

der-Waals-bonded matrices formed by deoxycholeic acid (Giglio, 1984) and perhydrotriphenylene (Farina, 1984).

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Geometry of the Iminium Moiety. I. Structure of Pyrazolinium Salts and an *N*-Isopropylidene Derivative

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Abstract. Compound (I; PYCL), 4,5-dihydro-3,5,5-trimethylpyrazolium chloride, $C_6H_{13}N_2^+Cl^-$, $M_r = 148.64$, orthorhombic, $P2_12_12_1$, $a = 8.324$ (1), $b = 8.381$ (1), $c = 12.121$ (1) Å, $V = 845.60$ (16) Å³, $Z = 4$, $D_m = 1.17$ (1), $D_x = 1.167$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 3.31$ cm⁻¹, $F(000) = 320$, $T = 294$ K, $R = 0.030$ for 782 observed reflections. Compound (II; PYRA), bis(4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate monohydrate, $2C_6H_{13}N_2^+ \cdot SnCl_6^{2-} \cdot H_2O$, $M_r = 575.8$, orthorhombic, $Fdd2$, $a = 16.975$ (2), $b = 30.729$ (4), $c = 8.987$ (10) Å, $V = 4687.8$ (27) Å³, $Z = 8$, $D_m = 1.62$ (1), $D_x = 1.631$ g cm⁻³, $\mu = 16.5$ cm⁻¹, $F(000) = 2304$, $R = 0.021$ for 1927 observed reflections. Compound (III; PYCS), bis(4,5-dihydro-3,5,5-trimethyl-1-isopropylidene)pyrazolium hexachlorostannate, $2C_9H_{17}N_2^+ \cdot SnCl_6^{2-}$, $M_r = 637.9$, monoclinic, $C2/c$, a

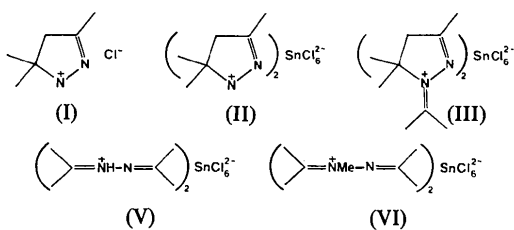
$= 14.145$ (1), $b = 11.630$ (1), $c = 17.054$ (6) Å, $\beta = 98.71$ (4)°, $V = 2773.1$ (10) Å³, $Z = 4$, $D_m = 1.52$ (1), $D_x = 1.528$ g cm⁻³, $\mu = 15.2$ cm⁻¹, $F(000) = 1288$, $R = 0.027$ for 1930 observed reflections. Compound (IV; MONS), $M_r = 654.8$, cubic, $Im\bar{3}$, $a = 17.886$ (4) Å, $V = 5721.9$ (42) Å³, $Z = 8$, $D_m = 1.52$ (1), $D_x = 1.520$ g cm⁻³, $\mu = 14.9$ cm⁻¹, $F(000) = 2400$, $R = 0.069$ for 644 observed reflections. The four structures arise from the condensation of hydrazine compounds with acetone. In (III) and (IV) the existence of the ternary iminium ion was confirmed. Strong hydrogen bonds exist in (I) and (II). (IV) is structurally disordered, containing an equal proportion of (II) and (III) and constraints were applied to several bond lengths of the rings during the final stages of refinement.

Introduction. The condensation product (Pugh, 1954) of hydrazine dihydrochloride with acetone, namely

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3,5,5-trimethylpyrazolinium chloride (I;* PYCL; $C_6H_{13}N_2^+.Cl^-$), was among the many salts of organic bases arising from these starting materials in the laboratories of W. Pugh and his collaborators. The majority of the salts prepared were hexachlorostannates, the complex anion conferring the desired insolubility and hence ease of crystallization. A key compound related to (I) was bis(3,5,5-trimethylpyrazolinium) hexachlorostannate (II; PYRA; $C_{12}H_{26}N_4^{2+}.SnCl_6^{2-}.H_2O$) which in a novel reaction was shown to condense further with acetone to yield bis(3,5,5-trimethyl-1-isopropylidene-pyrazolinium) hexachlorostannate (III; PYCS; $C_{18}H_{34}N_4^{2+}.SnCl_6^{2-}$) containing the ternary iminium ion. In the course of the reaction between acetone, hydrazine dihydrochloride and stannic chloride there were produced, in addition to prismatic crystals of (III), cubic crystals that have since proved to be an equimolar mixture (IV; MONS) of (II) and (III). The most convenient method of preparing (II) is by hydrolysis of the acid-sensitive iminium grouping present in (III) [either by using pure (III), or the mixture (IV)].

