

H(3), H(4) and H(5), the first one being statistically distributed on an eightfold position. So, two and 'a half' hydrogen bonds can start from this tetrahedron: the ordinary hydrogen bonds O(4)–H(4)···O(2) and O(5)–H(5)···O(2)' and the 'statistical' one O(3)–H(3)···O(3)'. The characteristic feature of the structural arrangement is the linkage of such a tetrahedron to an equivalent one by inversion symmetry [around the site 4(b)] through the 'statistical' hydrogen bonds: O(3)–H(3)···O(3)' and O(3)'–H(3)'···O(3). The result of this type of connection between the two P(2)O₄ tetrahedra can be considered as a cluster of formula (H₅P₂O₈)⁻. The detailed representation of such a group is schematically drawn in Fig. 2. The internal distance P(2)–P(2) is 4.7614 Å, shorter than in the (H₂P₂O₈)⁴⁻ cluster of (CH₂)₂(NH₃)₂·HPO₄ (4.847 Å) (Averbuch-Pouchot & Durif, 1987), but longer than in the (H₂P₂O₈)⁴⁻ group of the sodium salt (CH₂)₂(NH₃)₂·2Na₂HPO₄·6H₂O (4.320 Å) (Averbuch-Pouchot, Durif & Guitel, 1987).

The organic entity (CH₂)₂(NH₃)₂²⁺ is centrosymmetric with the inversion point located on the site 4(c).

So, the atomic arrangement of this compound is built up by (H₅P₂O₈)⁻ clusters interconnected by (H₂PO₄)⁻ units to form arrays in three dimensions. In this

manner, each (H₂PO₄)⁻ group which is centered on the 2 axis is surrounded by four clusters (H₅P₂O₈)⁻ at different levels: $z=0, 1$ along **c** and $z=\frac{1}{2}$ along **a** + **c**/2 (Fig. 1). The relative distances P(1)–P(2) between each type of anion are 4.4003, 4.7307 and 4.7577 Å. The (CH₂)₂(NH₃)₂ entities are isolated in this three-dimensional network of hydrogen bonds, alternating with the anionic arrays at $z=\frac{1}{4}$ and $\frac{3}{4}$.

Table 2 gives the main interatomic distances, bond angles and details of the hydrogen-bond scheme.

References

- VERBUCH-POUCHOT, M. T. & DURIF, A. (1987). *Acta Cryst.* **C43**, 1894–1896.
 AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J. C. (1987). *Acta Cryst.* **C43**, 1896–1898.
 ENRAF-NONIUS (1977). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (1974). Vol. IV, Table 2-2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.

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A Neutron Diffraction Study at 30 K of a Cage Compound, 5-Hydroxy-7,10-dimethyltetracyclo[4.4.0.0^{3,9}.0^{4,8}]decan-2-one

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Abstract. C₁₂H₁₆O₂, $M_r = 192.3$, monoclinic, $P2_1/c$, $a = 10.744$ (3), $b = 15.211$ (4), $c = 11.986$ (3) Å, $\beta = 93.94$ (3)°, $\lambda = 1.2602$ (2) Å (from measurements on a ruby crystal), $V = 1954$ (1) Å³, $Z = 8$, $D_x = 1.31$ g cm⁻³, m.p. 357.2–357.7 K, $T = 30$ K, $R = 4.79\%$ for 3196 reflexions. The structural unit is a dimer held together by weak hydrogen bonds. Dimerization occurs in two ways. Structural details for a reaction pathway involving intramolecular hydrogen

transfer of a methine hydrogen to a trans-annular keto-carbon atom are considered.

Introduction. The use of crystallographic data in mapping reaction pathways has been one of the more attractive developments in organic chemistry (Bürgi & Dunitz, 1983), with a link between the statics of the crystal structures and the dynamics of the reacting systems particularly well established for interactions of

nitrogen and oxygen nucleophiles with carbonyl, both in bond formation and cleavage (e.g. Allen & Kirby, 1984). Our own interest has focused on the reduction of ketonic carbonyl by hydride addition and we have considered the possibility that the hydride+carbonyl reaction might be susceptible also to analysis by structural correlation (Craze & Watt, 1981). To this end, a number of polycyclic hydroxyketones, exemplified by (1) to (4), have been prepared. These incorporate sterically constrained 4-hydroxycyclohexanone (1) to (3) or 4-hydroxycycloheptanone (4) substructures and rearrange by the depicted 1,4-hydride shift on treatment with base (Fig. 1).

