Notes

^{14}N–^{1}H Coupling in Some *N*-Alkylnitrilium Salts[1]

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While investigating[3] the reaction of *N*-alkylnitrilium salts[4] with sodium and dimethylammonium azide, proton magnetic resonance spectra of the nitrilium salts were studied. Although Goodrich and Treichel[5] reported pmr data for the *N*-methylacetonitrilium ion, no interpretation of the complex spectrum was given. Olah and Kiovsky[6] have studied a number of *N*-alkylnitrilium ions in sulfur dioxide using ^{15}N, ^{13}C, and ^{1}H nuclear magnetic resonance.

The first resolvable ^{14}N–^{1}H interaction was observed in several isonitriles.[7] Splitting in isonitriles has been attributed to an unusually small electric field gradient and spin–lattice relaxation times of ^{14}N.[7,8] The low electric field gradient is thought to result from axial symmetry of electron density near the nitrogen atom.[7] Although nitriles resemble isonitriles in being linear groups, nitriles have the lower electronic symmetry because of the nonbonding electrons on nitrogen. The observation of a singlet at δ 1.99 for CH_3CN rather than a 1:1:1 triplet is consistent with this theory. One would anticipate an approach toward electronic symmetry conditions in isonitriles when the lone-pair electrons on nitrogen are involved in bonding. Indeed, this is so in the case of some *N*-alkylnitrilium salts. In an effort to test the validity of the theory further, the pmr spectrum of $CH_3CN^+BF_3^-$ in CD_3CN was taken. The spectrum showed one singlet at δ 2.08 indicating no ^{14}N–^{1}H coupling or exchange with the solvent. The pmr spectrum of protonated acetonitrile in FSO_3H–SbF_5–SO_2 solution has been reported[6] as a sharp doublet at δ −3.25, relative to TMS, corresponding to the methyl group split by the NH proton. The NH^+ absorption is not observable at −90°. These results possibly suggest that, even though the electronic symmetry requirements may have been satisfied, improper relaxation times for ^{14}N cause decoupling through quadrupole relaxation.

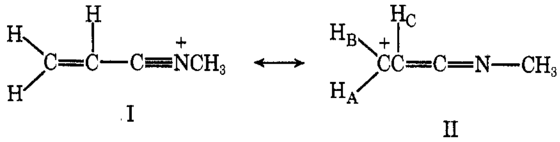
The pmr spectra of six *N*-alkylnitrilium ions in CD_3CN are summarized in Table I and representative spectra are given in Figures 1–3. The complex pmr spectra (*e.g.*, Figure 1) were due to long-range coupling of *N*- and *C*-alkyl protons through the C≡N bond in addition to coupling of the alkyl groups to the ^{14}N nucleus.[6] There was no change in the pmr spectrum of *N*-ethylacetonitrilium fluoroborate in CD_3CN at −40, 25, and 80°. Experiments were performed in which the alkyl groups were effectively decoupled from nitrogen by irradiation. Coupling between alkyl groups was minimized by substitution of ^{1}H by ^{2}H. The spectra of *N*-methyl- and *N*-ethylaceonitrilium ions after ir-

Table I

Pmr Data of Nitrilium Ions[a] in CD_3CN

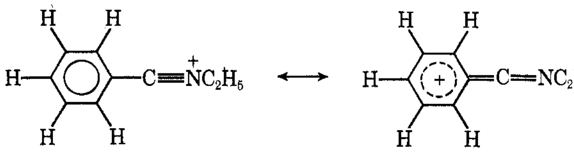
	δ_{RC}				δ_{NR}	
Compd (BF_4^-)	CH_3	CH	CH_2	C_6H_5	CH_3	CH_2
$CH_3CN^+CH_3$	2.78 m				3.71 m	
$CD_3CN^+CH_3$					3.71 t (J = 3)	
$CH_3CN^+C_2H_5$	2.78 m		4.03 m		1.46 m	
$C_2H_5CN^+C_2H_5$	1.40 m		3.10 m		1.40 m	4.01 m
$H_2C{=}CHCN$		5.77 q	6.08 m			
$H_2C{=}CHCN^+CH_3$		6.45 m	7.17 m		3.89 br	
C_6H_5CN				7.32 m		
$C_6H_5CN^+C_2H_5$				7.80 m	1.65 t (J = 7)	4.42 q (J = 7)

[a] Values are in ppm from TMS. J values are in Hz. Abbreviations used are br, broad; m, multiplet; t, triplet; q, quartet.



