

network leads to layers which interact by van der Waals forces in the crystal.

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Geometry of the Iminium Moiety. III. Structures of a Chiral Form of Bis[4,5-dihydro-3,5,5-trimethyl-1-(3'-methylcyclopentylidene)pyrazolium] Hexachlorostannate and the Racemate

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Abstract. Compound (I) MPDL, bis[4,5-dihydro-3,5,5-trimethyl-1-(3'-methylcyclopentylidene)pyrazolium] hexachlorostannate, [C₁₂H₂₁N₂]₂⁺[SnCl₆]²⁻, *M_r* = 718.0, monoclinic, *P*2₁/*n*, *a* = 10.002 (2), *b* = 10.639 (1), *c* = 15.616 (4) Å, β = 102.05 (2)°, *V* = 1625.1 (2) Å³, *Z* = 2, *D_m* = 1.46 (1), *D_x* = 1.467 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 13.1 cm⁻¹, *F*(000) = 732, *T* = 294 K, *R* = 0.035 for 2291 observed reflections with *I* > 2σ(*I*). Compound (II) MPCH, bis[(*R*)-4,5-dihydro-3,5,5-trimethyl-1-(3'-methylcyclopentylidene)pyrazolium] hexachlorostannate, [C₁₂H₂₁N₂]₂⁺[SnCl₆]²⁻, *M_r* = 718.0, monoclinic, *P*2₁, *a* = 9.998 (2), *b* = 10.649 (1), *c* = 15.637 (4) Å, β = 102.03 (2)°, *V* = 1628.3 (3) Å³, *Z* = 2, *D_m* = 1.48 (1), *D_x* = 1.493 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 13.1 cm⁻¹, *F*(000) = 732, *T* = 294 K, *R* = 0.039 for 2436 observed reflections with *I* > 2σ(*I*). The compounds (I) and (II) are condensation products of a 4,5-dihydropyrazolium ion with a racemic and a chiral five-membered carbocyclic ketone respectively. Their structures are compared crystallographically, compound (II) showing evidence of disorder.

Introduction. In part II of this series (Nassimbeni, Stephen & Van Schalkwyk, 1991) the structures of four cycloalkylidene derivatives formed by condensations of several ketones and a pyrazolinium com-

pound are reported. In this paper, a comparative study is reported of the condensation products of this compound, bis(4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate (PYRA), with the racemic and a chiral form of the ketone 3-methylcyclopentanone. The products are the iminium salts bis[4,5-dihydro-3,5,5-trimethyl-1-(3'-methylcyclopentylidene)pyrazolium] hexachlorostannate [(I) MPDL] and bis[(*R*)-4,5-dihydro-3,5,5-trimethyl-1-(3'-methylcyclopentylidene)pyrazolium] hexachlorostannate [(II) MPCH].

Experimental. A mixture of PYRA in dry ethanol (25% w/v) and excess (> 20 molar proportions) of either the racemic or the *R*(+) form of 3-methylcyclopentanone produced, after at least a day, stable prismatic crystals in small circular clusters. Crystal-density measurements were made by flotation in mixtures of bromoform and bromobenzene and by the use of a Paar DMA 35 density meter. The two compounds have almost identical unit-cell parameters. The space-group assignment was established photographically by taking long exposures of the zero and first layer photographs about *b* for both compounds. The photographs for compound (II) yielded a significant number of weak reflections which violated the *n*-glide condition *h* + *l* = 2*n*. This established the space group for compound (II) as *P*2₁, a subgroup of *P*2₁/*n*, which is the space group of (I). In addition, the reflections for the

