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Structure of 19-Methylstrychninium (*S*)-{*S*-[(*R*)-1,2-Di(ethoxycarbonyl)ethyl] *O*-Methyl Phosphorodithioate}

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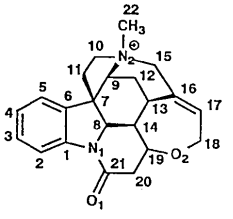
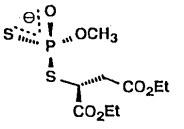
Abstract. $C_{22}H_{25}N_2O_2^+.C_9H_{16}O_6PS_2^-$, $M_r = 664.77$, monoclinic, $P2_1$, $a = 8.3925$ (14), $b = 8.0054$ (14), $c = 24.3050$ (42) Å, $\beta = 98.518$ (6)°, $V = 1614.9$ (6) Å^3, $Z = 2$, $D_m = 1.42$ (3), $D_x = 1.37$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å (Zr filter, no monochromator), $\mu = 2.2$ cm^{-1}, $F(000) = 704$, $T = 294$ (2) K, $R = 0.049$ and $wR = 0.046$ for 2417 unique observed reflections. The crystal structure consists of sheets of *N*-methylstrychninium cations in a bilayer, which alternate with sheets of phosphorodithioate anions, also in a bilayer. The anion is a dealkylated precursor to a specific stereoisomer of isomalathion, and its two chiral centers are identified as *S* at the P atom and *R* at the C atom.

Experimental. Berkman prepared the title compound using a procedure modified from that of Hilgetag (1969), and obtained suitable crystals (as large flat parallelepipids) from 1:5 methanol–ether. The crystal is composed of *N*-methylstrychninium cations (I) and phosphorodithioate diester anions (II).



(I)



(II)

Density was determined by flotation in a CCl_4–$CHCl_3$ mixture. All other measurements were made with a modified Picker FACS-I diffractometer using Zr-filtered Mo radiation without a monochromator. The data crystal was a cut fragment of dimensions 0.40 × 0.24 × 0.20 mm. Cell constants were determined from $\pm 2\theta$ values of 25 reflections in the range $22 < 2\theta < 28°$, and intensities were measured by θ–2θ scans of width $(1.25 + 0.5\tan\theta)°$, bracketed by stationary counting at edges for 10 s. Intensity data were collected to $2\theta_{max} = 50°$ (maximum $\sin\theta/\lambda = 0.59$ Å^{-1}) and encompassed h, $\pm k$, $\pm l$ indices spanning limits of 0→9, ±9 and ±28, respectively. Of the 5806 reflections surveyed, 3063 were unique ($R_{int} = 0.0459$) and 2417 were considered observed by the criterion $I > 2.5\sigma(I)$. Intensities of four standard reflections (112, 22$\bar{1}$, 1$\bar{2}$3 and 1$\bar{2}\bar{1}$), monitored after every 150 measurements, showed random variations of ±2%. Intensities of 0k0 reflections as a function of φ angle (with χ at 90°) showed less than 5% variation. Consequently, corrections for decay and absorption were not deemed necessary. No correction was made for extinction effects.

The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and was facilitated by input of model coordinates for strychnine. Refinement was based on least-squares minimization of $\sum w(\Delta F)^2$ using *SHELX*76 (Sheldrick, 1976). Atomic scattering factors and real and imaginary components for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All non-H atoms behaved well during anisotropic refinement except for the terminal atom C31 of an anion ester group which was too close to C30. Nevertheless, subsequent difference Fourier electron density maps revealed all H atoms. Refinement continued on 396 parameters with H atoms fixed at idealized positions ($d = 0.95$ Å, $U_H = 0.06$ Å^2), and with the C31—C30 distance set to match that of the similar C26–C27

