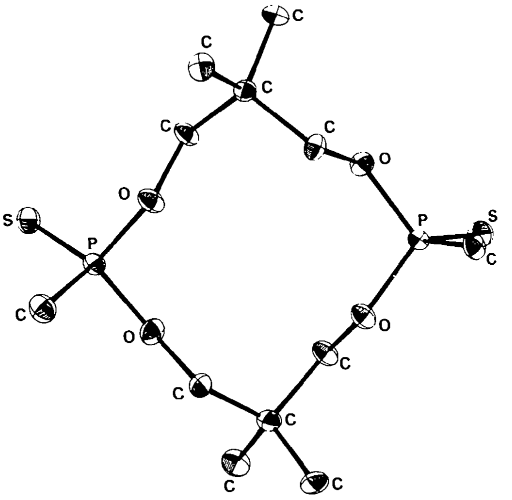

Fig. 1. *cis*-2,8-Dithioxo-2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane.

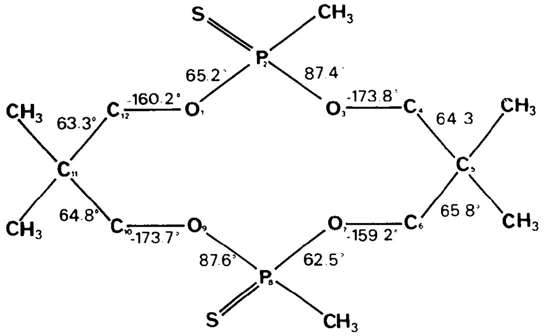

Fig. 2. Torsion angles across the ring.

the ring as a result of steric requirements (Dale, 1973). Similarly, 1,3,7,9-tetraoxacyclododecane adopts the same conformation with the O atoms placed across the corners, as found by NMR for 1,3,7,9-tetraoxacyclododecane (Borgen & Dale, 1974), and for 2,2,8,8-tetramethyl-1,3,7,9-tetraoxacyclododecane (Borgen, 1975). In (II), the P and the *gem*-dimethyl C atoms are situated at the corners. This conformation satisfies the steric requirements due to the P substituents and the preferred *gauche*(±),*gauche*(±) conformation around the P—O bond (Van der Veken & Herman, 1977).

At room temperature, the ^{1}H NMR spectrum of (II) shows the two coupling constants ^3J(POCH) to be nearly equal (5·5 and 6·5 Hz respectively). Such a value corresponds to a POCH dihedral angle close to 60° (Dutasta, Grand, Robert & Taieb, 1974), in agreement with the conformation observed in the solid state.

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Structure of Diethylammonium Diethyldithiocarbamate

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Abstract. $[(CH_3CH_2)_2NH_2]^+[(CH_3CH_2)_2NCS_2]^-$, $C_9H_{22}N_2S_2$, monoclinic, $P2_1/c$, $a = 11{\cdot}175$ (2), $b = 7{\cdot}755$ (1), $c = 15{\cdot}605$ (2) Å, $\beta = 90{\cdot}53$ (1)°, $Z = 4$, $V = 1352{\cdot}3$ Å^3, $D_m = 1{\cdot}094$, $D_x = 1{\cdot}092$ Mg m^{-3}, m.p. 354–355 K. The structure has been refined to $R(F^2) = 0{\cdot}048$ for 1546 reflexions and 206 varied parameters. It is built up of helical chains along **b**. The ammonium H and the dithiocarbamate S atoms link the ions together at H···S distances of 2·42 (2), 2·46 (3), 2·90 (3) and 3·12 (2) Å.

Introduction. This investigation follows the structural studies of dimethylammonium dimethyldithiocarbamate (M) (Wahlberg, 1978*a*), and diisopropylammonium diisopropyldithiocarbamate (iP) (Wahlberg, 1978*b*).

The compound was synthesized in benzene from diethylamine and CS_2 and was recrystallized from a mixture of CS_2 and petroleum (b.p. 333–358 K). The transparent colourless crystals appeared as long needles along [010]. The crystals sublimed markedly from *ca* 10 K below the melting point. The space-group assumption was made from systematically absent reflexions among *h*0*l* for *l* odd and 0*k*0 for *k* odd. The cell parameters were based on 26 lines from a Guinier–Hägg powder photograph. The internal standard was CoP_3 ($a = 7\cdot70778$ Å) and the radiation was Cr $K\alpha_1$.