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

| | (I) | (II) |
|--|----------------------------------|----------------------------------|
| Crystal dimensions (mm) | 0.13 × 0.25 × 0.25 | 0.16 × 0.16 × 0.19 |
| Range of indices <i>h</i> | -11→11 | -11→11 |
| <i>k</i> | 0→12 | 0→12 |
| <i>l</i> | 0→18 | 0→18 |
| Transmission factor minimum/maximum (%) | 82.2/99.4 | 92.6/99.5 |
| Standard reflections (<i>h,k,l</i>) | 811, 282, 3, 2, 11 | 1, 1, 12, 284, 723 |
| Minimum, maximum θ (°) | 1.0, 25.0 | 1.0, 25.0 |
| Stability (%) | -2.9 | -2.3 |
| Scan width parameter γ^* | 0.90 | 0.85 |
| Aperture width parameter x^\dagger | 1.12 | 1.12 |
| No. of reflections measured | 2966 | 3150 |
| No. of unique reflections, R_m | 2623, 0.016 | 2789, 0.016 |
| No. of observed reflections [$I > 2\sigma(I)$] | 2304 | 2426 |
| No. of variables | 175 | 368 |
| Minimum, maximum $\Delta\rho$ (e Å ⁻³) | -0.44, 0.90 | -0.89, 0.90 |
| Final Δ/σ | < 0.06 | < 0.16 |
| <i>R</i> | 0.035 | 0.039 |
| <i>wR</i> | 0.038 | 0.043 |
| <i>S</i> | 2.70 | 0.97 |
| Weighting scheme, <i>w</i> | $[\sigma^2(F) + 0.0004F^2]^{-1}$ | $[\sigma^2(F) + 0.0017F^2]^{-1}$ |

* Scan width, $\Delta\omega = (\gamma + 0.35\tan\theta)^\circ$.† Aperture width = $(x + 1.05\tan\theta)$ mm.

two compounds had matching intensities, showing that the two structures closely resemble one another.

Suitable crystals of (I) and (II) were each mounted on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation for intensity-data collection at 294 K. Lattice parameters were obtained by least-squares analysis of 24 reflections in the range of $16 < \theta < 17^\circ$. Intensity scans were carried out in the ω - 2θ mode with varying speeds and a recording time of 30 s. The intensities of three standard reflections were monitored and re-centring was performed every 100 measured reflections. The range scanned was $1 < \theta < 25^\circ$ and the data were corrected for Lorentz and polarization factors as well as absorption (North, Phillips & Mathews, 1968). In Table 1 additional experimental data and structure-refinement parameters are recorded. Both structures were solved by direct methods and refined by full-matrix least squares, based on F , using the *SHELX76* program system (Sheldrick, 1976). All non-H atoms were finally treated anisotropically and the H atoms were geometrically positioned to ride at 1.0 Å from the parent atoms with separate U_{iso} parameters for the methyl and methylene H atoms. Atomic scattering factors for non-H atoms were taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). The final fractional coordinates for (I) and (II) are listed in Table 2.* The melting point

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55434 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0308]