I

II



III

IV

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[1] Taken from the dissertation of L. A. Lee in partial fulfillment of the requirement for the Ph.D. degree, Howard University, 1970.

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[3] L. A. Lee, R. Evans, and J. W. Wheeler, *J. Org. Chem.*, **37**, 343 (1972).

[4] H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956).

[5] R. A. Goodrich and P. M. Trieichel, *J. Amer. Chem. Soc.*, **88**, 3509 (1966).

[6] G. A. Olah and T. E. Kiovsky, *ibid.*, **90**, 4666 (1968).

[7] I. D. Kuntz, P. v. R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1961).

[8] J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

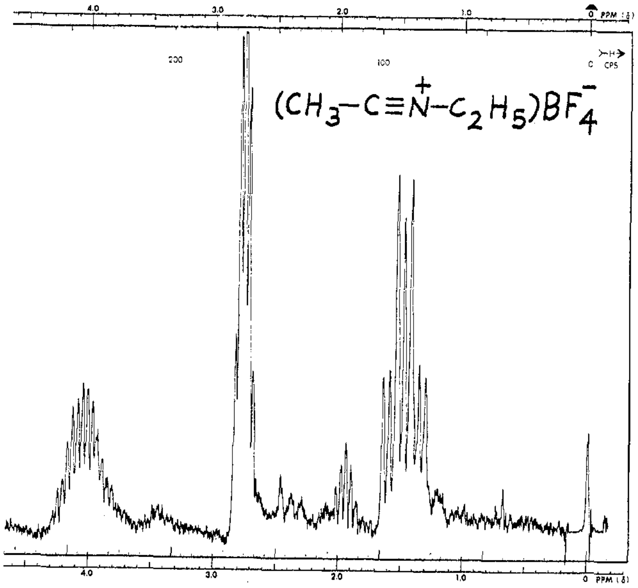

Figure 1.—Pmr spectrum of *N*-ethylacetonitrilium fluoroborate in CD_3CN.

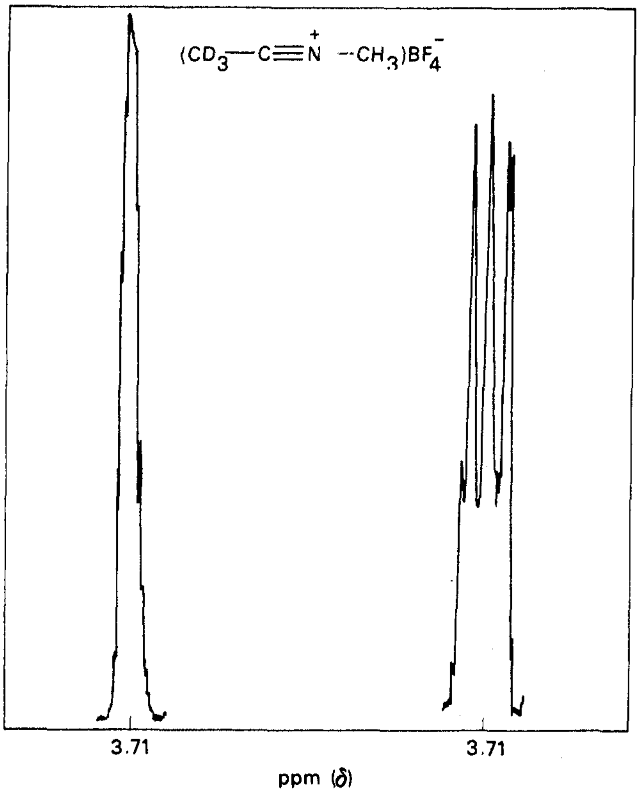

Figure 2.—Pmr spectra of *N*-methylacetonitrilium-d_3 ion, with irradiation of ^{14}N on left, in CD_3CN.

radiation and substitution of deuterium are shown in Figures 2 and 3.

