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A ^{19}F , ^{13}C AND ^{14}N -NMR STUDY OF TRIFLUOROMETHYL ISOCYANIDE

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SUMMARY

^{19}F , ^{13}C and ^{14}N -NMR spectra of trifluoromethyl isocyanide have been recorded at $-102\text{ }^\circ\text{C}$. The spectral data show only minor differences in comparison to those of hydrocarbon isocyanides.

INTRODUCTION

Although isocyanides were first reported 1867 [1], very little is known about perfluorinated isocyanides. Recently, an efficient synthesis of trifluoromethyl isocyanide was discovered [2]. Since that time, the chemical, structural, and physical properties of the molecule have been studied extensively.

A number of key properties (e.g. reactivity [3], ligand behaviour [4,5], isomerization barrier to the cyanide [6], PE-spectra [6], XPS-spectra [7]) of trifluoromethyl isocyanide were found to differ drastically from those of methyl isocyanide, even though there are only minor structural differences [8]. In particular the $\text{N}=\text{C}$ bond length is very similar to that of CNCH_3 [9] and HNC [10]. The $\text{N}-\text{C}$ bond length exhibits the expected fluorine substitution effect [11]. For these reasons we were interested in the fluorine substitution effect on the ^{13}C and ^{14}N resonance of trifluoromethyl isocyanide.

RESULTS AND DISCUSSION

Due to the instability of trifluoromethyl isocyanide in the condensed phase nmr spectra were recorded at $-102\text{ }^{\circ}\text{C}$. The ^{19}F -, ^{13}C -, and ^{14}N data for trifluoromethyl isocyanide are listed in table 1 and compared to those of methyl isocyanide and phenyl isocyanide. At $-102\text{ }^{\circ}\text{C}$ the ^{19}F nmr spectrum of trifluoromethyl isocyanide shows only one sharp resonance. On warming the sample a large number of signals from the decomposition products are formed. Nevertheless a small signal due to trifluoromethyl isocyanide remains, which broadens on warming and splits into a triplet at ambient temperature due to coupling with ^{14}N . The chemical shift and nitrogen-fluorine coupling constant are similar to those reported previously [12, 2]. The ^{13}C resonance of the isocyanide carbon atom of trifluoromethyl isocyanide is observed at lower field than that of methyl isocyanide and phenyl isocyanide.

In contrast to methyl isocyanide and phenyl isocyanide, no ^{14}N - ^{13}C coupling was observed for the isocyanide carbon. Although the lack of coupling may simply be due to the low temperature, the instability of trifluoromethyl isocyanide precluded measuring the ^{13}C nmr spectrum at higher temperatures, because the CF_3NC concentration rapidly decreases on warming. The resonance of the CF_3 -carbon atom is observed as a quartet due to coupling with ^{19}F . The individual lines are further splitted into poorly resolved triplets due to coupling with ^{14}N . The estimated coupling constant of 20 Hz is larger than that in methyl isocyanide and phenyl isocyanide. The chemical shift of the ^{14}N resonance is very similar to that of phenyl isocyanide.

In contrast to the drastic differences in reactivity and ligand behaviour, the fluorine substitution effect on the ^{13}C and ^{14}N nmr spectra of trifluoromethyl isocyanide is very small. Only a small down field shift and a larger ^{14}N - ^{13}C coupling constant can be observed in comparison with methyl isocyanide. However, upon complexation the effects can be drastic (e.g. $\text{Cp}^*\text{Mn}(\text{CO})_2(\text{CNCH}_3)$, $\delta_{\text{CN}}=182.2\text{ ppm}$; $\text{Cp}^*\text{Mn}(\text{CO})_2(\text{CNCF}_3)$, $\delta=257.7\text{ ppm}$ ($\text{Cp}^*=\text{C}_5(\text{CH}_3)_5$) [5]).

TABLE I

NMR data of isocyanides

| | ^{19}F -NMR ^a | ^1H -NMR | ^{13}C -NMR | ^{14}N -NMR ^b |
|--|--|--|---|-----------------------------------|
| CF_3NC | -52.0 ^[12, 21] $^2\text{J}(\text{NF})=15.5$ Hz at 25 °C | | $\delta(\text{CF}_3)=107.7$ $^1\text{J}(\text{CF})=262$ Hz $^1\text{J}(\text{CN})=20$ Hz $\delta(\text{CN})=169.0$ | -203.6 $1/2=57$ Hz |
| CH_3NC | | 2.73 ^[13] $^2\text{J}(\text{NH})=2.4$ Hz | $\delta(\text{CH}_3)=26.8$ ^[14] $^1\text{J}(\text{CN})=7.5$ Hz $\delta(\text{CN})=158.2$ | -216 ^[14] |
| CH_3NC (CCl_4) | | 2.85 ^[14] $^2\text{J}(\text{NH})=2.7$ Hz | $^1\text{J}(\text{CN})=5.8$ Hz | |
| PhNC | | | $\delta(\text{CN})=165.7$ ^[14] $^1\text{J}(\text{CN})=5.2$ Hz $\delta(\text{C1})=126.7$ $^1\text{J}(\text{CN})=13.2$ Hz | -200 ^[14] |

a

 CFCl_3 external reference

b

 NO_3^- of a saturated aqueous NH_4NO_3 solution as external reference

EXPERIMENTAL

Trifluoromethyl isocyanide was prepared according to [2]. NMR-Spectra were recorded using a JEOL FX 90Q (solution in $\text{CD}_2\text{Cl}_2/\text{CF}_2\text{Cl}_2$, ^{19}F -NMR 84.25 MHz, using CFCl_3 as an external reference; ^{13}C -NMR 22.49 MHz, using CD_2Cl_2 $\delta=53.61$ ppm as an internal reference; and ^{14}N -NMR 6.47 MHz, using an aqueous ammonium nitrate solution as an external reference) instrument. ^{13}C -NMR and ^{14}N -NMR spectra were measured at -102 °C. ^{19}F -NMR spectra were recorded between -102 °C and ambient temperature.

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