Table 2. *Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|------------------|------------|------------|-----------|----------|
| (I) MPDL | | | | |
| Sn(1) | 0 | 0 | 0 | 38 (1) |
| Cl(1) | 2327 (1) | 320 (1) | 813 (1) | 59 (1) |
| Cl(2) | -851 (1) | 1345 (1) | 1028 (1) | 68 (1) |
| Cl(3) | -236 (1) | -1838 (1) | 883 (1) | 63 (1) |
| N(1) | 5000 (3) | -1089 (3) | 2241 (2) | 45 (1) |
| N(2) | 4822 (4) | -2090 (3) | 1636 (2) | 58 (1) |
| C(3) | 5647 (6) | -1902 (5) | 1134 (3) | 70 (2) |
| C(4) | 6432 (7) | -739 (6) | 1287 (5) | 103 (3) |
| C(5) | 6205 (5) | -261 (4) | 2158 (3) | 57 (2) |
| C(6) | 5728 (10) | -2789 (7) | 409 (4) | 114 (4) |
| C(7) | 5826 (6) | 1119 (5) | 2088 (4) | 78 (2) |
| C(8) | 7370 (6) | -517 (9) | 2900 (5) | 112 (4) |
| C(9) | 4142 (4) | -993 (4) | 2755 (3) | 45 (1) |
| C(10) | 2971 (4) | -1852 (4) | 2724 (3) | 53 (2) |
| C(11) | 2189 (6) | -1279 (6) | 3351 (4) | 78 (2) |
| C(12) | 3162 (7) | -507 (7) | 3957 (4) | 89 (3) |
| C(13) | 4160 (6) | -16 (4) | 3438 (3) | 63 (2) |
| C(14) | 2592 (9) | 484 (8) | 4453 (5) | 117 (4) |
| (II) MPCH | | | | |
| Sn(1) | 2439 (1) | 0† | 2482 (1) | 36 (1) |
| Cl(1) | 4777 (2) | 300 (5) | 3283 (2) | 60 (2) |
| Cl(2) | 1608 (3) | 1355 (5) | 3503 (3) | 65 (1) |
| Cl(3) | 2223 (3) | -1835 (6) | 3355 (2) | 67 (1) |
| Cl(4) | 122 (2) | -326 (5) | 1669 (2) | 56 (1) |
| Cl(5) | 3305 (3) | -1327 (6) | 1438 (3) | 72 (2) |
| Cl(6) | 2687 (3) | 1838 (5) | 1594 (2) | 60 (1) |
| N(1) | 7443 (8) | -1046 (10) | 4727 (6) | 47 (4) |
| N(2) | 7218 (9) | -2029 (10) | 4112 (5) | 51 (4) |
| N(15) | -2524 (8) | 1115 (9) | 231 (5) | 40 (4) |
| N(16) | -2394 (9) | 2136 (10) | 820 (6) | 59 (4) |
| C(3) | 8020 (18) | -1829 (16) | 3594 (11) | 99 (8) |
| C(4) | 8915 (19) | -728 (16) | 3754 (11) | 119 (9) |
| C(5) | 8633 (19) | -214 (13) | 4605 (7) | 56 (5) |
| C(6) | 7943 (28) | -2661 (23) | 2812 (12) | 179 (15) |
| C(7) | 8240 (14) | 1163 (14) | 4498 (11) | 84 (7) |
| C(8) | 9775 (13) | -357 (26) | 5384 (13) | 164 (13) |
| C(9) | 6621 (9) | -959 (11) | 5266 (7) | 50 (4) |
| C(10) | 5475 (9) | -1856 (12) | 5268 (7) | 51 (4) |
| C(11) | 4796 (10) | -1377 (13) | 5995 (8) | 62 (4) |
| C(12) | 5508 (29) | -234 (25) | 6369 (22) | 245 (18) |
| C(13) | 6721 (11) | 17 (16) | 5985 (7) | 69 (5) |
| C(14A) | 3580 (21) | -547 (25) | 5691 (19) | 88 (11) |
| C(14B) | 5179 (29) | 634 (31) | 7056 (17) | 114 (16) |
| C(17) | -3239 (11) | 1932 (11) | 1317 (7) | 53 (4) |
| C(18) | -4022 (14) | 785 (16) | 1131 (10) | 95 (8) |
| C(19) | -3762 (9) | 294 (11) | 275 (8) | 58 (5) |
| C(20) | -3396 (15) | 2823 (15) | 2015 (9) | 77 (6) |
| C(21) | -3402 (13) | -1080 (12) | 325 (10) | 69 (5) |
| C(22) | -4920 (12) | 610 (15) | -468 (9) | 88 (6) |
| C(23) | -1653 (8) | 1018 (10) | -254 (5) | 37 (4) |
| C(24) | -460 (9) | 1859 (12) | -184 (7) | 54 (4) |
| C(25) | 424 (10) | 1249 (13) | -781 (8) | 61 (5) |
| C(26) | -622 (11) | 582 (12) | -1447 (6) | 56 (4) |
| C(27) | -1596 (9) | 21 (14) | -908 (7) | 61 (4) |
| C(28) | -13 (13) | -449 (11) | -1902 (8) | 64 (5) |

† Coordinate fixed to define origin for structure with non-centrosymmetric space group.

Table 3. *Microanalytical figures (%) for (I) and (II)*

| Element | Calculated | Found | |
|---------|------------|-------|------|
| | | (I) | (II) |
| C | 40.2 | 40.7 | 40.4 |
| H | 5.9 | 5.6 | 5.6 |
| N | 7.8 | 7.7 | 7.8 |

of (I) is 462 K and of (II) is 457 K. Microanalytical data are listed in Table 3.

