# Nuclear Magnetic Resonance Investigation of Iminium Ion Intermediates. Part VI.† A Hydrogen-1 and Carbon-13 Structural and Dynamic Study of Various Substituted Iminium Salts

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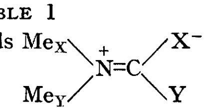
$^1$H and $^{13}$C chemical shifts and $^1J(^{13}C-H)$ of various substituted iminium salts and parent compounds are presented and correlated with the substituent parameters $\sigma_I$ and $\sigma_R$ and the energies of electronic transitions $\lambda_{\pi\rightarrow\pi^*}$. A $^{13}$C dynamic study shows that the rotation about the C–N bond is generally slow with respect to the n.m.r. time-scale and $T_1(^{13}C)$ measurements are applied to a qualitative description of the molecular motion of iminium salts. The results are discussed in terms of ion-pair constitution.

THE n.m.r. spectra of carbonium ions have been thoroughly reviewed and discussed[1] but similar data are scarcer for iminium salts.[2] However, a comprehensive review on this topic is to be published soon.[3] We have already investigated the formation, structure, and dynamic behaviour of the Vilsmeier–Haack intermediates by n.m.r.[4] and n.q.r.[5] spectroscopy. From a general point of view, it is worthwhile studying compounds having a carbon–nitrogen bond and in which the electronic deficiency is delocalized. Such a structure is found in the electrophilic derivatives of the Mannich, Vilsmeier, and Viehe reactions and knowledge of n.m.r. parameter–structure relationships may be very important for elucidating the reactivity of these species.[6] From another point of view, it is theoretically interesting to study the variation of the carbon screening constant and the carbon–proton coupling constant in terms of the electronic distribution of the molecules. We now present the results of a $^1$H and $^{13}$C structural and dynamic investigation of these widely used intermediates.

TABLE 1

$^1$H and $^{13}$C chemical shifts of the parent compounds



of the iminium salts $Me_2N=C(X)Y^+$, $B^-$

The proton chemical shifts were measured at 60 MHz (315 K) with 1M- or 2M-CDCl$_3$ solutions and are given in p.p.m. (±0.02 p.p.m.) from internal SiMe$_4$.

The carbon chemical shifts were recorded at 25.18 MHz (Varian XL 100–12) (305 K) and at 15.1 MHz (Brücker WP 60) (302 K). The accuracy of the $^{13}$C chemical shifts obtained in the broad band decoupling mode and reported in p.p.m. downfield from internal SiMe$_4$ is better than 0.1 p.p.m. Carbon line-shape measurements were carried out as previously described.[4b]

| Compounds | | | $^1$H | | | $^{13}$C | | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | X | Y | $\delta_{Me(X)}$ | $\delta_{Me(Y)}$ | $\delta_Y$ | $\delta_{Me(X)}$ | $\delta_{Me(Y)}$ | $\delta_Y$ | $\delta_{C=N}$ |
| (1) | O | H | 2.81 | 2.91 | 7.93 | 31.2 | 36.2 | | 161.7 |
| (2) | O | Me | 2.88 | 2.97 | 2.01 | 34.8 | 37.8 | 21.4 | 169.6 |
| (3) | O | Cl | 3.02 | 3.10 | | 36.2 | 38.1 | | 148.2 |
| (4) | O | OMe | 2.88 | | 3.66 | | | | |
| (5) | S | H | 3.27 | 3.35 | 9.25 | 36.8 | 45.0 | | 186.6 |
| (6) | S | Me | 3.44 | 3.34 | 2.59 | 44.0 | 42.3 | 32.8 | 198.7 |
| (7) | S | Cl | 3.47 | | | 44.9 | 45.4 | | 173.1 |
| (8) | S | SMe | 3.68 | | 2.75 | 41.0 | 44.8 | 20.2 | 196.1 |

EXPERIMENTAL

*Materials.—Origin of the compounds.* The amides, thioamides, carbamoyl, and thiocarbamoyl chlorides, ureas and thioureas were commercial products (Fluka). They were distilled twice before use and stored with molecular sieves. Some thioamides, $Et_2N{\cdot}CS{\cdot}Me_3$ and $PhCH_2(Me_3)$-$N{\cdot}CS{\cdot}Me$, were prepared by the reaction of phosphorus decasulphide on the corresponding amides. *NN*-Disubstituted dithiocarbamic esters were synthesized by the action of carbon disulphide on amines.[7]

*Preparation of the Iminium Salts.—Dichloromethyleneammonium salts and derivatives.* The 'phosgene immonium' salt (38) was obtained from Aldrich or was prepared according to the methods described in ref. 6*b*. Derivatives (17), (34), (37), and (35) were synthesized as described in ref. 6*b* and 8.

O- *and* S-*Alkylation of amides, thioamides, thiocarbamoyl chlorides, dithiocarbamic esters, ureas, and thioureas.* Three methylating agents were successfully used to treat these compounds to give the iminium salts: methyl iodide, dimethyl sulphate, and methyl fluorosulphate. Some of these reactions are described in the literature: the synthesis of (14),[9] (12),[10] (29), and (30),[11] for example. We have

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† Part V, G. J. Martin and N. Naulet, *Tetrahedron Letters*, 1976, 357.

[1] G. A. Olah and P. von R. Schleyer, 'Carbonium Ions,' Interscience, 1968, (*a*) vol. I, ch. 7; (*b*) vol. II, ch. 17; (*c*) vol. IV, ch. 28.

