*Acta Cryst.* (1979). B35, 1766–1769

# Hydrazine. XV. The Crystal Structures and Rates of Hydrolysis of Two Substituted Iminium Salts: Bis(1-*m*-chlorobenzylidene-3,5,5-trimethylpyrazolinium) Hexachlorostannate and Bis(1-*p*-hydroxybenzylidene-3,5,5-trimethylpyrazolinium) Hexachlorostannate

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(*Received* 23 *October* 1978; *accepted* 22 *December* 1978)

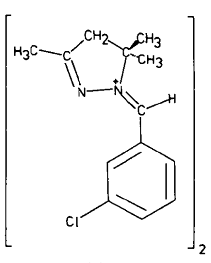
## Abstract

$[C_{13}H_{16}ClN_2]_2^+[SnCl_6]^{2-}$ crystallizes in the space group $P2_1/n$ with $a = 9{\cdot}522\,(5)$, $b = 13{\cdot}092\,(6)$, $c = 14{\cdot}597\,(7)$ Å, $\beta = 108{\cdot}2\,(2)°$, $Z = 2$. $[C_{13}H_{17}N_2O]_2^+[SnCl_6]^{2-}$ crystallizes in the space group $P2/n$ with $a = 12{\cdot}917\,(6)$, $b = 9{\cdot}277\,(5)$, $c = 14{\cdot}805\,(7)$ Å, $\beta = 112{\cdot}4\,(2)°$, $Z = 2$. The structures were refined to final $R$ values of 0·043 and 0·028 respectively. The pyrazolinium ring and the CNNC diene system in both structures are essentially planar. NMR spectroscopy was used to measure the rates of hydrolysis of the salts in dimethyl sulphoxide solution. Overall second-order kinetics were observed with rate constants of $2 \times 10^{-6}$ for the *m*-chloro salt and $1 \times 10^{-7}$ m$^3$ mol$^{-1}$ s$^{-1}$ for the *p*-hydroxy salt. The hydrolysis rate is a function of the benzene-ring substituent but no difference in length is detectable for the bond being hydrolysed.

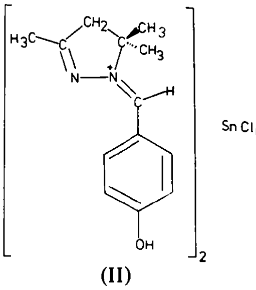
## Introduction

In part IX of a series of papers describing the preparation and properties of salts of hydrazine and derived bases (Lamchen, Pugh & Stephen, 1954), analytical evidence was presented for the existence of an iminium cation in the condensation products of the secondary amine salt bis(3,5,5-trimethylpyrazolinium) hexachlorostannate (III) with aldehydes and ketones. The condensed salts were also shown to be present in $Me_2SO$-$d_6$ solution by $^1$H-NMR spectroscopy (Rathbone & Stephen, 1971). More recently, X-ray crystallographic studies have characterized in detail the salts formed from (III) in ethanol solution, by addition of an excess of cyclooctanone and of 4-methylcyclohexanone (Van Schalkwyk, Stephen & Hodgson, 1976). We report the structural determination of (I) and (II) formed by the condensation of (III) with *m*-chloro- and *p*-hydroxybenzaldehyde.

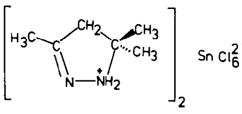
In addition, previous kinetic studies made on the hydrolysis of *p*-substituted benzaldehyde derivatives of (III) established the effect of the substituent groups upon rate and equilibrium constants (Ashford & Stephen, 1978). We report a similar study on the title compounds.



(I)



(II)



(III)

## Experimental

The compounds were prepared by the addition of the substituted benzaldehyde to a solution (approx. 1% weight/volume) of bis(3,5,5-trimethylpyrazolinium) hexachlorostannate in dry ethanol. Crystals formed after several days in a refrigerator.

The lattice constants were obtained by a least-squares method from the setting of 25 reflections measured on a four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å).

