Mono- and Di-protonation Sites in *N*-Ammonio-amidates: a Spectroscopic Study

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In a series of *N*-ammonio-amidates (1)—(6) the site of monoprotonation has been established as the formally negatively charged nitrogen atom by means of i.r., u.v., and ^1H n.m.r. spectroscopy with the aid of *O*- and *N*-methyl derivatives. Whereas in more strongly acidic media [65 : 35 (v/v) $HSO_3F-CF_3\cdot CO_2H$] *N*-(trimethylammonio)-methoxyformamidate (5) is diprotonated, once on nitrogen and once on oxygen, to give the internally hydrogen-bonded geometric isomers (16a and b), detectable by ^1H n.m.r. spectroscopy, the ethoxy-analogue (6) is diprotonated on nitrogen; this difference in behaviour is thought to be hyperconjugative in origin. The other *N*-ammonio-amidates are diprotonated on nitrogen. This preference for nitrogen as the location of the second proton, *vis à vis* amides, is ascribed to the strongly electron-withdrawing character of the trimethylammonio-group, which reduces the amide-like lone pair delocalisation in the monocation.

N-AMMONIO-AMIDATES are isoelectronic with nitrogen ylides, their essential feature being a quaternary nitrogen atom adjacent to a negatively charged nitrogen to which is bonded a group, *e.g.* acetyl or ethoxycarbonyl, which serves to delocalise the negative charge. The reactivity of these ylide-like species, which has recently been reviewed,[1,2] may be accounted for by the negatively charged heteroenolate moiety, which has ambident character. In view of their structure and against a background of previous investigations on amides,[3a] we have undertaken a spectroscopic investigation of the thermodynamic protonation sites of a series of *N*-ammonio-amidates (1)—(6) in acidic media of various strengths, chosen in order to effect both mono- and di-protonation.

RESULTS AND DISCUSSION

Monoprotonation of *N*-ammonio-amidates can be effected conveniently in aqueous hydrochloric acid to give salts. Formulation of these as hydrazinium salts (7)—(12) implicitly requires the presence of a carbonyl group. Table 1 contains the main features of the i.r. spectra of the *N*-ammonio-amidates (1)—(6), the hydrochloride salts (7)—(12), and the *N*-methyl and/or *O*-methyl salts relevant to the presence or absence of a carbonyl absorption.

The rather hygroscopic ylide (1) shows (Table 1) a broad absorption between 1 550 and 1 580 cm^{-1}, attributable to a strongly conjugated carbonyl. In the corresponding hydrochloride salt (7) the strong absorption at 1 690 cm^{-1} is assigned to a carbonyl stretching vibration, and a medium-strong absorption at 1 550 cm^{-1} to a CO·NH group, both being consequent upon protonation at nitrogen. This conclusion is supported by a comparison with the spectra of the *N*-methyl tosylate (13)

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[1] W. J. McKillip, E. A. Sedor, B. M. Culbertson, and S. Wawzonek, *Chem. Rev.*, 1973, **73**, 255.

[2] H. J. Timpe, *Z. Chem.*, 1972, **12**, 250.

[3] (*a*) See *e.g.* M. Liler, *Adv. Phys. Org. Chem.*, 1975, **11**, 328–344; (*b*) M. Liler and D. G. Morris, *J.C.S. Chem. Comm.*, 1975, 93.

and the *O*-methyl iodide (14). The first shows a strong absorption at 1 678 cm^{-1}, a frequency closely similar to that of (7), whereas the latter exhibits a strong absorption at 1 615 cm^{-1}, attributable to C=N bond stretching. Since this C=N stretching vibration appears at a significantly lower frequency than carbonyl stretching, we conclude that a carbonyl group is present in the hydrochloride salt (7).