Rates of rearrangement of the derived alkoxides have been determined, as have the X-ray crystal structures of derivatives of some nine hydroxyketones (Cernik, Craze, Mills & Watt, 1982; Cernik, Craze, Mills, Watt & Whittleton, 1984). Crucial to the intended correlations are the positions of the potentially hydridic hydrogens at the alcohol methine, but hydrogen is, of course, the least well determined atom type in any X-ray crystal structure investigation. The positions of H atoms should ideally be determined from neutron diffraction data, but only recently have crystals large enough for such measurements become available. We report here the first such determination of the structure of a reactive hydroxyketone, (5). Rates of its degenerate anionic rearrangement in Me₂SO solution, determined by dynamic NMR methods, show it to be the most reactive of the compounds we have studied in which the hydride shift occurs 1,4-fashion across a constrained 4-hydroxycyclohexanone, with a free energy of activation $\Delta G^* = 52.3 \text{ kJ mol}^{-1}$ at 298 K. It is, however, not as reactive as (4), in which the shift occurs, 1,4-fashion across a 4-hydroxycycloheptanone, but a suitable crystal of this compound has not, as yet, been prepared.

Experimental. A number of crystals of (5) were grown from ethyl acetate of which the two largest crystals occupied volumes of approximately 30 and 10 mm³. The larger had dimensions *ca* 7.5 × 2.3 × 2.0 mm. This crystal was inserted in a closed roll of Al foil of diameter such that the crystal was just contained within

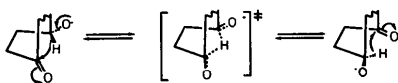
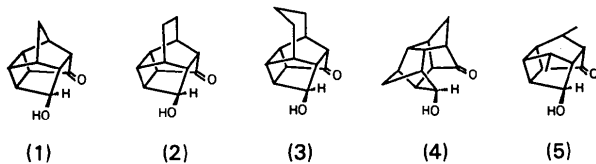


Fig. 1. Structures of hydroxyketones studied and mode of rearrangement by hydride shift.

the cross section and then secured by araldite onto a Cd pin. The measurements were made on the D10 diffractometer of the Institut Laue-Langevin and the crystal was cooled to 30 K using a helium-flow cryostat (Zeyen, Chagnon, Disdier & Morin, 1984). An orientation matrix was found with the aid of predicted diffraction directions based on a cell determined with X-rays at *ca* 160 K. D_m was not measured.

There are two molecules of (5) per asymmetric unit. The structure determination thus provided an internal test of consistency of molecular bonding parameters. The unit-cell parameters were obtained from a least-squares fit to 22 reflexions. Reflexion data were measured at some 4466 points. A reference reflexion was incorporated every 50 reflexions. No crystal deterioration was detected during the six-day data-collection period. Absorption corrections, using Gaussian integration, were applied to the observations. Plots of measurements, at 30° in φ apart, for the reflexions 300, 600, 900 showed similar variations in shape even though $I(900) \approx 10 I(300)$. An empirical variation of crystal-size parameters gave a best internal check with apparent dimensions 7.5 × 2.3 × 1.8 mm and absorption corrections derived for these values were used. The data were processed and a unique set of 3196 reflexions obtained. The structural parameters derived from the X-ray analysis at 160 K were used as starting set and the structure refined smoothly to $R \approx 6\%$. Scattering cross sections were taken from a compilation of Koester & Rauch (1981). Reflexions used in the least-squares refinement had limits of $h - 13$ to 13, $k 0$ to 19 and $l 0$ to 15. Unit weights were employed. A comparison of $\sum F_{\text{obs}}$ and $\sum F_{\text{calc}}$ as a function of F_{obs} indicated that no significant extinction was present. A few low-ordered reflexions for which $\theta < 7.6^\circ$ were removed; the beam is partially obscured in these cases and the reflexions ought not to have been measured. Refinement on F , by full-matrix least squares with all atoms given anisotropic thermal parameters, converged at $R = 4.79\%$. The maximum value of Δ/σ was 0.0001 for a coordinate and 0.05 for a thermal parameter. The final positional parameters are given in Table 1; * the non-hydrogen atoms in the two molecules in the asymmetric unit are numbered such that atom (n) in molecule I is equivalent to atom ($n + 14$) in molecule II. Fig. 2 shows the two molecules in the asymmetric unit rotated to give similar viewing aspects and details of the dimerization.