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Table 1. *Coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
O1	2912 (6)	−4827 (6)	9830 (2)	71 (5)
O2	6785 (5)	−3859 (5)	8683 (2)	61 (5)
N1	3271 (5)	−6397 (6)	9077 (2)	40 (4)
N2	5417 (6)	−9275 (6)	7702 (2)	47 (5)
C1	2397 (6)	−7832 (7)	9179 (2)	38 (5)
C2	1347 (5)	−8034 (7)	9560 (2)	47 (5)
C3	636 (6)	−9587 (8)	9581 (2)	54 (5)
C4	954 (6)	−10883 (7)	9246 (2)	51 (5)
C5	1989 (6)	−10652 (7)	8864 (2)	47 (5)
C6	2739 (6)	−9105 (6)	8836 (2)	35 (5)
C7	3786 (6)	−8501 (7)	8419 (2)	34 (5)
C8	4377 (6)	−6781 (7)	8672 (2)	35 (5)
C9	5153 (7)	−9675 (7)	8309 (2)	41 (6)
C10	4064 (7)	−8143 (8)	7463 (2)	48 (6)
C11	2790 (6)	−8320 (7)	7835 (2)	43 (6)
C12	6692 (7)	−9529 (7)	8699 (3)	48 (6)
C13	7264 (6)	−7725 (7)	8712 (2)	45 (6)
C14	6080 (6)	−6708 (7)	8996 (2)	37 (5)
C15	7028 (7)	−8438 (8)	7685 (3)	60 (7)
C16	7374 (7)	−7147 (7)	8124 (3)	52 (6)
C17	7816 (8)	5605 (8)	8018 (3)	69 (7)
C18	8157 (8)	−4305 (8)	8441 (3)	72 (7)
C19	6458 (7)	−4859 (8)	9135 (3)	48 (6)
C20	5034 (8)	−4033 (8)	9341 (3)	63 (8)
C21	3652 (8)	−5107 (8)	9450 (3)	51 (7)
C22	5411 (8)	−10876 (9)	7382 (3)	62 (7)
P	96390 (15)	2500	127903 (5)	470 (12)
S1	7870 (2)	1224 (3)	12379 (1)	61 (2)
S2	8653 (2)	3474 (3)	13482 (1)	53 (1)
O3	10439 (4)	3851 (5)	12530 (2)	65 (4)
O4	11063 (4)	1301 (5)	13063 (2)	61 (4)
O5	10172 (7)	6268 (8)	14634 (2)	102 (7)
O6	8520 (6)	7149 (6)	13885 (2)	73 (5)
O7	13503 (6)	6079 (8)	13913 (2)	90 (7)
O8	14260 (7)	4186 (8)	14553 (2)	91 (7)
C23	10745 (8)	−199 (9)	13346 (3)	75 (7)
C24	10297 (7)	4873 (7)	13770 (2)	57 (6)
C25	9664 (7)	6158 (9)	14149 (2)	66 (6)
C26	7941 (10)	8455 (10)	14216 (3)	91 (9)
C27	6559 (11)	9256 (11)	13871 (4)	113 (13)
C28	11690 (7)	3926 (9)	14076 (3)	72 (8)
C29	13204 (8)	4895 (11)	14170 (3)	64 (8)
C30	15814 (9)	4954 (13)	14628 (4)	112 (14)
C31	16880 (10)	4064 (14)	15053 (4)	153 (19)

Table 2. *Interatomic distances* (Å) *and angles* (°) *for the phosphorodithioate diester anion*

P—S1	1.951 (2)	O6—C26	1.446 (8)
P—S2	2.130 (2)	O7—C29	1.182 (8)
P—O3	1.466 (4)	O8—C29	1.315 (8)
P—O4	1.598 (4)	O8—C30	1.428 (9)
S2—C24	1.833 (5)	C24—C25	1.529 (8)
O4—C23	1.429 (7)	C24—C28	1.496 (8)
O5—C25	1.196 (7)	C26—C27	1.474 (11)
O6—C25	1.334 (7)	C28—C29	1.477 (9)
		C30—C31	1.449 (6)

S1—P—S2	104.0 (1)	S2—C24—C28	111.6 (4)
S1—P—O3	121.9 (2)	C25—C24—C28	110.9 (5)
S2—P—O3	109.1 (2)	O5—C25—O6	123.8 (6)
S1—P—O4	111.3 (2)	O5—C25—C24	122.6 (7)
S2—P—O4	104.3 (2)	O6—C25—C24	113.6 (5)
O3—P—O4	105.1 (2)	O6—C26—C27	107.5 (6)
P—S2—C24	99.6 (2)	C24—C28—C29	113.7 (6)
P—O4—C23	121.5 (4)	O7—C29—O8	123.1 (7)
C25—O6—C26	116.1 (5)	O7—C29—C28	125.8 (7)
C29—O8—C30	114.3 (6)	O8—C29—C28	110.9 (7)
S2—C24—C25	109.4 (4)	O8—C30—C31	109.6 (7)

atom pair. After the final cycle of refinement, R was unchanged from 0.0491 and wR from 0.0463, the goodness of fit (S) was 0.978, the weighting factor was $0.7838/[\sigma^2(F) + 0.000198F^2]$, $\Delta/\sigma < |0.02|$, $(\Delta\rho)_{max} = 0.2$ e Å^{-3} closest to C31, and $(\Delta\rho)_{min} =$

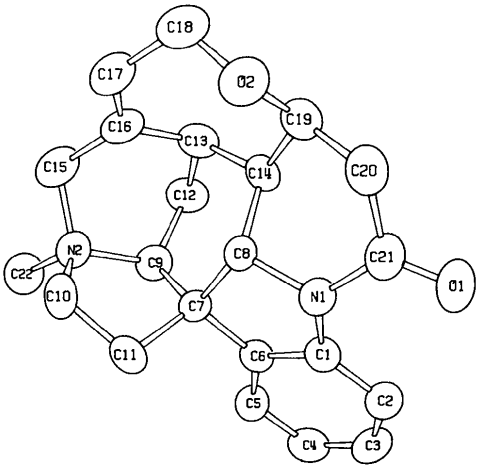

Fig. 1. An *ORTEP*II (Johnson, 1976) diagram of the *N*-methylstrychninium cation using 50% probability ellipsoids.