TABLE 1

I.r spectra of some *N*-ammonio-amidates, their hydrochlorides and some *N*- and/or *O*-methyl derivatives (solids, in KBr discs)

Compound	$\nu_{max.}$ (cm^{-1}) in the 1550—1800 cm^{-1} region
$MeCO{-}\bar{N}{-}\overset{+}{N}Me_3$	**1 550—1 580**vbr *
$PhCO{-}\bar{N}{-}\overset{+}{N}Me_3$	1 560s, 1 600s, 1 635sh
$p\text{-}MeO{\cdot}C_6H_4{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3$	1 555ms, 1 600s, br
$p\text{-}ClC_6H_4{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3$	1 550ms, 1 600s,br
$MeO{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3$	**1 630**s
$EtO{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3$	**1 630**s,br
$MeCO{-}\bar{N}{-}\overset{+}{N}Me_3,HCl$	*1 550*m, 1 627m, **1 690**s
$PhCO{-}\bar{N}{-}\overset{+}{N}Me_3,HCl$	*1 580*ms, **1 685**s
$p\text{-}MeO{\cdot}C_6H_4{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3,HCl$	*1 575*m, 1 608s, **1 678**s
$p\text{-}ClC_6H_4{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3,HCl$	*1 595*ms, **1 690**s
$MeO{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3,HCl$	*1 545*m, **1 725**s
$EtO{\cdot}CO{-}\bar{N}{-}\overset{+}{N}Me_3,HCl$	*1 548*ms, **1 722**s
$MeCO{-}NMe{-}\overset{+}{N}Me_3\ OTs^-$	1 600mw, **1 678**s
$MeO{\cdot}CMe{=}N{-}\overset{+}{N}Me_3\ I^-$	1 615s (C=N)
$MeO{\cdot}CO{-}NMe{-}\overset{+}{N}Me_3\ I^-$	**1 745**s

* Bold type refers to absorptions attributable to the CO group. Italics refer to absorptions attributable to the CONH group (see A. D. Cross, ' An Introduction to Practical Infra-red Spectroscopy,' Butterworths, 2nd edn., 1964, pp. 59—61).

The carbonyl band of the ammonio-amidate (2) is not clearly separated from the aromatic ring band at 1 600 cm^{-1}, but may be responsible for a shoulder at 1 635 cm^{-1}, a value considerably lower than the corresponding frequency for benzamide (1 656 cm^{-1}). This is in accord with the anticipated more extensive conjugation involving the negatively charged nitrogen. In the case of the derived hydrochloride (8) however, a strong absorption at 1 685 cm^{-1} is observed, closely similar to that of the corresponding aliphatic compound (7) and attributable to a carbonyl stretching vibration. This frequency is higher than that of the corresponding vibration in benzamide and may be accounted for by a relatively reduced amide-like conjugation in the cation $PhCO{-}\ddot{N}H{-}\overset{+}{N}Me_3$, due to the electrostatic attraction of the positive charge for the lone pair electrons involved in amide conjugation. The *p*-methoxy- and *p*-chloro-derivatives (3) and (4) also do not show distinct carbonyl absorptions, but their hydrochlorides (9) and (10) do show strong absorptions attributable to the carbonyl group at 1 678 and 1 690 cm^{-1}, respectively, as well as weaker absorptions attributable to CO·NH groups. These results are thus also consistent with proton additions to nitrogen. Here a substituent effect on the carbonyl frequency in the salts is also apparent, the frequency increasing with increasing electron withdrawal by the ring substituents (*i.e.* Cl > H > OMe).