Discussion. The asymmetric unit contains two molecules of (5) and each molecule is one half of a dimer

* Lists of X-ray structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51487 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal coordinates for (5)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{cu} (Å ²)
C(1)	0.4386 (2)	0.1170 (1)	-0.0507 (2)	0.86
C(2)	0.3430 (2)	0.1538 (1)	-0.1410 (1)	0.62
C(3)	0.3117 (2)	0.0766 (1)	-0.2287 (1)	0.64
C(4)	0.3935 (2)	-0.0025 (1)	-0.1942 (2)	0.82
C(5)	0.5255 (2)	0.0286 (1)	-0.2063 (2)	0.72
C(6)	0.5528 (2)	0.1057 (1)	-0.1203 (1)	0.67
C(7)	0.4172 (2)	0.2263 (1)	-0.1977 (2)	0.72
C(8)	0.5366 (2)	0.1745 (1)	-0.2177 (1)	0.67
C(9)	0.5085 (2)	0.0982 (1)	-0.3030 (1)	0.67
C(10)	0.3682 (2)	0.0934 (1)	-0.3424 (1)	0.67
C(11)	0.4378 (2)	0.3116 (1)	-0.1311 (2)	1.06
O(12)	0.4579 (2)	0.1754 (1)	0.0411 (2)	0.83
O(13)	0.3587 (2)	-0.0755 (1)	-0.1678 (2)	0.81
C(14)	0.3389 (2)	0.0188 (1)	-0.4259 (2)	1.13
C(15)	0.1016 (2)	0.0588 (1)	0.1125 (2)	0.60
C(16)	-0.0301 (2)	0.0730 (1)	0.1558 (1)	0.51
C(17)	-0.1019 (2)	0.1411 (1)	0.0735 (1)	0.57
C(18)	-0.0123 (2)	0.1698 (1)	-0.0127 (1)	0.60
C(19)	0.0900 (2)	0.2192 (1)	0.0545 (1)	0.63
C(20)	0.1585 (2)	0.1501 (1)	0.1356 (1)	0.58
C(21)	0.0003 (2)	0.1170 (1)	0.2708 (1)	0.69
C(22)	0.0895 (2)	0.1895 (1)	0.2361 (1)	0.62
C(23)	0.0206 (2)	0.2571 (1)	0.1551 (1)	0.67
C(24)	-0.1180 (2)	0.2323 (1)	0.1294 (1)	0.68
C(25)	0.0552 (2)	0.0575 (1)	0.3651 (2)	0.89
O(26)	0.1736 (2)	-0.0071 (1)	0.1704 (2)	0.74
O(27)	-0.0213 (2)	0.1566 (1)	-0.1133 (2)	0.84
C(28)	-0.1876 (2)	0.2985 (1)	0.0507 (2)	0.98
H(1)	0.4074 (4)	0.0532 (3)	-0.0184 (3)	1.85
H(2)	0.2566 (4)	0.1760 (3)	-0.1060 (4)	1.92
H(3)	0.2123 (4)	0.0602 (3)	-0.2364 (4)	1.94
H(5)	0.5966 (4)	0.0228 (3)	-0.2096 (4)	1.90
H(6)	0.6420 (4)	0.1010 (3)	-0.0720 (3)	1.94
H(7)	0.3704 (4)	0.2450 (3)	-0.2782 (3)	1.78
H(8)	0.6181 (4)	0.2157 (3)	-0.2333 (4)	2.02
H(9)	0.5715 (4)	0.0930 (3)	-0.3714 (3)	1.98
H(10)	0.3352 (4)	0.1554 (3)	-0.3811 (4)	1.80
H(12)	0.5198 (5)	0.1500 (3)	0.0925 (4)	2.12
H(15)	0.0959 (4)	0.0440 (3)	0.0222 (3)	1.46
H(16)	-0.0827 (4)	0.0110 (3)	0.1601 (3)	1.63
H(17)	-0.1890 (4)	0.1130 (3)	0.0356 (3)	1.60
H(19)	-0.1470 (4)	0.2613 (3)	0.0057 (3)	1.72
H(20)	0.2606 (3)	0.1515 (3)	0.1372 (4)	1.64
H(21)	-0.0850 (4)	0.1460 (3)	0.3012 (3)	1.58
H(22)	0.1476 (4)	0.2180 (3)	0.3052 (3)	1.69
H(23)	0.0368 (4)	0.3266 (3)	0.1755 (3)	1.70
H(24)	-0.1695 (4)	0.2269 (3)	0.2055 (3)	1.71
H(26)	0.1304 (4)	-0.0629 (3)	0.1592 (4)	1.82
H(111)	0.4957 (5)	0.3026 (3)	-0.0542 (4)	2.64
H(112)	0.3478 (5)	0.3398 (4)	-0.1108 (5)	3.23
H(113)	0.4827 (6)	0.3594 (3)	-0.1840 (4)	3.00
H(141)	0.2393 (5)	0.0103 (4)	-0.4423 (4)	1.77
H(142)	0.3763 (5)	-0.0438 (3)	-0.3958 (4)	2.59
H(143)	0.3786 (5)	0.0327 (3)	-0.5048 (4)	2.78
H(251)	0.1499 (5)	0.0371 (4)	0.3539 (4)	2.56
H(252)	-0.0015 (5)	-0.0022 (3)	0.3730 (4)	2.73
H(253)	0.0539 (5)	0.0932 (3)	0.4447 (3)	2.38
H(281)	-0.2825 (4)	0.2747 (4)	0.0266 (5)	2.78
H(282)	-0.1410 (5)	0.3092 (4)	-0.0257 (4)	2.88
H(283)	0.1952 (5)	0.3615 (3)	0.0930 (4)	2.78

