Generation, Isolation and Photoelectron Spectrum[1] of HC≡C–N≡C

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Thermal fragmentation of pentacarbonyl(1,2-dichlorovinylisocyanide)chromium, $(OC)_5Cr(CN\text{–}ClC{=}CHCl)$, yields acetylene isocyanide, a putative interstellar molecule, which, after purification by fractional condensation, is characterized by its helium(I) photoelectron spectrum.

In contrast to numerous saturated and unsaturated organic cyanides, R–CN (R = H, CH_3) and $H\text{–}(C{\equiv}C)_n\text{–}CN$ (n = 1 to 5)[2] found in interstellar space and especially in the Taurus molecular cloud,[2] only a few isocyanide isomers, H–NC and $H_3C\text{–}NC$,[2] have so far been detected. But also on Earth, known nitriles by far outnumber isonitriles and, therefore, new methods for their synthesis or that of their metal complexes are welcome.[3] In turn, thermal fragmentation of the latter can yield hitherto unprepared,[4] although precalculated[5] molecules such as the title compound.

Advantageously, acetylene isocyanide can be generated, isolated and characterized by its ionization pattern by performing the thermal fragmentation of the pentacarbonyl(1,2-dichlorovinylisocyanide)chromium complex [eqn. (1)] in a building block apparatus connected to a photoelectron spectrometer (Fig. 1), which allows the optimization of all essential reaction conditions by real-time photoelectron spectroscopic (PES) gas analysis.[6] The chromium complex, evaporated under 10^{-4} mbar (1 bar = 10^5 Pa) pressure at room temperature, passes through a quartz tube (length 40 cm, diameter 1.5 cm), which is heated to an oven temperature of 510 K. Except for CO, and HC≡C–N≡C, all other products of a nine hour fragmentation are frozen out in the intense cooling trap at 190 K. After closing the left-hand Teflon valve of the 78 K trap (Fig. 1) and on slow warming to 190 K, the liquid acetylene isocyanide can be evaporated into the spectrometer and its PES ionization fingerprint (Fig. 2) recorded.

$$(OC)_5Cr(CN\text{-}CCl{=}CCHCl) \xrightarrow[-CO]{} H\text{-}C{\equiv}C\text{-}N{\equiv}C \qquad (1)$$

The helium(I) PE spectrum recorded (Fig. 2) shows three vibrationally fine-structured bands corresponding to vertical ionizations at 11.23, 11.90 and 15.27 eV and, in addition, unresolved bands at 18.0 eV and, presumably, around 19.5 eV. The assignment to the three well-defined valence radical cation states of lowest energy, $\tilde{X}(^2\pi)$, $\tilde{A}(^2\Sigma^+)$ and $\tilde{B}(^2\pi)$ is straightforwardly supported by correlated Green function ionization energies[5b] and can even be achieved applying Koopman's theorem, $IE_n{}^v = -\varepsilon_J{}^{SCF}$, to the eigenvalue pattern from a fully geometry-optimized AM 1 calculation,[7] with only the 5σ value exhibiting a somewhat larger defect of 1.3 eV (Fig. 2). Especially with the almost 1 : 1 correspondence between the observed vibrational fine structures [Fig. 2 (insert)] and those predicted by anharmonic *ab initio* potential energy function calculations (Table 1), there remains hardly any doubt that the molecule generated from the chromium complex by thermal fragmentation and purified by fractionate condensation (Fig. 1) is the required acetylene isocyanide.

As concerns the other molecular properties of HC≡C–N≡C, now available on Earth, further results of the geometry-optimized AM 1 calculations (Scheme 1) are compared with those for the isomer HC≡C–C≡N: Accordingly, their semi-empirically predicted structures, which closely resemble the

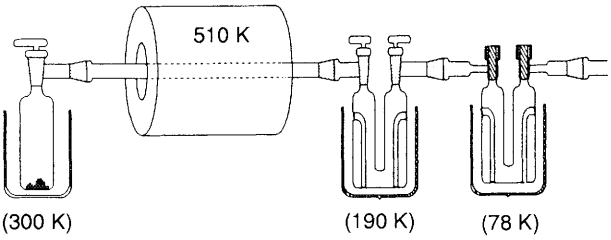


Fig. 1 Building block apparatus assembled for the 510 K thermolysis of the pentacarbonylchromium complex, for the fractionate condensation of side products in an 190 K intense cooling trap and for the isolation of acetylene isocyanide in a 78 K trap with Teflon valves. The photoelectron spectrometer (PES) connected is used both for the evaporation of the system and for the optimization of the reaction conditions and the product analysis.

