McCleverty, J. A. (1968). *Prog. Inorg. Chem.* **10**, 49–221.

Main, P., Fiske, S. J. Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Miller, J. S. (1982). Editor. *Extended Linear Chain Compounds.* New York: Plenum.

Schrauzer, A. N. & Mayweg, V. P. (1965). *J. Am. Chem. Soc.* **87**, 3585–3592.

Singh, H. B., Jacobson, R. H., Hinkelmann, K., Srdanov, G. & Wudl, F. (1989). *Inorg. Chem.* **28**, 4221–4225.

Steimecke, G., Sieler, H. J., Kirmse, R., Dietzsch, W. & Hoyer, E. (1982). *Phosphorous Sulfur*, **12**, 237–247.

Steimecke, G., Sieler, H. J., Kirmse, R. & Hoyer, E. (1979). *Phosphorus Sulfur*, **7**, 49–55.

Strouse, C. (1985). Locally modified version of *UCLA Crystallographic Program Package*. Univ. of California, Los Angeles, USA.

Wudl, F. (1975). *J. Am. Chem. Soc.* **97**, 1962–1963.

Acta Cryst. (1990). **C46**, 593–595

Structure of Sodium 4-Carbamoyl-5,5-dimethyl-5*H*-1,2-oxaphosphole 2,2-Dioxide Tetrahydrate

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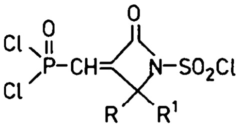
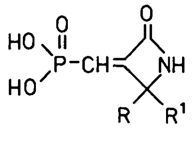
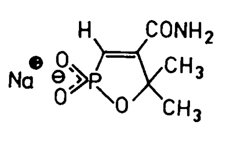
Abstract. $Na^+.C_6H_9NO_4P^-.4H_2O$, $M_r = 285{\cdot}17$, triclinic, $P\bar{1}$, $a = 6{\cdot}019\,(1)$, $b = 6{\cdot}676\,(1)$, $c = 16{\cdot}650\,(2)$ Å, $\alpha = 83{\cdot}88\,(1)$, $\beta = 86{\cdot}55\,(1)$, $\gamma = 74{\cdot}80\,(1)^\circ$, $V = 641{\cdot}6\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}476$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}710793$ Å, $\mu = 2{\cdot}66$ cm^{-1}, $F(000) = 300$, $T = 293$ K, $R = 0{\cdot}028$ for 2490 observed reflections with $I > 3\sigma(I)$. The oxaphosphole anions are linked *via* hydrogen bonds to positively charged zigzag chains of edge-shared $Na(H_2O)_6$ octahedra extending along the *a* axis. The distorted tetrahedral PO_3C group has essentially equal *exo* P—O bond lengths [1·497 (1) and 1·498 (1) Å], the *endo* P—O and P—C being 1·607 (1) and 1·773 (1) Å respectively. The carboxamide fragment is tilted from the plane of the five-membered oxaphosphole ring by 34·7°.

Introduction. The synthesis of 4,4-dialkyl-1-chlorosulfonyl-3-dichlorophosphonylmethylene-2-azetidinones (1), which appear to be stable only in inert organic solvents, has recently been reported (Mondeshka, Parashikov & Angelov, 1987). On treating (1) with NaOH/H_2O by known methods (Graf, 1963; Durst & O'Sullivan, 1970), aiming to obtain the more stable 4,4-dialkyl-3-dihydroxyphosphonylmethylene-2-azetidinones (2), crystalline substances were formed for which structures could not be unambiguously established by the known spectral methods: IR, MS and ^{1}H, ^{13}C and ^{31}P NMR. In the present paper we report the structure of the title compound (3) which was unexpectedly obtained instead of the corresponding derivative of (2). The details of the synthesis of (3) together with spectral and analytical data will be published elsewhere (Mondeshka, Parashikov & Angelov, 1990).