The interaction of a carbonyl compound with secondary N atoms in strongly acid solution, yielding (III), was of sufficient interest to give rise to an extensive investigation of the general reaction of aldehydes and ketones with secondary amines using $SnCl_6^{2-}$, among many others, as a suitable complex counter-ion. The components prepared included (Pugh & Stephen, 1953) the linear analogue (and isomer) of (II), bis(dimethylketazinium) hexachlorostannate (V; $C_{12}H_{26}N_4^{2+}.SnCl_6^{2-}$) and the corresponding ternary iminium salt (Lamchen, Pugh & Stephen, 1954a) bis(*N*-methyl-dimethylketazinium) hexachlorostannate (VI; $C_{14}H_{30}N_4^{2+}.SnCl_6^{2-}$) and many more complicated examples.



The existence of the iminium ion in salts typical of the many (Pugh, 1954; Lamchen, Pugh & Stephen, 1954a, b; Sohn, Marks & Pugh, 1955; Lamchen & Stephen, 1955) prepared in this way was demonstrated by 1H NMR spectroscopy of DMSO- d_6 solutions (Rathbone & Stephen, 1971), and the ease with which the ion could be decomposed by hydrolysis was investigated by this means. Hydrolysis rates depended, among other things, on the environments

of both the C atom and the doubly bonded, charged N atom. X-ray crystallography demonstrated the presence of the iminium cation in the condensation products of bis(3,5,5-trimethylpyrazolinium) hexachlorostannate (II) with the cyclic ketones cyclo-octanone and 4-methylhexanone (van Schalkwyk, Stephen & Hodgson, 1976), and with *m*-Cl- and *p*-HO-benzaldehydes (Galloway, Nassimbeni & Stephen, 1979); thus was proved the existence of the iminium ion, in both ketone and aldehyde condensation products, in the solid state. Furthermore, the nature of the geometrical isomerism about the $>C=N^+<$ system was confirmed [cf. the investigation by NMR (Rathbone, Stephen, Schwersenski & Tyler, 1975)] for the substituted benzylidene derivatives of (II).

The structures of (I), (II), (III) and (IV) are described in the present communication and those of (V) and (VI) are to follow.

Experimental. Using standard procedures (Pugh, 1954), (III) was prepared by the addition of a stoichiometric quantity of $N_2H_4.2HCl$ to a solution of $SnCl_4.3H_2O$ in excess acetone and boiling under reflux for *ca* 3 h. Crystals of prismatic (II) and sometimes cube-like (IV) formed on cooling. By dissolving this mixture of crystals in dry ethanol and heating under reflux for 1 h, prismatic crystals of (II) appeared on evaporation of excess ethanol. Prismatic crystals of (I) were obtained by boiling hydrazine dihydrochloride in dry acetone under reflux for *ca* 3 h. until dissolved, and removing excess acetone by distillation.

Density measurements of crystals were obtained by flotation in a water/saturated KI solution for (I), in a mixture of bromobenzene and bromoform for (II)-(IV), and measuring the density of the resulting liquids by means of a Paar DMA 35 density meter.

Crystals of all four compounds proved to be stable in air and were each mounted on glass fibres for preliminary photographic measurement and standard intensity data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $Mo K\alpha$ radiation. Accurate cell parameters were obtained by least-squares analysis of 24 reflections measured in the range $16 < \theta < 17^\circ$. The intensity data collection for all four crystals was carried out at 294 K, with scans in the $\omega-2\theta$ mode, variable speed and a maximum recording time of 40 s. Intensity variation of three standard reflections was monitored in each case and re-centring was carried out every 100 measured reflections. The range scanned was $1 < \theta < 25^\circ$ and all intensities were corrected for Lorentz and polarization factors as well as for absorption (North, Phillips & Mathews, 1968). Additional intensity and refinement data are given in Table 1.