A crystal was cut parallel to (010) and sealed in a thin-walled glass capillary. Distances between pairs of surfaces were: (010) 0·27, (100) 0·15, (001) 0·20, (101) 0·17 and $(\bar{1}01)$ 0·17 mm. Intensities were collected on a Stoe–Philips four-circle PDP 8/I computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The count rate was reduced by the factor 2^n ($0 \le n \le 5$). A unique set of intensities was thus obtained from one quadrant of reciprocal space ($4\cdot5 < 2\theta < 43°$). The longest scan time, in the ω–2θ mode, was 160 s. Background was measured on each side of a reflexion for 25 s. The intensities of three standards, measured every 40 reflexions, first increased by *ca* 1%, and then decreased by *ca* 5%. The variation could be described by two least-squares lines. The data were scaled to the mean level with the use of these lines, and corrected for background and for Lorentz, polarization and absorption effects [μ(Mo $K\alpha$) = 0·346 mm^{-1}]. The transmission factor varied from 0·94 to 0·96. 1967 intensities were reduced to 1546 structure factors [$F_m^2 > -1\cdot86\sigma(F^2)$ and $0\cdot060 < (\sin\theta)/\lambda < 0\cdot516$ Å^{-1}].

The structure was solved by direct methods (Long, 1965). The H atoms were located from a difference synthesis. 206 independent parameters were varied and all the structure factors were included in the last cycle of full-matrix least-squares refinement. The thermal parameters were anisotropic for the non-hydrogen and isotropic for the H atoms. The fractional coordinates are given in Table 1. The final parameter shifts were $< 0\cdot11\sigma$ for the non-hydrogen and $< 0\cdot24\sigma$ for the H atoms. The expression minimized was $\sum w\delta^2$, where $\delta = F_m^2 - F_c^2$ and $w^{-1} = \sigma^2(F^2) = \sigma^2_{\text{count}}(F^2) + (0\cdot03F_m^2)^2$. The refinements converged at $R(F^2) = \sum|\delta|/\sum F_m^2 = 0\cdot048$ and $R_w(F^2) = (\sum w\delta^2/\sum wF_m^4)^{1/2} = 0\cdot073$.* $|\delta|/\sigma(F^2)$ was > 2·0 for 206 reflexions. The largest value was 6·0 for the reflexion 200. A normal ΔR probability plot (Abrahams & Keve, 1971) had a slope of 0·75 and an intercept of −0·04. A difference synthesis showed some spurious peaks of density < 0·05 e Å^{-3}. The scattering factors for S, N, C and H, and the f' and f'' anomalous-dispersion corrections for S, N and C were taken from *International Tables for X-ray Crystallography* (1974). Lundgren (1976) has described the computer programs. The calculations were performed on the IBM 370/155 and 1800 computers in Uppsala.

Table 1. *Fractional coordinates (for* S $\times 10^5$, *for* N *and* C $\times 10^4$ *and for* H $\times 10^3$)

	x	*y*	*z*		*x*	*y*	*z*
S(1)	27400 (6)	55709 (9)	21426 (4)	H(6)	335 (3)	−65 (4)	162 (2)
S(2)	38192 (5)	32975 (8)	34797 (4)	H(7)	237 (3)	−1 (4)	109 (2)
N(1)	1551 (2)	4336 (2)	3471 (1)	H(8)	663 (3)	195 (4)	49 (2)
N(2)	4826 (2)	2154 (3)	1598 (1)	H(9)	561 (3)	284 (4)	−8 (2)
C(1)	2604 (2)	4399 (3)	3056 (1)	H(10)	669 (3)	391 (4)	28 (2)
C(2)	1399 (3)	3385 (4)	4272 (2)	H(11)	515 (3)	461 (4)	119 (2)
C(3)	929 (4)	1586 (5)	4135 (3)	H(12)	618 (2)	378 (3)	169 (2)
C(4)	419 (4)	7053 (5)	3540 (3)	H(13)	87 (3)	405 (3)	461 (2)
C(5)	488 (2)	5260 (4)	3164 (2)	H(14)	219 (3)	336 (3)	456 (2)
C(6)	3807 (2)	1640 (4)	1030 (2)	H(15)	96 (3)	102 (4)	469 (2)
C(7)	3003 (3)	391 (5)	1471 (2)	H(16)	9 (4)	171 (5)	387 (2)
C(8)	6223 (3)	2995 (6)	433 (2)	H(17)	147 (3)	97 (4)	378 (2)
C(9)	5617 (3)	3534 (4)	1246 (2)	H(18)	110 (3)	783 (4)	333 (2)
H(1)	454 (2)	250 (3)	208 (2)	H(19)	−25 (4)	754 (5)	341 (2)
H(2)	525 (2)	115 (4)	170 (2)	H(20)	48 (4)	699 (5)	419 (3)
H(3)	344 (2)	271 (4)	88 (2)	H(21)	−24 (3)	452 (3)	331 (2)
H(4)	415 (2)	109 (3)	52 (2)	H(22)	51 (2)	533 (3)	256 (2)
H(5)	268 (3)	85 (4)	201 (2)				

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33870 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. *The chain.* The ions are linked to form helical chains extending along **b** (Fig. 1). The chains are packed at approximately the van der Waals distances (Bondi, 1964).