(1)


(2)


(3)

Experimental. A transparent well formed crystal obtained from methanol with approximate dimensions 0·1 × 0·02 × 0·02 mm was investigated. D_m not determined. Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation); ω–2θ scan; speed 2 to 10° min^{-1}, width = $[1{\cdot}2 + 0{\cdot}40\tan(\theta)]^\circ$. Cell constants by least squares for 25 reflections with $20{\cdot}0 < \theta < 22{\cdot}0^\circ$. 6165 reflections measured with $(\sin\theta)/\lambda < 0{\cdot}660$ Å^{-1} (h: −7 to 7, k: −8 to 8, l: −21 to 21). Three standard reflections monitored every 4·0 h, intensity variation < 0·1%. No decay correction. Lorentz and polarization correction; empirical absorption correction based on ψ scans (program *EAC*), transmission factors from 96·810 to 99·715%. 3083 unique reflections with $R_{\rm int}$ = 0·014; 593 reflections considered unobserved [$I < 3\sigma(I)$]. Structure solved by combination of *MULTAN*11/82, which treated the normalized structure factors of the proposed (2), and a Patterson function analysis. The PO_3C_6 fragment was used in the initial phasing. Structure completed by subsequent difference Fourier syntheses and full-matrix least-squares refinement on F. H atoms refined isotropically. Final R = 0·0281, wR = 0·0381 and S = 1·366; $w = 4F_o^2/[\sigma^2(I) + (0{\cdot}04F_o)^2]$. Max. (Δ/σ) = 0·01; residual density within 0·27 and −0·34 e Å^{-3}. No correction for secondary extinction. Atomic scattering factors and anomalous-dispersion coefficients as quoted in *SDP*/*PDP V*.3.0 software package (Enraf–Nonius, 1985) operating on a PDP11/44 computer.

Discussion. Final fractional coordinates are given in Table 1* and the interatomic distances and angles are summarized in Table 2. The atom numbering scheme is depicted in Fig. 1 and the disposition of the structural fragments in the crystal is viewed in Fig. 2.

The first crystallographic evidence of the existence of the oxaphosphole moiety, the main feature of this structure, was given by Elder, Florian, Kennedy & Macomber (1973) for (4) and later by Macomber, Krudy, Seff & Rendon-Diazmiron (1983) for (5). The title compound (3), (4) and (5) have similar geometry of the common moieties with maximum differences in bond lengths of 0·023 Å and in angles of 3·8°. The five-membered POC_3 ring and the carbamoyl C(4) atom are coplanar within 0·009 Å. The two exocyclic P—O bonds are essentially equal in length [O(1) 1·497 (1), O(2) 1·498 (1) Å] but are at different distances from the molecular plane [1·244 (1) and −1·266 (1) Å respectively]. The O(1)PO(2) fragment makes a dihedral angle of 88·91 (5)° with the plane. Both O(1) and O(2) participate in three hydrogen bonds (see Table 2). The P—O(1), P—O(2) bond lengths fit well with the P═O *vs* O—H···O distance relation, established by Ichikawa (1987) for the $H_2PO_4^-$ group, *i.e.* P═O = 1·562 − 0·022 × (O···O). This, along with Blessing's (1988) conclusions that in H_3PO_4 molecules the P═O bond lengths are within 1·495–1·515 Å (libration corrected data, larger by 0·009 Å than the

Table 1. *Positional and equivalent isotropic thermal parameters and their e.s.d.'s*

