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Gas-Phase Protonation and Deprotonation of Acrylonitrile Derivatives $N{\equiv}C{-}CH{=}CH{-}X$ ($X = CH_3$, NH_2, PH_2, SiH_3)

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Abstract: A combined experimental and theoretical study on the gas-phase basicity and acidity of a series of cyanovinyl derivatives is presented. The gas-phase basicities and acidities of ($N{\equiv}C{-}CH{=}CH{-}X$, $X = CH_3$, NH_2) were obtained by means of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry techniques. The corresponding calculated values were obtained at the G3B3 level of theory. The effects of exchanging CH_3 for SiH_3, and NH_2 for PH_2, were analyzed at the same level of theory. For the neutral molecules, the *Z* isomer is always the dominant species under standard gas-phase conditions at 298 K. The loss of the proton from the substituent X was found systematically to be much more favorable than deprotonation of the $HC{=}CH$ linking group. The corresponding isomeric *E* ion is much more stable than the *Z* ion, so that only the former should be found in the gas phase. The most significant structural changes upon deprotonation occur for the methyl and amino derivatives because, in both cases, deprotonation of X leads to a significant charge delocalization in the corresponding anion. Protonation takes place systematically at the cyano group, whereby the isomeric *E* ion is again more stable than the *Z* ion. Push–pull effects explain the preference of aminoacrylonitrile to be protonated at the cyano group, which also explains the high basicity of this derivative relative to other members of the analyzed series that present rather similar gas-phase basicities, GB ≈ 780 $kJ\,mol^{-1}$, indicating that the different nature of the substituents has only a weak effect on the intrinsic basicity of the cyano group. The cyanovinyl derivatives have a significantly stronger gas-phase acidity than that of the corresponding vinyl compounds $CH_2{=}CH{-}X$. This acidity-strengthening effect of the cyano group is attributed to the greater stabilization of the anion with respect to the corresponding neutral compound.

Keywords: ab initio calculations · acidity · acrylonitrile derivatives · basicity · gas-phase reactions

Introduction

Among the molecules detected to date in interstellar media, cyanopolyynes constitute a rich and important subset.[1] These robust compounds exhibit special properties with respect to their reactivity and kinetic stability, and some have been found in other astrochemical environments, such as comets[2,3] or in lab simulations of planetary atmospheres.[4,5] These systems are supposed to be good starting materials for the formation of new, more complex, astrochemical species,[1] or amino acids on primitive Earth.[4] A paradigmatic example is cyanoacetylene ($HC{\equiv}C{-}C{\equiv}N$),[6] which readily reacts with ammonia, a compound also abundant in these media, to give the aminoacrylonitrile.[7,8] The introduction of a cyano group in a conjugative position in vinylamine dramatically modifies the properties of the unsaturated amine. In fact, although vinylamine ($H_2C{=}CH{-}NH_2$) is unstable at −80 °C in the condensed phase and decomposes in the pres-

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ence of several reactants, aminoacrylonitrile is a kinetically stable compound.

Very little is known about the chemistry of these and other similar cyanovinyl derivatives. Indeed, there is a complete lack of information regarding their intrinsic reactivity. The aim of this paper was to investigate the intrinsic basicity and acidity of NC−HC=CH−X compounds (X = CH_3, NH_2), which are the most relevant ones in the interstellar medium or in planetary atmospheres. We also investigated how the properties of the system change if X contains a second-row heteroatom instead of one from the first row, because, similarly to the addition of ammonia to cyanoacetylene, various heterocompounds, such as phosphines and silanes, have the potential to form adducts with cyanoacetylene.[8,9] With this in mind, we carried out a parallel theoretical study of the corresponding Si- and P-containing analogues. Furthermore, it is also interesting to investigate the effect that cyano substitution may have on the basicity and acidity of the corresponding vinyl derivatives CH_2=CH−X that were reported recently.[10–14]

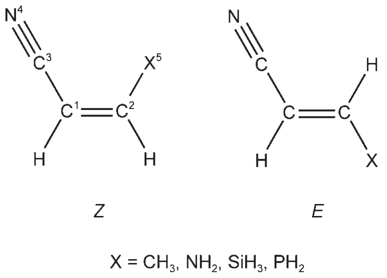
Results and Discussion

Experimental gas-phase acidities and basicities: All Fourier transform ion cyclotron resonance (FT-ICR) measurements were obtained at an ICR cell temperature of 338 K, as described in the Experimental Section. Literature values of gas-phase acidities and basicities of reference compounds[15] refer to the standard temperature of 298.15 K. The reported absolute acidities and basicities are not adjusted for the change from 338 to 298.15 K, because such corrections were assumed to be minor relative to other experimental uncertainties. The results of our gas-phase determinations are summarized in Tables 1 and 2 and comments regarding uncertainties in the experimental gas-phase acidities and basicities are given in the table footnotes.