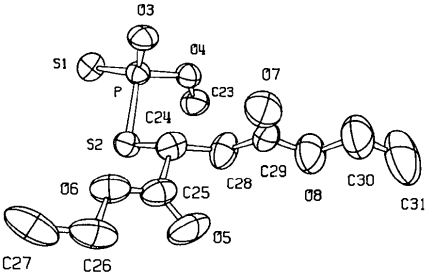

Fig. 2. An *ORTEP*II (Johnson, 1976) diagram of the phosphorodithioate diester anion using 50% probability ellipsoids.

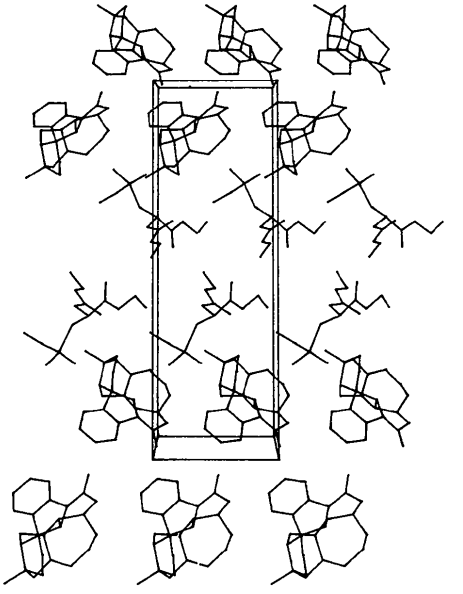

Fig. 3. An *ORTEP*II (Johnson, 1976) diagram of the unit cell and its surroundings showing the alternating bilayers of *N*-methylstrychninium cations and phosphorodithioate diester anions. The atoms are reduced to points and the view is almost normal to the *bc* plane.

-0.2 e Å^{-3}. Final parameters are given in Table 1,* and Table 2 shows anion bond distances and angles. *ORTEP*II (Johnson, 1976) diagrams of cation, anion and cell are shown in Figs. 1, 2 and 3, respectively.

Related literature. The absolute configuration of strychnine has been reported by Peerdeman (1956). Gould & Walkinshaw (1984) have reported on the bilayer packing pattern of strychnine salts. In a subsequent work, Gould, Taylor & Walkinshaw (1987) reported the structures of strychnine salts for both enantiomers of tartaric acid. The possibility of thermal and photochemically induced isomerization of the phosphorothionate entity in malathion, to the more toxic phosphorodithiolate present in isomalathion, is presented in several papers (Metcalf & March, 1953; Rengasammy & Parmar, 1988; Chukwudebe, March, Othman & Fukuto, 1989; Thompson, Frick, Natke & Hansen, 1989).

* Lists of anisotropic thermal parameters, H-atom coordinates, bond distances and angles for the *N*-methylstrychninium cation and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55585 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1007]

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Structure of (3aα,4α,7α,7aα)-2,2-Dimethyl-3a,4,7,7a-tetrahydro-1,3-benzodioxolane-4,7-diamine

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Abstract. $C_9H_{16}N_2O_2$, $M_r = 184.2$, rhombohedral, $R3$, $a = 12.594$ (2) Å, $\alpha = 118.03$ (1)°, $V = 720$ (2) Å^3, $Z = 3$, $D_x = 1.274$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 0.70$ mm^{-1}, $F(000) = 300$, $T = 290$ (1) K, final $R = 0.047$ for 1191 reflections with $I \geq 2\sigma(I)$. Although the title molecule (I) is a *meso* compound, it does not have exact mirror symmetry in the solid state. The observed distortions, which no doubt arise from the fusion of the two rings, results in two enantiomeric forms with any given crystal containing only the one enantiomer (*e.g.* with 3a*S*,-4*R*,7*S*,7a*R* configurations). The cyclohexene ring is in a fairly regular boat form with asymmetry parameter [Duax & Norton (1975). *Atlas of Steroid Structure*, Vol. I, pp. 18–19. New York: Plenum] $\Delta C_s = 5.8°$ and the amino substituents in equatorial positions. The conformation of the *cis*-fused oxolane ring is between a half chair and an envelope as is reflected by the pseudorotational parameters [Altona, Geise & Romers (1968). *Tetrahedron*, **24**, 13–32] $\Delta = 12.5°$ and $\varphi_m = 35.6°$. Intermolecular hydrogen bonds involving the exocyclic N atoms link each molecule to four adjacent molecules to form a three-dimensional network: the N(4)···N(4) [$(z, x, -1 + y)$,

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