The *N*-ammoniomethoxyformamidate (5) shows a strong absorption at 1 630 cm^{-1}, indicative of a strongly conjugated carbonyl group. In the spectra of the hydrochloride (11) and the methiodide (15) strong carbonyl absorptions are observed at 1 725 and 1 745 cm^{-1}, respectively, in the region associated with carbonyl

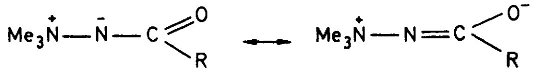
TABLE 2

Chemical shifts caused by protonation ($\Delta\delta$) of some *N*-ammonio-amidates at room temperature

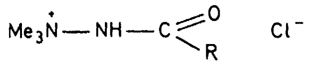
		Chemical shift (δ) (relative to internal Me_4Si)			Chemical shift (δ) (relative to internal $\overset{+}{N}Me_4$)		
Compound	Group	In $CDCl_3$	In TFA	$\Delta\delta$ (p.p.m.)	In water	In dil. HCl	$\Delta\delta$ (p.p.m.)
(1)	$\overset{+}{N}Me_3$	-3.40	-3.88	0.48	-0.16	-0.51	0.35
	CMe	-1.82	-2.29	0.47	$+1.31$	$+1.10$	0.21
(14)	$\overset{+}{N}Me_3$					-0.27 *	
	CMe					$+1.00$	
(13)	$\overset{+}{N}Me_3$					~ 0 *	
	CMe					$+0.95$	
	NMe					(-0.20)	
(2)	$\overset{+}{N}Me_3$	-3.49	-4.01	0.52	-0.30	-0.65	0.35
(5)	$\overset{+}{N}Me_3$	-3.40	-4.40	1.00	-0.14	-0.49	0.35
	OMe	-3.60	-4.52	0.92	-0.36	-0.62	0.26
(15)	$\overset{+}{N}Me_3$					-0.56 *	
	OMe					-0.65	
	NMe					(-0.25)	
(6)	$\overset{+}{N}Me_3$	-3.38	-4.58	1.20	-0.20	-0.48	0.28
	CH_2	-4.02	-5.19	1.17	Overlap with solvent peak	Overlap with solvent peak	
	CMe	-1.24	-2.16	0.92	$+2.00$	$+1.93$	0.07

* In water, for comparison with shifts of hydrochlorides immediately above.

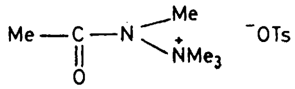
absorptions of saturated esters. Thus it appears that the amide-like conjugation is less strong in these cations, probably on account of competing conjugation from the methoxy-oxygen. Indeed the higher than usual carbonyl frequencies of (5) and (6) are attributable to the same cause. The close similarity of the carbonyl frequencies of (11), (12), and (15), together with the additional medium-strong absorptions at 1 545 and 1 548 cm^{-1} in the spectra of the hydrochloride salts, attributable to CO·NH, again support the cation structure with the proton on the nitrogen.



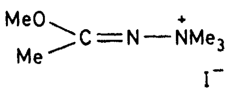
(1) R = Me
(2) R = C_6H_5
(3) R = C_6H_4·OMe-*p*
(4) R = C_6H_4Cl-*p*
(5) R = OMe
(6) R = OEt



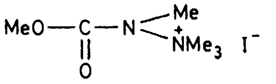
(7) R = Me
(8) R = Ph
(9) R = C_6H_4OMe-*p*
(10) R = C_6H_4Cl-*p*
(11) R = OMe
(12) R = OEt



(13)



(14)



(15)

The u.v. spectra of the *N*-ammoniobenzamidate (2), its hydrochloride (8), and benzamide, which serves as a model compound for the *N*-protonated cation, in aqueous solution, are shown in Figure 1. The absorption maximum of (2) at *ca.* 223 nm (ε 8 500) is very broad, whereas the absorptions of the cation and of benzamide are closely similar. A more pronounced absorption is noted in the carbonyl region (270—280 nm) for the cation. This may be accounted for in terms of a reduction of conjugation of nitrogen lone pair with carbonyl in the presence of a quaternary nitrogen. The small difference in the location of absorption maxima is probably due to the same effect, but detailed interpretation is more difficult.