Table 2. Experimental gas-phase basicities (GB) of aminoacrylonitrile and 2-butenenitrile [kJ mol^{-1}, 298.15 K].

B	Ref	GB(Ref)[a]	ΔGB[b]	GB(B)[c]
NH_2CH=CHCN	NH_3[d]	819.0	≤0	≤819
CH_3CH=CHCN	*n*PrCHO	760.8	+12.2	
	*n*PrCN	767.7	+5.81	
	*n*BuCN	771.7	+1.78	
	*i*PrCN	772.8	+3.20	
	*t*BuCN	780.2	−5.33	774.2 ± 1.1

[a] Reference [15]. [b] Gibbs free energies for the reaction $BH^+ + Ref \rightarrow B + RefH^+$ (338 K), in which RefH = reference acid. [c] No temperature correction; the indicated uncertainty corresponds to the standard deviation of the mean value of the five determinations enlarged by a factor of two, and represents the internal consistency. The uncertainty on the absolute values is in the order of 10 kJ mol^{-1}, that is, the average uncertainty of the basicity scale. [d] NH_3 was generated by the decomposition of NH_2CH=CHCN; see Experimental Section.



Scheme 1.

Structure, **relative stability**, **and bonding**: All compounds under scrutiny may exist in two different forms: the *Z* and the *E* isomer (Scheme 1). The total energies of all the neutral species investigated are given in Table S1 in the Supporting Information. For simplicity, the two isomers of the various structures investigated are named hereafter **XZ** and **XE** (X = CH_3, NH_2, SiH_3, PH_2). We denote the corresponding protonated and deprotonated species by adding H or A followed by a number that indicates the order of stability. For example, **NH_2ZH1** and **NH_2ZA1** are the most stable protonated and deprotonated forms, respectively, of the *Z* isomer of aminoacrylonitrile. The optimized geometries of all possible neutral species are shown in Figure 1. All of these species correspond to local minima on the potential energy surface (PES). In all cases, the *Z* isomer has a lower energy than the *E* isomer, as already found for aminoacrylonitrile.[16] This was attributed to an enhanced conjugation between the amino lone pair and the C=C π system in the former, and to an interaction between the nitrogen lone pair and the C=C π* antibonding orbital in the latter. Consistent with this, the C=C bond of the *Z* isomer (1.361 Å) is longer than that of the *E* isomer (1.356 Å), whereas the C−NH_2 bond in the former (1.358 Å) is shorter than that in the latter (1.364 Å), in agreement with an enhanced conjugative interaction between the amino-nitrogen lone pair and the π system. The same qualitative picture applies to the PH_2 derivative,

Table 1. Experimental gas-phase acidities (ΔG^0_{acid}) of aminoacrylonitrile and 2-butenenitrile [kJ mol^{-1}, 298.15 K].

AH	RefH	ΔG^0_{acid}(RefH)[a]	$\Delta\Delta G^0_{acid}$[b]	ΔG^0_{acid}(AH)[c]
NH_2CH=CHCN	cyclohexen-one-1	1464 ± 8.4	<0	bracketing
	PhOH	1432 ± 8.4	>0	1445 ± 22
		1426 ± 7.9		
CH_3CH=CHCN	MeSH	1467 ± 8.4	<0	bracketing
	EtSH	1460 ± 8.4	>0	1464 ± 4

[a] Reference [15]. [b] Gibbs free energies for the reaction $AH + Ref^- \rightarrow A^- + RefH$ (338 K), in which RefH = reference acid. [c] No temperature correction; the indicated uncertainty corresponds to the standard deviation between the limits of the bracketing, assuming a rectangular distribution, enlarged by a factor of two. The uncertainty on the absolute values is in the order of 10 kJ mol^{-1}, that is, the average uncertainty of the acidity scale.

