Notiz / Note

Gas-Phase Generation and Characterization of Hydrogen Cyanide *N*-Methylide[1]

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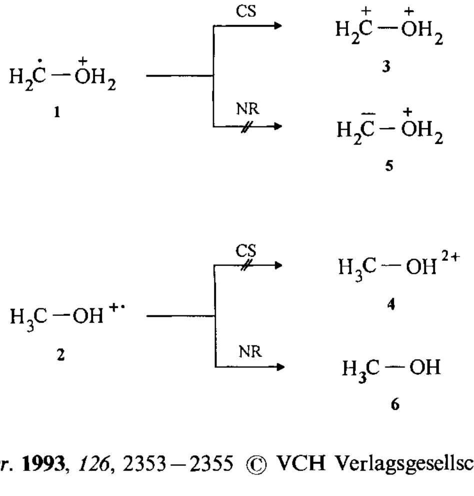
The recently described (Maier et al.[2]) title compound is not only viable in an argon matrix (10 K) but is also accessible in the gas phase. Electron impact ionization of $(CH_3)_3CCX_2NC$ (X = H, D) gives rise to $HCNCX_2^{+\bullet}$, which can be successfully neutralized in a beam experiment.

The increasing importance and conspicuous properties of distonic ions[3] – species in which the charge and radical centres are formally separated – as central intermediates in areas as diverse as chemistry in the gas phase or in frozen matrices are well documented in several review articles[4]. An interesting sub-class are the α-distonic cations which formally correspond to the ionized forms of ylides[5]. A typical example which highlights some of the unusual features of these molecules is $H_2\dot{C}{-}\overset{+}{O}H_2$ (**1**). This radical cation has indeed remarkable properties in comparison with its conventional isomer, the methanol molecular ion $CH_3OH^{+\bullet}$ (**2**) (Scheme 1). In contrast to the *neutral* counterparts **5** and **6**, ylide ion **1** is both thermochemically and kinetically more stable than **2**[6]. In charge stripping (CS) experiments[7], **1** can be oxidized in the gas phase to its corresponding dication $H_2C{-}OH_2^{2+}$ (**3**), while $CH_3OH^{+\bullet}$ upon gas-phase oxidation does not give rise to a detectable dication CH_3OH^{2+} (**4**)[8]. Similarly, if $CH_2OH_2^{+\bullet}$ (**1**) is subjected to a neutralization-reionization (NR)[9] experiment, in line with the theoretical predictions[6d], no recovery signal for the *neutral* ylide $H_2\overset{-}{C}{-}\overset{+}{O}H_2$ (**5**) is observed[10] in contrast to $CH_3OH^{+\bullet}$ which, of course, can be neutralized to methanol. The failure to neutralize $H_2C{-}OH_2^{+\bullet}$ is twofold: (i) The carbon-oxygen binding energy of the neutral ylide **5** is quite small (< 10 kcal/mol) and (ii) the large difference in equilibrium geometries of the charged and neutral species implies that vertically neutralized ylides will be formed with considerable excess energy, thus facilitating rearrangement and/or fragmentation processes.

Here we report our results on the gas-phase generation and characterization of another important ylide, i.e. hydrogen cyanide *N*-methylide $HCNCH_2$ (**8**) and its radical cation **7**. The neutral species

Scheme 1



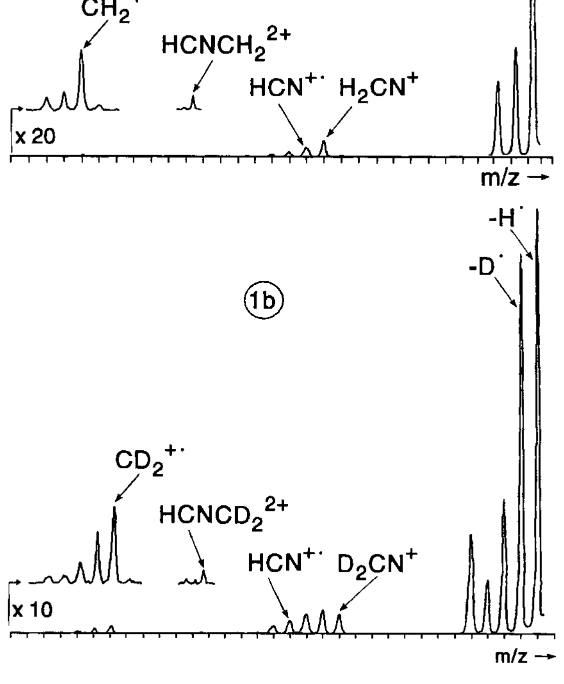


Figure 1. Collisonal activation mass spectra (helium, 80% T) of (a) $HCNCH_2^{+\bullet}$, (b) $HCNCD_2^{+\bullet}$

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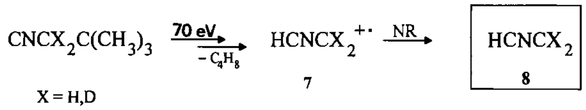
8 is one of the members of the intriguing C_2H_3N family[11], and in a recent exhaustive study[2] its preparation in an argon matrix (10 K), spectroscopic indentification, and its relationship with other C_2H_3N isomers has been described.