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$ (Å^2)
P	0·27524 (5)	0·04890 (5)	0·27018 (2)	1·650 (6)
O(1)	0·0811 (2)	−0·0521 (2)	0·26860 (6)	2·33 (2)
O(2)	0·3449 (2)	0·0655 (2)	0·35356 (6)	2·51 (2)
O(3)	0·2103 (2)	0·2746 (2)	0·22002 (6)	2·36 (2)
O(4)	0·6896 (2)	0·1403 (2)	0·01256 (6)	3·27 (2)
N	0·9265 (2)	−0·0665 (2)	0·10538 (7)	2·70 (3)
C(1)	0·5150 (2)	−0·0520 (2)	0·20581 (8)	1·81 (2)
C(2)	0·5377 (2)	0·0925 (2)	0·14651 (8)	1·74 (4)
C(3)	0·3608 (2)	0·3010 (2)	0·14887 (8)	1·95 (2)
C(4)	0·7252 (2)	0·0592 (2)	0·08191 (8)	2·05 (2)
C(5)	0·4746 (3)	0·4703 (2)	0·1634 (1)	3·08 (3)
C(6)	0·2079 (3)	0·3622 (3)	0·0762 (1)	2·94 (3)
Na	0·22208 (9)	0·55209 (9)	0·55527 (3)	2·46 (1)
O(W1)	0·2413 (2)	0·8717 (2)	0·60860 (7)	3·16 (2)
O(W2)	0·3875 (2)	0·6381 (2)	0·42235 (7)	3·00 (2)
O(W3)	0·0081 (2)	0·4234 (2)	0·66853 (7)	3·90 (3)
O(W4)	0·1582 (2)	0·2510 (2)	0·49420 (6)	2·75 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°) *and hydrogen bond geometry* (Å,°) *with e.s.d.'s in parentheses*

P—O(1)	1·497 (1)	N—C(4)	1·334 (2)
P—O(2)	1·498 (1)	C(1)—C(2)	1·332 (2)
P—O(3)	1·607 (1)	C(2)—C(3)	1·517 (2)
P—C(1)	1·773 (1)	C(2)—C(4)	1·501 (2)
O(3)—C(3)	1·471 (1)	C(3)—C(5)	1·514 (2)
O(4)—C(4)	1·228 (1)	C(3)—C(6)	1·520 (2)
O(1)—P—O(2)	113·87 (6)	C(3)—C(2)—C(4)	120·9 (1)
O(1)—P—O(3)	109·79 (5)	O(3)—C(3)—C(2)	105·1 (1)
O(1)—P—C(1)	114·51 (5)	O(3)—C(3)—C(5)	107·2 (2)
O(2)—P—O(3)	110·51 (5)	O(3)—C(3)—C(6)	107·0 (2)
O(2)—P—C(1)	112·32 (5)	C(2)—C(3)—C(5)	110·8 (2)
O(3)—P—C(1)	94·11 (5)	C(2)—C(3)—C(6)	114·3 (2)
P—O(3)—C(3)	115·46 (8)	C(5)—C(3)—C(6)	111·9 (1)
P—C(1)—C(2)	110·2 (1)	O(4)—C(4)—N	123·7 (1)
C(1)—C(2)—C(3)	115·2 (2)	O(4)—C(4)—C(2)	121·2 (1)
C(1)—C(2)—C(4)	124·0 (2)	N—C(4)—C(2)	115·2 (2)
Na—O(W1)	2·429 (1)	Na—O(W3)	2·428 (1)
Na—O(W2)	2·446 (1)	Na—O(W4)	2·472 (1)
Na—O(W2$^{\rm i}$)	2·390 (1)	Na—O(W4$^{\rm ii}$)	2·463 (1)
O(W1)—Na—O(W2)	94·46 (4)	O(W2)—Na—O(W4$^{\rm ii}$)	88·17 (5)
O(W1)—Na—O(W2$^{\rm i}$)	97·30 (5)	O(W2)—Na—O(W3)	103·81 (4)
O(W1)—Na—O(W3)	97·43 (4)	O(W2)—Na—O(W4)	89·38 (4)
O(W1)—Na—O(W4)	173·15 (4)	O(W2)—Na—O(W4$^{\rm ii}$)	169·49 (4)
O(W1)—Na—O(W4$^{\rm ii}$)	86·38 (5)	O(W3)—Na—O(W4)	82·39 (4)
O(W2)—Na—O(W2$^{\rm i}$)	81·75 (5)	O(W3)—Na—O(W4$^{\rm ii}$)	85·39 (4)
O(W2)—Na—O(W3)	166·08 (5)	O(W4)—Na—O(W4$^{\rm ii}$)	86·78 (4)
O(W2)—Na—O(W4)	84·94 (4)		

