Preparation, Structure and Vibrational Spectrum of the Dimethylmethyleniminium lon, including the Role of Cationic Polymers in its Formation

George R. Clark, Graeme L. Shaw, Peter W. J. Surman and Michael J. Taylor

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand Derek Steele

Chemistry Unit, Bourne Laboratory, Royal Holloway, University of London, Egham, Surrey, UK TW20 0EX

Crystalline $[(CH_3)_2N=CH_2]X$ (1X, where X = Br or I) results from the reaction of N,N,N',N'-tetramethylmethylenediamine with CH_2Br_2 or CH_2I_2 at room temperature. The structure of 1Br has been determined by X-ray crystallography. The crystals are orthorhombic, a = 6.262(2) Å, b = 7.428(3) Å, c = 5.651(2) Å, z = 2, space group *Pmmn*. The final R = 0.037 for 484 observed reflections. The dimethylmethyleniminium cation, 1, has crystallographically imposed *mm2* symmetry, with the C=N bond distance 1.263(5) Å, C-N bond distance 1.474(4) Å and the CH_3-N-CH_3 angle 114.4(4)°. The Raman spectrum of 1, investigated as the bromide and iodide salts, and supplemented by IR data for 1_2SnBr_6 , has been fully assigned with the aid of *ab initio* calculations using the 3-21G** basis at the SCF and MP2 levels. Isotopic labelling experiments which generate $[(CH_3)_2N=CD_2]^+$ from CD_2I_2 have been used in conjunction with NMR and Raman measurements to investigate the reactions leading to the iminium salt. The intermediate $[Me_2NCH_2NMe_2CH_2NMe_2]^+$ and a cationic polymer $[Me_2N(CH_2NMe_2)_nCH_2NMe_2]^{n+}$ are implicated in the reactions which form the basis of the synthesis of $[(CH_3)_2N=CH_2]I$.

The dimethylmethyleniminium ion $[(CH_3)_2N=CH_2]^+$ (1) belongs to the class of reactive carbocations which form useful organic reagents known as Mannich salts.¹ Such unsaturated cations, which are isostructural and/or isoelectronic with alkenes, are also of interest as ligands in the coordination chemistry of metal complexes.^{2,3} Our concern with the $[Me_2N=CH_2]^+$ ion stems from investigations of the reaction of diamines of the type $Me_2N(CH_2)_xNMe_2$ with dihalides $X(CH_2)_v X$ (X = Br or I) which yield cyclic cations where x + y = 3, 4 or 5.^{4,5} In these cases the ring size, including the two quaternary nitrogen centres, is five,⁶ six⁷ or seven,⁸ and each of these types has been characterised by an X-ray structure determination, for example $[Me_2N(CH_2CH_2)_2NMe_2]^{2+.7}$ According to this pattern the of N, N, N', N'-tetramethylmethylenediamine combination (TMMD) with CH_2Br_2 or CH_2I_2 corresponds to x + y = 2and could, in principle, generate a cyclic dication with a fourmembered ring, *i.e.* $[Me_2N(CH_2)_2NMe_2]^{2+}$. A possible alternative is a cationic polymer $[Me_2NCH_2]_n^{n+}$ with halide counterions. Such a product may seem unlikely since the numerous charges will tend to destabilise the structure; however, the present work indicates that materials of this sort are formed in solution during the reactions of TMMD with dibromomethane or diiodomethane.

The reaction of TMMD with $CH_2X_2(X = Br \text{ or } I)$ in acetonitrile, or an excess of the dihalomethane as the solvent, yields a colourless crystalline solid within a matter of hours at ambient temperture. This product proves to be the salt-like dimethylmethyleniminium halide, $[Me_2N=CH_2]X$ (1X, where X = Br or I) which we have identified by vibrational and NMR spectroscopy and by the X-ray structure determination of the bromide. Formation occurs according to the equation

$$Me_2NCH_2NMe_2 + CH_2X_2 \rightarrow 2[Me_2N=CH_2]X$$
$$(X = Br \text{ or } I)$$

to furnish the iminium salts 1Br or 1I in pure form without by-products. Other preparative methods for 1 are available, for example by the reaction of TMMD from acetyl chloride which gives $1Cl_{9}^{9,10}$ or from chloromethyldimethylamine with $AlCl_{3}$ or $SbCl_{5}^{1,11}$ II is obtained by heating iodomethyldimethylammonium iodide.¹² The cleavage of TMMD with $Me_{3}SiI^{13}$ or $CH_{2}CII^{14}$ has also been proposed. The ability of TMMD to react with $CH_{2}Br_{2}$ has been noted in this context¹⁵ but seems not to have been developed into a preparative method. This is surprising as the consumption of TMMD proceeds cleanly employing extra dihalomethane as the reaction medium. The commercial reagents require no special purification, and the crystalline product can be washed with dichloromethane (which does not itself react with TMMD) and collected by standard Schlenk-line techniques.