[2] H. O. Kalinowski and H. Kessler, *Org. Magnetic Resonance*, 1975, **7**, 128.

[3] R. Merenyi, 'Structure Determination of Iminium Compounds by Physical Methods,' *Adv. Org. Chem.*, in the press.

[4] (*a*) G. J. Martin and M. L. Martin, *Bull. Soc. chim. France*, 1963, 1637; (*b*) M. L. Martin, G. Ricolleau, S. Poignant, and G. J. Martin, *J.C.S. Perkin II*, 1976, 182.

[5] G. Jugie, G. J. Martin, and J. A. S. Smith, *J.C.S. Perkin II*, 1975, 925.

[6] (*a*) G. Hazebroucq, *Ann. pharm. franç*, 1966, **24**, 793; (*b*) H. G. Viehe, *Angew. Chem.*, 1973, **12**, 806; (*c*) J. Zabicky, 'The Chemistry of Amides,' Interscience, 1970, p. 731.

[7] 'Methoden der Organische Chemie,' Houben-Weyl, 4, Aufl, Bd IX, G. Thieme-Verlag, Stuttgart, 1955.

[8] (*a*) R. L. N. Harris, *Tetrahedron Letters*, 1970, 5217; (*b*) H. Eilingsfeld and L. Mobius, *Chem. Ber.*, 1965, **98**, 1293.

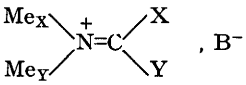
[9] R. J. Gillespie and T. Birchall, *Canad. J. Chem.*, 1963, **41**, 148.

[10] H. Bredereck, F. Effenberger, T. Brendle, and H. Muffler, *Chem. Ber.*, 1968, **101**, 1885.

[11] K. Hartke, E. Schmidt, M. Castillo, and J. Bartulin, *Chem. Ber.*, 1966, **99**, 3268.

### Table 2

$^1$H and $^{13}$C chemical shifts of the iminium salts

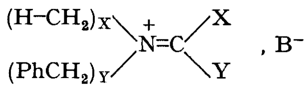


(Conditions: see Table 1). $CH_3SO_4^-$ $\delta(^1H)$ = 3.5—3.7 p.p.m. $\delta(^{13}C)$ = 54.0—54.4 p.p.m.

| Compounds | | | | $^1$H | | | | $^{13}$C | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | X | Y | $B^-$ | $\delta_{Me(X)}$ | $\delta_{Me(Y)}$ | $\delta_X$ | $\delta_Y$ | $\delta_{Me(X)}$ | $\delta_{Me(Y)}$ | $\delta_X$ | $\delta_Y$ | $\delta_{C=N}$ |
| (9) | H | H | Cl | 3.79 | | 8.48 | | 47.6 | | | | 167.6 |
| (10) | H | H | $OCOCF_3$ | 3.92 | | 7.95 | | 50.5 | | | | 170.0 |
| (11) | OMe | H | $OSO_2F$ | 3.19 | 3.36 | 4.34 | 8.33 | 35.9 | 41.1 | 64.7 | | 168.9 |
| (12) | OMe | H | $CH_3SO_4$ | 3.27 | 3.45 | 4.43 | 8.67 | 36.0 | 41.3 | 64.5 | | 168.6 |
| (13) | OMe | Me | $OSO_2F$ | (3.30 | 3.43) | 4.26 | 2.56 | (38.6 | 40.9) | 60.3 | 14.3 | 176.3 |
| (14) | OMe | Me | $MeSO_4$ | (3.33 | 3.52) | 4.32 | 2.68 | (38.2 | 40.7) | 59.8 | 14.2 | 176.0 |
| (15) | OMe | $NMe_2$ | $OSO_2F$ | 3.18 | | 4.16 | 3.18 | 39.8 | | 61.7 | 39.8 | 164.3 |
| (16) | OMe | $NMe_2$ | $MeSO_3$ | 3.23 | | 4.22 | 3.23 | 39.9 | | 61.8 | 39.9 | 164.1 |
| (17) | OPh | OPh | Cl | 3.72 | | 7.2 | | 40.7 | | | | 157.8 |
| (18) | OCOMe | H | Br | 3.60 | 3.95 | 2.64 | 10.1 | 39.7 | 43.3 | 21.5 | | 159.0 |
| (19) | OCOMe | Me | Br | 3.73 | 3.87 | 2.22 | 2.64 | 42.7 | 43.8 | 21.5 | 23.0 | 173.6 |
| (20) | SCOMe | H | Br | 3.57 | 3.78 | 2.95 | 9.80 | 47.6 | 50.8 | 33.9 | | 175.0 |
| (21) | SMe | H | Cl | 3.56 | 3.91 | 3.04 | 10.84 | 42.6 | 48.7 | 17.1 | | 183.3 |
| (22) | SMe | H | $OSO_2F$ | 3.43 | 3.68 | 2.89 | 9.48 | 42.2 | 48.9 | 16.7 | | 183.3 |
| (23) | SMe | H | $CH_3SO_4$ | 3.45 | 3.72 | 2.93 | 9.73 | 42.1 | 48.6 | 16.5 | | 183.6 |
| (24) | SMe | H | I | 3.58 | 3.92 | 3.20 | 10.52 | 43.7 | 49.0 | 17.1 | | 181.7 |
| (25) | SMe | Me | $OSO_2F$ | (3.58 | 3.68) | 2.86 | 2.73 | (44.8 | 45.7) | 16.8 | 21.1 | 191.6 |
| (26) | SMe | Me | $MeSO_4$ | (3.63 | 3.75) | 2.90 | 2.79 | (44.9 | 45.9) | 16.9 | 21.3 | 191.4 |
| (27) | SMe | Me | I | (3.68 | 3.86) | 3.03 | 2.96 | (46.3 | 48.0) | 18.8 | 24.3 | 191.3 |
| (28) | SMe | SMe | $OSO_2F$ | 3.87 | | 2.97 | | 47.7 | | 20.2 | | 193.7 |
| (29) | SMe | SMe | $CH_3SO_4$ | 3.48 | | 2.92 | | 48.0 | | 20.3 | | 193.4 |
| (30) | SMe | SMe | I | 3.92 | | 3.07 | | 49.5 | | 22.1 | | |
| (31) | SMe | $NMe_2$ | $OSO_2F$ | 3.3 | | 2.42 | 3.3 | 43.5 | | 16.4 | 43.5 | 176.5 |
| (32) | SMe | $NMe_2$ | $MeSO_4$ | 3.35 | | 2.62 | 3.35 | 43.6 | | 16.5 | 43.6 | 176.6 |
| (33) | SMe | $NMe_2$ | I | 3.5 | | 2.78 | 3.5 | 45.1 | | 18.7 | 45.1 | 176.2 |
| (34) | Cl | OPh | Cl | 3.81 | | | 7.46 | | | | | |
| (35) | Cl | SMe | Cl | 3.87 | 3.95 | | 3.07 | 46.5 | 48.6 | | 20.9 | 176.7 |
| (36) | Cl | SMe | $OSO_2F$ | 3.77 | 3.67 | | 2.78 | 46.1 | 48.1 | | 19.9 | 177.9 |
| (37) | Cl | NPh | Cl | 3.73 | 3.22 | | 7.52 | 46.2 | | | (b) | 156.2 |
| (38) | Cl | Cl | Cl | 4.07 | | | | 50.2 | | | | 160.5 |
| (39) | Cl | H | Cl | 4.20 | 3.96 | | 11.10 | 48.9 | 43.3 | | | 166.2 |
| (40) | $NMe_2$ | H | Cl | 3.45 | | | 8.80 | (39.7 | 45.8) | (39.7,<br>45.8) | | 156.4 |