* Alternative nomenclature for (I), (II) and (III) is used in the Introduction.

Table 1. *Experimental data and structure-refinement parameters*

	(I)	(II)	(III)	(IV)
Crystal dimensions (mm)	0.35 × 0.37 × 0.45	0.19 × 0.25 × 0.21	0.25 × 0.25 × 0.37	0.53 × 0.50 × 0.4
Range of indices <i>h</i>	0 → 9	0 → 20	-16 → 16	0 → 21
<i>k</i>	0 → 9	0 → 36	0 → 13	0 → 21
<i>l</i>	0 → 14	-10 → 10	0 → 20	0 → 21
Transmission factors				
Min. and max. (%)	97.2, 99.9	96.3, 99.9	91.5, 99.8	94.1, 98.6
Standard reflections (<i>h,k,l</i>)	3,6,2 6,2,3 1,2,9	3,15,9 4,10,10 11,11,3	1,9,2 11,1,6 2,6,10	10,6,8 10,6,8 6,8,10
Stability (%)	1.3	-0.8	0.7	10
Scan width ^a (y)	0.95	0.69	0.95	0.84
Aperture width ^b (x)	1.12	1.12	1.13	1.43
Total no. of reflections	853	2023	2184	888
Total no. of unique observed ^c	782	1927	1930	644
No. of variables	93	124	150	43
<i>R</i> _{int}	—	0.020	0.016	0.024
$\Delta\rho$ (min., max.) (e Å ⁻³)	-0.20, 0.10	-1.07, 0.34	-0.59, 0.29	-0.53, 0.39
Δ/σ (final)	< 0.35	< 0.12	< 0.13	< 0.001
<i>R</i>	0.030	0.021	0.027	0.069
<i>wR</i>	0.039	0.024	0.031	0.069
<i>S</i>	0.24	0.25	0.77	5.22
Weighting scheme, <i>w</i> ^d (g)	0.0077	0.0041	0.0021	unit

Notes: (a) Scan width, $\Delta\omega = (\gamma + 0.35\tan\theta)^\circ$. (b) Aperture width = $(x + 1.05\tan\theta)$ mm. (c) $I > 2\sigma(I)$. (d) $w = (\sigma^2F + gF^2)^{-1}$.

The structures were solved by normal heavy-atom and direct methods, and refined by full-matrix least squares using the *SHELX76* (Sheldrick, 1976) program system. Final refinements for (I), (II) and (III) were carried out with all non-H atoms treated anisotropically and the H atoms constrained to ride at 1.08 Å from the parent atom, linked with common isotropic temperature factors. Atomic scattering curves for non-H atoms are from Cromer & Mann (1968) and those for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were obtained for all non-H atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Positional parameters of (I) (space group *P*₂₁₂₁) were inverted in order to investigate absolute configuration, but no significant crystallographic differences resulted. The polarity of the crystal of (II) (space group *Fdd*₂) was established using the Hamilton (1965) significance test.

The structure of (IV) is disordered. Microanalysis data approximate very closely to the values required for a 1:1 mixture of (II) and (III) (Table 2). The structure was solved by interpretation of the electron density map (Fig. 1), which shows a section of the structure on the mirror plane at *z* = 0.

The structure was modelled by allowing equal contributions from (II) and (III), and using appropriate s.o.f.'s. Refinement could only be carried out by constraining the bond lengths of the pyrazolinium moiety to the mean distances found in (II) and (III). Thus, in the final refinement, the Sn and Cl atoms were treated anisotropically, the N and C isotropically, and H atoms were omitted [*cf.* the disordered structure of picric acid-naphthalene (1/1) π complex (Banerjee & Brown, 1985)]. Clearly the structure of

Table 2. *Microanalysis (%) for (II), (III) and (IV)*

Element	(II)		(III)		(IV)	
	Found	Calc.	Found	Calc.	Found	Calc.*
C	25.8	25.0	33.7	33.9	29.8	30.1
H	4.7	4.9	5.3	5.4	5.2	5.1
N	10.1	9.7	8.7	8.8	9.0	9.4
Sn					19.7	19.9
Cl					35.3	35.6

* Calculated for a 1:1 mixture of (III) and anhydrous (II).