Discussion. Perspective views with atomic nomenclature of molecules (I) and (II) and their packing diagrams are shown in Figs. 1 and 2. There is good

agreement between the corresponding bond lengths of (I) and those of the comparable compound PENT (Nassimbeni, Stephen & Van Schalkwyk, 1991), with standard deviations within the normal limits (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

In the final stages of refinement of (II), the bond lengths in the SnCl_6 moiety, M_1 , were quite consistent but the equivalent bond lengths obtained for the two organic moieties, M_2 and M_3 , yielded abnormally high standard deviations. The mean value of all the $\text{C}(sp^3)\text{—C}(sp^3)$ bond lengths was 1.515 (85) Å and for all the $\text{C}(sp^3)\text{—C}(sp^2)$ bond lengths 1.497 (80) Å. It was obvious that a measure of disorder existed in the crystal, which necessitated the application of certain constraints on some of the parameters in the refining process. For each and every corresponding pair of bonds in the two organic moieties, e.g. $\text{C}(3)\text{—C}(4)$ and $\text{C}(17)\text{—C}(18)$, a bond-length constraint equal to the mean of corresponding bond lengths in PENT and (I) was applied with a standard deviation of 0.01 Å. In addition to the integral methyl $\text{C}(28)\text{H}_3$, similar electron densities reflecting partial methyl groups $\text{C}(14A)\text{H}_3$ and $\text{C}(14B)\text{H}_3$ were located in the difference map. All of these groups were oriented in the expected *R* config-

uration with respect to the ring C atoms, which were not only $\text{C}(26)$ and $\text{C}(12)$, but also $\text{C}(11)$ (Fig. 2a). If for $\text{C}(14A)\text{H}_3$ and $\text{C}(14B)\text{H}_3$ the site-occupation factor was fixed at 0.5, the temperature factors were more satisfactory than for occupation factors on either side of 0.5. When this was done, the mean value for all the $\text{C}(sp^3)\text{—C}(sp^3)$ bond lengths was found to be 1.51 (2) Å and for all the $\text{C}(sp^3)\text{—C}(sp^2)$ bond lengths 1.48 (2) Å. The observed bond lengths and bond angles for (I) and (II) are shown in Table 4, alongside those for PENT.

For the purpose of the following argument, the geometrical isomer of (I) or (II) in which the $\text{C}(3')$ methyl lies to the same side of the iminium double bond as $\text{C}(5)$ which carries the *gem*-dimethyl groups, is referred to as *cis*. Comparing the packings of the cationic moieties in the crystals of (I) and (II), it is apparent that there are domains of (*R*)-*cis* in each case. Where in the racemate (I) these domains are interleaved with (*S*)-*cis* (Fig. 1b), the corresponding alternative domains for (II) contain approximately equal numbers of (*R*)-*cis* and (*R*)-*trans* (Fig. 2b). The

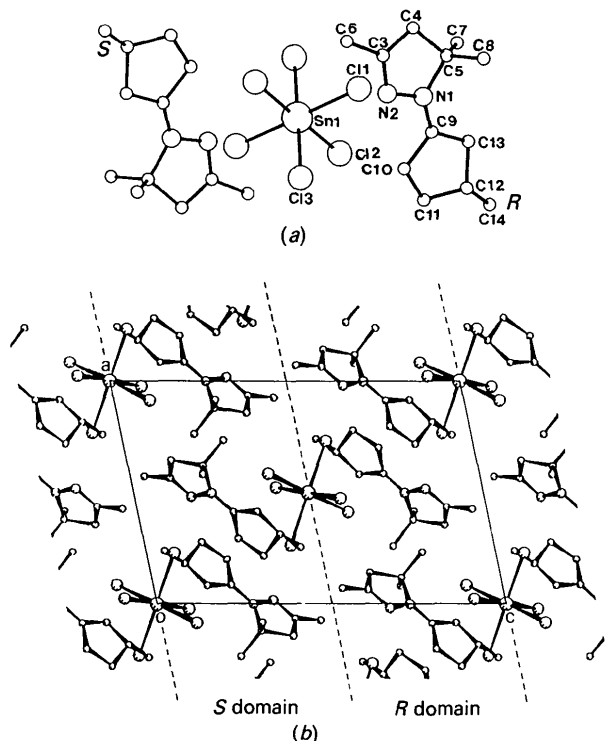


Fig. 1. Diagrams showing (a) perspective view of (I) with atomic nomenclature and (b) packing of (I) viewed along [010], showing domains in which molecules of *R* configuration lie parallel to those containing the *S* moiety. They are separated by sheets of $[\text{SnCl}_6]^{2-}$ ions.