### Table 3

$^1$H and $^{13}$C chemical shifts of both *Z* and *E* stereoisomers of the iminium salts



(Conditions: see Table 1). No attempt has been made to assign the methylene signals. The chemical shifts values are consistent with the relative percentage of both stereoisomers but not necessarily with the configurational description X or Y which could be reversed.

| | | | | | $^1$H | | | | $^{13}$C | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X | Y | $B^-$ | No. | % | $\delta_{CH_2(X)}$ | $\delta_{CH_2(Y)}$ | $\delta_X$ | $\delta_Y$ | $\delta_{CH_3(X)}$ | $\delta_{CH_2(Y)}$ | $\delta_X$ | $\delta_Y$ | $\delta_{C=N}$ |
| O | Me | | (41)[a] | 60 | 2.86 | 4.62 | | 2.10 | 33.2 | 50.2 | | 21.2 | 169.9 |
| Me | O | | (41′)[b] | 40 | 4.53 | 2.90 | 2.10 | | 53.8 | 35.2 | 21.5 | | 169.9 |
| S | Me | | (42) | 80 | 3.12 | 5.33 | | 2.68 | 39.2 | 57.9 | | 32.9 | |
| Me | S | | (42′) | 20 | 4.83 | 3.42 | 2.68 | | 57.9 | 42.6 | 32.4 | | |
| S | SMe | | (43)[a] | 70 | 3.17 | 5.38 | | 2.63 | 38.6 | 58.7 | | 20.3 | 180.0 |
| SMe | S | | (43′)[b] | 30 | 4.95 | 3.42 | 2.60 | | 57.0 | 43.3 | 20.5 | | 181.2 |
| OMe | Me | $OSO_2F$ | (44) | 70 | 3.33 | 4.88 | 4.37 | 2.68 | 39.0 | 54.5 | 61.0 | 15.1 | 177.5 |
| Me | OMe | $OSO_2F$ | (44′) | 30 | 4.97 | 3.20 | 2.72 | 4.37 | 56.8 | 36.9 | 14.9 | 61.0 | 177.5 |
| SMe | Me | I | (45) | 60 | 3.77 | 5.47 | 3.10 | 3.07 | 44.1 | 61.8 | 19.4 | 24.7 | 193.1 |
| Me | SMe | I | (45′) | 40 | 5.30 | 3.58 | 3.13 | 3.10 | 61.1 | 45.4 | 25.4 | 19.3 | 193.2 |
| SMe | SMe | $OSO_2F$ | (46) | | 3.67 | 5.40 | 2.95 | 2.95 | 46.0 | 63.7 | 20.9 | 20.9 | 197.0 |
| SMe | SMe | $MeSO_4$ | (47) | | 3.70 | 5.48 | 3.00 | 2.98 | 46.0 | 63.6 | 20.9 | 20.9 | 196.5 |

[a] 273 K($^1$H) and 305 K($^{13}$C). [b] 233K ($^1$H and $^{13}$C).

extended these reactions to other compounds: thioamides, thiocarbamoyl chlorides, ureas, and thioureas.

*Dialkylmethyleneammonium salts* (*Mannich reagents*). Dialkylmethyleneammonium chloride (9) was prepared from methylenebisdialkylamine and acid chloride using Böhme's method.[12a] The trifluoroacetate (10) was synthesized by the action of trifluoroacetic acid on the methylenebisalkylamine.[12b]

*N.m.r. Spectroscopy*.—Experimental conditions are indicated in the captions of Tables.