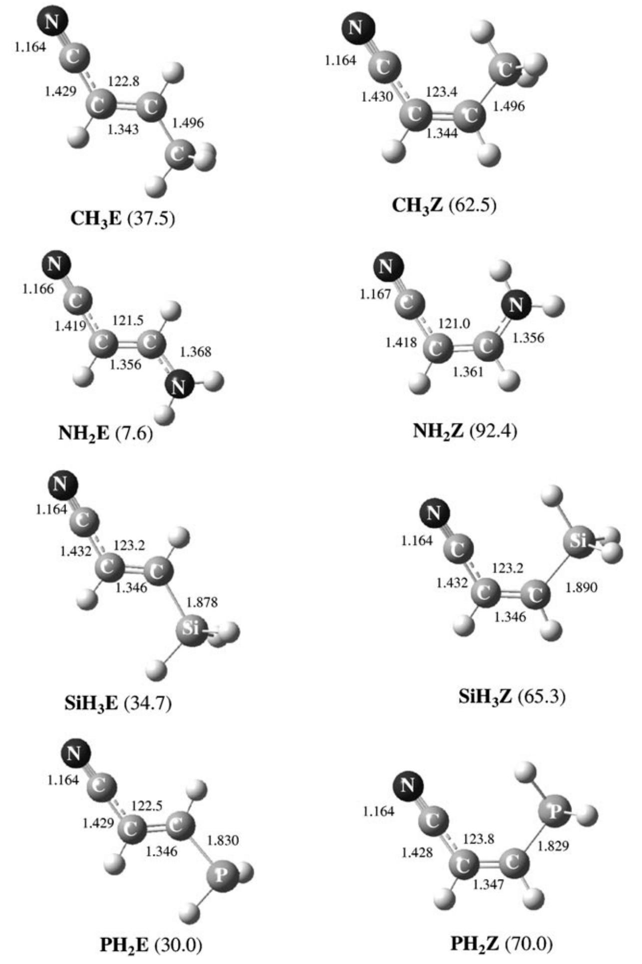


Figure 1. Optimized geometries (bond lengths [Å] and bond angles [°]) of different isomers of cyanovinyl derivatives. Numbers in parentheses indicate the percentage of each isomer present in the gas phase at 298.15 K.

although in this case, because the heteroatom is a second-row element, the conjugation is much weaker. Accordingly, although the *Z* isomer is still more stable than the *E* isomer, the respective lengthening and shortening of the C=C and C−P bonds upon going from the *E* to the *Z* isomer are much less (0.001 vs 0.005 Å and 0.001 vs 0.006 Å). The main consequence of these quantitative differences is that, although the *Z* isomer is predicted to be the dominant species (92 %) in the gas phase of aminoacrylonitrile, only 70 % of the species adopt this configuration in cyanovinylphosphine. These predictions for aminoacrylonitrile are in good agreement with the experimental abundances obtained after thermolysis at 750 °C under vacuo (95 % of isomer *Z*). The experimental values for cyanovinylphosphine (18 % of isomer *E*) are lower than the theoretical values, but they still show a clear increase in the amount of isomer *E* (see Table 3).

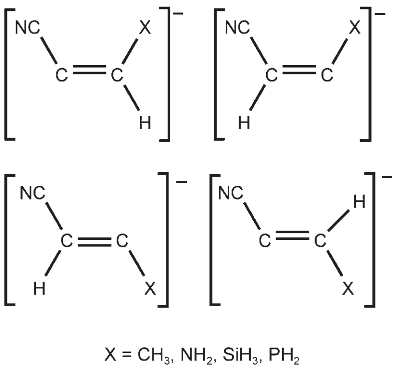
Results of a second-order natural bond order (NBO) analysis show that hyperconjugation of the methyl group with the C=C unsaturated moiety in the N≡C−CH=CH−CH$_3$ derivative is slightly more stabilizing for the *Z* isomer than for the *E* isomer, and accordingly, the former is 1.3 kJ mol^{-1} lower in energy than the latter. Consequently, the *Z* isomer is estimated to be only slightly dominant (62 %) in the gas phase, in fairly good agreement with the percentage of this isomer found after flash vacuum pyrolysis (FVP) of a sample (63 %). The hyperconjugation is rather weak, as expected, for the silyl derivative, however, the *Z* isomer is still slightly more stable in terms of Gibbs free energy, and should represent the 65 % of the species in the gas phase. As for the phosphorus derivative, agreement between experimental thermolysis measurements, which indicate the *Z* isomer to be present at ≈85 %, and theoretical estimates is not as good. Nevertheless, because we are dealing with rather small free-energy differences that are close to the average error of the theoretical scheme used, the theoretical percentages should be taken as a rough estimate of the real values.

