Fig. 1. A perspective view of funicin with the atomic-numbering scheme.

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Cyclohexylammonium μ-Disulfido-bis(trioxophosphate)(4—) Monohydrate, $4C_6H_{14}N_4^+.O_6P_2S_2^{4-}.H_2O$

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Abstract. $M_r = 640.82$, triclinic, space group $P\bar{1}$, $a = 10.646$ (3), $b = 14.469$ (4), $c = 11.565$ (3) Å, $\alpha = 102.62$ (2), $\beta = 96.34$ (1), $\gamma = 100.32$ (2)°, $V = 1689$ (1) Å³, $Z = 2$, $D_x = 1.260$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 2.63$ mm⁻¹, $T = 239$ K. Final $R = 5.7\%$ for 5118 unique X-ray diffractometer data. The anion displays P—O distances in the range 1.504 (3) to 1.522 (3) Å, the P—S and S—S bond lengths are 2.146 (2), 2.140 (1) and 2.072 (2) Å respectively, and the P—S—S—P torsion angle is 93 (1)°. The cyclohexyl-ammonium cations are hydrogen-bonded to phosphate and water O atoms, the latter being clathrated by three cyclohexyl groups in a basket-like arrangement.

Introduction. In the literature, the X-ray structures of several derivatives of dithiodiphosphonic acid have

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been reported such as μ-disulfido-bis(diisopropoxythio-phosphorus) (Lawton, 1970; Tkachev, Atovmayan & Shchepinov, 1976) and the μ-disulfido-bis(dimethyl-phosphine) coordination complex of Mn (Hoehne, Lindner & Ganz, 1978) but the unsubstituted anion as such has not yet been investigated. Because the recent application of nucleosidephosphorothioates and related molecules in biochemical studies has raised interest in the geometry of the thiophosphate group, the crystal-structure analysis of the tetrakis(cyclohexylammonium) salt of dithiodiphosphonic acid (I) was carried out.

Experimental. Dithiodiphosphonic acid was Syn-thesized according to Ladwig & Thilo (1965) and purified by column chromatography employing DEAE-Sephadex A25 equilibrated with 50mM triethylammon-ium bicarbonate (TEAB). Fractions eluted with a linear gradient (0·2–0·4M TEAB) were tested by addition of PdCl$_2$ which, if coordinated to dithiodiphosphonic acid, produces a yellow color. Pooled fractions were con-

centrated and converted to the corresponding cyclohex-ylammonium salt (I) by addition of cyclohexylamine. This was followed by repeated addition and evaporation of methanol and recrystallization from aqueous ethanol.

Needle-shaped colorless crystal, 0·4 × 0·2 × 0·17 mm, longest dimension along c axis, space group $P1$ or $P\bar{1}$ by photographic methods, 5118 data up to $\sin\theta/\lambda = 0·56$ Å^{-1}, Stoe four-circle diffractometer, Ni-filtered Cu $K\alpha$, $\omega/2\varphi$ scan mode with stationary background counts (7·5s each), 70 steps 0·01° wide, measuring time 0·5s per step, range of hkl $0\pm11, 0\pm16$, 0–12, 12 reflections used for measuring lattice parameters, no absorption correction applied, only $F_o > 3\sigma(F_o)$ included in refinement; centrosymmetric space group $P\bar{1}$ indicated by E statistics obtained with MULTAN (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) but because attempts to solve crystal structure on the basis were unsuccessful non-centrosymmetric space group $P1$ used and MULTAN provided positions of P and S atoms; remaining C, O, N atoms located from difference Fourier syntheses, atomic parameters refined by full-matrix least-squares methods (ORFLS 4, Busing, Martin & Levy, 1977) with $w = 1/\sigma^2(F)$ where $\sigma(F)$ is based on counting statistics; scattering factors taken from International Tables for X-ray Crystallography (1974), $F(000) = 696$, structure finally transformed into centrosymmetric space group $P\bar{1}$, further refinement included H atoms with constant isotropic temperature factors B (4·5 Å^2) and took anomalous-dispersion effects of P and S into account. Final $R_w = 5·0\%$.

Discussion. Atomic parameters and selected geometri-cal data are given in Tables 1 to 3.* Fig. 1 shows the coordination of two dithiodiphosphonate anions sur-rounded by cyclohexylammonium ions; the molecular packing is illustrated in Fig 2. Comparison of observed P–S and S–S bond lengths, Table 2, with those of related compounds mentioned in the Introduction reveals no unusual features and suggests that they are predominantly of single-bond character. For the P–O bond lengths in the range 1·504 (3) to 1·522 (3) Å, however, considerable double-bond contributions are indicated, i.e. the negative charge and double bond are evenly distributed over the three P–O bonds in each of the two thiophosphate groups.