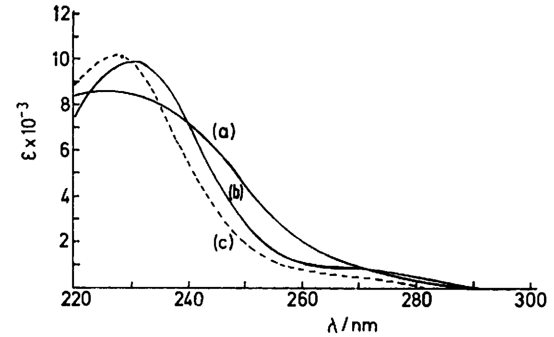


FIGURE 1 U.v. spectra of (a) *N*-trimethylammoniobenzamidate (in water), (b) its monocation (in 0.1N-hydrochloric acid), and (c) benzamide (in water)

The much weaker absorptions of the aliphatic compounds in the u.v. region have proved of little use for structural identification. Spectra in the far u.v. were not examined.

As the *N*-ammonio-amidates become protonated, the n.m.r. absorptions of the $\overset{+}{N}Me_3$ and other protons undergo substantial downfield shifts (Table 2). Such shifts are expected whether the proton is attached to N or O, but the fact that downfield shifts of the $\overset{+}{N}Me_3$ protons are greatest suggests that proton addition is occurring at the adjacent nitrogen atom. Additionally, the downfield shifts of the signals of the methiodide (15) closely resemble those of the hydrochloride (11) of compound (5); this is not so for the *O*-methyl iodide (14) and the hydrochloride (7) of compound (1), but neither is there a close similarity of chemical shifts of the *N*-methyl tosylate (13) and the hydrochloride (7).

We have attempted to observe the resonances of the captured protons in the cations in pure trifluoroacetic acid (TFA) at low temperature; in the majority of cases no additional resonances were observed as far as −20 p.p.m. from Me_4Si, a range which embraces the solvent peak at −11.47 p.p.m., and down to a temperature of −17 °C. However compounds (5) and (6), the most basic compounds studied (pK_a *ca.* 5.6), gave an additional absorption at −9.5 p.p.m. (one proton) which becomes detectable below 0 °C. Further evidence on the site of this proton was obtained by recording spectra of the dications in more acidic media.

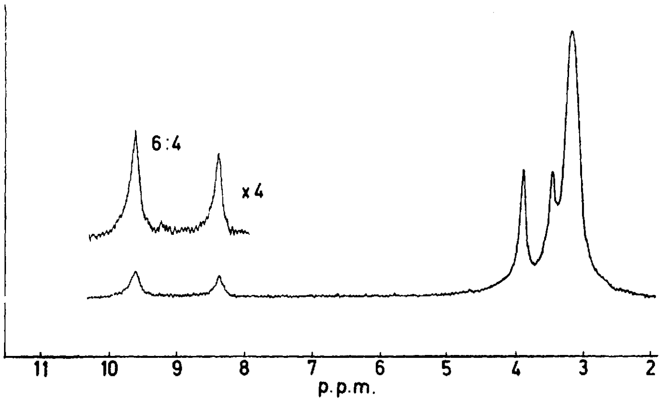


FIGURE 2 N.m.r. spectrum of *N*-(trimethylammonio)methoxyformamidate (5) in 65 : 35 (v/v) HSO_3F–TFA at 90 MHz and 233 K

The low temperature spectrum of the methoxyformamidate (5) in 65 : 35 (v/v) HSO_3F–TFA, chosen because most *N*-ammonio-amidates are more stable in it than in pure fluorosulphuric acid, is shown in Figure 2. Two non-equivalent OCH_3 resonances and a pair of low-field signals gradually appear as the temperature is lowered, and the process is reversible with temperature. The $^{+}NMe_3$ resonance remains a singlet even at low temperature, although it is broadened. These features of the spectrum are consistent with an equilibrium of *cis*- (16a) and *trans*- (16b) forms of the *O*-protonated dication, as previously reported;[3b] the relative amounts of the two forms are 6 : 4. No OH resonance was observed in this medium, but in the more acidic solvent, pure fluorosulphuric acid, in which this solute gave a stable solution, an additional resonance was observed at still lower field (Figure 3), attributable to OH in the above dication. The appearance of a single resonance is not unexpected, because the *cis–trans* structure of the $-NH-\overset{+}{N}Me_3$ group is rather far removed from the hydrogen-bonded hydroxy-proton, which is probably, owing to this intramolecular hydrogen bonding, shielded from other environmental influences. Interestingly, this hydrogen bonding stabilisation is provided in a situation where the angle subtended at the hydrogen atom in question is far from the purported optimum of 180°. We note that most esters give cations in which intramolecular hydrogen bonding occurs.[4] The dominating influence of the positive charge upon the chemical shift serves to rationalise the observation of a single rather than two absorptions for $^{+}NMe_3$.