(IV) must be regarded only as an approximate model, but the best obtainable under the circumstances of severe disorder. The final fractional atomic coordinates for (I)–(IV) are listed in Table 3.*

Discussion. Perspective views of molecules of (I), (II) and (III) and their packing diagrams are shown in Figs. 2(a) and 2(b), Figs. 3(a) and 3(b), and Figs. 4(a) and 4(b) respectively. The observed bond lengths and angles that are common in structures of (I), (II) and (III) are in good agreement with one another as well as with other comparable structures completed in this laboratory. These are shown in Table 4, along with the deviations of the relevant atoms from the mean plane of the pyrazolinium ring. The closest approach, less than the van der Waals distance (3.3 Å), between an anion (Cl⁻) and the cation (N⁺) is for (I) and (II) 3.086 (2) and 3.375 (3) Å respectively. The three pyrazolinium rings are not flat, but

* Lists of structure factors, anisotropic thermal parameters, bond angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53159 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$), with *e.s.d.*'s in parentheses

$$U_{eq} = 1/3(\text{orthogonalized } U_{ij} \text{ matrix}).$$

(I) (PYCL)	x	y	z	U_{eq}
Cl(1)	2431 (1)	-3225 (1)	6030 (1)	49 (1)
N(1)	3713 (2)	-1147 (2)	4122 (2)	34 (1)
N(2)	3485 (3)	497 (3)	4477 (2)	40 (1)
C(3)	2290 (3)	1049 (3)	3930 (2)	39 (1)
C(4)	1555 (3)	-80 (3)	3121 (2)	41 (1)
C(5)	2811 (3)	-1413 (3)	3039 (2)	35 (1)
C(6)	1701 (5)	2700 (4)	4096 (3)	62 (1)
C(7)	2128 (4)	-3085 (3)	3020 (3)	56 (1)
C(8)	3974 (4)	-1095 (4)	2091 (2)	51 (1)

(II) (PYRA)	x	y	z	U_{eq}
Sn(1)	0	0	0	35 (1)
Cl(1)	713 (1)	-395 (1)	1897 (1)	46 (1)
Cl(2)	1023 (1)	557 (1)	44 (1)	51 (1)
Cl(3)	706 (1)	-409 (1)	-1888 (1)	60 (1)
N(1)	979 (2)	609 (1)	3794 (3)	39 (1)
N(2)	559 (2)	954 (1)	4585 (3)	45 (1)
C(3)	950 (2)	1036 (1)	5753 (4)	41 (1)
C(4)	1692 (2)	776 (1)	5937 (4)	51 (1)
C(5)	1824 (2)	592 (1)	4389 (4)	42 (1)
C(6)	669 (3)	1360 (1)	6862 (5)	60 (1)
C(7)	2305 (3)	891 (1)	3426 (6)	68 (2)
C(8)	2120 (2)	126 (1)	4379 (6)	60 (1)
O(1)	0	0	5238 (5)	54 (2)

(III) (PYCS)	x	y	z	U_{eq}
Sn(1)	0	0	0	36 (1)
Cl(1)	1744 (1)	-131 (1)	199 (1)	57 (1)
Cl(2)	-92 (1)	-1990 (1)	440 (1)	56 (1)
Cl(3)	-70 (1)	-660 (1)	-1347 (1)	60 (1)
N(1)	1996 (2)	3070 (2)	2472 (2)	42 (1)
N(2)	1357 (2)	3838 (2)	2019 (2)	47 (1)
C(3)	1545 (2)	3826 (3)	1312 (2)	46 (1)
C(4)	2311 (3)	3031 (3)	1166 (2)	57 (1)
C(5)	2771 (2)	2667 (3)	2000 (2)	46 (1)
C(6)	987 (3)	4545 (3)	683 (2)	63 (1)
C(7)	3661 (2)	3365 (4)	2283 (2)	73 (1)
C(8)	2922 (4)	1367 (3)	2021 (3)	83 (2)
C(9)	1893 (2)	2881 (3)	3202 (2)	46 (1)
C(10)	2554 (3)	2128 (4)	3733 (2)	64 (1)
C(11)	1111 (3)	3436 (4)	3550 (2)	66 (1)