Scheme 2



In the context of our earlier work on the identification of the potentially interstellar C_2H_3N isomer aminoacetylene[12], we also reported on the collisional activation (CA)[13] mass spectra of several $C_2H_3N^{+\bullet}$ isomers, including also $HCNCH_2^{+\bullet}$ (**7**). This species is easily accessible by electron-impact-induced fragmentation of aliphatic isonitriles (Scheme 2), and a typical CA mass spectrum for this ion, generated from 2,2-dimethylpropyl isocyanide, is given in Figure 1a. In Figure 1b, the CA mass spectrum of the isotopomer $HCNCD_2^{+\bullet}$ is reproduced[14].

The interpretation of Figure 1 is straightforward in that — in addition to the structure-unspecific losses of H_x ($x = 1-3$) — we observe three diagnostic features one would indeed expect for an $HCNCX_2^{+\bullet}$ (X = H, D) connectivity: Formations of $CX_2^{+\bullet}$, NCX_2^{+}, and of the doubly charged ion $HCNCX_2^{2+}$. This signature is not only different from that of the other $C_2H_3N^{+\bullet}$ isomers, described earlier[12], it is also in keeping with the connectivity of ionized hydrogen cyanide *N*-methylide **7**.

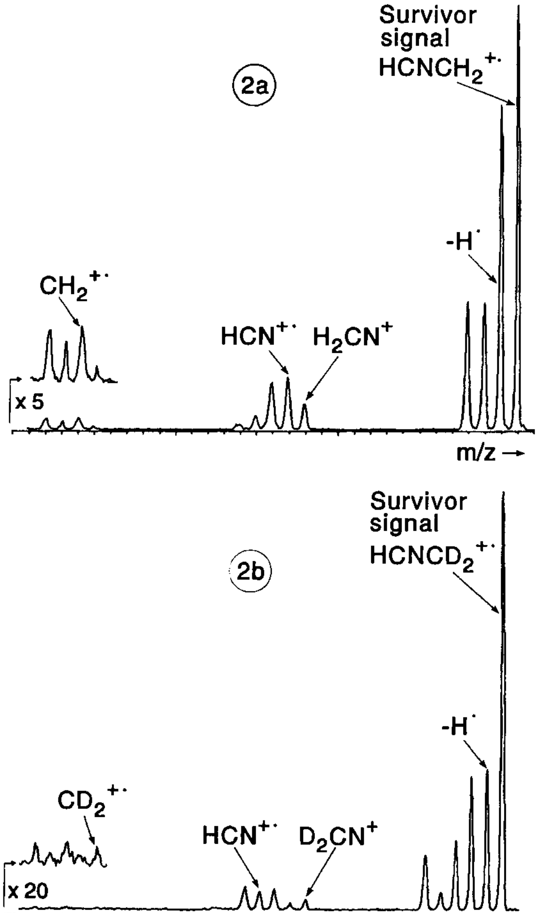


Figure 2. Neutralization-reionization mass spectra (xenon, 80% T/oxygen 80% T) of (a) $HCNCH_2^{+\bullet}$, (b) $HCNCD_2^{+\bullet}$

Can **7** also be successfully neutralized? As evidenced by the spectra shown in Figure 2, the structure-indicative fragments are indeed retained, when $HCNCX_2^{+\bullet}$ ions are subjected to a neutralization-reionization experiment. In addition, we observe a very intense survivor signal. These two observations clearly demonstrate that — in line with the theoretical expectations[2] — the neutral $HCNCX_2$ (X = H, D) is a stable molecule also in the gas phase. The relatively high abundances of the $HCNCX_2$ signals in the NR spectra are no surprise if one takes into account, that — in contrast to $H_2\overset{-}{O}\text{–}\overset{+}{O}H_2$ — no low-energy dissociation paths are available for hydrogen cyanide *N*-methylide (**8**). In particular, Maier's calculations[2] indicate that the two carbon–nitrogen bonds of **8** are of nearly equal bond length, thus favouring the ylide form **8a** in comparison to the *N*-methylide form **8b**, which would be expected to fall apart more easily to HCN and CH_2.

$HC{=}N{=}CH_2$ $HCN\text{–}CH_2$
8a **8b**

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[1] Dedicated to Professor *Hans Bock*, Frankfurt, on the occasion of his 65th birthday.

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[14] The mass-spectrometric experiments were performed using our modified ZAB-HF machine which is of *BEBE* configuration (*B* stands for magnetic and *E* for electric sector) (ref.[15]). $C_2H_3N^{+\bullet}$ and $C_2HD_2N^{+\bullet}$ ions were generated by 70-eV ionization of $(CH_3)_3CCH_2NC$ and $(CH_3)_3CCD_2NC$, respectively, employing the following ion-source conditions: ion-source temperature 200°C; trap current 100 μA; repeller voltage 30 V; acceleration voltage 8 kV; mass resolution $m/\Delta m = 3000$. In the NRMS experiment, a beam of $B(1)E(1)$ mass-selected $C_2H_3N^{+\bullet}$, having 8 keV translational energy, was neutralized in the first cell of a differentially pumped tandem collision cell by colliding it with xenon (80% transmission, T). Unreacted ions were deflected away from the beam of neutral species by putting a voltage on a deflector electrode which is situated between the two collision cells. Subsequent reionization of the beam of neutral C_2H_3N is brought about in a second collision cell by collision with oxygen (80% T). The mass spectra of the resulting ions were recorded by scanning $B(2)$. The *minimal* lifetime *t* (identical with the transit time from collision cell I to cell II) in the present experiments is > 10 μs. In the CA experiments, helium was used as a collision partner (80% T). In order to improve the S/N ratio, signal averaging techniques were used by accumulating 25 – 50 scans and on-line processing the data with the AMD-Intectra data system.

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