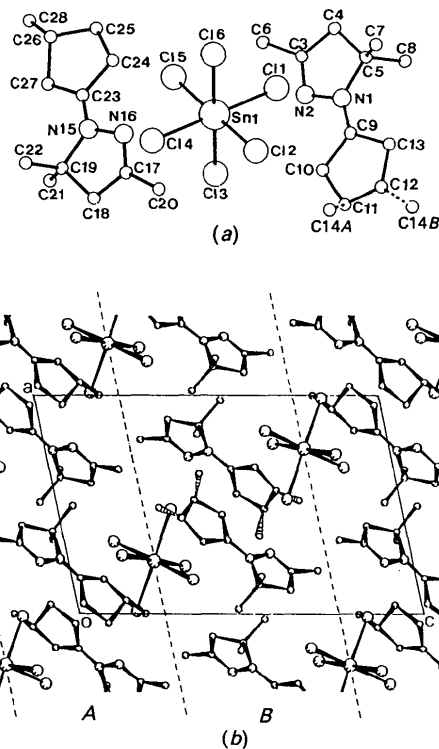
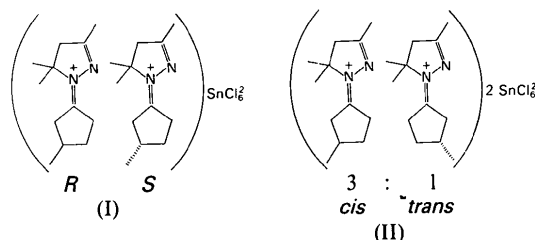


Fig. 2. Diagrams showing (a) perspective view of (II) with atomic nomenclature and (b) packing of (II) viewed along [010], showing domains (A) containing molecules of *R* configuration in which the cyclopentylidene methyl is *cis* to the *gem*-dimethyl groupings in the pyrazolinium ring. Parallel to these are sheets (B) comprising both *cis* and *trans* isomers in similar proportions. Domains (A) and (B) are separated by sheets of $[\text{SnCl}_6]^{2-}$ ions.

scheme below illustrates the equal proportions of *R*- and *S*-moieties in (I) and the appropriate ratio (3:1) of (*R*)-*cis* to (*R*)-*trans* in (II).



¹H NMR spectra of (I) and (II) in DMSO-*d*₆ show chemical shifts comparable with those for the cyclopentylidene derivative (Table 5). The two signals of equal intensity for the *gem*-dimethyl groups in (I), at δ 1.62 and 1.65 (Fig. 3), may reflect the effects of the

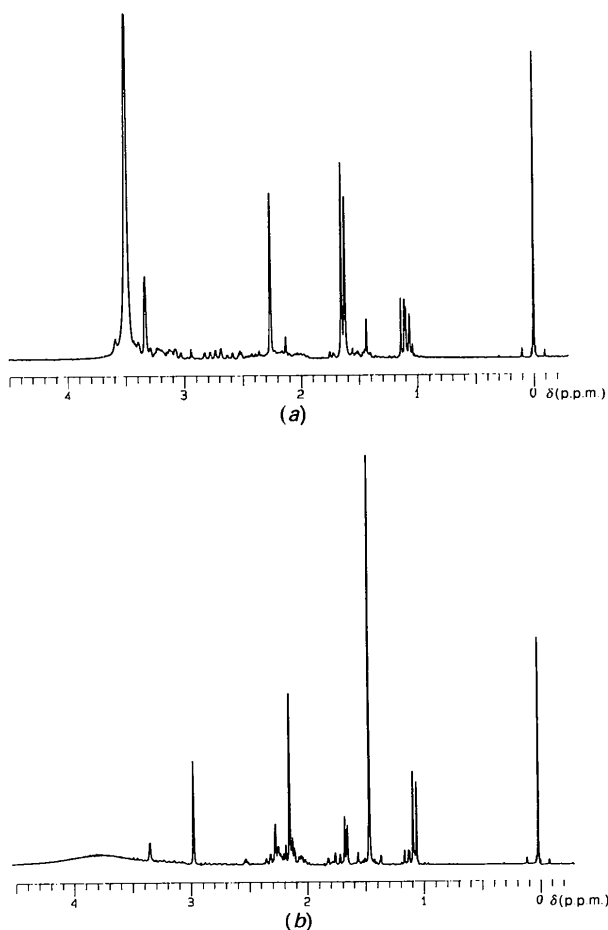


Fig. 3. ¹H NMR spectra (a) for (I) in DMSO-*d*₆ at 298 K, and (b) for extensively hydrolysed (I) (therefore mainly PYRA), at 333 K. Internal reference Me₄Si, $\delta = 0$. Assignment of signals in spectrum (a) is as given in Table 5. For PYRA [spectrum (b)], C(4)H₂, C(3)H₃ and C(5)(CH₃)₂ resonate at δ 2.96, 2.14 and 1.45 respectively.