## RESULTS AND DISCUSSION

$^1$H and $^{13}$C chemical shifts of thioamides, thiocarbamoyl derivatives and iminium salts are collected in Tables 1—3.

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[12] (*a*) H. Bohme, W. Lehners, and G. Keitzer, *Ber.*, 1968, **91**, 340; (*b*) A. Ahmond, A. Cave, C. Kan-Fan, and P. Potier, *Bull. Soc. chim. France*, 1970, 2707.

*Influence of Solvents on Chemical Shifts*.—The Mannich derivative $Et_2N{:}CH_2^+$, $Cl^-$ shows typical behaviour with respect to solvent effects.

| | $CDCl_3$ | $CH_3CN$ | $CHCl_2CHCl_2$ (TCE) | DMF |
|---|---|---|---|---|
| $\delta_{CH_3-N}$ | 4.1 | 4.05 | 4.18 | 4.22 |
| $\delta_{CH_2=N}$ | 8.3 | 8.4 | 8.68 | 8.72 |

The lowfield shifts of both methyl and methylene resonance may be related to the extent of ion-pair dissociation although other processes such as ion solvation and the anisotropy properties of the solvent probably intervene. The same trend is observed for *C*-substituted iminium salts $N\overset{+}{=}CH-X$, $B^-$; the more polar the solvent, the greater the shift of the methine resonance with regard to those of methyl groups. It is also worthwhile to note the upfield shifts when $CH_3CN$ is used instead of $CDCl_3$ [$f = (CH_3CN)/(CDCl_3)$; $T = 312$ K; salt (22)].

| | $f$ | 1 | 0.75 | 0.5 | 0.25 | 0 |
|---|---|---|---|---|---|---|
| $\Delta\nu_{(Hz)}{}^1H$ | $N-CH_3$ | 0 | 1 | 2.5 | 4 | 6 |
| | $=CH$ | 0 | 2 | 6 | 10 | 14 |

These results may be explained by the diamagnetic influence of $CH_3CN$ on the organic cation separated from the anion by a solvent molecule [13] or linked to the solvent through weak charge-transfer association. The role of TCE is not clear, since a simple consideration of dielectric properties does not explain the drastic lowfield shifts. However, the peculiar nature of this halogenated solvent has been already noted from chemical [1] or n.m.r.[14a,b] evidence.

The solvent dependence of amidinium ion chemical shifts has also been studied [15] and explained by an ion-pairing mechanism. No quantitative explanation of the solvent effect observed in iminium salts has been attempted here.

*Discussion of Structure–Chemical-shift Relationships*.—*Assignment of* $^1H$ *resonances: nuclear Overhauser measurements*. The nuclear Overhauser effect is the one method which gives unequivocal assignments of $^1H$ resonance in compounds containing $N\overset{+}{=}C$.[16]

The data collected in Table 4 permit us to assign the methyl resonances of some typically substituted iminium salts ($SMe_3$, OMe, and Cl) and show the unreliability of long-range coupling constants $^4J$ for configuration determination in these compounds. The differences in *C*-substituent electronegativities (Me, OMe, and Cl) rather than conformational effects may explain the inversion of the relative magnitude of the *cis–trans* allylic coupling constants.

If the salts are *C*-methyl substituted, a selective irradiation of the *C*-substituent when observing the intensities of the *N*-methyl groups is no longer possible and no assignments were made for these cases.

*Assignment of* $^{13}C$ *resonances*. Since the $^1H$ methyl resonances may be unequivocally determined, the $^{13}C$ signals are easily assigned using off-resonance data. Successive irradiation of the $^1H$ $CH_3$ lines at a high or a low field and measurement of the residual $^1J^{13}C$–H coupling constants, permit application of the Ernst relationship [17] which leads to the appropriate results (Tables 1—3).

*Structure chemical-shifts correlation*. Discussion of the $^1H$ and $^{13}C$ chemical shifts involves some common considerations: [18] the screening constants of both nuclei imply an electronic charge dependence and proximity effects (anisotropy, electric field, and steric contributions). However, the $^{13}C$ resonance is strongly affected by the nature of the excited electronic levels of the molecule which appear as a mean excitation energy $\Delta E$ in the Karplus–Pople [19] formulation of the $^{13}C$ screening constant. Similar behaviour was observed for the variation of the energies of $\pi \longrightarrow \pi^*$ transitions of olefinic derivatives ($CH_2=CH-X$) and iminium salts [$Me_2N^+=CHX$] (Table 6) with the auxochromic properties of substituents and offers a basis for discussion.

$\delta^{13}CO$ Data for acyl derivatives and $\delta^{13}CH=$ data for alkenes and iminium salts correlate reasonably well ($R^2 = 0.89$, 0.86, and 0.98 respectively) with the $\lambda_{n\rightarrow\pi^*}$ or $\lambda_{\pi\rightarrow\pi^*}$ values when the X = $NMe_2$ substituent is not taken in account (Table 6). As will be shown later, the double-bond character of the salt (40) (X = $Me_2N$) is low when compared to the other monosubstituted salts and the electronic transition energies are probably high. Thus the paramagnetic contribution $\sigma_{para}$ of the iminoyl carbon atom exhibits an increase with $\lambda_{max.}$ (u.v.).

