Rosenstein, 1968; Kim, Jeffrey & Rosenstein, 1969) the C—C bonds have the staggered conformation leading to a planar zigzag chain of C atoms. The terminal O atoms of the *p*-chlorobenzoate groups do not form an extension to the planar carbon chain (*anti* conformation) but rather adopt the *gauche* conformation [defined by the O(1)—C(1)—C(2)—C(3) torsion angle]. The conformation of the O—C—C—O fragments of the main chain is *ap* [C(1)—C(2)], *Msc* [C(2)—C(3)] and *ap* [C(3)—C(3′)] as follows from the pertinent O—C—C—O torsion angles (Table 2) (for nomenclature, see Klyne & Prelog, 1960).

The investigated compound differs in structure from the parent compound, galactitol, which has only approximate $\bar{1}$ symmetry in the crystal and crystallizes in the centrosymmetric space group as a racemate of unsymmetrical conformers. In addition, in the crystal structure of galactitol the planar carbon chain is extended by two terminal O atoms and so the conformation of the terminal groups is *anti*, while the *gauche* conformation is favoured in the present case.

Angles between ring 1 (C12–C17) and rings 2 (C22–C27), and 3(C32–C37) are 55·9 (2) and 77·9 (2)°, respectively, whereas the angle between rings 2 and 3 is 23·5 (3)°. The three rings form angles of 46·7 (5), 69·9 (3) and 77·9 (3)° with the plane of the planar carbon chain and angles of 14·0 (2), 5·8 (3) and 8·1 (3)° with the respective carboxylic moieties.

The geometrical parameters of the aromatic rings, which are planar within experimental error, are normal, the mean C—C distances and the mean C—C—C angles being 1·381 (14) Å and 120·0 (10)°, respectively. As in other benzoic acid derivatives the exocyclic angles have different values, the angle smaller than 120° being on the side of the carbonyl O atom. Significant narrowing of the angles opposite to the C═O bonds is also systematically observed.

The three C_{sp^3}—C_{sp^3} distances have a mean value of 1·524 (9) Å. Packing of the molecules in the crystal is determined primarily by normal van der Waals contacts.

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References

Berman, H. M., Jeffrey, G. A. & Rosenstein, R. D. (1968). *Acta Cryst.* **B24**, 442–449.

Berman, H. M. & Rosenstein, R. D. (1968). *Acta Cryst.* **B24**, 435–441.

Gawroński, J. & Gawrońska, K. (1990). *Carbohydr. Res.* Submitted.

Jaskólski, M. (1982). *Collect. Abstr. Symp. Org. Cryst. Chem.* edited by Z. Kałuski, p.70. Poznań, Poland.

Kim, H. S., Jeffrey, G. A. & Rosenstein, R. D. (1969). *Acta Cryst.* **B25**, 2223–2230.

Klyne, W. & Prelog, V. (1960). *Experientia,* **16**, 521–523.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–584.

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.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO78.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1990). **C46**, 606–609

Structure of Pyridinium Dihydrogenphosphate Phosphoric Acid

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Abstract. $C_5H_6N^+.H_2PO_4^-.H_3PO_4$, $M_r = 275·1$, triclinic, $P\bar{1}$, $a = 7·708\ (5)$, $b = 8·176\ (5)$, $c = 9·566\ (5)$ Å, $\alpha = 115·39\ (5)$, $\beta = 98·47\ (5)$, $\gamma = 90·80\ (5)°$, $V = 536·7\ (9)$ Å^3, $Z = 2$, $D_x = 1·702$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 4·405$ cm^{-1}, $F(000) = 284$, $T = 295$ K, final $R = 0·034$ for 3404 unique reflexions. The aggregates of $H_2PO_4^-$ anions and H_3PO_4 molecules bridged by hydrogen bonds form a three-dimensional anionic subnetwork inside which the pyridinium ions are anchored. The existence of an $(H_5P_2O_8)_n^{n-}$ polymeric anion is supported by structural considerations.

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Introduction. An important feature of $H_2PO_4^-$ anions is their arrangement in chains or layers in the presence of alkyl- or arylammonium ions. The number of functional groups with hydrogen donors and the dimension of the organic cation promote the anionic layered arrangement and determine the participation of solvent in the crystallization. A second important feature is the effect of chiral cations on the $(H_2PO_4^-)_n$ layers (Masse & Durif, 1989). The structural determination of $C_5H_6N^+.H_2PO_4^-.H_3PO_4$ shows clearly that the pyridinium ion which is a single hydrogen donor cannot induce an $(H_2PO_4^-)_n$ layer structure, as we were hoping.