Table 4. Bond lengths (Å) and bond angles (°) of PENT (for comparison), (I) and the various moieties M₁, M₂ and M₃ of (II)

The structure (II)M₁ refers to the SnCl₆ moiety of (II). The structures (II)M₂ and (II)M₃ refer to the organic moieties of (II) with atoms numbered from 1 to 14 and 15 to 28 respectively, in the same numerical order.

| | PENT | (I) | (II)M ₁ | (II)M ₂ | (II)M ₃ |
|--------------------|------------|------------|--------------------|--------------------|--------------------|
| Sn(1)—Cl(1) | 2.438 (1) | 2.431 (1) | 2.433 (2) | | |
| Sn(1)—Cl(2) | 2.435 (1) | 2.434 (1) | 2.424 (5) | | |
| Sn(1)—Cl(3) | 2.425 (1) | 2.432 (1) | 2.422 (6) | | |
| Sn(1)—Cl(4) | | | 2.423 (2) | | |
| Sn(1)—Cl(5) | | | 2.450 (5) | | |
| Sn(1)—Cl(6) | | | 2.422 (5) | | |
| N(1)—N(2) | 1.404 (7) | 1.410 (4) | | 1.408 (14) | 1.413 (14) |
| N(1)—C(5) | 1.540 (7) | 1.520 (6) | | 1.527 (15) | 1.529 (14) |
| N(1)—C(9) | 1.301 (8) | 1.296 (6) | | 1.297 (15) | 1.273 (12) |
| N(2)—C(3) | 1.282 (8) | 1.267 (7) | | 1.271 (21) | 1.280 (16) |
| C(3)—C(4) | 1.459 (10) | 1.458 (9) | | 1.465 (25) | 1.446 (20) |
| C(3)—C(6) | 1.495 (12) | 1.489 (9) | | 1.499 (27) | 1.479 (19) |
| C(4)—C(5) | 1.545 (9) | 1.513 (9) | | 1.519 (22) | 1.510 (21) |
| C(5)—C(7) | 1.520 (9) | 1.515 (7) | | 1.518 (20) | 1.505 (17) |
| C(5)—C(8) | 1.534 (8) | 1.487 (8) | | 1.494 (18) | 1.495 (15) |
| C(9)—C(10) | 1.488 (8) | 1.478 (6) | | 1.493 (15) | 1.477 (14) |
| C(9)—C(13) | 1.485 (9) | 1.487 (6) | | 1.520 (18) | 1.484 (16) |
| C(10)—C(11) | 1.528 (10) | 1.504 (8) | | 1.528 (17) | 1.555 (17) |
| C(11)—C(12) | 1.485 (12) | 1.460 (9) | | 1.470 (30) | 1.493 (15) |
| C(12)—C(13) | 1.531 (10) | 1.505 (9) | | 1.485 (35) | 1.536 (16) |
| C(12)—C(14) | | 1.491 (12) | | | 1.504 (18) |
| C(11)—C(14A) | | | | 1.499 (25) | |
| C(12)—C(14B) | | | | 1.505 (45) | |
| Cl(5)—Sn(1)—Cl(6) | | | 89.5 (2) | | |
| Cl(4)—Sn(1)—Cl(6) | | | 90.9 (1) | | |
| Cl(4)—Sn(1)—Cl(5) | | | 90.0 (1) | | |
| Cl(3)—Sn(1)—Cl(6) | | | 179.1 (1) | | |
| Cl(3)—Sn(1)—Cl(5) | | | 89.7 (2) | | |
| Cl(3)—Sn(1)—Cl(4) | | | 89.5 (1) | | |
| Cl(2)—Sn(1)—Cl(6) | | | 89.2 (2) | | |
| Cl(2)—Sn(1)—Cl(5) | | | 178.7 (2) | | |
| Cl(2)—Sn(1)—Cl(4) | | | 90.6 (1) | | |
| Cl(2)—Sn(1)—Cl(3) | 88.8 (1) | 90.6 (1) | 91.5 (1) | | |