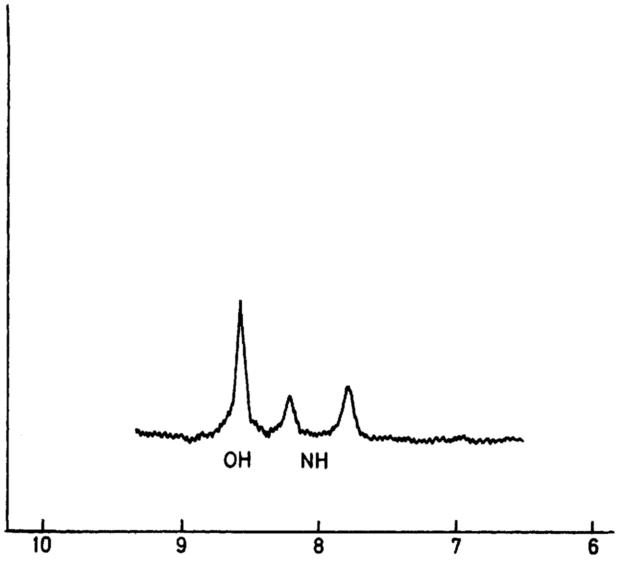
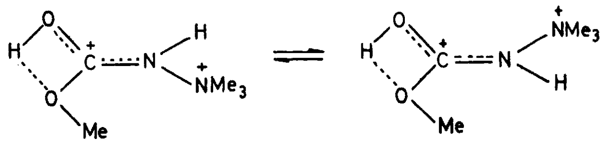


FIGURE 3 Low-field n.m.r. spectrum of *N*-(trimethylammonio)-methoxyformamidate (5) in pure fluorosulphuric acid at 90 MHz and 233 K, showing the resonances of both captured protons

As the non-equivalent OMe and NH resonances shown in Figure 2 are not coupled, definitive assignment of the *cis*- and *trans*-forms is not possible. Accordingly we examined the ^1H n.m.r. spectrum of the ethoxyformamidate (6) under the same conditions in the hope that the bulkier ethyl group might lead to a change in the *cis* : *trans* ratio of dications in strongly acidic media. However the spectrum of (6) in fluorosulphuric acid gave no evidence of *cis–trans* isomerism, but showed a single low-field two-proton absorption (Figure 4). Hence both captured protons in this case are equivalent and must reside on nitrogen. Thus a minor structural change in the base has changed the site of the second protonation, a finding for which the change of protonation sites observed in phenols and phenol ethers provides reasonable precedent.[5] It thus appears that the stability of the *O*-protonated dication depends critically on the presence of the methyl group and may therefore be hyperconjugative in origin. With the reduced hyperconjugation



(16a) (16b)