Table 1. *Fractional atomic coordinates of non-H atoms and equivalent isotropic temperature factors* (Å^2)

Mean $\bar{B}$'s were obtained from anisotropic β's $[\bar{B} = \frac{1}{3}(B_{11} + B_{22} + B_{33})]$. Figures in parentheses refer to last digits given and are calculated from the least-squares correlation matrix.

	x	y	z	B_{eq}
P(1)	0·5879 (1)	1·0098 (1)	0·7365 (1)	3·3 (1)
P(2)	0·1606 (1)	0·9519 (1)	0·7520 (1)	3·4 (1)
S(1)	0·4393 (1)	1·0877 (1)	0·7041 (1)	4·9 (1)
S(2)	0·3167 (1)	1·0731 (1)	0·8292 (1)	4·2 (1)
O(11)	0·6255 (2)	1·0279 (2)	0·8709 (2)	4·5 (1)
O(12)	0·6925 (2)	1·0570 (2)	0·6770 (2)	4·4 (1)
O(13)	0·5313 (3)	0·9045 (2)	0·6781 (3)	4·3 (1)
O(21)	0·0649 (2)	0·9747 (2)	0·8349 (2)	4·6 (1)
O(22)	0·2101 (3)	0·8611 (2)	0·7614 (2)	5·3 (1)
O(23)	0·1184 (2)	0·9530 (2)	0·6239 (2)	4·0 (1)
O(W)	0·9195 (5)	0·3288 (4)	0·2850 (5)	15·2 (3)
C(11)	0·7109 (4)	0·2581 (3)	0·5203 (4)	3·8 (1)
C(12)	0·8480 (4)	0·2984 (3)	0·5698 (5)	6·1 (2)
C(13)	0·8735 (5)	0·4101 (4)	0·6038 (6)	8·1 (3)
C(14)	0·7849 (7)	0·4462 (3)	0·6868 (5)	8·2 (3)
C(15)	0·6493 (6)	0·4031 (4)	0·6402 (6)	9·3 (3)
C(16)	0·6231 (4)	0·2918 (3)	0·6061 (5)	6·7 (2)
N(1)	0·6843 (3)	0·1493 (2)	0·4870 (3)	3·8 (1)
C(21)	0·9574 (4)	0·1814 (3)	0·9806 (4)	4·1 (2)
C(22)	1·0940 (4)	0·1966 (3)	1·0447 (4)	4·8 (2)
C(23)	1·1562 (5)	0·3038 (4)	1·0801 (5)	6·3 (2)
C(24)	1·1541 (6)	0·3474 (4)	0·9730 (5)	8·3 (3)
C(25)	1·0184 (6)	0·3304 (4)	0·9080 (6)	10·1 (3)
C(26)	0·9536 (5)	0·2220 (4)	0·8712 (4)	6·4 (2)
N(2)	0·8968 (3)	0·0761 (2)	0·9477 (3)	3·6 (1)
C(31)	0·5445 (4)	0·2326 (3)	0·0809 (4)	4·2 (1)
C(32)	0·6354 (5)	0·2785 (3)	0·0101 (4)	7·3 (2)
C(33)	0·6142 (6)	0·3812 (4)	0·0068 (6)	9·9 (3)
C(34)	0·6278 (6)	0·4429 (3)	0·1341 (5)	7·7 (2)
C(35)	0·5382 (5)	0·3967 (3)	0·2057 (5)	7·1 (2)
C(36)	0·5564 (5)	0·2942 (3)	0·2068 (4)	5·8 (2)
N(3)	0·5686 (3)	0·1341 (2)	0·0853 (3)	4·0 (1)
C(41)	0·2222 (3)	0·1555 (3)	0·4836 (3)	3·7 (1)
C(42)	0·2094 (4)	0·2036 (3)	0·3785 (4)	4·9 (2)
C(43)	0·2803 (5)	0·3091 (3)	0·4188 (4)	6·2 (2)
C(44)	0·2299 (5)	0·3634 (3)	0·5262 (5)	6·8 (2)
C(45)	0·2392 (5)	0·3128 (3)	0·6301 (4)	6·6 (2)
C(46)	0·1691 (4)	0·2069 (3)	0·5906 (4)	5·3 (2)
N(4)	0·1527 (3)	0·0523 (2)	0·4445 (3)	4·2 (1)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and the geometrical data of the cyclohexyl groups have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38178 (46 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 (°)*

P(1)—S(1)	2·146 (2)	P(2)—S(2)	2·140 (1)
S(1)—S(2)	2·072 (2)		
P(1)—O(11)	1·514 (3)	P(2)—O(21)	1·504 (3)
P(1)—O(12)	1·510 (3)	P(2)—O(22)	1·522 (3)
P(1)—O(13)	1·508 (3)	P(2)—O(23)	1·504 (3)

Mean value of C—C = 1·51 (3), C—N = 1·49 (7)