related to its moiety across a centre of symmetry. In particular, molecule I is centred on $\frac{1}{2}, 0, 0$ and molecule II on $0, 0, 0$. The hydroxyl hydrogen, H12, lies between the associated hydroxyl oxygen and the ketonic oxygen of the symmetry-related molecule. The plane defined by the hydroxyl oxygen, O12, and ketonic oxygen, O13, of one molecule, together with the carbon atoms, C1 and C4 respectively, to which they are attached, does not contain the centre of symmetry and hence does not coincide with the symmetry-related plane. The hydrogen-bonding H12 is rotated out of the above plane so that it lies between O12 and O13' and corresponds to a torsion about C1—O12. This rotation could be performed in two ways which correspond to

positive and negative values of the torsion angle. The second set of four molecules which make up the complement of the cell contents corresponds to dimers with this rotation in the opposite direction. The two rotamers must therefore be energetically similar over the range 30–300 K. This effect is shown in Fig. 2. In spite of the systematic occurrence of these two conformations dictated by the hydrogen bonds, these bonds can only be described as weak. The averaged O...O distance is 2.85 Å which shows no reduction from that expected from twice the van der Waals radius for oxygen although the H...O distance, 1.91 Å, is reduced by ~0.7 Å from the sum of van der Waals radii for hydrogen and oxygen. In consequence the angle O12—H12...O13' is 166°.

Table 2 contains a comparison of bonding parameters for the two dimers. That the majority of these parameters agree within one standard deviation is an indication of good internal consistency in the analysis.

The best plane defined by C4, O13, C1, H1 and O12 shows that these molecule-I atoms lie within ± 0.005 Å of the plane and that the centre ($\frac{1}{2}, 0, 0$) lies +1.197 Å off the plane. In the case of molecule II the defining atoms are not as coplanar but lie within ± 0.03 Å with the corresponding centre -1.196 Å away. In both dimers the symmetry-related plane is thus 2.40 Å away from the defining plane. In molecule I the hydroxyl

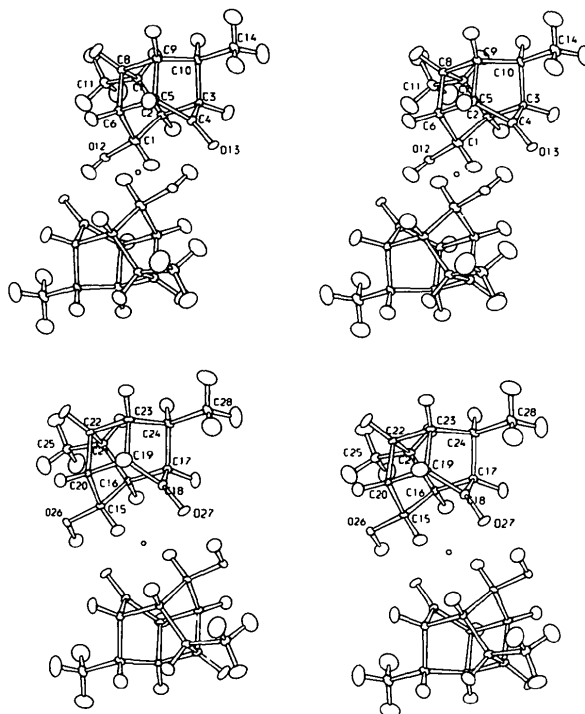


Fig. 2. Stereodrawings, after Johnson (1976), of the two independent dimers viewed from similar directions and showing numbering scheme.

Table 2. *Molecular geometry for (5)*

The values for the corresponding bond lengths, bond angles and torsion angles in molecule II are printed immediately below those for molecule I.