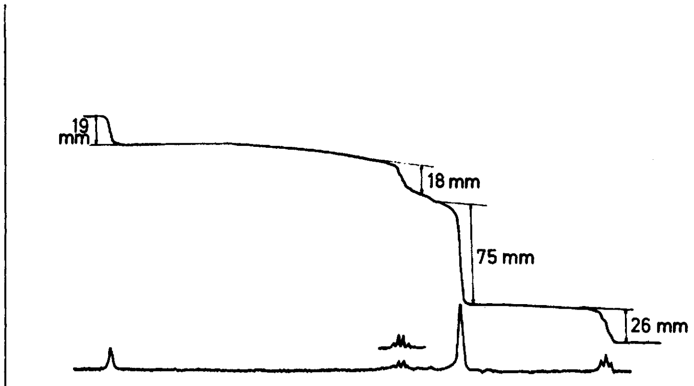


FIGURE 4 N.m.r. spectrum of *N*-(trimethylammonio)ethoxyformamidate (6) in pure fluorosulphuric acid at 90 MHz and 237 K

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[4] G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, 1967, **89**, 5694.

[5] G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 1973, **38**, 353.

involving the ethyl group, the alternative dication, with both protons on nitrogen, becomes relatively more stable under the same conditions. Attempts to investigate the t-butoxy-analogue of (5) and (6) were vitiated by its instability in strong acid.

Although *N*-ammonio-amidates are rather unstable in pure fluorosulphuric acid, meaningful spectra were obtained in 65 : 35 (v/v) HSO_3F–TFA, and for compounds (1) and (2) (and some ring substituted derivatives) (Figures 5 and 6, respectively) these showed two equivalent captured protons. The spectra can also be attributed to the *N*-diprotonated dications, $RCO{\cdot}\overset{+}{N}H_2{\cdot}\overset{+}{N}Me_3$, as reported previously.[3b] The considerable broadening of the NH resonances is not due to exchange with the solvent protons, which give a far removed peak at lower field, but rather to coupling with the ^{14}N quadrupole.

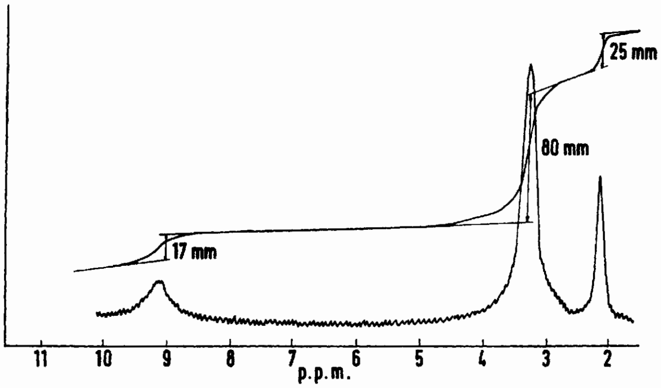

FIGURE 5 N.m.r. spectrum of *N*-trimethylammonioacetamidate (1) in 65 : 35 (v/v) HSO_3F–TFA at 90 MHz and 223 K

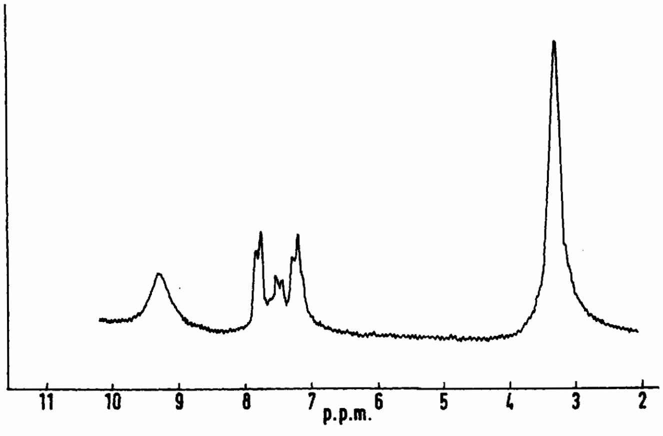

FIGURE 6 N.m.r. spectrum of *N*-trimethylammoniobenzamidate (2) in 65 : 35 (v/v) HSO_3F–TFA at 90 MHz and 222 K