This study describes the crystal and molecular structure of $[(CH_3)_2N=CH_2]Br$, determined by single-crystal X-ray diffraction and reports the vibrational spectrum of the iminium cation which is assigned using Raman and IR data supported by *ab initio* calculations. Investigations by NMR and Raman spectroscopy of the reactions concerned in the formation of the iminium salts by the present route are also reported.

Experimental

TMMD (Aldrich Chemicals), dibromomethane, diiodomethane and $[^{2}H_{2}]$ diiodomethane were commercial materials and were used without further purification. Reaction mixtures were made up under the fume hood.

Crystalline $[(CH_3)_2N=CH_2]X$ (X = Br or I) was prepared by the direct reaction of TMMD with CH_2Br_2 or CH_2I_2 at room temperature using an excess (usually threefold) of the dihalomethane as the solvent and simply allowing the mixture to stand for some days. The product appeared as a colourless crystalline solid, from which the liquid phase was withdrawn and set aside to continue the process of crystallisation. Dry dichloromethane was used to wash the crystals which were collected and stored under dry nitrogen.

empirical formula	C ₂ H ₂ NBr
	138.01
$F(0 \ 0 \ 0)$	136
crystal system	orthorhombic
space group	Pmmn
a/Å	6.262(2)
\dot{b}/\dot{A}	7.428(3)
c/Å	5.651(2)
$V/Å^3$	262.85(15)
Z	2
$D_{\rm r}/{\rm g}~{\rm cm}^{-3}$	1.74
$D_{\rm m}/{\rm g}$ cm ⁻³ by flotation in CH ₂ Cl ₂ /CH ₂ Br ₂	1.69
radiation used	Mo-Ka (Zr filter)
linear absorption coefficient/cm ⁻¹	80.88
max. and min. transmission coefficients	1.000, 0.434

Structure Determination

Crystallographic data are collected in Table 1. A single crystal was transferred to a capillary and sealed under nitrogen. The crystal selected for data collection, measuring 0.74 $m \times 0.44 mm \times 0.28 mm$, was positioned on an Enraf-Nonius CAD-4 diffractometer. Intensities were recorded with Zr-filtered Mo-K α radiation ($\lambda = 0.71069$ Å) using the $\omega/2\theta$ scan mode and a variable scan speed. Three standard reflections monitored every hour showed a 4% variation in intensity during the data collection and all intensities were rescaled on standards. Data were corrected for Lorentz and polarisation effects, and for absorption using empirical psi scans.¹⁶ Of 558 unique reflections measured within the range $1 < \theta/\text{degrees} < 32$, 484 reflections with $I/\sigma > 3$ were considered observed and used in the calculations. The structure was solved by direct methods using SHELX86¹⁷ and refined by full-matrix least-squares on F using SHELX76.¹⁸ Hydrogen atoms were located and refined individually.

The final refinement of 29 parameters converged at R = 0.037 and $R_w = 0.036$ ($w = 1/[\sigma^2(F) + 0.0131F^2]$). The (maximum shift)/ σ for any parameter in the final cycle was 0.001; the highest peak in the difference map was 0.48 Å⁻³. Final coordinates and thermal parameters are given in Table 2. The bond lengths and angles are listed in Table 3.†

Spectroscopy

IR spectra were recorded on Perkin-Elmer 983 and Digilab FTS60 spectrometers. Raman spectra were measured using a Jobin Yvon U1000 spectrometer system with a Spectra Physics argon-ion laser tuned to the green line at 514 nm with a power of 20–50 mW. NMR spectra were recorded using a Bruker AM400 spectrometer operating at 400.137 MHz for ¹H or 100.614 MHz for ¹³C. Locking signals were provided by the deuterium resonance of CDCl₃, CD₂I₂ or CD₃CN.

† Structure factor tables have been deposited at the Cambridge Crystallographic Data Centre.