O(13)—P(1)—O(12)	114·9 (2)	O(21)—P(2)—O(23)	114·7 (2)
O(13)—P(1)—O(11)	112·2 (2)	O(21)—P(2)—O(22)	113·5 (2)
O(12)—P(1)—O(11)	113·2 (1)	O(23)—P(2)—O(22)	112·1 (2)
S(1)—P(1)—O(11)	107·9 (1)	S(2)—P(2)—O(21)	99·7 (1)
S(1)—P(1)—O(12)	101·0 (1)	S(2)—P(2)—O(22)	107·2 (1)
S(1)—P(1)—O(13)	106·6 (1)	S(2)—P(2)—O(23)	108·6 (1)
S(2)—S(1)—P(1)	107·18 (6)		
S(1)—S(2)—P(2)	108·77 (6)		

Mean value of C—C—C = 111·3 (9), N—C—C = 109·9 (6)

Table 3. *Structural characteristics of the hydrogen bonds*

|	O···O (Å)	O—H (Å)	H···O (Å)	O—H···O (°)
N(1)—H(N1A)···O(12)	2·812 (5)	0·899 (4)	1·922 (3)	170·2 (2)
N(1)—H(N1B)···O(13)	2·695 (4)	0·871 (3)	1·843 (3)	165·5 (2)
N(1)—H(N1C)···O(23)	3·022 (4)	0·907 (3)	2·134 (3)	166·2 (2)
N(2)—H(N2A)···O(21)	2·770 (4)	0·927 (3)	1·902 (3)	155·0 (2)
N(2)—H(N2B)···O(21)	2·778 (4)	0·850 (4)	1·963 (3)	160·3 (2)
N(2)—H(N2C)···O(11)	2·839 (4)	0·971 (3)	1·897 (2)	162·8 (2)
N(3)—H(N3A)···O(22)	2·769 (4)	0·822 (3)	1·970 (3)	163·6 (2)
N(3)—H(N3B)···O(11)	3·006 (4)	0·840 (3)	2·257 (3)	148·6 (2)
N(3)—H(N3C)···O(11)	2·807 (4)	0·930 (3)	1·898 (3)	165·2 (2)
N(4)—H(N4A)···O(23)	2·889 (4)	0·906 (3)	2·002 (3)	166·1 (2)
N(4)—H(N4B)···O(12)	2·768 (4)	0·908 (3)	1·881 (3)	165·3 (2)
N(4)—H(N4C)···O(23)	2·789 (4)	0·908 (3)	1·881 (3)	167·3 (4)
O(W)···O(22)	2·753 (5)	—	—	—
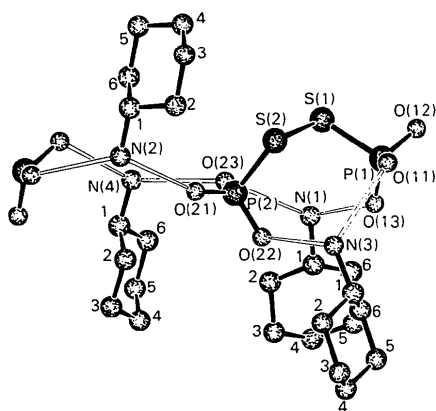
Fig. 1. *SCHAKAL* plot (Keller, 1980) showing coordination of two dithiodiphosphonate anions (in *x,y,z* and *x*+1,*y,z*) surrounded by cyclohexylammonium ions. Atoms are labelled according to the convention used in Table 1 and hydrogen bonds are indicated by open lines. N atoms are designated N(1) to N(4) and C atoms of respective attached cyclohexyl rings are numbered 1 to 6.
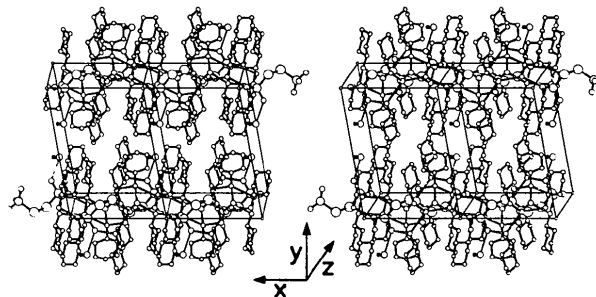

Fig. 2. *ORTEP* stereo picture (Johnson, 1965) illustrating the molecular packing of the title compound in the unit cell. H atoms are not shown, for the sake of clarity. Spheres of increasing size are C, N, O, P, S. Covalent bonds are filled and hydrogen bonds are indicated by thin lines.

The bond angles in the anion are in the usual range except in S(1)—P(1)—O(12), 101·0 (1)°, and S(2)—P(2)—O(21), 99·7 (1)°, which are about 7° smaller than the other S—P—O angles in this molecule. This distortion can be attributed to crystal-packing forces which might be sufficiently strong to influence molecular geometry especially if the relatively long and 'soft' P—S bonds are involved.