(IV) (MONS)	x	y	z	†	U_{iso}/U_{eq}^*
Sn(1)	2500	2500	2500	0	86 (1)*
Cl(1)	1299 (2)	2870 (2)	2011 (2)	1-0	152 (2)*
N(1)	2721 (10)	5262 (8)	0	0	90 (5)
N(2)	2090 (8)	4762 (9)	0	0	104 (6)
C(3)	2331 (11)	4086 (10)	0	0	79 (6)
C(4)	3146 (11)	3963 (11)	0	0	106 (8)
C(5)	3445 (9)	4785 (12)	0	0	115 (8)
C(6)	1774 (15)	3478 (15)	0	0	99 (11)
C(7)	3879 (8)	5000	728 (8)	0	135 (5)
C(9)	2642 (15)	5981 (10)	0	0	37 (6)
C(10)	1876 (17)	6321 (25)	0	0	54 (10)
C(11)	3261 (13)	6530 (15)	0	0	43 (7)

† Occupation factor (not refined).

show significant deviations of up to 0.17 Å from their mean planes.

There are no significant differences in the bond lengths and endocyclic angles of (I) and (II), but, upon formation of the isopropylidene derivative (III), the N(1)—N(2) bond length of 1.414 Å is sig-

nificantly shorter than in the parent compounds, for which the average is 1.459 (4) Å. We interpret this by the formation of a conjugate system C(9)=N(1)—N(2)=C(3) in (III), and note that the angles C(5)—N(1)—N(2) and N(1)—N(2)—C(3) both increase.

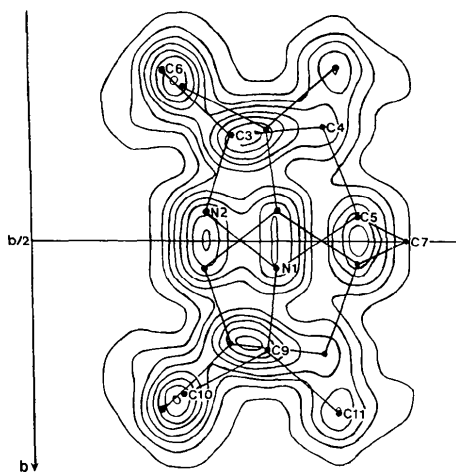
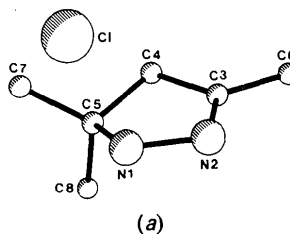
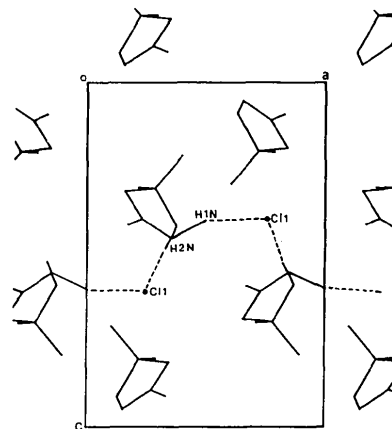


Fig. 1. Electron density map of (IV) on the mirror plane at $z = 0$. Contours are drawn at 1 e \AA^{-3} , zero included.



(a)



(b)

Fig. 2. (a) Perspective view of (I) with atomic nomenclature and (b) packing diagram of (I) viewed along [010] showing the hydrogen-bonding scheme.

The packing of (I) is shown in Fig. 2(b). The distance between the chloride and N(1) is 3.086 (2) Å which is less than the sum (3.30 Å) of the van der Waals radii (Bondi, 1964), and is therefore indicative of an N—H...Cl hydrogen bond. The pyrazolinium rings are linked by a series of N—H...Cl bonds which spiral about the diads running parallel to *a*. Both of the protons bonded to N(1) are involved in the hydrogen-bonding scheme and the distances N(1)...Cl(1) of 3.086 (2) and N(1)...Cl(1') of 3.145 (2) Å are indicative of strong H bonds between N and Cl.