J. CHEM. SOC. FARADAY TRANS., 1994, VOL. 90

Table 3 Bond distances and angles for $[(CH_3)_2N=CH_2]Br$

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.8(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.4(4) 5(4) 6(5) 5(2) 0(8) 9(4) 9(4) 9(4) 1(5) 7.2(4)

Results and Discussion

Crystal Structure

Fig. 1 shows the cation geometry and atomic numbering. The dimethylmethyleniminium ion possesses crystallographically imposed *mm2* site symmetry and is thus required to be planar, apart from the hydrogens of the methyl groups. Coordination at the nitrogen atom is trigonal with a CH_3-N-CH_3 angle of 114.4(4)°. The bond angle within the CH_2 group is 90(8)°. The C-N bonds measure 1.474(4) and the C=N distance is 1.263(5) Å, which is at the short end of the range of values in other iminium ions.^{1,19} For comparison, in the [$(CH_3)_2N=C(CH_3)_2$]⁺ ion the C-N-C angle is 125.4°, the C-N distance is 1.51(3) Å, and the C=N distance is 1.30(2) Å.²⁰ X-Ray identification of [$(CH_3)_2N=CH_2$]Cl, formed as a by-product of the action of HCl on Me₂N(H)CH₂SO₃,²¹ revealed the dimensions C-N, 1.464(6); C=N, 1.264(9) Å and C-N-C, 114.1°, which are very close to the present values. This compound and



Fig. 1 Cation geometry and atomic numbering for $[(CH_3)_2N=CH_2]Br$

Table 2 Final positional and thermal parameters for $[(CH_3)_2N=CH_2]Br$

atom	x	у	Ζ	<i>U</i> ₁₁	U 22	U 33	U 23	U ₁₃	U ₁₂
Br N C(1) C(2) H(1) H(21) H(22)	0.250 0.750 0.750 0.750 0.750 0.750 0.750 0.874 (7)	0.250 0.250 0.250 0.0832(5) 0.156(9) -0.013(12) 0.097(6)	0.04454(7) 0.5428(5) 0.7663(7) 0.4016(7) 0.890(14) 0.511(15) 0.290(8)	0.0447(3) 0.037(1) 0.055(3) 0.0479(17) 0.046(14) 0.043(14) 0.048(8)	0.0318(3) 0.037(2) 0.048(3) 0.0382(17)	0.0367(3) 0.026(1) 0.025(1) 0.0353(12)	0.00 0.00 0.00 - 0.0056(14)	0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00

 $[(CH_3)_2N=CH_2]Br$ have the same orthorhombic space group, and are essentially isostructural. The distances of the bromide ion from atoms of the cation $[Br\cdots C(1), 3.50;$ $Br\cdots C(2), 3.53; Br\cdots N, 4.21 Å$] are such that there appears to be no significant bonding between the two, other than electrostatic interaction.

Vibrational Spectra and Assignment of the $[(CH_3)_2N=CH_2]^+$ Ion

The $[(CH_3)_2N=CH_2]^+$ cation has C_{2v} symmetry according to the X-ray analysis of 1Br. Hence this point group can be made the basis of the vibrational assignment since, although the cell has D_{2h} symmetry and contains two formula units, no site group or correlation effects appear in the spectrum. The number of fundamental modes of $[(CH_3)_2N=CH_2]^+$ is 30, comprising $10a_1 + 5a_2 + 6b_1 + 9b_2$. All are Raman active and all except the a2 species should appear in the IR spectrum. Crystals of 1Br and 1I, examined in sealed glass tubes under nitrogen, gave good quality Raman spectra, free of fluorescence. IR spectra were difficult to obtain because the compounds are highly deliquescent and react with water to give formaldehyde and MeNH₂Br (or I). Salts of 1 with a large anion are easier to handle so that we were able to record the IR spectrum of 1₂SnBr₆ which matches that of 1SbCl₆ reported in earlier work.²²

Fig. 2 shows the Raman spectrum of II, partially labelled by deuterium substitution in the methylene group. NMR study confirms that the reaction of TMMD with CD_2I_2 occurs without scrambling of the hydrogen atoms and hence the spectrum is that of a mixture of $[(CH_3)_2N=CH_2]^+$ and $[(CH_3)_2N=CD_2]^+$. Despite the problem of moisture sensitivity the IR spectrum was also measured, enabling many of the bands to be located amongst others due to the decomposition products. These IR data are included in Table 4 and show close correspondence with the Raman values.

Assignment of the CH₃ modes requires little comment, being guided by the results of *ab initio* modelling of the spectrum, as shown in Table 4. The CD₂ stretching modes are plainly visible in the spectra of the deuteriated sample and lend support to the assignment of the corresponding CH₂ modes. Of the skeletal modes, those of C=N and C-N stretching are of particular interest. The former gives an intense Raman band at 1683 cm⁻¹ and this mode drops by 35 cm⁻¹ upon deuteriation owing to a contribution from the CH₂ deformation (the replacement of CH₂ by CD₂ is computed to have an effect of 48 cm⁻¹). Even more pronounced is the effect on the modes identified as C-N stretches, espe-



Fig. 2 Raman spectrum of $[Me_2N=CH_2]I$ containing a proportion of $[Me_2N=CD_2]I$. Starred bands arise from $[Me_2N=CD_2]I$. Inset: The C=N bands of a sample in the liquid phase.