Atoms				Bond lengths (Å)			Bond angles (°)		τ (°)
A	B	C	D	A-B	B-C	C-D	ABC	BCD	
C1	C2	C3	C4	1.545 (2)	1.596 (3)	1.530 (3)	107.1 (3)	108.1 (3)	-3.2 (2)
				1.555 (2)	1.594 (3)	1.521 (3)	107.2 (3)	107.8 (3)	-2.8 (2)
C1	C2	C3	C10			1.554 (3)	112.3 (3)	112.3 (3)	-108.5 (2)
						1.555 (3)	112.1 (3)	112.1 (3)	-109.1 (2)
C1	C2	C7	C8		1.545 (3)	1.537 (3)	103.1 (3)	99.6 (3)	48.4 (2)
					1.546 (3)	1.537 (3)	102.6 (3)	99.6 (3)	49.5 (2)
C1	C2	C7	C11			1.534 (3)	115.8 (3)	115.8 (3)	-75.3 (2)
						1.535 (3)	116.6 (3)	116.6 (3)	-73.5 (2)
C1	C6	C5	C4	1.539 (3)	1.575 (3)	1.510 (3)	108.6 (3)	107.8 (3)	3.5 (2)
				1.538 (3)	1.579 (3)	1.517 (3)	109.2 (3)	106.7 (3)	3.0 (2)
C1	C6	C5	C9			1.571 (3)	89.4 (3)	89.4 (3)	106.7 (1)
						1.572 (3)	89.8 (3)	89.8 (3)	106.4 (1)
C1	C6	C8	C7		1.570 (3)		106.0 (3)	106.1 (3)	2.6 (2)
					1.577 (3)		106.1 (3)	105.7 (3)	2.9 (2)
C1	C6	C8	C9			1.564 (3)	89.8 (3)	89.8 (3)	-109.2 (1)
						1.565 (3)	90.2 (3)	90.2 (3)	-109.3 (1)
C2	C1	C6	C5				100.4 (3)	100.0 (3)	-69.2 (2)
							100.0 (3)	100.0 (3)	-68.5 (2)
C2	C1	C6	C8						26.6 (2)
									26.9 (2)
C2	C3	C4	C5				104.7 (3)	104.6 (3)	-64.1 (2)
							104.6 (3)	104.6 (3)	-65.2 (2)
C2	C3	C4	O13		1.220 (3)		127.3 (3)	127.3 (3)	118.9 (2)
					1.221 (3)		127.9 (3)	127.9 (3)	115.1 (2)
C2	C3	C10	C9		1.551 (3)		99.8 (3)	99.8 (3)	60.0 (2)
					1.546 (3)		99.8 (3)	99.8 (3)	60.8 (2)
C2	C3	C10	C14		1.533 (3)		112.0 (3)	112.0 (3)	179.5 (1)
					1.538 (3)		112.6 (3)	112.6 (3)	-179.7 (1)
C2	C7	C8	C6						-30.6 (2)
									-31.5 (2)
C2	C7	C8	C9				110.9 (3)	111.3 (3)	65.5 (2)
							111.3 (3)	111.3 (3)	64.9 (2)
C3	C2	C1	C6						67.9 (2)
									67.6 (2)
C3	C2	C1	O12		1.419 (3)		111.9 (3)	111.9 (3)	-170.4 (2)
					1.417 (3)		114.5 (3)	114.5 (3)	-174.1 (2)
C3	C2	C7	C8				109.0 (3)	109.5 (3)	-65.1 (2)
							109.5 (3)	109.5 (3)	-64.1 (2)
C3	C2	C7	C11						171.1 (1)
									172.9 (1)
C3	C4	C5	C6						63.7 (2)
									65.0 (2)
C3	C4	C5	C9				102.8 (3)	102.9 (3)	-29.8 (2)
							102.9 (3)	102.9 (3)	-28.8 (2)
C3	C10	C9	C5				104.7 (3)	105.0 (3)	35.9 (2)
							105.0 (3)	105.0 (3)	35.5 (2)
C3	C10	C9	C8				111.8 (3)	111.7 (3)	-60.8 (2)
							111.7 (3)	111.7 (3)	-61.0 (2)
C4	C3	C2	C7						107.7 (2)
									107.8 (2)
C4	C3	C10	C9				96.6 (3)	97.5 (3)	-52.6 (1)
							97.5 (3)	97.5 (3)	-52.0 (1)
C4	C3	C10	C14						66.9 (2)
									67.5 (2)
C4	C5	C6	C8				90.2 (3)	89.7 (3)	-103.5 (1)
							89.7 (3)	89.7 (3)	-104.0 (1)
C4	C5	C9	C8				90.6 (3)	90.4 (3)	108.3 (1)
							90.4 (3)	90.4 (3)	107.7 (1)
C4	C5	C9	C10						-4.5 (2)
									-4.9 (2)
C5	C4	C3	C10						52.0 (2)
									50.9 (2)
C5	C6	C1	O12				114.3 (3)	110.7 (3)	170.9 (2)
							110.7 (3)	110.7 (3)	170.4 (1)
C5	C6	C8	C7						112.0 (1)
									112.8 (1)
C5	C6	C8	C9						0.3 (1)
									0.6 (1)
C5	C9	C8	C6						-0.3 (1)
									-0.6 (1)
C5	C9	C8	C7						-107.4 (1)
									-107.5 (1)
C5	C9	C10	C14				112.7 (3)	112.5 (3)	-83.1 (2)
							112.5 (3)	112.5 (3)	-84.1 (2)
C6	C1	C2	C7						-47.0 (2)
									-47.7 (2)
C6	C5	C4	O13				128.0 (3)	127.5 (3)	-119.3 (2)
							127.5 (3)	127.5 (3)	-115.4 (2)
C6	C5	C9	C8						0.3 (1)
									0.6 (1)