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Table 1. *Crystal data and experimental and refinement parameters for the crystal structures of the m-chloro salt* (I) *and the p-hydroxy salt* (II)

| | (I) | | (II) | |
|---|---|---|---|---|
| Crystal data | | | | |
| Molecular formula | $[C_{13}H_{16}ClN_2]_2^+[SnCl_6]^{2-}$ | | $[C_{13}H_{17}N_2O]_2^+[SnCl_6]^{2-}$ | |
| $M_r$ | 802·91 | | 766·03 | |
| Space group | $P2_1/n$ | | $P2/n$ | |
| $a$ | 9·522 (5) Å | | 12·917 (6) Å | |
| $b$ | 13·092 (6) | | 9·277 (5) | |
| $c$ | 14·597 (7) | | 14·805 (7) | |
| $\beta$ | 108·2 (2)° | | 112·4 (2)° | |
| $V$ | 1728·98 Å$^3$ | | 1640·43 Å$^3$ | |
| $D_m$ | 1·51 Mg m$^{-3}$ | | 1·66 Mg m$^{-3}$ | |
| $D_c$ | 1·54 for $Z = 2$ | | 1·68 for $Z = 2$ | |
| $\mu$(Mo $K\alpha$) | 1·43 mm$^{-1}$ | | 1·41 mm$^{-1}$ | |
| $F$(000) | 804 | | 772 | |
| Analysis | found | required | found | required |
| C | 38·50% | 38·89% | 40·85% | 40·76% |
| H | 4·15% | 4·02% | 4·50% | 4·48% |
| N | 6·95% | 6·98% | 7·25% | 7·31% |
| Melting point | 506 K (decomposition) | | 521 K (decomposition) | |
| Data collection | | | | |
| Crystal dimensions | 0·2 × 0·2 × 0·6 mm | | 0·1 × 0·3 × 0·5 mm | |
| Scan mode | $\omega$–$2\theta$ | | $\omega$–$2\theta$ | |
| Scan width | 0·9° $\theta$ | | 0·9° $\theta$ | |
| Scan speed | 0·03° $\theta$ s$^{-1}$ | | 0·03° $\theta$ s$^{-1}$ | |
| Range scanned ($2\theta$) | 6–45° | | 8–46° | |
| Stability | ±2% | | ±3% | |
| Number of reflections collected | 2463 | | 2426 | |
| Number of observed reflections | 1977 with $I$(rel.) > $2\sigma I$(rel.) | | 1991 with $I$(rel.) > $2\sigma I$(rel.) | |
| Final refinement | | | | |
| Number of variables | 114 | | 192 | |
| $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$ | 0·043 | | 0·028 | |
| $R_w = \sum w^{1/2}\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum w^{1/2}\lvert F_o\rvert$ | 0·047 | | 0·028 | |
| Weighting scheme $w$ | $(\sigma^2 F + 8\cdot9 \times 10^{-4} F^2)^{-1}$ | | $(\sigma^2 F)^{-1}$ | |
| $U$ of constrained H atoms | | | | |
| Benzene ring | 0·100 Å$^2$ | | 0·079 Å$^2$ | |
| Methyl | 0·089 | | 0·108 | |
| Hydroxy | – | | 0·116 | |

During the data collection three reference reflections were periodically monitored to check crystal stability. Crystal data and experimental details are listed in Table 1. The data were corrected for Lorentz–polarization effects but not for absorption.

### Solution and refinement of the structures

*m*-Chloro derivative (I): Stoichiometric considerations and requirements of space group $P2_1/n$ restrict the Sn atom to the origin. Hence the Patterson map resembles the electron density map, but since it has $P2/m$ symmetry, care was exercised in selecting three unique peaks corresponding to the Cl atoms. Subsequent least-squares refinement followed by a difference map yielded the positions of the remaining non-hydrogen atoms. After further refinement with Sn and all Cl atoms treated anisotropically, most of the H atoms appeared in a difference map. These were included in the final model and were constrained at 1·08 Å from their corresponding C atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were refined as two single parameters.