cially that of b_2 type which is mixed with the CH_2 wagging mode of the same symmetry. The result is to move the band from 1030 to 813 cm⁻¹ (measured in the IR spectrum where it is adjacent to a weaker band at 820 cm⁻¹ attributable to the a_1 C–N stretch of the CH_2 containing molecule). The same near coincidence occurs in the Raman spectrum where it explains a gain in the intensity of the band at 817 cm⁻¹ compared with the spectrum of the sample without the labelled component. In support of the assignment of the C=N and C–N stretches we note that the earlier IR study of 1 as the [SbCl₆]⁻ salt²² includes a footnote citing Raman lines in solution at 1706 and 818 cm⁻¹, both polarised, which confirms their identity as a_1 vibrations.

Skeletal deformations, which are chiefly bending modes of the C-N-C group, occur at 429 and 499 cm⁻¹ and the assignment of these to a_1 and b_2 species, respectively, receives qualitative support from their Raman intensities and is backed up by fair agreement with the computed values. This calculation also suggests that the bands at 113 and 157 cm⁻¹ may be the CH₃ torsional modes, although their attribution to lattice modes is an obvious alternative. Using the frequencies provided by the Raman and IR spectra of 1, 25 of the 30 fundamentals of the [(CH₃)₂N=CH₂]⁺ ion have been assigned. Table 4 also includes the values of the other fundamentals (mainly those of a_2 or b_1 type) which have not been observed, but for which estimates are furnished by the computational results.

All the bands in the Raman spectra of crystalline 1Br and 1I can be ascribed to fundamentals of the iminium ion, except for the two weak features at 2050 and 2775 cm⁻¹. These can be explained as overtones of the C–N mode at 1030 and the CH₂ deformation at 1409 cm⁻¹, respectively. Apart from the suspected lattice modes, only the band at 1030 cm⁻¹ of 1I changes its position appreciably (to 1055 cm⁻¹) in the spectrum of 1Br. This band is assigned to a mixed mode comprising antisymmetric C–N–C stretching and CH₂ wagging.

A further check on the validity of the vibrational assignment according to C_{2v} symmetry can be made by comparison with that of 2-methylpropene, $(CH_3)_2C=CH_2$, the molecule with which the present iminium ion is isoelectronic. Of particular note in that assignment²³ are the C-C stretches at 802 (a₁) and 970 (b₂), and the C=C stretch at 1655 cm⁻¹. The cationic species can be expected to exhibit higher frequencies than the isoelectronic molecular counterpart and this is so for the C-N and C=N modes, and indeed for most of the other vibrations. Symmetry coordinates and force constants for the [Me₂N=CH₂]⁺ ion are given in Table 5. These are derived from the *ab initio* calculations described in the following section.

Ab initio Calculations of the Structure and Vibrational Frequencies of $[(CH_3)_2N=CH_2]^+$

Ab initio structures and vibrational spectra were computed with the GAUSSIAN 92 package using the in-built 3-21G** basis at both the SCF and the MP2 levels. The Raman intensities were not calculated at the MP2 level owing to the absence of the necessary software for the analytic polarisability derivatives.

The cartesian force fields were extracted from GAUSSIAN and transferred into the symmetrical valence basis shown in Table 5 using the author's software, VIBRA90.²⁴ In the absence of scaling of the force field the results of the GAUSS-IAN package were reproduced.

It is well established that the SCF values are too large and that, to a first approximation, the experimental vibrational frequencies are reasonably reproduced by scaling all calcu-

I	CHEM	SOC	FARADAY	TRANS	1994	VOL	90
J.	CHEW.	30C.	FARADAT	1 KANO.,	1774,	VOL.	70

Table 4 V	ibrational assignments	for $[(CH_3)_2N=C$	$[H_2]^+$ (1) ^a and	$[(CH_3)_2N=0]$	$[D_2]^+$ (2)
-----------	------------------------	--------------------	--------------------------------	-----------------	---------------