The hydrogen-bonding scheme of (II) (Fig. 3b) interlinks the hexachlorostannate ions, the pyrazolinium rings and the water of crystallization in ribbons running along *c*. Thus Cl(1) has a weak H bond to N(1) with Cl(1)...N(1) 3.554 (3) Å. The ring is linked to the water *via* an H bond N(1)—H...O(1), the N to O distance being 2.819 (4) Å. The water in turn interacts with a symmetry-related hexachloro-

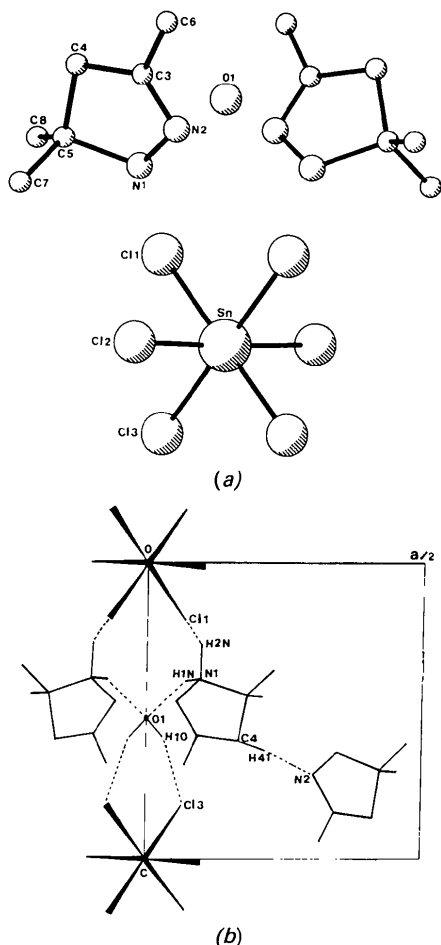


Fig. 3. (a) Perspective view of (II) with atomic nomenclature and (b) part of the packing diagram of (II) along [010] showing the hydrogen-bonding scheme.

stannate, the O(1)—H(1)...Cl(3) bond having an O to Cl distance 3.112 (4) Å. There are thus three distinct hydrogen bonds linking the SnCl₆²⁻ ions in the [001] direction. These three H bonds are doubled by the diad running parallel to *c*, giving rise to parallel chains of chlorostannate, pyrazolinium and water moieties. These chains are in turn linked by C(4)—H...N(2) hydrogen bonds, having a C(4)...N(2) distance of 3.471 (5) Å.

(III) is shown in perspective with atomic nomenclature in Fig. 4(a). The packing viewed along [010] is shown in Fig. 4(b). The chlorostannate anions are located at the centres of inversion at Wyckoff position *a*, the pyrazolinium moieties are stacked about the screw axes and are linked by C(8)—H...N(2) interactions having C(8)...N(2) distances of 3.445 (5) Å. There are no other close contacts below 3.5 Å.

Interest in the properties of the iminium moiety with regard to planarity, bond lengths, distances between ions and anion size has led to the solution of a number of related crystal structures which will be published as a series.

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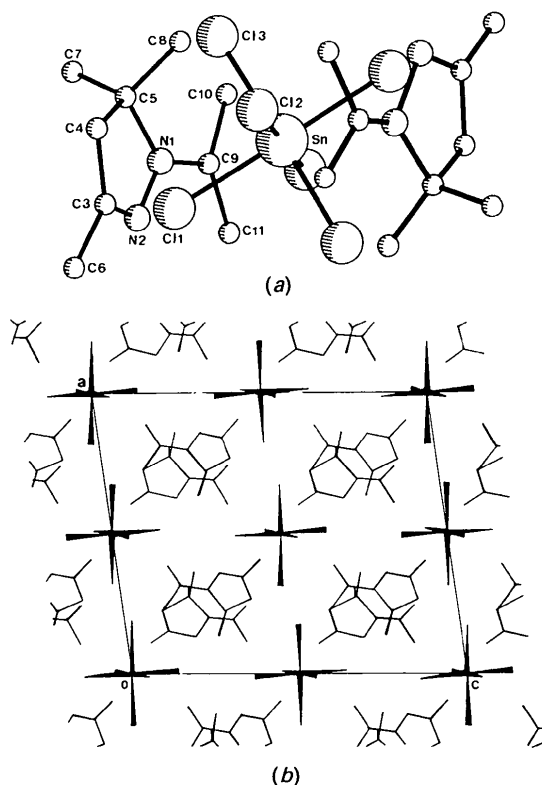