Table 2 (cont.)

Atoms				Bond lengths (Å)			Bond angles (°)		τ (°)
A	B	C	D	A-B	B-C	C-D	ABC	BCD	
C6	C5	C9	C10						-112.5 (1)
									-112.0 (1)
C6	C8	C7	C11						114.9 (3)
									113.9 (3)
C6	C8	C9	C10						105.8 (1)
									105.7 (1)
C7	C2	C1	O12						74.6 (2)
									70.6 (2)
C7	C2	C3	C10						2.4 (2)
									1.6 (2)
C7	C8	C9	C10						-1.3 (2)
									-1.2 (2)
C8	C6	C1	O12						-93.3 (2)
									-94.2 (2)
C8	C6	C5	C9						-0.2 (1)
									-0.6 (1)
C8	C9	C10	C14						-179.8 (1)
									179.4 (1)
C9	C5	C4	O13						147.3 (2)
									150.9 (2)
C9	C8	C7	C11						-170.1 (1)
									-170.3 (1)
									-125.0 (2)
C10	C3	C4	O13						-128.7 (2)

hydrogen H12 is twisted out of the defining plane and lies 0.767 Å on the same side as the centre ($\frac{1}{2}, 0, 0$). Similarly H26 lies -0.774 Å out of the defined plane for molecule II. The normal to the defined plane for molecule I makes an angle of 58.7° to the normal to the plane defined by O12, O13 and the centre at $\frac{1}{2}, 0, 0$ whilst the principal axis of thermal motion for H12 makes an angle of 21.5° with respect to the latter normal. The corresponding values for molecule II are 58.5 and 13.7° respectively.

Details of molecular geometry at the sites involved in the rearrangement are shown in Fig. 3. Where parameters differ significantly in the two molecules, these have been averaged to yield the values displayed. The most obvious differing intramolecular parameters are the torsion angles H1-C1-O12-H12, which are 59 and -63°. Other more subtle differences occur, but all seem related to this torsional variation by some kind of conformational transmission (Barton, Head & May, 1957). For example, the H1-C1-O1 angles are 107.9 and 109.2° respectively and displacements of C1 from the plane of its heavy-atom ligands are 0.510 and 0.522 Å. The other differing parameters all involve the pendant methyl groups, C11 and C14, and their attached hydrogens and we comment on these below. It is reasonable, however, that these should show most variation, since the constraints upon them are very much less than on atoms forming the rings of the rigid cage structure. With the exception of the hydrogen-bonding arrangements, there are no unusually close intermolecular contacts involving either hydrogen or heavier atoms. The closest (2.17 Å) occur between hydrogens at C7 and C6 or at C6 and C3 of a non-hydrogen-bonded pair. The molecular geometry thus reflects intramolecular constraints rather than any strong crystal packing forces.

As in the related hydroxyketones (1), (2) and (3), the functionalized six-membered ring is a boat with the reacting carbons at the prow and stern positions, and, as noted above, those atoms most directly involved (O12, C1, H1, C4 and O13) are close to their mean plane. The interatomic angles within this group of atoms in (5) seem to be typical of the 4-hydroxycyclohexanone series, although it must be remembered that the angles involving H1 in the X-ray structures of derivatives of (1), (2) and (3) are subject to large uncertainties. There is no obvious trend in these angles which can be related to either reactivity or other structural features. The C1...C4 non-bonded distances in (1), (2) and (3) decrease from 2.76 to 2.48 Å, and are related to the size of the methylene bridge spanning C7 and C10 in these compounds. Close C1...C4 approaches, and therefore close C4...H1 contacts, are associated with variation of reactivity reflecting relief of differing amounts of ground state strain. It is interesting that (5) is anatopic in this respect. Its C1...C4 distance (2.524 Å) is close to that in (2) (2.526 Å), but it is *ca* 10³-fold more reactive. Possibly the absence of the methylene bridge in (5) permits a more flexible framework which combines high ground-state strain with a more comfortable fit for the preferred arrangement of reacting atoms in the transition state.