mode		a _i	a ₂	b _i	b ₂
CH ₃ asym. str.	1	3012 m (2964) 3010	(2948)	(2952)	3115 w (3052) 3114
	2	(2964)	(2948)	(2952)	(2962)
CH, sym str.	1	2982 m (2952)	()	(====)	2950 w (2962)
	2	(2862)			(2857)
CH ₂ stretch	1	2935 m (2861)			2890 w (2857)
	2	2202 (2172)			<u>2890</u> 2260 (2283) 2270
C=N stretch	1	1683 vs (1692)			
		<u>1683</u>			
	2	1648 (1644)			
		<u>1648</u>			
CH ₃ asym. def.	1	1480 w (1466)	(1417)	(1437)	1445 w (1436)
		<u>1490</u>			<u>1443</u>
	2	(1447)	(1417)	(1437)	(1435)
CH ₃ sym. def.	1	1462 m (1425)			1395 m (1400)
	-	1465			<u>1395</u>
	2	(1403)	((00)	(1157)	(1399)
CH_2 wag	1	1409 s (1403)	(699)	(1156)	— (1290)
	2	$\frac{1410}{1180}$ (1172)	(507)	(1012)	1204 (1221)
	2	1180 (1172)	(307)	(1013)	(1221)
CH tock	1	$\frac{1150}{1163}$ s (1151)	(1103)	(1200)	(1071)
C113 100K	•	1164	(1105)	(1200)	1004
	2	1066 m (1047)	(1090)	(1164)	(952)
		1065	()	()	876
C-N stretch	1	817 w (787)			1030 s (963)
		<u>820</u>			1030
	2	(749)			817 (835)
					<u>813</u>
skeletal def.	1	429 m (381)		(439)	499 w (473)
		<u>428</u>			<u>499</u>
	2	(378)		(425)	445 (421)
CH ₃ torsion	1		113 vs (140)	157 s (178)	

^a Wavenumbers (cm⁻¹) from Raman spectra (with IR data underlined) are compared with the values calculated by *ab initio* methods which are shown in parentheses.

lated wavenumbers by a single scaling factor. The deficiencies of the SCF results are partially removed by the application of Møller–Plesset corrections. At the MP2 level rather more than 50% of the configuration interaction error is corrected for. Thus for the 6-13G* basis Pople *et al.* recommended the correction factors at the SCF and MP2 levels of 0.8929 and 0.9427.²⁵ For the 3-21G*/SCF level a scaling of *ca.* 0.9 is frequently applied (0.81 to the force constants).

It is recognised, however, that such a general scaling is not uniformly effective through the spectrum. Configuration interaction (CI) has a far greater impact on bonds with high electron density. Thus we find that the MP2 correction results in an increase in bond length for all the CH bonds of the dimethylmethyleniminium ion of 0.2%. For the N-CH₃ and the N=CH₂ bonds the increases are 1.2 and 2.5%, respectively. Vibrational force constants change in an exponential manner with bond length. Thus for C-C bonds the relation: $f/mdyn Å^{-1} = 1170 \exp(-3.65r/Å)$, has been given.²⁶ The error due to the lack of CI is therefore nonuniform. In addition it is usual to compare with experimental frequencies, not with harmonic data.

Anharmonicity has a far greater effect on CH stretching than for other bonds. It is for such reasons that better results are obtained by applying different scaling factors to different types of motions. While this introduces a further degree of empirical correction, such differential scaling is likely to be important for the current case in view of the substantial MP2 corrections to the structure. As the object of the present calculations is to gain guidance in understanding the spectra, the number of parameters is kept to the minimum required to explain the major unequivocal bands. Thus adjustments were made in the factors for stretching force constants of the C-H and N=C bonds and for the HCH/NCH bending modes to centralise the computed band centres in the observed regions. These factors for the N=C, N-C and C-H bonds are 0.80, 0.95 and 0.76 at the SCF level. For the MP2 calculations the N=C bond frequency is now clearly too low by nearly 2%, even though the scaling factor has been greatly increased to 0.99. To reproduce the observed band at 1681 cm^{-1} would require the factor to be near 1.04. This is due to the MP2 calculations giving a structure in which the CN bonds are too long. The SCF structure with N-C, 1.503 Å and N=C, 1.264 Å is in much better accord with that resulting from the X-ray analysis. In an effort to understand this, the effect of placing a chloride ion 3.2 Å above the N=C bond was explored. The N=C bond was virtually unaltered, but the nitrogen became almost tetrahedral and the N-C bonds extended by 0.021 Å. No frequencies changed by more than 20 cm^{-1} . It appears that the 3-21G** basis might be inadequate to reproduce the structure of this ion at the MP2 level in that the NC bonding is not quite of high enough order. The best reproduction of the structure is at the SCF level, and for this reason the vibrational spectra referred to in the remainder of the text will be that calculated at this level. The scaling factors used are given in Table 5 where the diagonal force constants are listed in the symmetry coordinate basis.