Deprotonated species: The situation is completely different as far as the most stable deprotonated species are concerned. We investigated all possible anions, the total energies of which are summarized in Table S2 of the Supporting Information. In all cases, the loss of a proton from the substituent was much more favorable than deprotonation of the HC=CH group. Therefore, the anions shown in Scheme 2 should not be observed in the gas phase. On the other hand, if the proton is lost from the substituent, the *E* conformer is systematically more stable than the *Z* conformer (see Figure 2). More importantly, in all cases, the Gibbs free-energy gap is large enough so that only the *E* conformer should be observed in the gas phase at room temperature.

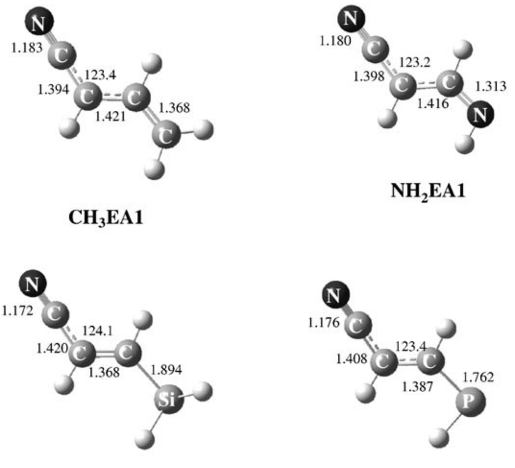
Table 3. Calculated gas-phase basicities (enthalpy, PA; Gibbs free energy, GB) and gas-phase acidities (enthalpy, ΔH^0_{acid}, Gibbs free energy, ΔG^0_{acid}). All values[a] are in kJ mol^{-1}. The last column gives the percentage[b] of each isomer in the gas phase at 298.15 K.

	PA	PA$_{av}$	GB	GB$_{av}$	ΔH_{acid}	$(\Delta H_{acid})_{av}$	ΔG_{acid}	$(\Delta G_{acid})_{av}$	%
CH$_3$Z	808.7 (828.1)	809.4	779.5	780.3	1506.7 (1485.0)	1506.2	1475.9	1475.4	62 (63)
CH$_3$E	809.9		780.8		1505.5		1474.6		37 (36)
NH$_2$Z	853.6 (876.6)	854.2	821.5	822.1	1467.5 (1445.8)	1466.9	1437.0	1436.4	92 (95)
NH$_2$E	861.9		829.9		1459.2		1428.6		8 (5)
SiH$_3$Z	796.2 (811.8)	796.8	766.9	768.7	1486.1 (1473.7)	1485.5	1455.6	1453.5	65 (85)
SiH$_3$E	799.0		768.5		1484.1		1448.6		35 (15)
PH$_2$Z	803.8 (828.0)	804.4	775.4	776.3	1407.9 (1395.6)	1407.3	1378.5	1377.9	70 (82)
PH$_2$E	805.8		777.4		1405.9		1376.5		30 (18)

[a] Values calculated at the G3B3 level of theory. Values in parenthesis were obtained at the B3LYP7/6-311+G(3df,2p) level. Average PAs were obtained by taking account of the Boltzmann distribution at 298.15 K for the different neutral and protonated isomers. Average gas-phase acidities only take account of the distribution of the different neutral isomers because all anions are exclusively in the *E* form. [b] Values calculated by using Gibbs free energies evaluated at the G3B3 level. Values in parenthesis were obtained from experimental thermolysis measurements.



Scheme 2.



CH$_3$EA1 **NH$_2$EA1** **SiH$_3$EA1** **PH$_2$EA1**

Figure 2. Optimized geometries (bond lengths [Å] and bond angles [°]) of the most stable deprotonated structures of cyanovinyl derivatives.