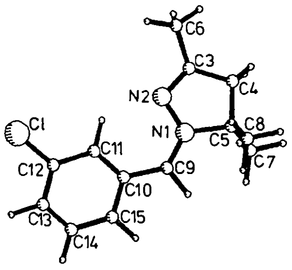

Fig. 1. The *m*-chlorobenzylidene-3,5,5-trimethylpyrazolinium cation.

Table 2. *Fractional coordinates of the heavy atoms* (×10$^4$)

| | (I) | | | (II) | | |
|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| Sn | 0 | 0 | 0 | 2500 | 1876 (0) | 2500 |
| Cl(1) | 978 (2) | 1707 (1) | 33 (1) | 532 (1) | 1943 (1) | 1440 (1) |
| Cl(2) | 1312 (2) | −517 (1) | −1121 (1) | 2094 (1) | 57 (1) | 3489 (1) |
| Cl(3) | 2121 (2) | −472 (1) | 1367 (1) | 2133 (1) | 3733 (1) | 3500 (1) |
| Cl(4) | 858 (4) | 5533 (2) | −1856 (2) | – | – | – |
| O | – | – | – | −678 (3) | 3022 (4) | 2915 (2) |
| N(1) | 4401 (5) | 3173 (4) | 1221 (3) | 230 (2) | 2463 (3) | 7568 (2) |
| N(2) | 4302 (5) | 2921 (4) | 267 (3) | 983 (2) | 1348 (4) | 7599 (2) |
| C(3) | 4659 (6) | 1965 (5) | 283 (4) | 1333 (3) | 855 (4) | 8473 (3) |
| C(4) | 4997 (7) | 1445 (5) | 1223 (4) | 894 (4) | 1553 (4) | 9151 (3) |
| C(5) | 4994 (6) | 2305 (5) | 1928 (4) | 241 (3) | 2832 (4) | 8579 (3) |
| C(6) | 4652 (7) | 1430 (5) | −606 (5) | 2143 (3) | 9585 (4) | 8774 (3) |
| C(7) | 6550 (8) | 2595 (6) | 2554 (5) | −928 (4) | 2950 (6) | 8552 (3) |
| C(8) | 3962 (7) | 2112 (6) | 2512 (5) | 889 (4) | 4222 (5) | 8898 (3) |
| C(9) | 4020 (7) | 4057 (5) | 1459 (5) | −376 (3) | 3105 (4) | 6770 (3) |
| C(10) | 3339 (7) | 4892 (5) | 835 (5) | −409 (3) | 2948 (4) | 5790 (3) |
| C(11) | 2587 (8) | 4806 (6) | −146 (5) | 317 (3) | 2112 (4) | 5508 (3) |
| C(12) | 1865 (9) | 5667 (6) | −651 (6) | 237 (4) | 2127 (5) | 4551 (3) |
| C(13) | 1937 (8) | 6593 (6) | −201 (5) | −568 (3) | 2956 (4) | 3863 (3) |
| C(14) | 2696 (8) | 6682 (6) | 752 (5) | −1312 (3) | 3747 (5) | 4120 (3) |
| C(15) | 3393 (7) | 5844 (5) | 1283 (5) | −1233 (3) | 3757 (4) | 5074 (3) |

*p*-Hydroxy derivative (II): The space group *P*2/*n* requires the two Sn atoms to lie either at the origin or on a twofold axis. A Patterson map showed the Sn to be on a diad at ($\frac{1}{4}$,0·189,$\frac{1}{4}$) and revealed the Cl positions. Subsequent refinement followed by difference maps yielded the positions of the remaining atoms including many H atoms. The latter were included in the model by constrained refinement (C—H = 1·08, O—H = 1·00 Å) as previously described. Details of the final refinement parameters for both structures are given in Table 1, and the positional parameters in Table 2.*

### Description of the structures

Views of the molecules with atoms numbered are shown in Figs. 1 and 2 and bond lengths and angles given in Tables 3 and 4. In both cases the expected geometric isomer about N$^{+}$(1)=C(9), with the aromatic ring *trans* to the bulky geminal dimethyl group, is found in the crystal structures. The near planarity of the pyrazolinium ring and of the iminium ion system C(9)=N$^{+}$(1) may be seen from the perpendicular distance from least-squares planes (1 and 2) in the molecules (Table 5).