Spectroscopic Investigations of the Reaction of CH_2X_2 (X = Br or I) with TMMD

This reaction generates the dimethylmethyleniminium halides. NMR spectra of $[(CH_3)_2N=CH_2]Br$ in acetonitrile

J. CHEM. SOC. FARADAY TRANS., 1994, VOL. 90

Table 5 Comparison of the SCF/3-21G** and MP2/3-21G** force fields, both scaled and unscaled, in mdyn Å⁻¹

	$f_{unsc}(SCF)$	$f_{\rm scal}({\rm SCF})$	$f_{unsc}(MP2)$	$f_{\rm scal}({ m MP2})$
$S_1 = R[N=C]$	12.94	10.35	10.27	10.17
$S_{2} = R[N - C(3)] + R[N - C(7)]$	4.71	4.48	4.11	4.07
$S_3 = r_4 + r_5 + r_6 + r_8 + r_9 + r_{10}$	6.26	4.76	6.03	4.73
$S_4 = r_{11} + r_{12}$	6.49	4.93	6.26	4.91
$S_5 = 2r_4 - r_5 - r_6 + 2r_8 - r_9 - r_{10}$	6.20	4.71	6.01	4.72
$S_6 = \alpha [H(11)CH(12)]$	0.851	0.673	0.798	0.702
$S_7 = \theta[C(3)NC(7)]$	1.517	1.214	1.315	1.183
$S_8 = R[N-C(3)] - R[N-C(7)]$	4.45	4.23	3.95	3.91
$S_9 = \tau_{3,1,2,11} + \tau_{7,1,2,12}$	0.135	0.115	0.112	0.101
$S_{10} = r_4 + r_5 + r_6 - r_8 - r_9 - r_{10}$	6.24	4.74	6.02	4.73
$S_{11} = r_{11} - r_{12}$	6.49	4.93	6.27	4.92
$S_{12} = 2r_4 - r_5 - r_6 - 2r_8 + r_9 + r_{10}$	6.19	4.70	6.00	4.71
$S_{13} = r_5 - r_6 + r_9 - r_{10}$	6.13	4.66	5.96	4.68
$S_{14} = r_5 - r_6 - r_9 + r_{10}$	6.15	4.67	5.97	4.69
$S_{15} = \beta_4 + \beta_5 + \beta_6 - \alpha_{4,5} - \alpha_{4,6} - \alpha_{5,6}$				
$S_{16} = \beta_8 + \beta_9 + \beta_{10} - \alpha_{8,9} - \alpha_{8,10} - \alpha_{9,10}$				
$S_{15}' = S_{15} + S_{16}$	0.819	0.647	0.765	0.673
$S_{16}' = S_{15} - S_{16}$	0.796	0.629	0.745	0.656
$S_{17} = 2\beta_4 - \beta_5 - \beta_6 + 2\beta_8 - \beta_9 - \beta_{10}$	1.016	0.813	0.909	0.782
$S_{18} = 2\beta_4 - \beta_5 - \beta_6 - 2\beta_8 + \beta_9 + \beta_{10}$	0.951	0.761	0.849	0.730
$S_{19} = \beta_5 - \beta_6 + \beta_9 - \beta_{10}$	0.957	0.765	0.850	0.731
$S_{20} = \beta_5 - \beta_6 - \beta_9 + \beta_{10}$	0.958	0.767	0.850	0.731
$S_{21} = 2\alpha_{5.6} - \alpha_{4.5} - \alpha_{4.6} + 2\alpha_{9.10} - \alpha_{8.10} - \alpha_{8.9}$	0.642	0.507	0.593	0.521
$S_{22} = 2\alpha_{5.6} - \alpha_{4.5} - \alpha_{4.6} - 2\alpha_{9.10} + \alpha_{8.10} + \alpha_{8.9}$	0.629	0.497	0.582	0.513
$S_{23} = \alpha_{4.5} - \alpha_{4.6} - \alpha_{8.10} + \alpha_{8.9}$	0.615	0.486	0.570	0.502
$S_{24} = \alpha_{4.5} - \alpha_{4.6} + \alpha_{8.10} - \alpha_{8.9}$	0.623	0.492	0.575	0.506
$S_{25} = \beta_{11} - \beta_{12}$	3.877	3.063	3.602	3.170
$S_{26} = \beta C[(3)] - \beta [C(7)]$	3.964	3.171	3.535	3.040
$S_{27} = \tau_{CH_3} + \tau_{CH_3}$	0.0146	0.0124	0.0149	0.0127
$S_{28} = \tau_{CH_3} - \tau_{CH_3}$	0.0219	0.0186	0.0193	0.0165
$S_{29} = \gamma_{11} + \gamma_{12}$	0.184	0.156	0.148	0.133
$S_{30} = \gamma_3 + \gamma_7$	0.308	0.262	0.293	0.263

The following scaling factors were applied to the force field in the symmetry coordinate basis