Because the *Z* isomer is dominant in the gas phase of all neutral compounds investigated, this implies that the formation of the most stable deprotonated species requires an isomerization of the system through an internal rotation around the C=C double bond. To assess whether this *Z*–*E* isomerization of the anion can occur under normal ICR conditions, we evaluated the corresponding energy barrier by using aminoacrylonitrile as a suitable model compound. The activation barrier, estimated at the G3B3 level, is 60 kJ mol^{-1}. As previously suggested,[17,18] one may reasonably guess that this energy is provided by the strong interactions (hydrogen bonds and ion–dipole) that, under normal experimental conditions, occur between the neutral and deprotonated bases. These interaction energies are typically[15] between 70 and 125 kJ mol^{-1}. Therefore, we can safely assume that the anion formed in the deprotonation process of the *Z* isomer will have sufficient internal energy to rearrange to the most stable *E* isomer.

The most significant structural effects upon deprotonation are observed for the methyl and the amino derivatives. Loss of a proton from the amino group of aminoacrylonitrile leads to an enhancement in conjugation of the remaining imino group with the C=C moiety. In the second-order NBO analysis, this is viewed as a stronger donation from the imino-nitrogen lone pairs to the π_{CC}^* antibonding orbital, which is reflected in an increase in the electron density at the C−NH bond and in a concomitant decrease at the C=C bcp (bcp = bond critical point; see Figure 3). In agreement with this, the C−NH bond shortens by 0.055 Å and the C=C bond lengthens by 0.012 Å. This effect is even more dramatic for the methyl derivative, because of the large increase in conjugation triggered by the carbon lone-pair created by deprotonation of the methyl group. The obvious consequence is that the C−C single bond acquires significant double-bond character, as evidenced by a shortening of 0.128 Å and an increase in the electron density at the bcp of 0.06 a.u. (See Figure 3). This conjugation significantly populates the π_{CC}^* antibonding orbital, and consequently, the charge density at the bcp decreases by 0.05 a.u., and the ethylenic bond lengthens by 0.078 Å. Similar effects to those described above for aminoacrylonitrile, although quantitatively weaker, are observed for the phosphorus derivative. The silicon derivative behaves in a very different fashion to the carbon derivative, because conjugation between the silicon lone pair and the C=C π system is much less efficient, and deprotonation leads to a small lengthening of both C−Si and C−C bonds.

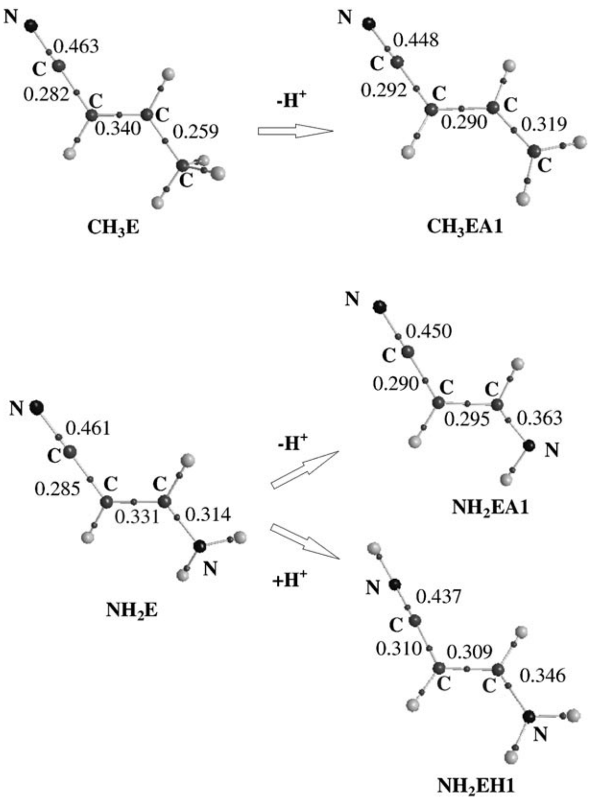
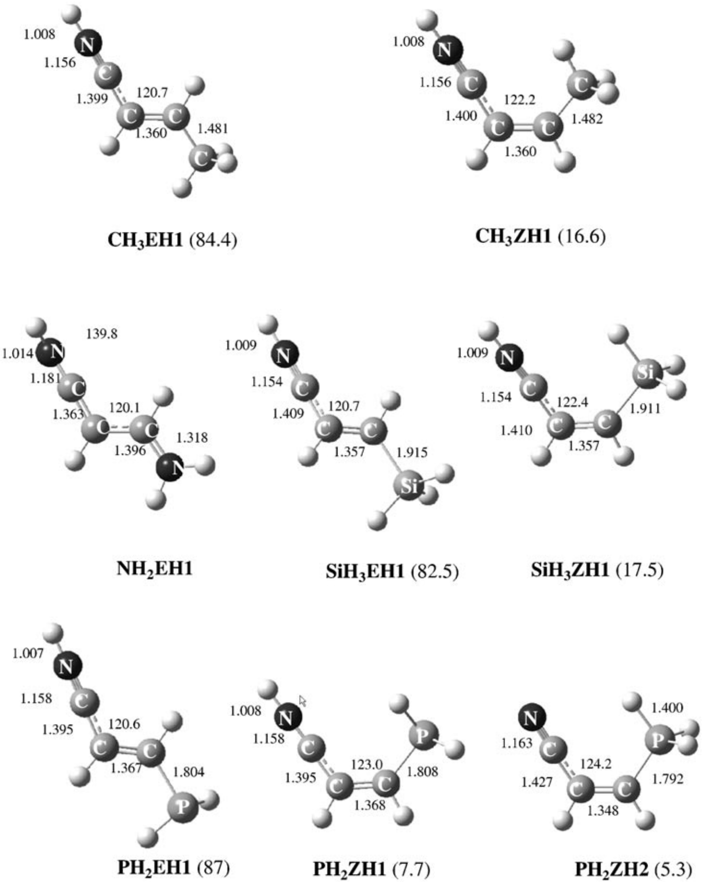