The P—S—S—P torsion angle, 93·3 (7)°, is in the synclinal range and different from the antiperiplanar angle observed in μ-disulfido-bis(diisopropoxy-thiophosphorus) (Lawton, 1970), the synclinal (120°) found in the μ-disulfido-bis(dimethylphosphine) coordination complex of Mn (Hoehne *et al.*, 1978) and the synclinal (72·8°) in cyclic P_2S_4 (Minshall & Sheldrick, 1978). Thus it appears that the rotation about the S—S bond in these systems is not severely inhibited by steric factors. In the case of (I), the conformation of the dithiodiphosphonate anion is stabilized by two cyclohexylammonium cations forming two pairs of hydrogen bonds to the two terminal phosphate groups.

The crystal-packing scheme displays clear separation into hydrophobic and hydrophilic zones, the former being constituted by cyclohexyl residues whereas dithiodiphosphonate anions are held together by hydrogen bonds to ammonium groups and form extended hydrophilic layers, Table 3. The two water of hydration molecules per unit cell are fixed by clathration through three cyclohexyl groups in a basket-like arrangement. In addition, the water molecules are hydrogen-bonded to phosphate oxygen at the bottom of the basket whose open top is closed by a nearby cyclohexyl group.

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Methyldigitoxigenin, $C_{24}H_{36}O_4$ *†

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Abstract. $M_r = 388.54$, orthorhombic, $P2_12_12_1$, $a = 7.249$ (1), $b = 15.109$ (1), $c = 19.268$ (3) Å, $V = 2110.33$ Å^3, $Z = 4$, $D_c = 1.223$ Mg m^{-3}, $\lambda(Cu K\alpha_1) = 1.5406$ Å, $\mu = 0.61$ mm^{-1}, $T = 296$ K. Final $R = 0.075$ for 1210 observed reflections. The structure is similar to that of digitoxigenin. The ring junctions A/B and C/D are cis. The molecules are linked together by hydrogen bonds between terminal OH and C=O groups, forming infinite chains parallel to the b axis.

Introduction. The naturally occurring *Digitalis* glycosides are the most effective drugs used in the treatment of heart disease, but at the same time they are highly toxic. Until recently it was believed that the inotropic and the toxic effects of *Digitalis* cardenolides could not be separated. However, in an effort to prepare cardenolide analogues with low toxicity, the two epimeric methyldigitoxigenins (I and II) have been synthesized by Professor K. Wiesner and his colleagues at the University of New Brunswick, Canada. In one of the epimers, one face of the active lactone group is blocked by a methyl group. If the inotropic and toxicity receptors used opposite faces of the lactone group, then one of the derivatives will be inotropic while the other will be toxic. Investigations are in progress to study the toxic and inotropic effects of methyldigitoxigenin. We report here the crystal-structure analysis of the major epimer of methyldigitoxigenin, which has been undertaken to determine the conformation of the lactone group and the configuration at C(21).

(I) a = H, b = Me
(II) a = Me, b = H
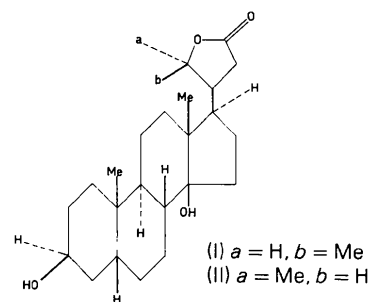
Experimental. Colourless, irregular plate-like crystals of the major epimer of methyl-digitoxigenin supplied by Professor K. Wiesner, 0.15 × 0.3 × 0.35 mm crystal, graphite-monochromatized Cu $K\alpha$, Picker four-circle automatic diffractometer, 3111 reflections up to 110° in 2θ measured by $\theta/2\theta$ scan method, line-profile analysis (Grant & Gabe, 1978), 1554 unique, 1210 had $I_{net} \geq 2.5\sigma(I_{net})$, corrected for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979) but not for absorption; cell parameters from least-squares refinement of the setting angles of 56 reflections with $2\theta > 60°$; structure solved using MULTAN (Germain, Main & Woolfson, 1971) and 241 largest E values; H atoms located in a difference map but parameters not refined; least-squares refinement with anisotropic parameters for C and O, $w = 1/\sigma^2(F)$ where $\sigma(F)$ is based on counting statistics, final $R = 0.075$, $R_w = 0.047$ for observed reflections and $R = 0.096$, $R_w = 0.048$ for all reflections, extinction correction included (Larson, 1970); $F(000) = 848$, scattering curves for neutral atoms from *International Tables for X-ray*

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* 3β,14β-Dihydroxy-21-methyl-5β-card-20(22)-enolide.
† NRCC publication No. 20720.