	N=C	N-C	С—Н	α	β	CNC	τ
sym. coord.	1	2, 7	3–5, 10–15	6, 15, 16, 21–25	17–20	7	26–30
SCF	0.80	0.90	0.76	0.88	0.86	0.80	0.85
MP2	0.99	0.99	0.785	0.88	0.86	0.90	0.90

show ¹H signals at 3.74 and 8.21 ppm, and ¹³C signals at 47.4 and 165.9 ppm, due to the CH₃ and CH₂ groups, respectively. These figures match the values of 3.66 and 7.79 ppm (¹H) and 50.4 and 169.0 ppm (¹³C) reported for 1SbCl₆ in the same solvent^{22,27} and confirm the identity of the iminium ion. The possibility that the compound might exist in solution as the covalent form Me₂NCH₂Br is thus eliminated and this general conclusion is support by the fact that the spectra of reaction mixtures and products are similar whether CH₂Br₂ or CH₂I₂ is employed in the reaction with TMMD.

As an adjunct to the preparative work we have investigated the formation of 1I by following the changes in NMR spectra of reaction mixtures over time. (The iodide system was chosen because the reaction with CH_2I_2 is faster than with CH_2Br_2 .) Fig. 3 shows results for a mixture of CH_2I_2 with TMMD in a mole ratio of 5:1. The ¹H spectrum consists of a fixed signal due to CH_2I_2 at 3.95 ppm and a pair of signals which move progressively as the reaction proceeds. At the outset these are the CH_3 resonance at 2.15 and the CH_2 resonance at 2.63 ppm of TMMD. After 6 h at room temperature these signals had moved to 2.65 and 4.05 ppm, respectively. Subsequently they reached 2.85 and 4.65 ppm and then remained near these positions while crystals of the iminium salt, 1I, were deposited by the solution.

This behaviour points to a sequence in which CH_2I_2 reacts in a slow step with TMMD and the iminium ion (a strong electrophile) combines immediately with the diamine in an equilibrium which is rapid on the NMR timescale:

$$CH_2I_2 + Me_2NCH_2NMe_2 \rightarrow 2[Me_2N=CH_2]^+I^- \quad (1)$$

 $[Me_2N=CH_2]^+ + MeNCH_2NMe_2$

$$\approx [Me_2NCH_2(NMe_2)CH_2NMe_2]^+ \quad (2)$$

Once the initial stage, represented by the sum of eqn. (1) and (2), is complete the reaction becomes much slower, presumably because free TMMD is unavailable to react with CH_2I_2 .

In the next stage, during which crystals of the iminium salt are produced, the mixture becomes viscous and may separate into two layers, one of which consists mainly of the reagents. The product layer seems to comprise a polymer, believed to be of the type $[Me_2N(CH_2NMe_2)_nCH_2NMe_2]^{n+}$ in which iminium ions form the repeat unit while a molecule of TMMD furnishes the end groups. The chain length will increase as more of the iminium material is generated by the reaction of CH_2I_2 with the amine substrate (either TMMD or the subsequent complex of the diamine with iminium ions).

Crystallisation of 1I can be brought about by seeding the mixture, or by adding ether to drive the iminium salt out of solution. Stirring or moving the sample appears to retard the onset of crystal formation and in some instances the reaction mixture has remained liquid for several weeks.



Fig. 3 ¹H NMR spectra of a reaction mixture of $CH_2(NMe_2)_2$ and CH_2I_2 . Labels a-d denote the CH_3 signal and a'-d' the CH_2 signal at times of 15 min, 1 h, 6 h and 48 h after mixing. h denotes the CH_2I_2 signal.

To provide further insight on the mechanism, the reaction of TMMD with deuterio-diiodomethane, CD₂I₂, was investigated by Raman spectroscopy. The NMR data had already confirmed that no exchange occurs to produce CHD groups. Hence CD_2 groups from the CD_2I_2 reagent carry through into the iminium ion as such, and the system contains labelled ions $[Me_2N=CD_2]^+$ alongside unlabelled ions in the liquid phase and in the solid material which crystallises from the solution. The Raman experiment used a mixture of CD_2I_2 and TMMD (in the ratio 3:1) stored within a thinglass vial. Periodically the Raman spectrum was surveyed over the full range from 100 to 4000 cm^{-1} and in addition the region from 1500 to 1800 cm⁻¹ was acquired. In the early stage of the reaction CCD multichannel detection was employed. Alternatively, 10 scans were co-added to get a satisfactory signal-to-noise ratio. Of particular interest are the Raman bands at 1648 and 1683 cm⁻¹ (C=N stretching with a contribution from the methylene group) which can be used to measure the relative amounts of labelled and unlabelled iminium ions in the mixture as the reaction progresses.