Figure 3. Molecular graphs of **CH$_3$E** and its most stable deprotonated species, and **NH$_2$E** and its most deprotonated and protonated forms. Charge densities at the bcps (small spheres) are in a.u.

Protonated species: Protonation takes place preferentially at the cyano group, the protonation at the ethylenic (unsaturated) carbon atoms being less favorable (see Table S3). This is at variance with the behavior of the vinyl compounds $CH_2{=}CH{-}X$ that were found to be carbon bases.[10–14] In all cases, the *E*-protonated isomers are predicted to be lower in energy than the corresponding *Z* conformers. There are, however, some quantitative differences, depending on the nature of the substituent. For $X = NH_2$, 100% of the protonated species should correspond to the *E* isomer, but for the remaining X substituents, some proportion of the *Z*-protonated isomers are predicted to coexist at room temperature (Figure 4). The fact that aminoacrylonitrile is protonated preferentially at the cyano group may be surprising, as hydrogen cyanide is a much weaker base (gas-phase basicity, GB = 712.9 kJ mol^{-1}) than ammonia (GB = 853.6 kJ mol^{-1}). However, in the case of hydrogen-bond formation between OH acids (another type of acid/base interaction) and cyano bases, a similar preference for association to the CN group has been reported.[19,20] If an amino group is either directly linked to the cyano function (cyanamides), or connected through a double bond (C=C or C=N), or by a benzene ring (1,4 positions), the strong conjugation between the electron-donating nitrogen and the strong electron-withdrawing cyano group induces the so-called "push–pull effect". These conclusions were reached from the analysis of crystallographic data, spectroscopic shifts, association-constant measurements, and ab initio calculations.[19,20]



CH$_3$EH1 (84.4) **CH$_3$ZH1** (16.6)

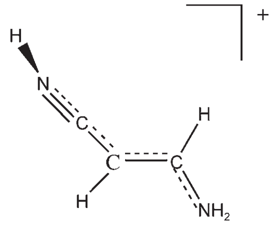
NH$_2$EH1 **SiH$_3$EH1** (82.5) **SiH$_3$ZH1** (17.5)

PH$_2$EH1 (87) **PH$_2$ZH1** (7.7) **PH$_2$ZH2** (5.3)

Figure 4. Optimized geometries (bond lengths [Å] and bond angles [°]) of the most stable protonated forms of cyanovinyl derivatives. Numbers in parentheses indicate the percentage of each isomer present in the gas phase at 298.15 K.