These dications represent *N*-protonated *N*-substituted amides carrying a strongly electron-withdrawing *N*-substituent. The question now arises as to why these derivatives should give *N*-protonated cations under the same conditions as primary, secondary, and tertiary amides give *O*-protonated cations.[6] The reason seems to lie in the strong electron withdrawal by the trimethylammonio-group, which reduces conjugative electron donation of the amide nitrogen lone pair of electrons to the carbonyl group and thereby makes the lone pair more available for proton addition. The interpretation of the i.r. and u.v. spectra also requires a lesser involvement of the nitrogen lone pair with the carbonyl group, as discussed above. *N*-Protonation has also been reported[7] for 2,4-dinitroformanilide, in which the electron-withdrawing substituents on the ring thus seem to produce the same effect as the localised *N*-ammonio-charge in the present compounds. In the carbamate type of structure, *N*-protonation has also been reported for ethyl *NN*-diisopropylcarbamate[8] in 90—98% sulphuric acid below 0 °C and in HSO_3F–SO_2ClF above −30 °C, whereas the *O*-protonated cation is observed at still lower temperatures.[9] Under the same conditions the *NN*-dimethyl and *NN*-diethyl derivatives are *O*-protonated, presumably on account of better hyperconjugative stabilisation of the planar *O*-protonated cations.

EXPERIMENTAL

M.p.s were recorded with a Kofler hot-stage apparatus. Microanalytical determinations were carried out by the Microanalytical Department, University of Glasgow. I.r. spectra were recorded for KBr discs with an Infrascan Hilger–Watts spectrometer. U.v. spectra were recorded for 0.1M- or 0.05M-solutions of the neutral solutes and their hydrochlorides, *i.e.* in 0.1—0.5M-hydrochloric acid, which converts the neutral solutes into cations, in view of the pK_a values of the substances studied (4—5.6). A Cecil CE202 spectrophotometer at 25 °C was used. N.m.r. spectra of the *N*-ammonio-amidates were recorded for solutions in deuteriochloroform, in water, and in aqueous hydrochloric acid (at a pH 1—1.5 all these substances are present as hydrochlorides) and in strongly acidic solvents, *viz.* trifluoroacetic acid, trifluoroacetic acid–fluorosulphuric acid [35 : 65 (v/v)], and pure fluorosulphuric acid (where possible), either with a Varian EM-360 60 MHz spectrometer, for work at room temperature (21 ± 2 °C), or with a Brüker HFX 90 MHz spectrometer, for work at low temperatures. Solutions of the organic substances in the strongly acidic solvents were prepared directly in n.m.r. tubes by adding precooled acids (either in ice–water or in ice–salt) to the organic substrate with cooling. Spectra of the fresh solutions were recorded as soon as possible. Solutions of *N*- and *O*-methyl iodides and a tosylate in strong acids, prepared in the manner described, were unstable, even though kept below −20 °C, and no meaningful n.m.r. spectra of the dications at low temperature were obtained. In strong acid solvents, the solvent peaks were used as reference and lock signals. Their chemical shifts were determined with respect to water as external reference and the abscissae in the spectra (Figures 2—6) have been marked accordingly.

Benzamide was a B.D.H. laboratory reagent, and was recrystallised from ethanol before use (m.p. 129.5 °C).

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[6] M. Liler, *J.C.S. Perkin II*, 1972, 720, 816; 1974, 71.

[7] S. R. de Lockerente, O. B. Nagy, and A. Bruylants, *Org. Magnetic Resonance*, 1970, **2**, 179.

[8] V. C. Armstrong, D. W. Farlow, and R. B. Moodie, *Chem. Comm.*, 1968, 1362.

[9] G. A. Olah, A. M. White, and A. T. Ku, *J. Org. Chem.*, 1971, **36**, 3585.

Trifluoroacetic acid was a B.D.H. laboratory reagent and fluorosulphuric acid a product of the Ozark-Mahoning Co.; both were used without purification. Deuteriochloroform (99.5%) was supplied by Beta Scientific Ltd.

