The First Nitrogen NMR Spectroscopic Study of Nitrile Imides (Nitrilimines)

Klaus Horchler von Locquenghien, Régis Réau and Guy Bertrand*

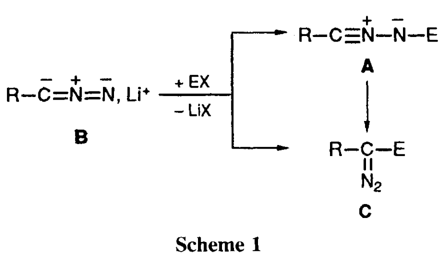
Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse, Cédex, France

^{14}N NMR spectroscopy provides a powerful tool to distinguish easily nitrile imides from the isomeric diazo compounds; the chemical shift variations of the N$_\alpha$ resonance reflect the electronic interaction between the substituents and the nitrile imide skeleton (–CN$_\alpha$N$_\beta$–).

Until recently, nitrile imides **A** were considered as transient intermediates and, thus, had been spectroscopically characterized only by IR and UV spectroscopy in matrices at 85 K[1a–c] or by mass[1c] and real time photoelectron spectroscopy[1d] in the gas phase. The first derivatives of type **A**, stable at ambient temperatures, were prepared using heteroatom substituents.[2] The key step in the synthesis is electrophilic attack at the terminal nitrogen atom of a diazo lithium salt **B**. Depending on the nature of the reagents, the reaction can also occur at carbon leading to isomeric diazo compounds **C**. Moreover, the rearrangement of nitrile imides **A** into diazo compounds **C** has been observed.[2a–c,f,g] Thus, it was of interest to find a rapid and reliable method to distinguish nitrile imides **A** from their diazo isomers **C** (Scheme 1).

The IR absorptions for both types of compounds are found in a similar range.[2] For phosphorus-substituted derivatives ^{31}P NMR spectroscopy has proved to be valuable,[2a–e] but this is, of course, not generally applicable.

In Table 1, the nitrogen and ^{13}C NMR data for the CN$_\alpha$N$_\beta$ skeleton of some nitrile imides **1–8** and of related diazo compounds **9–14** are given. It is clear from the data that the ^{13}C chemical shift of the carbon atom bound to nitrogen can serve as a criterion to differentiate between the two isomeric structures. However, observation of these ^{13}C resonances is hampered owing to the fairly long longitudinal relaxation time T_1(^{13}C). In addition, the transverse relaxation time T_2(^{13}C) is considerably shortened by scalar relaxation of the second kind caused by the adjacent ^{14}N nucleus.[3] Further difficulties arise when heteronuclei like ^{11}B or ^{31}P are attached to these carbon atoms, giving rise to additional broadening or splitting, respectively.



Scheme 1

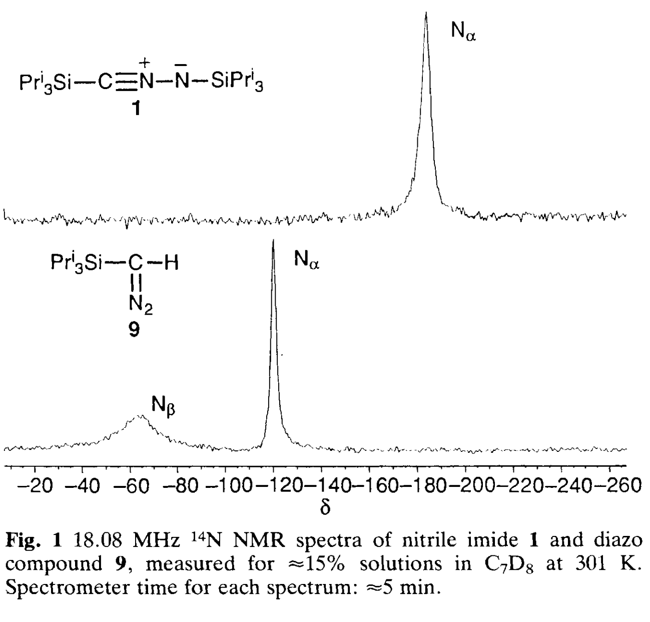
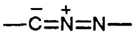


Fig. 1 18.08 MHz ^{14}N NMR spectra of nitrile imide **1** and diazo compound **9**, measured for ≈15% solutions in C$_7$D$_8$ at 301 K. Spectrometer time for each spectrum: ≈5 min.