The carbon and proton chemical shifts of aromatic nuclei have been correlated many times with Hammett-type parameters.[20] Some data concerning styrenes $\delta^{13}C$ [21] and benzylideneanilines $\delta^1H$ [22] have been recently published; in the latter case, an unexpected positive $\rho$ value * for the imino-proton in Ar–CH=N–Ar′ has been observed, although a normal downfield shift is obtained when electron-withdrawing groups are substituted in the *para*-position of the Ar cycle. The coefficients of the correlations concerning iminium salts were computed using multilinear regression analysis. The validity of the correlations were checked by means of the

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* When plotting $\Delta\delta$ against $\sigma$, a negative $\rho$ value is generally observed if a negative sign is used for a downfield shift of the X substituent with respect to the H substituent. In our work, the plotting of $\delta$ against $\sigma$ should give a positive $\rho$ value.

[13] M. Szwarc, 'Ions and Ion Pairs in Organic Reactions,' Interscience, 1974, vol. 2, p. 247.

[14] (*a*) G. J. Martin and S. Poignant, *J.C.S. Perkin II*, 1972, 1964; (*b*) G. J. Martin and S. Poignant, *J.C.S. Perkin II*, 1974, 642.

[15] R. C. Neuman and V. Jonas, *J. Phys. Chem.*, 1971, **75**, 3550.

[16] A. H. Lewin and M. Frucht, *Org. Magnetic Resonance*, 1975, **7**, 206.

[17] R. R. Ernst, *J. Chem. Phys.*, 1966, **45**, 3845.

[18] G. J. Martin, M. L. Martin, and O. Odiot, *Org. Magnetic Resonance*, 1975, **7**, 2.

[19] M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803.

[20] (*a*) R. W. Taft, S. Erhenson, I. C. Lewis, and R. E. Glick, *J. Amer. Chem. Soc.*, 1959, **81**, 5352; (*b*) R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343; (*c*) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323; (*d*) C. Laurence and B. Wojtkowiak, *Ann. Chim. France*, 1970, **5**, 163.

[21] G. K. Harner, I. R. Peat, and W. F. Reynolds, *Canad. J. Chem.*, 1973, **51**, 897; 915.

[22] (*a*) N. Inamoto, K. Kuslida, S. Masuda, H. Ohta, S. Satoh, Y. Tamura, K. Tokumaru, K. Tori, and M. Yoshida, *Tetrahedron Letters*, 1974, 3617; (*b*) N. Inamoto, S. Masuda, K. Tokumaru, K. Tori, and M. Yoshida, *Tetrahedron Letters*, 1975, 3701.

regression coefficient $R^2$ of a linear analysis of the calculated and experimental values of the chemical shifts. The results show that the nature of the anion plays an important part in all evaluations of the shifts since the correlations are always closer when data relative to the same anion are used in the computation. The ion-pair nature of the salts seems to be well established:

$$\mathrm{Me_2\overset{+}{N} = C(X)Y,B^-}$$

$$\mathrm{B = OSO_2F}\begin{cases}\delta^{13}\overline{\mathrm{CH}}_3 = 61.0 - 83.5\,\sigma_I\,(\mathrm{X}) + 4.8\,\sigma_I\,(\mathrm{Y}) \\ \quad R^2 = 0.92 \\ \delta^{13}\overline{\mathrm{CH}}_3 = 50.7 + 27.0\,\sigma_R\,(\mathrm{X}) + 1.3\,\sigma_R\,(\mathrm{Y}) \\ \quad R^2 = 0.88\end{cases}$$

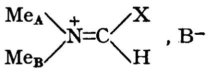
$$\mathrm{B = Cl, Br, I, OSO_2F, SO_4CH_3}\ R^2 < 0.7$$

From this point of view, the close correlation obtained between $\delta^1\mathrm{H(CH_3)}$ and $\sigma_I(\mathrm{X}) + \sigma_R(\mathrm{X})$ may be understood: the transmission of inductive and resonance effects of a substituent are not affected by the presence of another bulky and electron-donating or -withdrawing group of the anion moiety.

TABLE 4

Assignment of both *N*-methyl groups in some iminium salts (2M, $\mathrm{CDCl_3}$, 305 K) by means of the nuclear Overhauser effect and long range coupling $^4J_{\mathrm{H,H}}$

The carbon resonances were identified from the proton data using the off-resonance technique; [a] data measured in $\mathrm{CD_2Cl_2}$ at 213 K; from ref. 28. The proton Overhauser enhancement has been recorded from carefully degassed samples at 100 MHz (305 K). The intensity of the =CH line was first measured with an irradiating power of ≃95 dB at the resonance frequency $\mathrm{Me_A}$ and the same procedure was repeated for $\mathrm{Me_B}$.



| | | | $\mathrm{Me_A}$ | | | $\mathrm{Me_B}$ | | |
|---|---|---|---|---|---|---|---|---|
| No. | X | $\mathrm{B^-}$ | Resonance $^1$H, $^{13}$C | % NOE | $^4J_{\mathrm{HH}}$ Hz | Resonance $^1$H, $^{13}$C | % NOE | $^4J_{\mathrm{HH}}$ Hz |
| (23) | SMe | $\mathrm{MeSO_4}$ | Upfield | 4 | 0.45 | Low field | 14 | 0.70 |
| (22) | SMe | $\mathrm{OSO_2F}$ | Upfield | 3 | 0.45 | Low field | 15 | 0.70 |
| (24) | SMe | I | Upfield | 2 | 0.50 | Low field | 14 | 0.70 |
| (12) | OMe | $\mathrm{MeSO_4}$ | Upfield | 3 | 1.05 | Low field | 12 | 0.65 |
| (11) | OMe | $\mathrm{OSO_2F}$ | Upfield | 4 | 1.0 | Low field | 13 | 0.65 |
| (39) | Cl | Cl [a] | Low field | 5 | ~1.0 | Upfield | 10 | ~0.5 |

$$\mathrm{Me_2N^+{=}CHX,\ B^-}$$

$$\delta^1\mathrm{H}(\overline{\mathrm{CH}}_3) = 3.80 + 1.16\,\sigma_I(\mathrm{X}) + 1.65\,\sigma_R\,(\mathrm{X})\ R^2 = 0.95$$