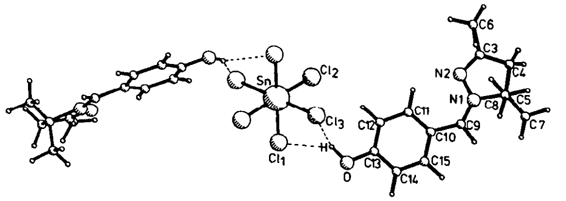

Fig. 2. *p*-Hydroxybenzylidene-3,5,5-trimethylpyrazolinium cations showing hydrogen bonding.

Slight distortions in internal bond angles occur in the benzene ring. Thus the angle at the point of substitution is 121·0 (7) for (I) and 120·2 (4)° for (II). This compares well with the results of Domenicano, Mazzeo & Vaciago (1976).

The diene system C(3)=N(2)—N$^{+}$(1)=C(9) which is near planar (Table 5) is not in the plane of the benzene ring for either compound, as can be seen from the torsion angle N(1)—C(9)—C(10)—C(11) which is 19·3 (6) for (I) and 6·3 (6)° for (II). The substituent has little effect on bond lengths in the diene system, C(3)=N(2), N(1)—N(2), N(1)=C(9), which are essentially the same in both structures (Table 3).

Hydrogen bonding exists in the *p*-hydroxy salt between the hydroxy H and two Cl atoms of the SnCl$_6^{2-}$ anion. This bifurcated hydrogen bond has distances of 2·46 [H—Cl(1)] and 2·90 Å [H—Cl(3)], Fig. 2.

### Rate of hydrolysis

In common with a large number of other products of condensation of carbonyl compounds with (III) (Rathbone & Stephen, 1971), (I) and (II) give $^1$H-NMR spectra in Me$_2$SO-$d_6$ which show sharp singlets for the geminal-dimethyl (6-proton), methylene (2-proton) and

Table 3. *Bond lengths* (Å)

| | (I) | (II) | | (I) | (II) | | (I) | (II) |
|---|---|---|---|---|---|---|---|---|
| Sn—Cl(1) | 2·415 (1) | 2·427 (1) | C(5)—N(1) | 1·521 (7) | 1·529 (4) | C(13)—O | – | 1·358 (4) |
| Sn—Cl(2) | 2·444 (1) | 2·419 (1) | N(1)—C(9) | 1·292 (7) | 1·288 (4) | C(13)—C(14) | 1·358 (9) | 1·373 (5) |
| Sn—Cl(3) | 2·435 (1) | 2·432 (1) | C(9)—C(10) | 1·442 (8) | 1·443 (5) | C(14)—C(15) | 1·387 (9) | 1·376 (5) |
| N(1)—N(2) | 1·407 (6) | 1·408 (4) | C(10)—C(11) | 1·392 (9) | 1·398 (5) | C(15)—C(10) | 1·401 (8) | 1·400 (5) |
| N(2)—C(3) | 1·294 (7) | 1·280 (4) | C(11)—C(12) | 1·404 (9) | 1·381 (5) | C(3)—C(6) | 1·473 (8) | 1·526 (5) |
| C(3)—C(4) | 1·475 (7) | 1·478 (5) | C(12)—Cl(4) | 1·730 (7) | – | C(5)—C(7) | 1·526 (8) | 1·500 (5) |
| C(4)—C(5) | 1·526 (8) | 1·514 (5) | C(12)—C(13) | 1·370 (9) | 1·379 (5) | C(5)—C(8) | 1·510 (8) | 1·512 (5) |