Table 1 Nitrogen and ^{13}C NMR data[a] of nitrile imides **1–8** and related diazo compounds **9–14**

	Compound								
No.	R	E	$\delta N_{\alpha}(\nu_{1/2})$	$\delta N_{\beta}(\nu_{1/2})$	$\delta N_{misc.}(\nu_{1/2})$	Solv.	*T*/K	$\delta(^{13}C)(CN)$	Solv.
1[2g]	Pr^i_3Si	$SiPr^i_3$	−189.0 (78)	n.o.	—	C_7D_8	301	46.7	C_6D_6
2[2d]	$Pr^i_2N)_2B$	$B(NPr^i_2)_2$	−186.4 (140)	n.o.	≈ −285 (1300)	C_7D_8	348	65.8	C_7D_8
3[12]	$(c\text{-}Hex_2N)_2B$	$B(NPr^i_2)_2$	−188.0 (175)	n.o.	≈ −320 (1000)	$CDCl_3$	328	68.0	$CDCl_3$
4[12]	$(c\text{-}Hex_2N)_2B$	$B(Nc\text{-}Hex_2)_2$	−191 (550)	n.o.	≈ −315 (>1600)	$CDCl_3$	298	66.5	$CDCl_3$
5[2d]	$(Pr^i_2N)_2B$	$P(NPr^i_2)_2$	−184.4 (220)	n.o.	≈ −320 (>1500)	C_6D_6	298	67.0	C_6D_6
6[12]	$(Pr^i_2N)_2P$	$P(NPr^i_2)_2$	−191.9 (250)	n.o.	≈ −320 (1300)	$CDCl_3$	328	63.4	C_6D_6
7[2b]	$(Pr^i_2N)_2P(S)$	$P(NPr^i_2)_2$	−173.1 (107)	n.o.	≈ −320 (>1500)	C_6D_6	343	61.0	$CDCl_3$
8[2e]	$(Pr^i_2N)_2P(S)$	$P^+(Me)(NPr^i_2)_2$[b]	−215.0 (200)	n.o.	n.o.	C_6D_6	343	69.8	$CDCl_3$
9[2f]	Pr^i_3Si	H	−121.4 (45)	−62 (315)	—	C_7D_8	301	15.0	$CDCl_3$
10[2d]	$(Pr^i_2N)_2B$	H	−114.2 (80)	−44.6 (430)	−306 (670)	C_7D_8	348	36.5[c]	C_7D_8
11[2b]	$(Pr^i_2N)_2P$	H	−113.0 (50)	−23.8 (470)	−302.6 [78.2][d]	C_6D_6	338	31.0	C_6D_6
12[2b]	$(Pr^i_2N)_2P(S)$	H	−123.8 (62)	−26 (870)	≈ −320 (1070)	C_6D_6	338	40.3	C_6D_6
13[13]	$(Pr^i_2N)_2P$	Me_3Si	−120.9 (115)	−74 (720)	−305.5 [72.1][d]	C_6D_6	338	28.7	C_6D_6
14[14]	$(Pr^i_2N)_2P$	$(Pr^i_2N)_2P$	−114.8 (150)	≈ −38 (1150)	−307.3 [77.3][d]	C_7D_8	338	40.9	C_7D_8

[a] Bruker WM 250 and AM 300 spectrometers; solutions *ca.* 15–30% v/v; positive signs indicate high frequency shifts; chemical shift references: ^{13}C [$SiMe_4$, $\delta(^{13}C)$ (solvent) 20.4 (C_7D_8), 77.0 ($CDCl_3$), 128.0 (C_6D_6)]; ^{14}N, ^{15}N (neat $MeNO_2$, external $\Xi(^{14}N)$ = 7 226 455 Hz, $\Xi(^{15}N)$ = 10 136 767 Hz (n.o. = not observed). [b] Counter ion: $SO_3CF_3^-$. [c] $^1J(^{13}C^{11}B) \geqslant 93$ Hz, estimated from the ^{13}C linewidth at 348 K. [d] ^{15}N NMR data, recorded with the INEPT pulse sequence assuming a coupling constant $J(^{15}N^1H) \approx 2.5$ Hz;[11] $^1J(^{31}P^{15}N)$ in square brackets in Hz.



$$-\overset{-}{C}=\overset{+}{N}=N-$$

I

$$-C\equiv\overset{+}{N}-\overset{-}{N}-$$

II

We found that ^{14}N NMR spectroscopy provides a simple and quick way to distinguish the two CNN structural isomers.[4] Of particular interest, ^{14}N NMR spectroscopy can be applied to reaction solutions. The $^{14}N_{\alpha}$ nuclei give rise to comparatively narrow ^{14}N NMR signals, which are easily observed even for larger molecules (*e.g.* **4**) at room temperature. This behaviour is similar to that found in related molecules such as azides R–NNN,[5] nitrile oxides R–CNO[6] and isocyanamides R_2NNC,[7] where the ^{14}N nuclei of the linear dicoordinated nitrogen atoms experience only small electric field gradients. The N_{α} chemical shift difference between nitriles imides **A** and the corresponding diazo compounds **C** (≈70 ppm between, *e.g.* **1/9**, **2/10**, and **6/14**) is sufficient for a definitive assignment of the structure (Fig. 1). As expected, the nitrogen chemical shifts for the nitrile imides are found in a similar range to those of nitrile oxides.[6]

The $^{14}N_{\beta}$ resonance of nitrile imides was never observed. When compared with covalent azides,[5,8] this resonance can be expected around $\delta_N \approx -300$. Unfortunately, for compounds **2–8** this region in the ^{14}N NMR spectra is dominated by the broad and intense signals due to the amino substituents which would therefore overlap with the $^{14}N_{\beta}$ resonance. However, even in the case of **1** only the narrow $^{14}N_{\alpha}$ NMR signal was observed even at +80 °C (Fig. 1). This would indicate that the electric field gradient at the site of the $^{14}N_{\beta}$ nucleus is very large, causing the $^{14}N_{\beta}$ relaxation time T_Q to be very short.