It should be noticed that using the Swain and Lupton field [23] and resonance constants (*E*, *R*) [15] does not improve the correlations involving proton and carbon chemical shifts. Neither does the use of the Brown substituent parameters [24] improve the correlations.

The correlations obtained from $\delta^{13}\mathrm{C{=}N}$ data are generally poor, the nature of the anion having a strong influence; magnetic anisotropy, electric field,[25] and steric [26] effects of X(Y) substituents may partially account for these discrepancies. However, owing to the difficulty of accurately calculating such effects in multifunctional molecules, no quantitative treatment has been attempted here.

$^1J^{13}\mathrm{C{-}H}$ *Coupling constants*. Since consideration of $^1$H or $^{13}$C chemical shifts of the iminoyl moiety of the cation X–CH= fails to give a satisfactory explanation for the observed behaviour in terms of inductive and resonance effects, it was decided to investigate the dependence of $^1J^{13}\mathrm{C{-}H}$ on the electronic properties of the X substituent. It is known [27] that the direct $^{13}$C–H coupling constant constitutes a very sensitive probe to test the linkage of a substituent with the carbon atom involved in the coupling under consideration.

When the data collected in Table 5 are correlated with the Taft substituent constants, we obtain a reasonably good regression coefficient:

$$\mathrm{Me_2N^+{=}CHX,\ B^-}$$

$$J^{13}\mathrm{C{-}H} = 185.0 + 107.7\sigma_I\,(\mathrm{X}) - 2.2\sigma_R\,(\mathrm{X})\ R^2 = 0.92$$

The correlation is poorer in the Swain–Lupton systematic, which attributes a greater role to resonance effects ($R^2 = 0.77$). It is noteworthy that inductive effects have a major responsibility in the variation of the charge density and *s*-character of iminoyl carbon atom. These observations support our previous conclusions which were inferred from a consideration of the chemical shift.

*Dynamic Measurements.—Carbon line-shape measurements*. The dynamic carbon resonance method has proved to be very useful for the study of hindered rotation processes around C–N bonds when diastereotopic protons are fortuitously equivalent [29] or when the barrier is low.[30] We have already shown that $^1$H Fourier transform spectroscopy gives good values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ from total line-shape analysis in a series of amide derivatives.[14b,29] However, when a monomolecular process may be assumed to hold, the free enthalpy of activation $\Delta G_\mathrm{T}^\ddagger$ is also a good parameter for evaluating the energetic contribution to the barrier height. We have compared, on these bases, the $\Delta G_\mathrm{T}^\ddagger$ values of the C–N rotation for some iminium salts and parent compounds.

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[23] C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, 1968, **90**, 4328.

[24] D. H. MacDaniel and H. C. Brown, *J. Org. Chem.*, 1968, **23**, 420.

[25] R. F. Zurcher, *Progr. N.M.R. Spectroscopy*, 1967, **2**, 205.

[26] B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 5319.

[27] J. H. Goldstein, V. S. Watts, and L. S. Rottet, *Progr. N.M.R. Spectroscopy*, 1971, **8**, 103.

[28] S. Poignant, Thèse d'Etat Nantes 1976.

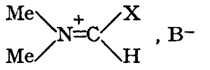
[29] M. L. Filleux, N. Naulet, J. P. Dorie, G. J. Martin, J. Pornet, and L. Miginiac, *Tetrahedron Letters*, 1974, 1435.

[30] G. J. Martin and J. P. Gouesnard, *Tetrahedron Letters*, 1975, 4251.

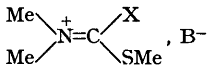
The results collected in Table 7 show the drastic influence of the electron-donating power of the X substituent: *C*-disubstituted iminium salts are characterized by a relatively low barrier. When studying the salts (15) and (31), two restricted rotation processes around the C–N and the C–O (or C–S) bonds have to be considered. We have synthesized however the dissymmetrical salt $Et_2N\overset{...}{=}C(OMe)\overset{...}{=}NMe_2^+$ and observed two successive coalescence temperatures for the *N*-alkyl groups (*ca.* 190 and 200 K) and no broadening of the OMe signal down to 165 K. Thus, it may be concluded that the coalescence phenomenon observed for the salts

TABLE 5

$^1J(^{13}C–H)$ coupling constants (Hz) in some iminium salts and parent compounds