The six-membered ring containing C7 and C10 is also held in a boat conformation with these atoms at prow and stern positions, and the bonds to the attached methyls at these sites are nearly collinear. The non-bonded distance (1.86 Å) between H7 and H10 is well below the van der Waals radius sum for two hydrogen atoms, closer H...H contacts only being found in constrained seven- and eight-membered rings (Ermer, Mason, Anet & Miura, 1985). The resulting non-bonded interaction replaces the steric effect of the methylene bridges and may be transmitted to the reacting atoms by a second close non-bonded approach which occurs between the C11 methyl group and the alcoholic oxygen, O12, on the cyclopentanol face of the molecule. These C11...O12 distances (2.925 and

2.904 Å) differ in the two molecules, as do the torsional arrangements of the methyl hydrogens. The largest H7-C7-C11-H angles are -172° and -167° respectively, the remaining angles of the series being accurately spaced at 120° intervals. By comparison, on the cyclopentanone face of the molecule the corresponding distance between the carbonyl oxygen, O13, and its methyl, C14, whilst showing variation between the two molecules (3.403 and 3.493 Å), is over 0.5 Å greater so that non-bonded repulsion here is minimal. The difference in steric compression at the two five-membered ring faces is also reflected in a 2° difference between the H-C-methyl angles at C10 (108.1°) and at C7 (106.3°).

There is at least one adjustment in angles at a reacting atom in apparent response to these contacts. The displacement of alcohol carbon C1 from the plane of O12, C2, and C6 (0.501 or 0.522 Å) is small compared with corresponding displacements in (1) (0.579 Å), (2) (0.557 Å), and (3) (0.548 Å) where the pendant methyls are absent. Since C1 is transformed into a planar carbonyl in the rearrangement, the distortion is in the sense expected for motion along a reaction coordinate. Disappointingly, we find no corresponding displacement from planarity of the carbonyl carbon in response to the enforced close approach of the alcoholic methine hydrogen. In this structure pyramidalization in the sense expected at the carbonyl would move the oxygen, O13, closer to its methyl group, C14, and this balancing non-bonded repulsion may reduce its response to the approach of the hydride donor. A small displacement (0.019 Å) has been found in the structure of (3), which is only marginally less reactive, and a much larger one (0.074 Å) in the structure of (4). In this latter, the functional groups are in a 4-hydroxycycloheptanone with different angular arrangements and a very short H...C=O contact (2.18 Å by X-ray diffraction methods). Neither is there any anomaly in the length of the alcoholic C-H bond (1.108 Å) which is only just outside the range of values (1.090 to 1.106 Å) found in neutron diffraction structures (mainly sugars) containing cyclic secondary alcohol groups.

In conclusion, the structure of (5) has revealed clear evidence of steric compression of the potential hydride donor and accepting carbonyl. There is, however, no evidence of any adjustment in molecular geometry to show coupling between the functional groups. Presumably, the hydridic character of the alcoholic methine is not sufficiently well developed in the alcohol itself. Rate measurements and theory agree that this is enhanced by ionization. Theory (Steigerwald, Goddard & Evans, 1979; Williams, 1983) further predicts that there should be measurable differences in C-H bond lengths in alcohols and their alkoxides. This structural difference has yet to be confirmed by experiment and we hope that comparison of this alcohol structure with those of its

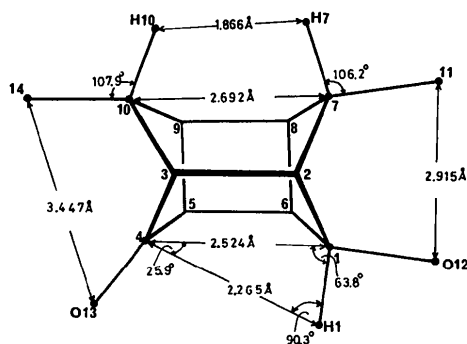


Fig. 3. Aspects of molecular geometry important to the rearrangement.

salts will provide confirmation of this prediction, as well as revealing coupling between molecular geometry of the more strongly interacting groups.

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References

- ALLEN, F. H. & KIRBY, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6197–6200.
 BARTON, D. H. R., HEAD, A. J. & MAY, P. J. (1957). *J. Chem. Soc.* p. 935.
 BÜRGI, H.-B. & DUNITZ, J. D. (1983). *Acc. Chem. Res.* **16**, 153–161.