A 2_1 screw axis is situated at the centre of the chain. The ammonium H and the dithiocarbamate S atoms are involved in two ordinary and two long intermolecular H···S distances (corresponding N···S distances are given in square brackets): H(1)···S(2) 2·42 (2) [3·277 (2)], H(1)···S(1) 3·12 (2) [3·636 (2)], H(2)···S($2^{\rm i}$) 2·46 (3) [3·355 (3)] and H(2)···S($1^{\rm i}$) 2·90 (3) [3·560 (2) Å]. The two longest S···H distances are not very different from the van der Waals distance between uncharged atoms (3·00 Å, Bondi, 1964).

The shortest intermolecular ammonium H···H distance is the intrachain H(1)···H($2^{\rm i}$) = 3·42 (4) Å. No others are < 4·0 Å. The shortest intermolecular S···S distance is the intrachain S(1)···S($2^{\rm i}$) = 4·503 (2) Å.

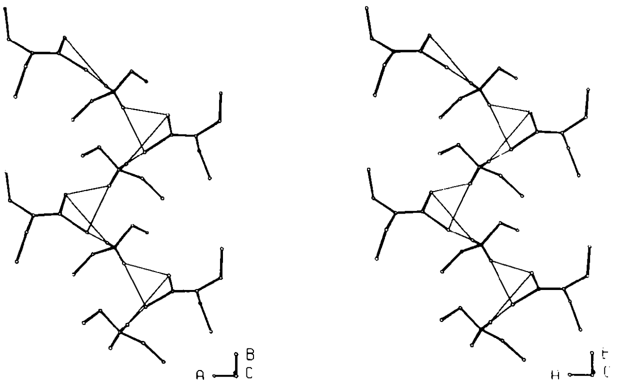

Fig. 1. Part of the helical chain; only the ammonium H atoms have been drawn.

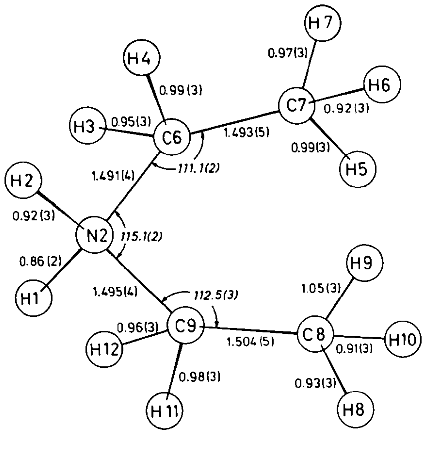

Fig. 2. Distances (Å) and angles (°) in the diethylammonium cation.

The diethylammonium cation (*Fig.* 2). C(7) and C(8) are −0·139 (4) and 1·228 (4) Å, respectively, from the plane through N(2), C(6) and C(9).

The diethyldithiocarbamate anion (*Fig.* 3). The non-hydrogen atom arrangement is similar to that in Cu$^{\rm I}$ diethyldithiocarbamate (Hesse, 1963) and in Tl$^{\rm I}$ diethyldithiocarbamate (Pritzkow & Jennische, 1975). The anion possesses an approximate twofold symmetry axis along C(1)—N(1).

The mean C—S distance is 1·715 Å. However, C(1)—S(1) is 16σ shorter than C(1)—S(2). This discrepancy probably originates from the intermolecular H···S bonding: S(1) participates in the two longest, S(2) in the two shortest distances. A similar effect on the C—S bonding in iP is obtained, with one H···S distance of 2·85 (3) *versus* two of 2·41 (3) and 2·52 (3) Å.

The dithiocarbamate plane is a little bent. Distances of some atoms from the least-squares plane through S(1), S(2), C(1), N(1), C(2) and C(5) are: S(1) 0·001 (1), S(2) 0·000 (1), C(1) −0·012 (2), N(1) −0·009 (2), C(2) 0·018 (3), C(5) 0·008 (3), C(3) −1·354 (4) and C(4) 1·420 (4) Å. C(1) and N(1) lie significantly below the other dithiocarbamate-plane atoms. The same tendency was also observed in M.