The relative proportion of labelled material was estimated from the band areas of the 1648 and 1683 cm⁻¹ bands (shown inset in Fig. 2), allowing for the overlapping which occurs. After one day the reaction mixture contained labelled and unlabelled products in the ratio of *ca*. 1 to 3. Reference to eqn. (1) shows that $[Me_2N=CD_2]^+$ and $[Me_2N=CH_2]^+$ are formed in equal amounts from CD_2I_2 and TMMD. Each will then combine with a further molecule of TMMD (which is unlabelled) according to eqn. (2) so that the net result is the sum of the two processes. Invoking probabilities, the consequence of the equilibrium between TMMD and the iminium

J. CHEM. SOC. FARADAY TRANS., 1994, VOL. 90

ion is to expect $[Me_2N=CH_2]^+$ to be three times more abundant than $[Me_2N=CD_2]^+$ during the early stage of the reaction, as is observed. Subsequently the proportion of labelled material should increase and approach the limit of equal amounts of labelled and unlabelled product, and the Raman spectra bear out this trend.

Reaction of $Me_2NCH_2NMe_2$ with CH_2Br_2 or CH_2I_2 is an attractive route to these dimethylmethyleniminium halides using a simple mixture of the reagents. The crystalline product can be collected and the reaction then allowed to continue, making good the supply of TMMD if the process has become unduly slow.

We are grateful to the New Zealand Research Grants' Committee and the University of Auckland Research Committee for financial support. P.W.J.S. acknowledges the receipt of a William Georgetti Research Scholarship.

References

- 1 E. C. Taylor, H. Böhme and H. G. Viehe, *Advanced Organic Chemistry Methods and Results*, Wiley, New York, 1976, vol. 9, part 1.
- 2 C. W. Fong and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1975, 1100.
- 3 R. D. Adams, J. E. Babin and H-S. Kim, Organometallics, 1987, 6, 749.
- 4 J M. Coddington and M. J. Taylor, Spectrochim. Acta, Part A, 1990, 46, 1487.
- 5 J. A. Creighton and M. J. Taylor, Can. J. Chem., 1987, 65, 2526.
- 6 M. A. Khan, C. Peppe and D. G. Tuck, Can. J. Chem., 1984, 62, 1662.
- 7 G. R. Clark, C. E. F. Rickard and M. J. Taylor, Can. J. Chem., 1986, 64, 1697.
- 8 D. A. House and W. T. Robinson, University of Canterbury, New Zealand, personal communication.
- 9 G. Kinast and L-F. Tietze, Angew. Chem., Int. Ed. Engl., 1976, 15, 239.
- 10 H. Böhme and K. Hartke, Chem. Ber., 1961, 93, 1305.
- 11 F. Knoll and U. Krumm, Chem. Ber., 1971, 104, 31.
- 12 J. Schreiber, H. Maag, N. Hashimoto and A. Eschenmoser, Angew. Chem., Int. Ed. Engl., 1971, 10, 330.
- 13 T. A. Bryson, G. H. Bonitz, C. J. Riechel and R. E. Dardis, J. Org. Chem., 1980, 45, 524.
- 14 S. Miyano, H. Hokari and H. Hashimoto, Bull. Chem. Soc. Jpn., 1982, 55, 534.
- 15 H. Böhme, M. Hilp, L. Koch and E. Ritter, Chem. Ber., 1971, 104, 2018.
- 16 A. C. T. North, D. C. Phillips and F. S. Mathews, Acta Crystallogr., Sect. A, 1968, 24, 351.
- 17 G. M. Sheldrick, Acta Crystallogr., Sect. A, 1990, 46, 467.
- 18 G. M. Sheldrick, SHELX76, Program for Crystal Structure Determination, University of Cambridge, UK, 1976.
- 19 R. Minkwitz, W. Mechstroth and H. Preut, Z. Naturforsch., B, 1993, 48, 19.
- 20 L. M. Trefonas, R. L. Flurry, Jr., R. Majeste, E. A. Meyers and R. F. Copeland, J. Am. Chem. Soc., 1966, 88, 2145.
- 21 A. B. Burg, Inorg. Chem., 1989, 28, 1295.
- 22 K. E. Elmer, P. Volgnandt, G. Heckmann and A. Schmidt, Spectrochim. Acta, Part A, 1979, 35, 473.
- 23 A. J. Barnes and J. D. R. Howells, J. Chem. Soc., Faraday Trans. 2, 1973, 69, 532.
- 24 D. Steele, VIBRA 90, available to users of University of London Computer Centre.
- 25 J. A. Pople, A. P. Scott, M. W. Wong and L. Radom, Israel J. Chem., 1993, 33, 345.
- 26 D. Steele, Spectrochim. Acta, 1966, 22, 1275.
- 27 G. A. Olah and D. J. Donovan, J. Org. Chem., 1978, 43, 860.

Paper 4/03442B; Received 7th June, 1994