N-*Trimethylammonioacetamidate* (1).—To a solution of *NN*-dimethylacetohydrazide [10,11] (5.1 g, 5×10^{-2} mol) in chloroform was added an excess of methyl iodide. After overnight stirring at room temperature the precipitated salt was filtered off, washed with ether, and dried (yield 11.2 g, 93%). This salt (8.1 g, 3×10^{-2} mol), as a solid, was titrated with 0.1M-sodium hydroxide until neutral; sodium chloride was then added to saturation and the solution was exhaustively extracted with chloroform to yield the *ammonioamidate* (1) (2.6 g, 69%). A sample obtained by recrystallisation from redistilled n-propyl chloride (no propylation occurred) had m.p. 68—70° (Found: C, 51.4; H, 10.45; N, 23.5. $C_5H_{12}N_2O$ requires C, 51.7; H, 10.4; N, 24.1%).

The N-*Trimethylammonioalkoxyformamidates* (5) *and* (6).—These were prepared analogously from the respective alkoxyformohydrazides.[11,12] The *methoxy-derivative* (5) had m.p. 172—174° (Found: C, 45.3; H, 9.1; N, 21.05. $C_5H_{12}N_2O_2$ requires C, 45.45; H, 9.15; N, 21.2%); the *ethoxy-derivative* (6) had m.p. 156—158° (Found: C, 49.1; H, 9.7; N, 19.05. $C_6H_{14}N_2O_2$ requires C, 49.3; H, 9.65; N, 19.15%).

N-*Trimethylammoniobenzamidate* (2).—This was prepared by the method of Smith *et al.*[13] (see also ref. 14). The *N*-trimethylammoniobenzamidates (3) and (4) were prepared analogously. The p-*methoxy-derivative* (3) had m.p. 142—143° (Found: C, 63.7; H, 7.85; N, 13.3. $C_{11}H_{16}N_2O_2$ requires C, 63.45; H, 7.75; N, 13.45%); the p-*chloroderivative* (4) had m.p. 103—104° (Found: C, 56.5; H, 6.3; N, 13.25. $C_{10}H_{13}ClN_2O$ requires C, 56.45; H, 6.15; N, 13.15%).

*Methyl Di-*N-*methylacetohydrazonate Methiodide* (14).—To the *N*-ammonioamidate (1) (1.45 g, 1.25×10^{-2} mol) in chloroform (15 ml) was added an excess of methyl iodide and the solution was stirred at 55 °C overnight. On cooling and removal of solvent a white crystalline *solid* was obtained whose spectral characteristics (Tables 1 and 2) did not change on recrystallisation from ethanol; m.p. 125—127° (Found: C, 27.65; H, 5.75; N, 11.1. $C_6H_{15}IN_2O$ requires C, 27.9; H, 5.85; N, 10.85%) was obtained. Similarly, compound (5) gave *methyl* 2,3,3-*trimethylcarbazate methiodide* (15), m.p. 141—142° (Found: C, 26.0; H, 5.2; N, 10.35. $C_6H_{15}IN_2O_2$ requires C, 27.9; H, 5.85; N, 10.85%).

NNN′-*Trimethylacetohydrazide Methotoluene*-p-*sulphonate* (13).—To *NNN′*-trimethylacetohydrazide [15] (1.45 g, 1.25×10^{-2} mol) in chloroform (10 ml) was added methyl toluene-*p*-sulphonate (2.35 g, 1.3×10^{-2} mol). After stirring overnight at 60 °C the solvent was evaporated off and the white *solid* was recrystallised from ethyl acetate–ethanol without alteration of spectral· characacteristics (Tables 1 and 2); m.p. 132—133° (Found: C, 51.7; H, 7.6; N, 9.45. $C_{13}H_{22}N_2O_4S$ requires C, 51.6; H, 7.35; N, 9.25%).

The hydrochlorides were prepared by evaporating to dryness aqueous solutions of *N*-ammonio-amidates containing an excess of hydrochloric acid.

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