The bonds between the alkyl C and the N atoms are *ca* 8σ shorter in the anion than in the cation (Figs. 2 and 3), and are intermediate between those in M and iP, for the cation and for the anion.

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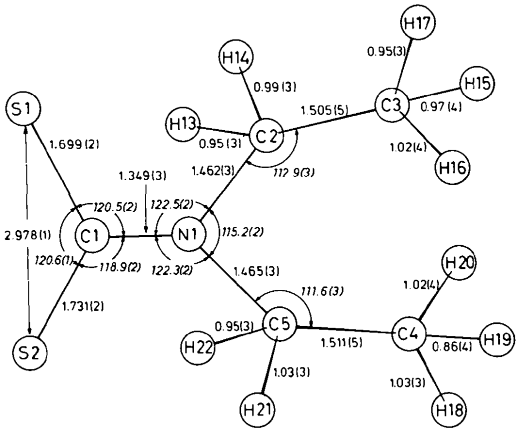

Fig. 3. Distances (Å) and angles (°) in the diethyldithiocarbamate anion.

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Acta Cryst. (1978). B**34**, 3825–3827

6-Acetoxy-5-methoxy-1-methyl-1,2,3,9a-tetrahydrocyclohexa[*ij*]isoquinoline-7-spiro-4′-(2′-methoxy-2′,5′-cyclohexadien-1′-one) Methiodide (Acetyl Dienone II Methiodide)

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Abstract. $C_{22}H_{25}NO_5.CH_3I$, $M_r = 525{\cdot}4$, m.p. 255 ~ 256 °C (crystallized from methanol solutions), $C2/c$, $a = 20{\cdot}435$ (10), $b = 11{\cdot}899$ (5), $c = 21{\cdot}379$ (10) Å, $\beta = 113{\cdot}74$ (1)°, $U = 4758$ Å^3, $Z = 8$, $D_x = 1{\cdot}467$ g cm^{-3}, μ(Mo $K\alpha$) = 13·6 cm^{-1}. The configuration around the spiro C atom has been determined to be such that the methoxy group of ring *D* is oriented *syn* with respect to the H atom at the junction of rings *B* and *C*.

Introduction. Kreysiginone (dienone I), a minor alkaloid of *Kreysigia multiflora*, is a homoproaporphine alkaloid existing as one of the two possible spiro isomers (Battersby, McDonald, Munro & Ramage, 1967; Battersby, Bradbury, Hervert, Munro & Ramage, 1974). The stereostructures of these two isomers, dienone I and dienone II (Fig. 1), have been proposed on the basis of chemical reactivity towards hydrochloric acid (Kametani, Satoh, Yagi & Fukumoto, 1967, 1968). Apart from the natural product, dienone II has been synthesized from a phenolic 1-phenethyltetrahydroisoquinoline and the structure of its methiodide derivative has been determined by X-ray methods. A brief account of the stereospecific synthesis has been published along with a preliminary report of the present structure determination (Hara, Hoshino, Umezawa & Iitaka, 1977).

Diffraction data were obtained from a crystal of approximate dimensions 0·13 × 0·18 × 0·25 mm. The lattice constants were determined by the least-squares treatment of the setting angles of 23 reflexions measured on a Philips PW 1100 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The 2θ angles ranged from 21 to 35°.

Intensities were measured by the θ–2θ scan method at a scan speed of 6° min^{-1} in θ. When the total counts during the first scan were less than 3000, scans were repeated twice. The background was measured at each end of the scan for half the total scan time.

2852 reflexions were measured in a θ range of 3 ~ 23°; of these, 2767 reflexions with $I > 2\sigma(I)$ were used for the subsequent structure analysis. The intensities were corrected for Lorentz and polarization factors but not for absorption. The crystal structure was determined by the heavy-atom method. The locations of almost all the lighter atoms were found on the electron density map synthesized by using the phase angles of the calculated structure factors with the iodide ion. Refinement of the structural parameters was carried out by the block-diagonal least-squares method using the program *HBLS* (Okaya & Ashida, 1967). The atomic scattering factors of C, N, O and I$^-$ and the dispersion corrections of the iodine atom for Mo $K\alpha$ radiation were taken from *International Tables for X-ray Crystallography* (1974). The following weighting system was adopted: $w^{1/2} = 0{\cdot}1$ for $F_o < 5$, $w^{1/2} = 5/|F_o|$ for $F_o > 5$. The final *R* value was 0·05. The atomic parameters are given in Table 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33848 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.