-dimensional network of H bonds is constructed; there are no H bonds between the networks. Bulky $N(CH_3)_4^+$ ions exist in the hollow space of the network. As shown in Table 3, the H bonds along the chain are strong and the interchain H bonds weak according to the criterion of O—O distances less than or greater than 2·7 Å (Brown, 1976).

Following Baur (1974), the distortion indices (DI's) related to a PO_4 tetrahedron have been calculated for P—O distances, O—P—O angles and O—O distances: DI(TO) = 0·021 (0·017), DI(OTO) = 0·021 (0·025) and DI(OO) = 0·007 (0·011); the average values given by Baur (1974) for several acidic orthophosphates are shown in parentheses. All the DI's are zero for a regular PO_4 tetrahedron.

The arrangement of C atoms around N in the $N(CH_3)_4^+$ ion is almost ideally tetrahedral. The N—C lengths range from 1·476 (1) to 1·488 (1) Å, and the C—N—C angles from 108·77 (7) to 110·9 (1)° with average values of 1·483 (1) Å and 109·47 (8)° respectively (Table 2).

The experiment and analysis were carried out at the Center of Advanced Instrumental Analysis, Kyushu University.

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Dimethyl 3,3-Dimethyl-2,4,7-trioxa-*cis*-bicyclo[3.3.0]octane-*exo*-6,*exo*-8-dicarboxylate

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Abstract. $C_{11}H_{16}O_7$, $M_r = 260·2$, monoclinic, $P2_1/n$, $a = 13·724$ (4), $b = 6·543$ (2), $c = 14·507$ (3) Å, $\beta = 102·99$ (2)°, $U = 1269$ (1) Å³, $Z = 4$, $D_x = 1·36$ g cm⁻³, Mo $K\bar{\alpha}$ radiation, $\lambda = 0·71069$ Å, μ(Mo $K\bar{\alpha}$) = 1·1 cm⁻¹, $F(000) = 552$, $T = 298$ K, $R = 0·051$ for 974 reflections with $I \geq 3\sigma(I)$. X-ray analysis indicates that the two methoxycarbonyl groups at C(6) and C(8) are *exo* to the *cis* ring junction and