Fig. 4. (a) Perspective view of (III) with atomic nomenclature and (b) packing diagram of (III) viewed along [010].

Table 4. Bond distances (Å), bond angles (°) and deviations from the pyrazolinium ring plane (Å), with *e.s.d.'s* in parentheses

	(I)	(II)	(III)
Bonds			
N(1)—N(2)	1.456 (3)	1.462 (4)	1.414 (4)
N(2)—C(3)	1.282 (4)	1.267 (5)	1.274 (5)
C(3)—C(4)	1.494 (4)	1.501 (5)	1.474 (5)
C(4)—C(5)	1.533 (4)	1.518 (5)	1.531 (5)
C(5)—N(1)	1.529 (3)	1.532 (5)	1.529 (5)
C(3)—C(6)	1.482 (4)	1.487 (5)	1.489 (5)
C(5)—C(7)	1.512 (4)	1.503 (6)	1.514 (5)
C(5)—C(8)	1.526 (4)	1.518 (4)	1.527 (5)
N(1)—C(9)			1.294 (5)
C(9)—C(10)			1.485 (5)
C(9)—C(11)			1.480 (5)
Endocyclic angles			
N(1)—N(2)—C(3)	106.9 (2)	107.0 (3)	107.6 (3)
N(2)—C(3)—C(4)	115.4 (2)	115.2 (3)	115.5 (3)
C(3)—C(4)—C(5)	103.0 (2)	102.8 (3)	103.7 (3)
C(4)—C(5)—N(1)	100.0 (2)	99.7 (3)	99.6 (3)
C(5)—N(1)—N(2)	109.1 (2)	108.2 (3)	110.9 (3)
Atoms included in LS plane			
N(1)	-0.098 (2)	-0.136 (3)	0.061 (3)
N(2)	-0.072 (3)	0.063 (3)	-0.030 (3)
C(3)	0.039 (3)	0.045 (3)	-0.028 (3)
C(4)	-0.123 (3)	-0.132 (3)	-0.107 (4)
C(5)	0.160 (3)	0.170 (3)	-0.105 (3)

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Structure du Tétraméthyl-3,3,5,5 Oxa-7 Bicyclo[4.1.0]heptanyl-1 Méthyl Sulfoxide $R_S SS$ (ou $S_S RR$)

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Abstract. $C_{11}H_{20}O_2S$, $M_r = 216.34$, monoclinic, $P2_1/c$, $a = 12.538$ (1), $b = 8.587$ (2), $c = 11.411$ (4) Å, $\beta = 90.71$ (2)°, $V = 1228.4$ (8) Å³, $Z = 4$, $D_x = 1.17$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.24$ mm⁻¹, $F(000) = 472$, $T = 294$ K, $R = 0.039$, $wR = 0.039$ for 1412 independent reflections. Simple C—C bonds in the six-membered ring are shorter near the epoxide ring. The epoxide and sulfinyl O atoms are *syn* with respect to the S—C bond. The cyclohexyl ring has a half-chair conformation. The crystalline structure appears to be in accord with ¹H NMR indicating that the relative configurations of

the molecule are identical in both the solid state and solution.

Introduction. Les deux époxysulfoxydes (1) et (2), séparables par chromatographie sur silice, ont été préparés par action de l'ozone sur le méthylthio-1 tétraméthyl-3,3,5,5 cyclohexène (Barillier, Strobel, Morin & Paquer, 1982). Une étude comparée en RMN ¹H, basée sur les effets de solvants, nous a permis de proposer les structures (1) et (2) pour ces diastéréoisomères en solution (Barillier & Vazeux, 1986). L'arrangement spatial des substituants de