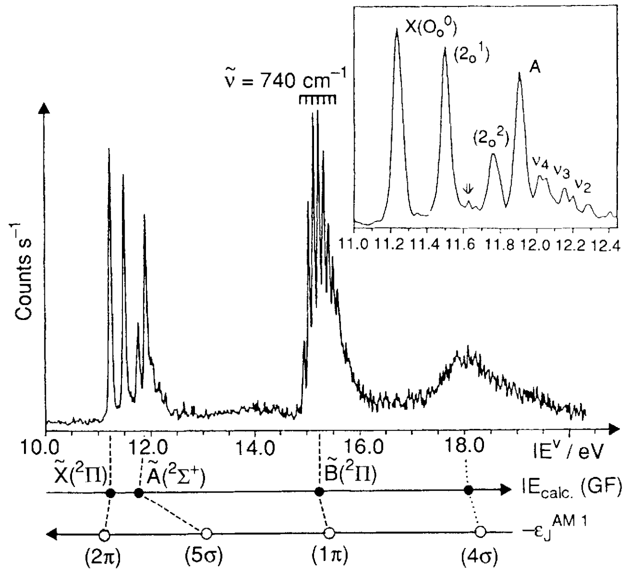
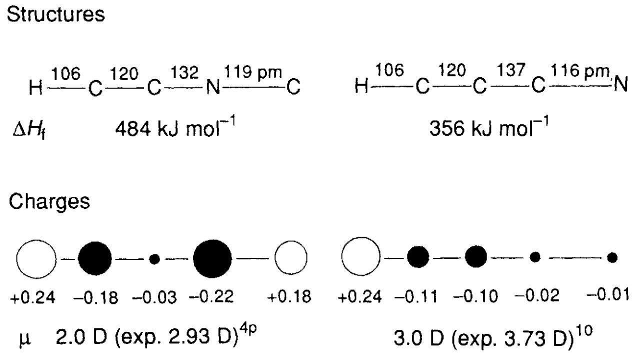


Fig. 2 He I PE spectrum of HC≡C–N≡C [calibrated with $^2P_{3/2}$ (Ar) = 15.76 eV] and its assignment based on correlated Green function ionization energies, $IE^v_{calc.}$ (GF), and on Koopmans' correlation, $IE^v_n = -\varepsilon_J^{AM1}$, with eigenvalues from a fully geometry-optimized AM 1 calculation. Insert: expanded record between 11.1 and 12.60 eV with assignment of the vibrational radical cation states observed according to anharmonic *ab initio* potential energy function calculations,[5c] (*cf.* Table 1); the rather weak peak at 11.60 eV (↓) could be owing to traces of the acetylene cyanide isomer formed in the thermal fragmentation (see, text).

Table 1 Assignment of the vibrational fine structures observed for the radical cation states $\tilde{X}(^2\pi)$ and $\tilde{A}(^2\Sigma^+)$ of HC≡C–N≡C (Fig. 1: insert) including the comparison of experimental and calculated relative intensities $I_{rel.}$ (%) as predicted by the anharmonic *ab initio* potential energy function approximation[5c]

Assignment		Experimental IE^v_n/eV	Experimental $I_{rel.}$ (%)	Calculated ΔIE^v_n/eV	Calculated $I_{rel.}$ (%)
$X(^2\Pi)$	0^0_0	11.23	100	0	100
	2^1_0	11.50	90	0.27	76
	2^2_0	11.77	35	0.54	29
	2^3_0	12.04	10	0.81	7
$A(^2\Sigma^+)$		11.90	80	0	80
		12.01	10	0.11	8
		12.16	5	0.27	6
		12.20	4	0.29	6



Scheme 1 Comparison of the HC_3N isomers based on selected results of fully geometry-optimized AM 1 calculations (see text)

experimental ones,[4,8] expectedly only reverse the bond distances in the isomeric subunits CNC and CCN. The estimated difference in the heats of formation, $\Delta\Delta H_f \approx +128$ kJ mol^{-1} for the isocyanide isomer agrees reasonably well with the result from an SCF Cl calculation,[5a] and would yield a plausible explanation for the unassigned weak peak at 11.60 eV in the PE spectrum (Fig. 2: insert, ↓). The charge distributions calculated, expectedly reflect the difference in effective nuclear charges, $Z_{eff}(N) > Z_{eff}(C)$ and, although the values for the individual centres are subject to caution, the difference in the resulting dipole moments of the two isomers approaches the experimentally (exp.) determined value of 0.8 D.[4,10]

With reference to its considerable dipole moment,[4] the novel molecule HC≡C–N≡C stands a reasonable chance of being detected radioastronomically in interstellar space (see below).

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