Experimental. An aqueous solution of monophosphoric acid (85%, $d = 1·70$) was mixed with a pyridine solution (99%, $d = 0·983$) in the ratio 0·02 M H_3PO_4/0·01 M C_5H_5N and slowly evaporated at room temperature. Several crystallizations were repeated. Large prisms, up to 8 mm long, without specific symmetry of faces were observed. Crystal size used for data collection: 0·80 × 0·80 × 0·80 mm. Density not measured. Philips PW 1100, graphite monochromator. 19 reflexions ($11 < \theta < 22^\circ$) used for refining unit-cell dimensions. ω scan. 4295 non-zero unique reflexions collected ($3 < \theta < 35^\circ$). $h_{\rm min} = k_{\rm min} = -12$, $l_{\rm min} = 0$, $h_{\rm max} = k_{\rm max} = 11$, $l_{\rm max} = 14$. Scan width 1·20°, scan speed 0·03° s^{-1}, total background measuring time 10 s. Orientation reference reflexions: 316 and $\overline{3}\overline{1}\overline{6}$, no variation. Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN*77; Main, Lessinger, Woolfson, Germain & Declercq, 1977). Patterson and successive Fourier syntheses. H atoms were located from difference Fourier map. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinement cycles with 3404 reflexions corresponding to $F_o > 3\sigma_{F_o}$. Final $R = 0·034$ ($wR = 0·040$). Max. $\Delta/\sigma = 0·05$. $S = 0·375$. Max. peak height in the final difference Fourier synthesis 0·44 e Å^{-3}. No extinction correction. $R = 0·041$ for the complete set of 4149 reflexions. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer: MicroVaxII. Table 1 reports the final atomic coordinates. Table 2 gives the main interatomic distances, bond angles and details of the hydrogen bonds.*

Table 1. *Final atomic coordinates, B_{eq} values for non-*H *atoms and B_{iso} values for* H *atoms*

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

	x	y	z	$B_{\rm eq}/B_{\rm iso}$(Å^2)
P(1)	0·31779 (5)	0·24140 (4)	0·51912 (4)	1·870 (5)
P(2)	0·89331 (5)	0·39717 (4)	0·75503 (4)	1·838 (5)
O(11)	0·1655 (2)	0·0977 (1)	0·4080 (1)	2·74 (2)
O(12)	0·3333 (2)	0·2553 (2)	0·6876 (1)	2·81 (2)
O(13)	0·4879 (1)	0·1666 (2)	0·4602 (1)	2·63 (2)
O(14)	0·2840 (2)	0·4181 (1)	0·5151 (1)	2·94 (2)
O(21)	0·7757 (2)	0·4838 (2)	0·8833 (1)	3·59 (3)
O(22)	0·9332 (2)	0·5401 (2)	0·6954 (2)	4·59 (3)
O(23)	0·2103 (2)	0·7692 (1)	0·3751 (1)	2·82 (2)
O(24)	0·0672 (1)	0·3613 (2)	0·8270 (1)	2·46 (2)
N	0·3036 (2)	0·7271 (2)	0·7838 (2)	2·66 (3)
C(1)	0·2136 (2)	0·8583 (2)	0·7714 (2)	2·92 (3)
C(2)	0·1896 (2)	0·0065 (2)	0·9052 (2)	3·25 (3)
C(3)	0·2595 (3)	0·0140 (3)	0·0492 (2)	3·52 (4)
C(4)	0·3523 (3)	0·8755 (2)	0·0587 (2)	3·41 (3)
C(5)	0·3729 (3)	0·7306 (2)	0·9212 (2)	3·11 (3)
H(11)	0·175 (4)	0·008 (3)	0·404 (3)	5·1 (6)
H(12)	0·249 (4)	0·299 (4)	0·732 (3)	5·5 (6)
H(13)	0·425 (3)	0·800 (3)	0·475 (3)	4·7 (6)
H(21)	0·179 (4)	0·479 (3)	0·036 (3)	5·6 (7)
H(22)	0·136 (4)	0·458 (3)	0·370 (3)	5·5 (6)
H(N)	0·311 (3)	0·658 (3)	0·716 (2)	3·4 (4)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°)

PO_4 tetrahedron in the H_3PO_4 molecule

P(1)	O(11)	O(12)	O(13)	O(14)
O(11)	1·553 (2)	2·543 (3)	2·469 (3)	2·471 (3)
O(12)	109·9 (1)	1·553 (2)	2·472 (3)	2·521 (3)
O(13)	106·2 (1)	106·4 (1)	1·535 (2)	2·526 (3)
O(14)	108·7 (1)	112·0 (1)	113·4 (1)	1·487 (2)