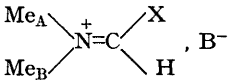
| No. | X | $B^-$ | $^1J(N{=}^{13}C–H)$ Hz | $^1J(N–^{13}CH_3)$ Hz |
|---|---|---|---|---|
| (5) | S | | 179.5 | 139.5 |
| (1) | O | | 189.0 | 139.0 |
| (9) | H | Cl | 188.0 | 144.5 |
| (40) | $NMe_2$ | Cl | 192.0 | 143.0 |
| (24) | SMe | I | 195.0 | 143.5 |
| (21) | SMe | Cl | 195.5 | 143.5 |
| (23) | SMe | $MeSO_4$ | 196.5 | 143.5 |
| (22) | SMe | $OSO_2F$ | 198.0 | 143.5<br>144.5 |
| (20) | SCOMe | Br | 202.0 | 144.5 |
| (11) | OMe | $OSO_2F$ | 214.5 | 144.0 |
| (12) | OMe | $MeSO_4$ | 216.0 | 144.0 |
| (18) | OCOMe | Br | 223.0 | 145.0 |
| (35) | Cl | Cl | 236.0 | 146.0 |



| No. | X | $^1J(N–^{13}CH_3)$ Hz | $^1J(S–^{13}CH_3)$ Hz |
|---|---|---|---|
| (31) | $NMe_2$ | 142 | 143.5 |
| (22) | H | 143.5 | 144.5 |
| (28) | SMe | 144.0 | 145.0 |
| (25) | Me | 145.0 | 146.5 |
| (35) | Cl | 146.0 | 146.0 |

TABLE 6

Substituent parameters and spectroscopic properties of iminium salts and analogous vinylic and carbonyl compounds

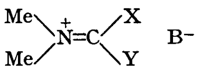


| $Me_2N^+{=}CHX, B^-$ | Taft substitution constants | | I.r. data[3,4] KBr | | U.v. data (this work) MeCN | | U.v. and $\delta^{13}C$ data for analogous $sp^2$ compounds | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $CH_2{=}CHX$ | | MeCOX | |
| X | $\sigma_I$ | $\sigma_R$ | $\nu(C{=}N)$ $cm^{-1}$ | $B^-$ | $\lambda(\pi\rightarrow\pi^*)$ nm | $B^-$ | $\lambda(\pi\rightarrow\pi^*)$ nm | $\delta^{13}C\alpha$ p.p.m. | $\lambda(n\rightarrow\pi^*)$ nm | $\delta^{13}CO$ p.p.m. |
| H | 0 | 0 | 1 675 | Cl | 188 | Cl | 165 | 122.8 | 293 | 200.5 |
| Ph | 0.10 | −0.10 | 1 660 | $BF_4$ | 275 | | | | 325 | 196.9 |
| Cl | 0.47 | −0.20 | 1 660 | Cl | 201 | Cl | 170 | 126.1 | 235 | 169.5 |
| OMe | 0.26 | −0.41 | 1 700 | $MeSO_4$ | 202 | $OSO_2F$ | 195 | 153.1 | 210 (OH)<br>205 (OEt) | 171.0 |
| SMe | 0.19 | −0.17 | 1 635 | $MeSO_4$ | 252 | $OSO_2F$ | 210 | | | |
| OCOMe | 0.30 | −0.25 | | | | | 197 | 141.7 | 217 | 167.3 |
| SCOMe | 0.15 | −0.10 | | | | | | | | |
| $NMe_2$ | 0.05 | −0.52 | 1 715 | Cl | 223 | Cl | 205 | 138.9 | 215 | 169.3 |

TABLE 7

Carbon dynamic resonance study of iminium salts

The $\Delta G_{T_c}^{\ddagger}$ values were computed following the Eyring equation $\Delta G_{T_c}^{\ddagger} = 4.57\,T\,(9.97 + \log T_c - \log \Delta\nu_\infty)$ assuming $f$(transmission-factor) = 1 for dissymmetrical salts and $f = \frac{1}{2}$ for the salts (40), (15), and (31). The values reported for the salt (39) correspond to an intermolecular exchange process.[14b]



| No. | X | Y | $B^-$ | $\Delta\nu_\infty$/Hz (at 25.18 MHz) | $T_c$/K | $\Delta G_{T_c}^{\ddagger}$ / kcal mol⁻¹ | Solvent concentration |
|---|---|---|---|---|---|---|---|
| (1) | O | H | | $^1H$ 11.3 (100 MHz) | 400 | 21.0 | TCE[2b] |
| (5) | S | H | | $^1H$ 2.7 (60 MHz) | 433 | 24.1 | ODCB[31] |
| (11) | OMe | H | $OSO_2F$ | 130.9 | >413 | >19.7 | TCE 2M |
| (21) | SMe | H | Cl | 168.7 | >413 | >19.5 | TCE 2M |
| (40) | $NMe_2$ | H | Cl | 159.4 | 341 | 15.6 | $CDCl_3$ 2M |
| (48) | $NEt_2$ | H | Cl | 192.0 | 343 | 15.5 | $CDCl_3$ 2M |
| (39) | Cl | H | Cl | $^1H$ 18.0 (60 MHz) | 240 | 11.3 | MeCN 0.2M[14b] |
| (15) | OMe | $NMe_2$ | $OSO_2F$ | 34.5 | 209 | 10.3 | $CH_2Cl_2$ 1.5M |
| (31) | SMe | $NMe_2$ | $OSO_2F$ | 26.0 | 193 | 9.5 | $CH_2Cl_2$ 1.5M |

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[31] T. H. Siddal, W. E. Stewart and F. D. Knight, *J. Phys. Chem.*, 1970, **74**, 3580.

(15) and (31) are due to a slow rotation around the C–N bonds.

*Spin Lattice Relaxation Time Measurements.*—We measured the carbon spin lattice relaxation times $T_1$ of some iminium ions and of the corresponding parent compounds (amide or thioamide) with a view to checking the possibility of using these parameters to investigate ion-pairing phenomena in such compounds.