Table 4. *Bond angles* (°)

| | (I) | (II) | | (I) | (II) | | (I) | (II) |
|---|---|---|---|---|---|---|---|---|
| Cl(1)—Sn—Cl(2) | 89·7 (1) | 89·7 (0) | C(4)—C(5)—N(1) | 100·0 (4) | 99·7 (3) | C(9)—C(10)—C(15) | 115·8 (6) | 115·5 (3) |
| Cl(1)—Sn—Cl(3) | 90·2 (0) | 88·7 (0) | C(4)—C(5)—C(7) | 112·5 (5) | 114·3 (4) | C(10)—C(11)—C(12) | 119·1 (6) | 120·2 (4) |
| Cl(2)—Sn—Cl(3) | 90·7 (0) | 89·3 (0) | C(4)—C(5)—C(8) | 113·3 (5) | 111·7 (3) | C(11)—C(12)—C(13) | 121·0 (7) | 120·3 (4) |
| C(5)—N(1)—C(9) | 124·3 (5) | 124·7 (3) | N(1)—C(5)—C(7) | 107·8 (5) | 110·9 (3) | C(11)—C(12)—Cl(4) | 118·5 (5) | – |
| C(5)—N(1)—N(2) | 113·1 (4) | 112·5 (3) | N(1)—C(5)—C(8) | 109·8 (4) | 107·2 (3) | Cl(4)—C(12)—C(13) | 120·4 (6) | – |
| N(2)—N(1)—C(9) | 122·7 (5) | 122·7 (3) | C(7)—C(5)—C(8) | 112·6 (5) | 112·2 (4) | C(12)—C(13)—C(14) | 119·8 (7) | 120·2 (4) |
| C(3)—N(2)—N(1) | 105·8 (4) | 105·6 (3) | N(1)—C(9)—H(9) | 116·0 (3) | 114·8 (2) | C(12)—C(13)—O | – | 122·8 (4) |
| C(4)—C(3)—N(2) | 116·4 (5) | 116·8 (3) | N(1)—C(9)—C(10) | 128·1 (5) | 130·6 (3) | O—C(13)—C(14) | – | 117·0 (4) |
| C(4)—C(3)—C(6) | 122·7 (5) | 122·6 (3) | C(10)—C(9)—H(9) | 115·9 (3) | 114·6 (2) | C(13)—C(14)—C(15) | 120·9 (7) | 120·1 (4) |
| C(6)—C(3)—N(2) | 120·9 (5) | 120·7 (4) | C(11)—C(10)—C(15) | 119·0 (6) | 118·3 (3) | C(14)—C(15)—C(10) | 120·1 (6) | 120·7 (4) |
| C(3)—C(4)—C(5) | 103·9 (4) | 103·8 (3) | C(9)—C(10)—C(11) | 125·1 (6) | 126·2 (3) | | | |

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* Lists of hydrogen positional coordinates, temperature factors and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34115 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

methyl (3-proton) groups, downfield from the corresponding signals given by (III), Table 6.

The hydrolysis reaction involved the addition of measured amounts of $D_2O$ to 0·03 $M$ solutions of (I) and (II) in dimethyl sulphoxide-$d_6$ following the procedure of Rathbone & Stephen (1971). A Brüker 90 NMR spectrometer was used to monitor the course of reaction by means of multiple scans of the geminal-dimethyl peak. The use of integrated proton values yielded quantitative information on the disappearance of the benzylidene derivative and the appearance of the hydrolysed product.

Second-order rate constants for the hydrolysis of the salts ($R$) carried out at 303 K are summarized in Table 7.

These results are in agreement with the Hammett plots obtained by Ashford & Stephen (1978) as can be seen from Fig. 3.

## Conclusion

The work of Ashford & Stephen (1978) clearly shows the effect of substituents on the ease of hydrolysis of iminium salts. For the two compounds studied here their rates of hydrolysis differ by more than a factor of ten. However, this substituent effect is not reflected in the $C{=}N^+$ length, the bond cleaved in the hydrolysis reaction. Our results indicate that no difference in bond length can be detected in these two compounds within the limits of experimental error.