P(1)—O(11)—H(11)	114 (4)
P(1)—O(12)—H(12)	114 (3)
P(1)—O(13)—H(13)	115 (3)

PO_4 tetrahedron in the $H_2PO_4^-$ anion

P(2)	O(21)	O(22)	O(23)	O(24)
O(21)	1·559 (2)	2·500 (4)	2·470 (3)	2·510 (3)
O(22)	107·2 (2)	1·548 (2)	2·513 (3)	2·454 (3)
O(23)	107 (1)	110·8 (1)	1·504 (2)	2·530 (2)
O(24)	109·9 (1)	106·9 (1)	114·4 (1)	1·506 (2)

P(2)—O(21)—H(21)	115 (4)
P(2)—O(22)—H(22)	116 (4)

Pyridinium cation

N—C(1)	1·324 (4)	N—C(1)—C(2)	119·3 (3)
N—C(5)	1·332 (4)	C(1)—C(2)—C(3)	119·0 (3)
C(1)—C(2)	1·374 (4)	C(2)—C(3)—C(4)	120·5 (3)
C(2)—C(3)	1·378 (5)	C(3)—C(4)—C(5)	118·2 (3)
C(3)—C(4)	1·376 (5)	C(4)—C(5)—N	119·9 (3)
C(4)—C(5)	1·375 (5)	C(5)—N—C(1)	123·1 (3)
N—C(1)—H(C1)	108 (3)	C(3)—C(4)—H(C4)	125 (3)
C(2)—C(1)—H(C1)	133 (3)	C(5)—C(4)—H(C4)	116 (3)
C(1)—C(2)—H(C2)	115 (2)	C(4)—C(5)—H(C5)	128 (2)
C(3)—C(2)—H(C2)	126 (2)	N—C(5)—H(C5)	112 (2)
C(2)—C(3)—H(C3)	118 (3)	C(1)—N—H(N)	115 (4)
C(4)—C(3)—H(C3)	121 (3)	C(5)—N—H(N)	122 (4)

Hydrogen bonds

	O(N)—H	H···O	O(N)···O	O(N)—H···O
O(11)—H(11)···O(23)	0·72 (5)	1·88 (5)	2·600 (3)	174 (5)
O(12)—H(12)···O(24)	0·83 (5)	1·74 (5)	2·569 (3)	171 (5)
O(13)—H(13)···O(23)	0·80 (5)	1·74 (5)	2·519 (3)	164 (5)
O(21)—H(21)···O(24)	0·73 (5)	1·86 (5)	2·591 (3)	175 (5)
O(22)—H(22)···O(14)	0·77 (5)	1·80 (5)	2·567 (3)	171 (5)
N—H(N)···O(14)	0·66 (4)	2·06 (4)	2·705 (3)	167 (5)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and interatomic distances and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52400 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Fig. 1 shows a detail of the crystal structure arrangement. The two pyridinium ions are surrounded by four $H_2PO_4^-$ and four H_3PO_4 tetrahedra. Each pyridinium ion is anchored by an N—H(N)···O(14) hydrogen bond to an H_3PO_4 molecule. O(14) is a double H acceptor. The H_3PO_4 and $H_2PO_4^-$ units form a three-dimensional framework of tetrahedra bound by hydrogen bridges (Fig. 2) (Fischer, 1985). The aim here is not to discuss the detailed geometrical features of the pyridinium ion based on a LCAO–MO treatment, but to underline its specific geometry supported by X-ray investigations. The low melting point of pyridine (231·4 K) is probably responsible for the time spent in order to achieve with precision its molecular and crystal structure. Investigated for the first time by Schomaker & Pauling (1939), using electron microscopy, the molecular structure of pyridine was approached by repeated investigations of its microwave spectra (Bak, 1953; Bak & Rastrup-Andersen, 1953; Bak, Hansen & Rastrup-Andersen, 1954; Bak, Hansen-Nygaard & Rastrup-Andersen, 1958; Sorensen, Mahler & Rastrup-Andersen, 1974). The X-ray crystal structure, determined at 153 K by Mootz & Wussow (1981), is our reference for the geometrical features of the pyridine heterocycle. The crystal structure of pyridinium chloride (Rerat, 1962) does not give information about hydrogen positions but reveals enlargement of the C—N—C angle (128°) due to the capture of a proton, compared to the C—N—C angle in pyridine [115 (9)°] (Mootz & Wussow, 1981). The C—N—C angle observed in this material is 123 (3)°. This protonation reduces the N—C distances by 0·01 Å and enlarges the C—N—C angle by about +7°, two related geometrical features of the same phenomenon: a small decrease in all the C—C and N—C distances compared to those of pyridine due to the ability of the nitrogen to act as an H donor toward the counter anion and then to affect the 6π molecular orbital of the heterocycle. One can expect some appreciable changes in the geometry of the pyridinium ion following the nature of the acceptor: halogenide, oxoanion, sulfoanion, *etc.* The dynamical disorder of the pyridinium ion observed in pyridinium iodide (Hartl, 1975) and in pyridinium dichloroiodide (Tucker & Kroon, 1973) did not allow an accurate determination of the C—N—C angle in these compounds.