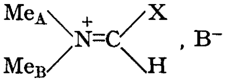
For dimethylformamide, lower $T_1$ values than those reported by Levy and Nelson[34] are observed but it should be noticed that the H-bond existing between amide and $CDCl_3$ increases the correlation time of the molecules and decreases the $T_1$ values. An examination of the other data collected in Table 8 reveals several interesting properties. First of all, methylation of the basic atom of dimethylformamide and DMTF leads to a bulky salt and causes a drastic decrease of the $T_1$ values of both *N*-methyl groups. By measuring the nuclear Overhauser enhancement of the $^{13}C$ resonances, we obtained good evidence for a major contribution of a dipole–dipole relaxation for methyl carbons[35] ($CDCl_3$; 5M):

| | | |
|---|---|---|
| DMF | $Me_A\ \eta = 1.0$ | $Me_B\ \eta = 1.4$ |
| $Me_2N{=}CHX$, OMe | $\eta = 1.3$ | $\eta = 1.0$ |

Since the rotation about the C–N bond is slow with respect to the n.m.r. time scale for the compounds under study, it may be assumed from the measurements of $T_1$ that molecular motion is considerably reduced in the salts by the intimate ion-pair structure. Furthermore, the rate of anisotropic motion $R = T_1(A)/T_1(B)$ of *N*-methyl groups seems to be slightly higher in salts [$R \simeq 1.9$ (OMe) and 1.7 (SMe)] than in amides or thioamides ($R = 1.5$) for $CDCl_3$ solutions. Although no systematic measurements were carried out for the iminoyl carbon atom, we observed short $T_1$ values ($\simeq$ 2 s). As suggested by Levy and Nelson,[34] the rotational process of *N*-methyl groups may be understood in terms of favourable rotameric conformations for $Me_B$. Our results suggest also that the anion $B^-$ is linked through an ion-pair to the iminoyl carbon atom near to the $=C=X$ bond.

[5/2545 *Received*, 30*th December*, 1975]

TABLE 8

Spin-lattice relaxation times $T_1$ (s) of iminium salts  $Me_AMe_B\overset{+}{N}{=}CHX,\ B^-$ and parent compounds determined at 25.18 MHz ($T$ = 305 K) and using IRFT method[32]

Each reported value gives the average for three runs; 18 runs were performed with salt (21) (B = Cl) to check the procedure statistically.[33] For twelve identical runs, the mean and standard deviations for grouped data were computed.

| | $Me_A$ | $Me_B$ | $SMe_3$ |
|---|---|---|---|
| $\overline{T_1}$ (mean) | 3.7 | 2.2 | 3.5 |
| Standard deviation | 0.7 | 0.5 | 0.5 |
| Standard error | ±0.3 | ± 0.2 | ±0.3 |

The relative accuracy of a $T_1$ value with respect to the other values corresponding to the compounds of the sequence under study may be estimated to 10%. Some measurements were also carried out at 15.1 MHz ($T$ = 302 K) (Brüker WP 60 DS) in the IRFT mode. A close agreement is observed between both series of data ($\Delta T_1 < 0.4$). $R^2$ is the coefficient of confidence of the exponential curve fit and is the average of values obtained in 3 runs: SW = 1 000 Hz, PW ($\pi/2$) = $92.10^{-6}$ s, $k$ = −0.72 (offset parameter).

| | | | | $Me_A$ | | $Me_B$ | | X | | $B^-$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | X | $B^-$ | Conditions | $T_1$(s) | $R^2$ | $T_1$(s) | $R^2$ | $T_1$(s) | $R^2$ | $T_1$(s) | $R^2$ |
| (1) | O | | 5M-$CDCl_3$ | 13.4 | 0.989 | 9.2 | 0.979 | | | | |
| (5) | S | | | 14.7 | 0.985 | 9.7 | 0.921 | | | | |
| (23) | SMe | $MeSO_4$ | 5M-$CDCl_3$ | 3.9 | 0.959 | 2.8 | 0.904 | 4.2 | 0.951 | 4.5 | 0.951 |
| (22) | | $OSO_2F$ | | 3.9 | 0.971 | 2.3 | 0.975 | 3.3 | 0.973 | | |
| (24) | | I | | 4.5 | 0.949 | 2.6 | 0.964 | 4.0 | 0.957 | | |
| (21) | | Cl | | 3.7 | 0.969 | 2.2 | 0.970 | 3.5 | 0.970 | | |
| (12) | OMe | $CH_3SO_4$ | 5M-$CDCl_3$ | 4.9 | 0.987 | 2.6 | 0.975 | 3.0 | 0.982 | 4.5 | 0.971 |
| (23) | SMe | $CH_3SO_4$ | 3M-$CDCl_3$ | 4.6 | 0.990 | 2.5 | 0.982 | 4.2 | 0.990 | 5.4 | 0.962 |
| (23) | | | 5M-$CDCl_3$ | 3.9 | 0.959 | 2.8 | 0.904 | 4.2 | 0.951 | 4.5 | 0.951 |
| (23) | | | 7M-$CDCl_3$ | 3.6 | 9.080 | 2.2 | 0.984 | 3.4 | 0.972 | 4.0 | 0.993 |

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[32] R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, 1971, **54**, 3367.

[33] K. A. Brownlee, 'Statistical Theory and methodology in Science and Engineering,' Wiley, London, 1965.

[34] G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, 1972, **94**, 4897.

[35] H. Nakanishi and O. Yamamoto, *Chem. Phys. Letters*, 1975, **35**, 407.