The pmr spectra of *N*-ethylbenzonitrilium and *N*-methylacrylonitrilium fluoroborate show only slight long-range $^1H-^1H$ and/or $^1H-^{14}N$ coupling. These results suggest the importance of other resonance structures of the nitrilium salts such as II and IV. The pmr spectrum of *N*-methylacrylonitrilium fluoroborate shows that the H_A and H_B protons are deshielded more than the H_C proton by 1.09 ppm relative to H_A and H_B protons in acrylonitrile. The phenyl protons in *N*-ethylbenzonitrilium fluoroborate are deshielded by 0.48 ppm relative to the phenyl protons in benzonitrile.

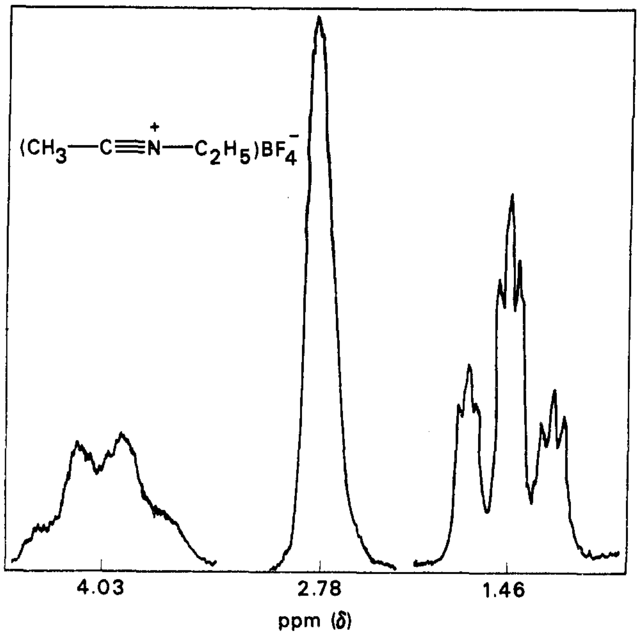

Figure 3.—Pmr spectrum of *N*-ethylacetonitrilium ion, with irradiation of ^{14}N, in CD_3CN.

Similar results have been reported[6] for *N*-methylbenzonitrilium fluoroborate and protonated acrylonitrile in SO_2 and $FSO_3H-SbF_5-SO_2$, respectively.

Experimental Section

***N*-Alkylnitrilium Fluoroborates.**—All nitrilium salts used in this study were prepared according to the procedure of Meerwein and coworkers.[4]

Boron Trifluoride-Acetonitrile Complex.—The addition compound was prepared by the method of Coerver and Curran[9] which requires passing BF_3 into an ice-cooled flask containing acetonitrile until the whole mass solidifies, mp 119–120°.

Pmr Spectra.—Proton magnetic resonance spectra of freshly prepared solutions of nitrilium salts in CD_3CN were taken on a Varian Associates A-60 or HR-60 spectrometer. Positions are reported in parts per million from tetramethylsilane (δ). Nitrogen decoupling experiments were performed with the aid of an nmr Specialties Model SD-60B heteronuclear spin-spin decoupler.

Registry No.—$CH_3CN^+CH_3BF_4^-$, 21353-63-9; $CD_3CN^+CH_3BF_4^-$, 32830-03-8; $CH_3CN^+C_2H_5BF_4^-$, 462-35-1; $C_2H_5CN^+C_2H_5BF_4^-$, 333-94-8; $H_2C{=}CHCN$, 107-13-1; $H_2C{=}CHCN^+CH_3BF_4^-$, 32830-06-1; C_6H_5CN, 100-47-0; $C_6H_5CN^+C_2H_5BF_4^-$, 459-39-2.

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(9) H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, **80**, 3522 (1958).