- CERNIK, R. V., CRAZE, G.-A., MILLS, O. S. & WATT, I. (1982). *J. Chem. Soc. Perkin Trans. 2*, pp. 361–367.
 CERNIK, R. V., CRAZE, G.-A., MILLS, O. S., WATT, I. & WHITTLETON, S. N. (1984). *J. Chem. Soc. Perkin Trans. 2*, pp. 685–690.
 CRAZE, G.-A. & WATT, I. (1981). *J. Chem. Soc. Perkin Trans. 2*, pp. 175–184.
 ERMER, O., MASON, S. A., ANET, F. A. L. & MIURA, S. S. (1985). *J. Am. Chem. Soc.* **107**, 2330–2334.
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KOESTER, L. & RAUCH, H. (1981). *Summary of Neutron Scattering Lengths*. IAEA Contract 2517/RB. Vienna: International Atomic Energy Agency.
 STEIGERWALD, M. L., GODDARD, W. A. & EVANS, D. A. (1979). *J. Am. Chem. Soc.* **101**, 1994–1999.
 WILLIAMS, I. H. (1983). *Theochem.* **105**, 105–117.
 ZEYEN, C. M. E., CHAGNON, R., DISDIER, F. & MORIN, H. (1984). *Rev. Phys. Appl.* **19**, 789–791.

Acta Cryst. (1989). **C45**, 428–430

Structure of Bis(ethylenediammonium) *cyclo*-Tetraphosphate Monohydrate

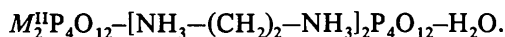
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Abstract. $[\text{C}_2\text{H}_{10}\text{N}_2]_2[\text{P}_4\text{O}_{12}]\cdot\text{H}_2\text{O}$, $M_r = 458.13$, orthorhombic, *Pcca* (D_{2h}^8), $a = 13.168$ (9), $b = 8.599$ (6), $c = 15.152$ (10) Å, $V = 1704$ (3) Å³, $Z = 4$, D_m not measured, $D_x = 1.786$ g cm⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 2.76$ cm⁻¹, $F(000) = 952$, $T = 293$ K, final R value 0.033 for 1983 independent reflexions. Layers ($z \sim 0$ and 0.5) of the P_4O_{12} ring anions and water molecules alternate with corrugated layers of ethylenediammonium dications ($z \sim 0.25$ and 0.75). The two independent ethylenediammonium groups, the P_4O_{12} ring anion and the water molecule have twofold symmetry.

Introduction. The present description of the crystal structure of ethylenediammonium *cyclo*-tetraphosphate monohydrate is part of an investigation of the system

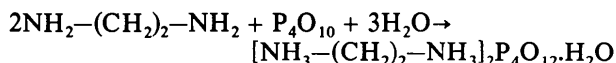


Some compounds belonging to such systems have previously been described. Up to now they correspond to three different structure types.

The first, common to a series of salts: $M^{\text{II}}[\text{NH}_3-(\text{CH}_2)_2-\text{NH}_3]_3\text{P}_4\text{O}_{12}\cdot 14\text{H}_2\text{O}$ has been determined by using the copper salt (Averbuch-Pouchot, Durif & Guitel, 1989). The second is represented by the calcium salt: $\text{Ca}[\text{NH}_3-(\text{CH}_2)_2-\text{NH}_3]_2\text{P}_4\text{O}_{12}\cdot 15/2\text{H}_2\text{O}$

(Averbuch-Pouchot, Durif & Guitel, 1988). The third has recently been described for the strontium salt: $\text{Sr}[\text{NH}_3-(\text{CH}_2)_2-\text{NH}_3]_2\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$ (Bagieu-Beucher, Durif & Guitel, 1988).

Experimental. To an aqueous solution of ethylenediamine, kept at a temperature $T < 278$ K, is slowly added an amount of P_4O_{10} corresponding to the reaction:



After evaporation for some days at room temperature orthorhombic plates of the title compound appear in the solution.

Density not measured. Prism fragment: $0.34 \times 0.32 \times 0.32$ mm. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: $0kl$: $l = 2n$; $h0l$: $l = 2n$; $hk0$: $h = 2n$. 16 reflexions ($11 < \theta < 12^\circ$) for refining unit-cell dimensions. ω scan, scan width: 1.20° , scan speed: $0.03^\circ \text{ s}^{-1}$, total background measuring time: 10 s. 2608 reflexions measured ($3 < \theta < 27.5^\circ$), $h, k, l, h_{\text{max}} = 22, k_{\text{max}} = 14, l_{\text{max}} = 26$.

Two intensity and orientation reference reflexions (006 and 820) every two hours, no significant variation. Lorentz and polarization corrections, no absorp-