D—H···A	D—H	H···A	D···A	D—H···A
N—H(N1)···O(4$^{\rm iii}$)	0·87 (2)	2·04 (2)	2·916 (1)	177 (1)
H—H(N2)···O(1$^{\rm iv}$)	0·87 (2)	2·11 (2)	2·944 (1)	161 (1)
O(W1)—H(W11)···O(1$^{\rm ii}$)	0·78 (2)	2·10 (2)	2·867 (1)	171 (2)
O(W1)—H(W12)···O(2$^{\rm i}$)	0·85 (2)	1·90 (2)	2·751 (1)	174 (2)
O(W2)—H(W21)···O(W3$^{\rm ii}$)	0·83 (2)	2·24 (2)	3·034 (2)	162 (2)
O(W2)—H(W22)···O(2$^{\rm v}$)	0·79 (2)	2·13 (2)	2·911 (2)	171 (2)
O(W3)—H(W31)···O(1$^{\rm vi}$)	0·80 (2)	1·96 (2)	2·758 (1)	172 (2)
O(W3)—H(W32)···O(3$^{\rm ii}$)	0·88 (3)	2·02 (2)	2·890 (1)	169 (2)
O(W4)—H(W41)···O(W1$^{\rm vii}$)	0·81 (2)	2·14 (2)	2·952 (2)	175 (2)
O(W4)—H(W42)···O(2)	0·77 (2)	2·04 (2)	2·802 (1)	178 (2)

Symmetry codes: (i) $1-x,1-y,1-z$; (ii) $-x,1-y,-z$; (iii) $2-x,-y,-z$; (iv) $1+x,y,z$; (v) $x,1+y,z$; (vi) $-x,-y,1-z$; (vii) $x,y-1,z$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52485 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

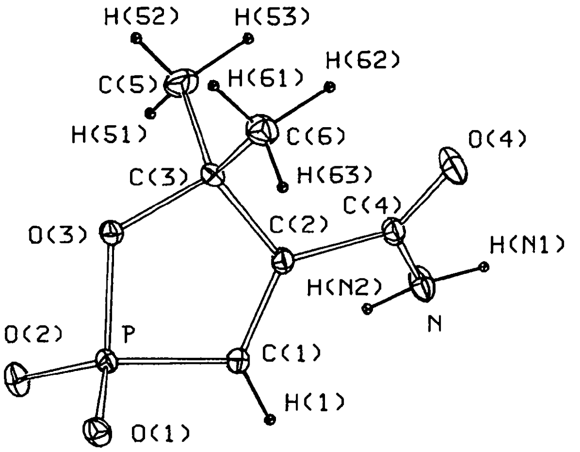


Fig. 1. Oxaphosphole anion with the atomic numbering scheme. 30% probability thermal ellipsoids. H atoms arbitrarily reduced.

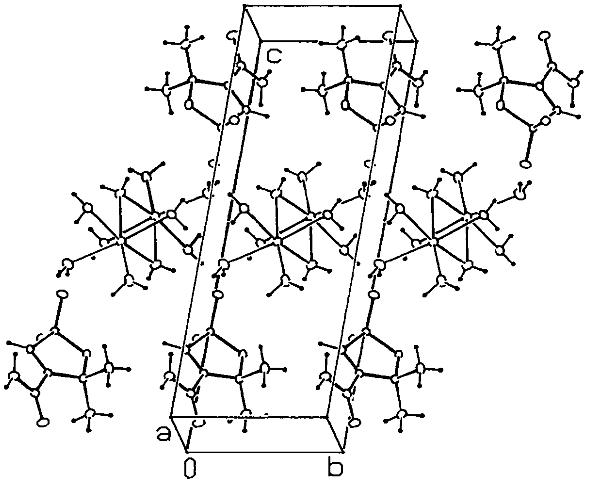


Fig. 2. Crystal packing diagram. The hydrated sodium cations are sandwiched by the oxaphosphole anions.