Table 5. *Least-squares planes*

Equations of the planes expressed in orthogonalized space as $lx + my + nz = P$ and perpendicular distance (Å) from each atom to the plane ($d$)

| Compound (I) | | Compound (II) | |
|---|---|---|---|
| Plane 1: Pyrazolinium ring<br>$9·1342x + 3·1791y - 2·3644z = 4·7841$ | | Plane 1: Pyrazolinium ring<br>$9·7051x + 5·6540y - 0·7717z = 3·7830$ | |
| | $d$ | | $d$ |
| N(1) | −0·044 | N(1) | 0·068 |
| N(2) | 0·011 | N(2) | −0·030 |
| C(3) | 0·029 | C(3) | −0·024 |
| C(4) | −0·050 | C(4) | 0·060 |
| C(5) | 0·055 | C(5) | −0·074 |
| Plane 2: Iminium system<br>$8·8564x + 4·5567y - 2·6047z = 5·0253$ | | Plane 2: Iminium system<br>$9·1895x + 6·3580y - 1·8828z = 4·1144$ | |
| | $d$ | | $d$ |
| N(1) | 0·000 | N(1) | 0·009 |
| N(2) | 0·046 | N(2) | 0·032 |
| C(5) | −0·054 | C(5) | −0·046 |
| C(9) | 0·004 | C(9) | 0·007 |
| C(10) | −0·056 | C(10) | 0·047 |
| H(9) | 0·061 | H(9) | 0·045 |
| Plane 3: Diene system<br>$8·9708x + 3·6733y - 1·7415z = 4·8693$ | | Plane 3: Diene system<br>$8·9941x + 6·2878y - 0·6924z = 4·4126$ | |
| | $d$ | | $d$ |
| C(3) | −0·022 | C(3) | 0·033 |
| N(2) | 0·015 | N(2) | −0·022 |
| N(1) | 0·032 | N(1) | −0·048 |
| C(9) | −0·025 | C(9) | 0·038 |

Table 6. *Signals obtained from* 90 MHz *spectrum in* $(CD_3)_2SO$

Chemical shifts ($\tau$ scale, $Me_4Si_{int.}$ = 10·00)

| Compound | $C(4)H_2$ | $C(3){-}CH_3$ | $C(5){<}^{CH_3}_{CH_3}$ |
|---|---|---|---|
| (III) | 7·04 | 7·86 | 8·56 |
| (I) | 6·62 | 7·52 | 8·25 |
| (II) | 6·70 | 7·57 | 8·31 |

Table 7. *Second-order rate constants for the hydrolysis of the salts at* 303 K

| *m*-Chloro salt | $[R]_0(M)$ | $[D_2O]_0(M)$ | $k \times 10^6$ ($m^3 mol^{-1} s^{-1}$) |
|---|---|---|---|
| | 0·024 | 1·833 | 2·0 (3) |
| | 0·035 | 1·067 | 2·3 (3) |
| | 0·035 | 1·078 | 2·2 (3) |
| *p*-Hydroxy salt | $[R]_0(M)$ | $[D_2O]_0(M)$ | $k \times 10^7$ ($m^3 mol^{-1} s^{-1}$) |
| | 0·026 | 1·100 | 1·2 (3) |
| | 0·018 | 1·100 | 1·1 (3) |

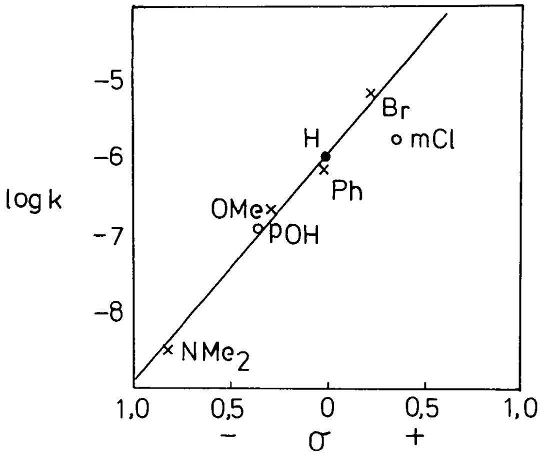

Fig. 3. Relationship between rate of hydrolysis and Hammett sigma function ($\sigma$). Crosses, Ashford & Stephen's (1978) results; open circles, this work.

All calculations were carried out on a Univac 1106 computer at the University of Cape Town.

We thank the CSIR (Pretoria) for the diffractometer data collection and the CSIR and the University of Cape Town for research grants.

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