For **7**[2b] and **8**[2e] the structures have been determined by X-ray crystallography. Considering the possible resonance structure of nitrile imides, these compounds represent two extremes: **7** is best described as a heteroallenic compound **I** while **8** shows a heteropropynylic structure **II**.

In solution these findings are reflected by the $\delta(^{14}N_{\alpha})$ values which compare with the corresponding ^{13}C chemical shifts of ketenimines[9] (>C=C=N–) and amino-substituted alkynes[10] (–C≡C–N<). This comparison shows the correlation existing between the $^{14}N_{\alpha}$ shielding and the corresponding resonance structures of the nitrile imide skeleton ($-CN_{\alpha}N_{\beta}-$). This method could probably be extended to other derivatives, thus providing a simple and straightforward tool in the deduction of electronic structures.

Support of this work by the CNRS is gratefully acknowledged. K. H. v. L. thanks the Alexander von Humboldt-Foundation and Conseil Régional Midi-Pyrénées for a post-doctoral fellowship.

Received, 29th April 1991; Com. 1/02005F

References

1 (*a*) H. Toubro and A. Holm, *J. Am. Chem. Soc.*, 1980, **102**, 2093; (*b*) H. Meier, W. Heinzelmann and H. Heimgartner, *Chimia*, 1980, **34**, 504, 506; (*c*) C. Wentrup, S. Fisher, A. Maquestiau and R. Flammang, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 56; (*d*) H. Bock, R. Dammel, S. Fisher and C. Wentrup *Tetrahedron Lett.*, 1987, **28**, 617.

2 (*a*) G. Sicard, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1988, **110**, 2663; (*b*) M. Granier, A. Baceiredo, Y. Dartiguenave, M. Dartiguenave, M. J. Menu and G. Bertrand, *J. Am. Chem. Soc.*, 1990, **112**, 6277; (*c*) M. Granier, A. Baceiredo and G. Bertrand, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1350; (*d*) M. P. Arthur, A. Baceiredo and G. Bertrand, *Organometallics*, in the press; (*e*) M. Granier, A. Baceiredo, V. Huch, M. Veith and G. Bertrand, *Inorg. Chem.*, 1991, **30**, 1161; (*f*) F. Castan, A. Baceiredo, D. Bigg and G. Bertrand, *J. Org. Chem.*, 1991, **56**, 1801; (*g*) F. Castan, A. Baceiredo and G. Bertrand, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1250.

3 O. Howarth in *Multinuclear NMR*, ed. J. Mason, Plenum Press, New York, 1987, ch. 5, p. 133.

4 R. O. Duthaler, H. G. Förster and J. D. Robert, *J. Am. Chem. Soc.*, 1978, **100**, 4974.

5 J. Müller, *J. Organomet. Chem.*, 1973, **51**, 119.

6 F. de Sarlo, A. Brandi, A. Guarna and N. Niccolai, *J. Magn. Reson.*, 1982, **50**, 64.

7 K. Barlos, G. Hübler, H. Nöth, P. Wanninger, N. Wiberg and B. Wrackmeyer, *J. Magn. Reson.*, 1978, **31**, 363.

8 D. M. Kanjia, J. Mason, I. A. Stenhouse, R. E. Banks and N. D. Venayak, *J. Chem. Soc., Perkin Trans. 2*, 1981, 975.

9 (*a*) H. O. Kalinowski, S. Berger and S. Braun, *^{13}C-NMR Spectroscopy*, Wiley, London 1988; (*b*) K. Eberl and J. D. Roberts, *Org. Magn. Reson.*, 1981, **17**, 180.

10 B. Wrackmeyer and K. Horchler, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1990, **22**, 209.

11 B. Wrackmeyer, S. Kerschl, C. Stader and K. Horchler, *Spectrochim. Acta, Part A*, 1986, **42**, 1113.

12 R. Réau, F. Castan, A. Baceiredo and G. Bertrand, unpublished results.

13 A. Igau, H. Grützmacher, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1988, **110**, 6463.

14 A. Baceiredo, A. Igau, G. Bertrand, M. J. Menu, Y. Dartiguenave and J. J. Bonnet, *J. Am. Chem. Soc.*, 1986, **108**, 7868.