| Cl(1)—Sn(1)—Cl(6) | | | 89.1 (1) | | |
| Cl(1)—Sn(1)—Cl(4) | | | 179.0 (1) | | |
| Cl(1)—Sn(1)—Cl(3) | 90.9 (1) | 90.7 (1) | 90.3 (1) | | |
| Cl(1)—Sn(1)—Cl(2) | 89.7 (1) | 90.1 (1) | 90.4 (1) | | |
| C(5)—N(1)—C(9) | 130.7 (5) | 130.3 (4) | | 130.9 (10) | 129.9 (9) |
| N(2)—N(1)—C(9) | 117.9 (4) | 117.8 (3) | | 117.8 (9) | 118.6 (9) |
| N(2)—N(1)—C(5) | 111.3 (4) | 111.8 (3) | | 111.3 (8) | 112.1 (8) |
| N(1)—N(2)—C(3) | 106.8 (5) | 106.7 (4) | | 106.2 (11) | 106.4 (9) |
| N(2)—C(3)—C(6) | 120.6 (6) | 121.1 (5) | | 119.3 (17) | 121.6 (11) |
| N(2)—C(3)—C(4) | 116.7 (6) | 115.5 (5) | | 118.0 (15) | 114.8 (11) |
| C(4)—C(3)—C(6) | 122.6 (6) | 123.3 (6) | | 122.6 (16) | 123.6 (11) |
| C(3)—C(4)—C(5) | 103.4 (5) | 104.8 (5) | | 102.7 (13) | 106.6 (12) |
| N(1)—C(5)—C(4) | 98.9 (4) | 98.8 (4) | | 101.1 (10) | 97.8 (9) |
| C(4)—C(5)—C(8) | 112.3 (5) | 113.5 (5) | | 115.3 (11) | 111.2 (12) |
| C(4)—C(5)—C(7) | 111.3 (5) | 110.1 (4) | | 110.0 (11) | 112.0 (11) |
| N(1)—C(5)—C(8) | 108.3 (4) | 109.5 (4) | | 108.8 (11) | 109.8 (9) |
| N(1)—C(5)—C(7) | 113.4 (5) | 112.2 (4) | | 112.6 (9) | 111.8 (9) |
| C(7)—C(5)—C(8) | 112.0 (5) | 112.2 (5) | | 108.9 (13) | 113.4 (11) |
| N(1)—C(9)—C(13) | 127.3 (5) | 126.1 (4) | | 125.3 (10) | 126.7 (9) |
| N(1)—C(9)—C(10) | 121.0 (5) | 123.6 (4) | | 123.6 (10) | 123.4 (9) |
| C(10)—C(9)—C(13) | 111.6 (5) | 110.3 (4) | | 111.6 (9) | 109.5 (8) |
| C(9)—C(10)—C(11) | 103.4 (5) | 104.1 (4) | | 104.4 (9) | 104.7 (9) |
| C(10)—C(11)—C(14A) | | | 114.7 (14) | | |
| C(10)—C(11)—C(12) | 104.1 (6) | 106.4 (5) | | 108.6 (14) | 102.4 (9) |
| C(12)—C(11)—C(14A) | | | 86.0 (17) | | |
| C(11)—C(12)—C(14) | | 117.3 (6) | | | 112.6 (9) |
| C(11)—C(12)—C(14B) | | | | 129.3 (23) | |
| C(11)—C(12)—C(13) | 105.7 (6) | 105.9 (5) | | 110.9 (19) | 103.6 (8) |
| C(13)—C(12)—C(14) | | 113.8 (6) | | | 110.0 (10) |
| C(13)—C(12)—C(14B) | | | | 119.7 (23) | |
| C(9)—C(13)—C(12) | 102.2 (6) | 103.5 (4) | | 104.1 (14) | 102.8 (10) |

3'-methyl groups, which occur to an equal extent above the plane of the pyrazolinium ring (for the 3'-*R* moiety) and below (for the 3'-*S* moiety), on those at C-5. A corresponding shift difference of 0.034 p.p.m. was observed for the 4'-methylcyclohexylidene derivative of PYRA (Van