The centrosymmetrical anionic aggregate ($2H_2PO_4^-$, $2H_3PO_4$), clearly drawn in Fig. 2, is the basis of the three-dimensional anionic subnetwork. The equivalence of all the hydrogen bonds inside the anionic aggregate and the value of the O(13)—H(13)···O(23) distance, 2·519 (3) Å, which is of the same order of magnitude as the O—O distances in both PO_4 tetrahedra, retains our attention. This means that the two entities $H_2PO_4^-$ and H_3PO_4 are not independent in this crystal. Moreover, N—H(N)···O(14) is the unique bond of the pyridinium ion to the anionic subnetwork. Then the negative charge cannot be localized on the H_2PO_4 unit. The formula of the counter anion must be written $(H_5P_2O_8)_n^{n-}$. Accurate electron density maps $\rho_{x-x'}$ or ρ_{x-n} would be necessary to gain information on the charge distribution in the pyridinium ion and in the polymeric anion.

Blessing (1986), for L-histidinium $H_2PO_4^-.H_3PO_4$, has pointed out a two dimensional and non-centric anionic aggregate, where the hydrogen bonds are of the same order of magnitude as in this pyridinium salt. The ethylenediammonium salt $C_2H_{10}N_2^{2+}$.-

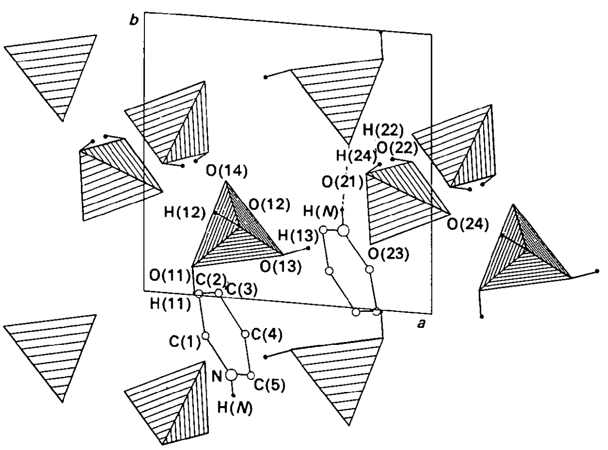

Fig. 1. A partial c projection of $C_5H_6N^+.H_2PO_4^-.H_3PO_4$.

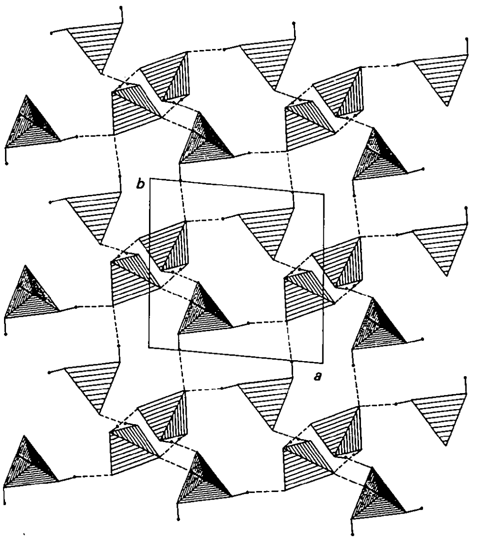

Fig. 2. Projection along the c direction of the $(H_5P_2O_8)_n^{n-}$ anionic subnetwork.

$H_5P_2O_8^-.H_2PO_4^-$ (Bagieu-Beucher, Durif & Guitel, 1989) is noteworthy due to its anionic aggregate. The anion should be written $H_7P_3O_{12}^{2-}$. These three materials which show various steps in the aggregation of $H_2PO_4^-$ anions and H_3PO_4 molecules allow us to imagine the possible formation of clathrate structures with monophosphoric acid.