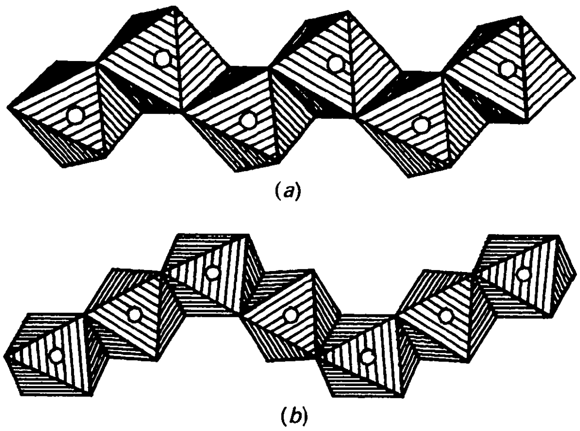
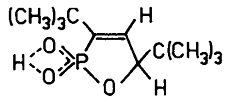


Fig. 3. Configurations of the $[Na(H_2O)_4]$ octahedral zigzag chains (*a*) in the present structure and (*b*) in Glauber's salt and borax (Levy & Lisensky, 1978).

experimentally obtained values) and the P—OH bond lengths vary from 1·530 to 1·577 Å, indicates that the phosphonyl groups in the oxaphosphole anion have predominantly double-bond character. The carbamoyl group has a normal geometry and its twisting along the C(2)—C(4) bond [torsional angles C(1)—C(2)—C(4)—O(4) 145·2 (1), C(1)—C(2)—C(4)—N −33·3 (1)°] is a result of the participation of both amino and carboxyl groups in the hydrogen bonded system. This rotation hinders the π-bonding interaction between the conjugated systems of the five-membered ring and carbamoyl group and causes an elongation of the C(2)—C(4) bond to 1·501 (1) Å.



(4)

(5)

The sodium ions are octahedrally surrounded by six water molecules with Na—O distances ranging from 2·390 (1) to 2·472 (1) Å [average 2·44 (3) Å]. The octahedra are condensed in a zigzag $[Na(H_2O)_4]_\infty$ chain through sharing their two *cis* disposed (having no common vertex) edges [O(W2)—O(W2) and O(W4)—O(W4)]. The midpoints of the shared edges coincide with the space group symmetry centres as they are extended along **a**. The zigzag chain has a *cis-cis* configuration with Na—Na separation of 3·586 (1) and 3·657 (1) Å and Na—Na—Na angle of 112·40 (3)°. Similar isolated chains of *cis-trans-cis* edge-sharing $Na(H_2O)_6$ octahedra (Fig. 3) exist in the structures of Glauber's salt $[Na_2SO_4.10H_2O]$ and borax $[Na_2B_4O_5(OH)_4.8H_2O]$ (Levy & Lisensky, 1978).

References

Blessing, R. H. (1988). *Acta Cryst.* **B44**, 334–340.
Durst, T. & O'Sullivan, M. J. (1970). *J. Org. Chem.* **35**, 2043–2044.
Elder, R. C., Florian, L. R., Kennedy, E. R. & Macomber, R. S. (1973). *J. Org. Chem.* **38**, 4177–4184.
Enraf-Nonius (1985). *Structure Determination Package, SDP/PDP V.*3.0 *Users Guide.* Enraf-Nonius, Delft, The Netherlands.
Graf, R. (1963). *Justus Liebigs Ann. Chem.* **661**, 111–155.
Ichikawa, M. (1987). *Acta Cryst.* **B43**, 23–28.
Levy, H. A. & Lisensky, G. C. (1978). *Acta Cryst.* **B34**, 3502–3510.
Macomber, R. S., Krudy, G. A., Seff, K. & Rendon-Diazmiron, L. E. (1983). *J. Org. Chem.* **48**, 1425–1430.
Mondeshka, D. M., Parashikov, V. A. & Angelov, C. M. (1987). Proc. 31st IUPAC Congress, 13–18 July, 1987, Sofia, Bulgaria. Posters 2, 6.132.
Mondeshka, D. M., Parashikov, V. A. & Angelov, C. M. (1990). *Tetrahedron Lett.* In the press.