Table 5. Signals obtained from 200 MHz ^1H NMR spectra of derivatives of bis(4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate (PYRA) in $(\text{CD}_3)_2\text{SO}$

| Carbonyl moiety | Chemical shifts (δ , TMS _{int} = 0) | | |
|--------------------------|--|----------------------|---------------------------------------|
| | C(4)H ₂ | C(3)—CH ₃ | H ₃ C—C(5)—CH ₃ |
| Cyclopentanone* | 3.36 | 2.28 | 1.66 |
| 3-Methylcyclopentanone | 3.33 | 2.26 | 1.62, 1.65 |
| 3-R-Methylcyclopentanone | 3.32 | 2.25 | 1.62, 1.64 |

* Rathbone, Stephen, Schwersenski & Tyler (1975).

Schalkwyk, Stephen & Hodgson, 1976). The NMR result is consistent with the presence in (I) of the *cis* (C-3'/C-5) isomers only, as shown by crystal analysis (Table 2). Two NMR signals for the *gem*-dimethyl groups at C-5 in (II) are consistent with the different relative effects of the C-3' methyl. The proton integral values for the two sets of *gem*-dimethyl protons are similar, but could allow for a preponderance of the unaffected methyls, as would be the case for the small proportion of the alternative *trans* (C'-3/C-5) isomer which X-ray crystallographic analysis indicates.

The molecular conformations of the cycloalkylidene rings, one in compound (I) and two in compound (II), can be expressed (Table 6) as linear combinations of the standard primitive forms of five-membered puckered rings, such as envelope (*E*) and twist (*T*), with the program *CONFOR* (Evans & Boeyens, 1989). The normalized numerical coefficients *a* and *b* indicate the relative contributions of the primitive forms in order of increasing mode *m* in the linear sum. The phase angles φ_m of the relevant primitive form, *E* or *T*, are expressed as multiples of

Table 6. Conformational analysis of five-membered alkylidene rings using computer program *CONFOR*

| Molecule | Puckering parameters | | Assignment $a\varphi(E) + b\varphi(T)$ | Classic form |
|----------------------------|----------------------|-----------------|---|-----------------------------|
| | Q_2 (Å) | φ_2 (°) | | |
| (I) | 0.297 (7) | 277.0 (9) | 39 (16) + 61 (15) | Mixed <i>E</i> and <i>T</i> |
| (II) <i>M</i> ₂ | 0.062 (20) | 129.9 (12) | 22 (8) + 78 (7) | Mixed <i>E</i> and <i>T</i> |
| (II) <i>M</i> ₁ | 0.400 (12) | 100.4 (16) | 58 (6) + 42 (5) | Mixed <i>E</i> and <i>T</i> |

$\pi/2N$, for an *N*-membered polygon, where *N* = 5. From Table 6 it is clear that all three rings are mixed forms of *E* and *T*, with relative percentages indicated by the *a* and *b* values.

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Geometry of the Iminium Moiety. IV. Structure of 4,5-Dihydro-3,5,5-trimethylpyrazolium Aquapentachlorostannate Monohydrate

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Abstract. Compound PYFA, 4,5-dihydro-3,5,5-trimethylpyrazolium aquapentachlorostannate monohydrate, $[\text{C}_6\text{H}_{13}\text{N}_2]^+[\text{SnCl}_5(\text{H}_2\text{O})]^- \cdot \text{H}_2\text{O}$, $M_r = 469.2$, monoclinic, $P2_1/n$, $a = 10.788$ (1), $b = 18.560$ (1), $c = 8.158$ (1) Å, $\beta = 96.18$ (1)°, $V = 1624.0$ (3) Å³, $Z = 4$, $D_m = 1.92$ (1), $D_x =$

1.919 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.1$ cm⁻¹, $F(000) = 920$, $T = 294$ K, $R = 0.026$ for 2304 observed reflections with $I > 2\sigma(I)$. The modified anion was formed on treatment of a dihydropyrazolium hexachlorostannate (PYRA) with hexafluoroacetone trihydrate. The water present causes replacement of a Cl⁻ ion from the hexachlorostannate anion by an H₂O molecule, one base

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