References

BAGIEU-BEUCHER, M., DURIF, A. & GUITEL, J. C. (1989). *Acta Cryst.* C**45**, 421–423.

BAK, B. (1953). *Kem. Maanedobl. Danm.* **34**, 43–46.

BAK, B., HANSEN, L. & RASTRUP-ANDERSEN, J. (1954). *J. Chem. Phys.* **22**, 2013–2017.

BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spectrosc.* **2**, 361–368.

BAK, B. & RASTRUP-ANDERSEN J. (1953). *J. Chem. Phys.* **21**, 1305–1306.

BLESSING, R. M. (1986). *Acta Cryst.* B**42**, 613–621.

Enraf–Nonius (1977). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

HARTL, H. (1975). *Acta Cryst.* B**31**, 1781–1783.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MASSE, R. & DURIF, A. (1989). *Z. Kristallogr.* Submitted.

MOOTZ, D. & WUSSOW, H. G. (1981). *J. Chem. Phys.* **75**, 1517–1522.

RERAT, C. (1962). *Acta Cryst.* **15**, 427–433.

SCHOMAKER, V. & PAULING, L. (1939). *J. Am. Chem. Soc.* **61**, 1769–1780.

SORENSEN, G. O., MAHLER, L. & RASTRUP-ANDERSEN, J. (1974). *J. Mol. Struct.* **20**, 119–126.

TUCKER, P. A. & KROON, P. A. (1973). *Acta Cryst.* B**29**, 2967–2968.

Acta Cryst. (1990). C**46**, 609–614

Structures of 2,3,5,6-Tetrahalogeno-3′,4′-diphenylspiro[2,5-cyclohexadiene-1,2′-oxetan]-4-one, $C_{20}H_{12}O_2X_4$ (X = F, Cl and Br)

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Abstract. Fluoro compound: $C_{20}H_{12}F_4O_2$, M_r = 360·31, $F(000)$ = 736, (I): *cis* isomer, triclinic, $P\overline{1}$, a = 10·938 (1), b = 16·336 (2), c = 9·925 (2) Å, α = 93·82 (1), β = 103·92 (1), γ = 104·00 (1)°, V = 1655·5 (5) Å^3, Z = 4, D_m = 1·43, D_x = 1·45 Mg m^{-3}, Cu $K\alpha$, λ = 1·5418 Å, μ = 1·093 mm^{-1}, R = 0·057 for 4740 observed reflections. (II): *trans* isomer, monoclinic, $P2_1/c$, a = 7·895 (2), b = 13·708 (4), c = 15·456 (3) Å, β = 94·54 (2)°, V = 1667·5 (7) Å^3, Z = 4, D_m = 1·42, D_x = 1·44 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 0·133 mm^{-1}, R = 0·058 for 1655 observed reflections. Chloro compound: $C_{20}H_{12}Cl_4O_2$, M_r = 426·13, $F(000)$ = 432, (III): *trans* isomer, triclinic, $P\overline{1}$, a = 10·060 (2), b = 10·652 (2), c = 10·030 (2) Å, α = 98·98 (2), β = 116·36 (1), γ = 76·76 (1)°, V = 935·6 (3) Å^3, Z = 2, D_x = 1·51 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 0·644 mm^{-1}, R = 0·034 for 3211 observed reflections. Bromo compound: $C_{20}H_{12}Br_4O_2$, M_r = 603·93, $F(000)$ = 576, (IV): *trans* isomer, triclinic, $P\overline{1}$, a = 10·354 (2), b = 10·885 (2), c = 10·149 (2) Å, α = 98·91 (2), β = 114·55 (2), γ = 75·72 (2)°, V = 1006·5 (4) Å^3, Z = 2, D_x = 1·99 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 8·480 mm^{-1}, R = 0·042 for 2434 observed reflections. All measurements were made at 296 K. In the oxetane rings of all the compounds, the bond lengths of O—C(3′) and C(1)—C(4′) are longer than those of O—C(1) and C(3′)—C(4′), respectively. The lengthening is caused by the strong electron-attracting ability of the halogen-substituted quinone moiety. The puckering angles [the dihedral angles between the C(1)—O—C(3′) and C(1)—C(4′)—C(3′) planes] range from 10·2 to 18·7° in all the *trans* halogen-substituted spirooxetanes. One of the two crystallographically independent molecules in (I) has a planar oxetane ring and the other has a puckered form with a puckering angle of 6·8 (3)°.

Introduction. Only a few X-ray analyses have been made of substituted oxetane derivatives. In the struc-