Returning to proton transfer in the gas phase, an ab initio study of $Me_2N{-}CH{=}N{-}CN$ concluded that the *N*-cyano atom is the most basic among the three nitrogen sites.[21] A similar effect was observed for anilines: from an analysis of the substituent effect on their gas-phase basicity, it was concluded that 4-cyanoaniline and 4-nitroaniline are protonated on the cyano and on the nitro groups, respectively, rather than on the amino nitrogen.[22] Another electronic push–pull system related to aminoacrylonitrile is 3-aminocyclohex-2-enone (and *N*-alkyl derivatives), which is protonated on the carbonyl group either in the gas phase or in aqueous solution. Owing to the strength of their push–pull effect, aminocyclohexenones are among the strongest carbonyl bases known.[23]

All these observations related to the basic site of push–pull systems are a direct consequence of the conjugation of the amino lone pair with the cyano group (or another strong electron acceptor) through a C=C or benzene link. Actually, protonation of the nitrogen in the cyano group of aminoacrylonitrile leads to dramatic geometrical changes that are not observed for the other derivatives. The first significant difference affects the local structure of the C−N−H group, which is linear for all protonated systems, except in **NH$_2$EH1**, for which an angle of 139.8° is predicted. This indicates a drastic reorganization of the bonding in the system upon protonation. As shown in Figure 3, the charge density at the bond critical points (bcps) of the C≡N and C=C bonds decreases significantly on going from **NH$_2$E** to **NH$_2$EH1**, whereas that at the formally single bonds C−C and C−N bcps also increases appreciably. In agreement with this, a NBO analysis indicates that these bonds acquire double-bond character. A second-order perturbation analysis also shows strong interactions between the atomic orbitals of C1 and the C3–N4 and C2–N6 antibonding orbitals (numbering as in Scheme 1). Both analyses indicate that an adequate description of the bonding of **NH$_2$EH1** is that presented here.



Calculated gas-phase basicities and acidities: The calculated gas-phase basicities (enthalpy, PA; Gibbs free energy, GB) and acidities (enthalpy, ΔH^0_{acid}; Gibbs free energy, ΔG^0_{acid}) of the compounds under investigation are summarized in Table 3. The first conspicuous fact is that the compounds under investigation have rather similar gas-phase PAs or GBs of ≈800 kJ mol^{-1} and 780 kJ mol^{-1}, respectively, indicating that the influence of the substituents on the intrinsic basicity of the cyano group is rather weak. However, aminoacrylonitrile has larger PA and GB than the other compounds, reflecting the resonance stabilization of the protonated form discussed above. The silicon derivative has a slightly lower PA and GB than the other compounds, which probably reflects the lack of hyperconjugation between a silyl group and the unsaturated moiety. Because the corresponding vinyl compounds $CH_2{=}CH{-}X$ are carbon bases (see above)[10–14] no correlation exists between their PAs or GBs and those of their cyano derivatives. Nevertheless, with the exception of aminoacrylonitrile that displays an enhanced gas-phase basicity as described above, all cyano derivatives are weaker bases than the unsubstituted vinyl derivatives.[10–14]

Unfortunately, accurate experimental basicities were obtained only for cyanopropene, because aminoacrylonitrile decomposes under normal ICR conditions with loss of NH_3 (see Experimental Section). Taking into account the experimental and calculations errors, an upper GB limit of 819.0 kJ mol^{-1} for this compound can be considered satisfactory. The agreement between the calculated and the experimental basicity for $NC{-}CH{=}CH{-}CH_3$ is very good.

It is also observed that values calculated at the B3LYP level are systematically larger than G3B3 values. Similar findings have already been reported;[24,25] however, it is worth noting that for cyanovinyl derivatives, the differences between both sets of values is quite large, ranging from 13 to 29 kJ mol^{-1}. Furthermore, a linear correlation between both sets of values ($PA_{G3B3} = 1.0704\ PA_{B3LYP} - 35.843$) gives a slope greater than unity, a significant intercept, and a relatively low correlation coefficient ($r = 0.974$).

As far as the gas-phase acidities are concerned, the calculated values are in reasonably good agreement with the experimental values, which indicates that cyanovinyl derivatives have an enhanced intrinsic acidity (i.e., decrease in ΔH^0_{acid} or ΔG^0_{acid}) with respect to the corresponding $CH_2{=}CH{-}X$ vinyl compounds. The acidity strengthening lies between 70 kJ mol^{-1} for the SiH_3 derivative and 120 kJ mol^{-1} for the CH_3 derivative.

To gain some insight into the origin of this acidity strengthening, we employed the following isodesmic reactions:

Reaction (1) was devised to measure the effect of the CN substituent on the relative stability of neutral species, whereas Reaction (2) is a means to evaluate this effect on the corresponding anion produced by deprotonation of the substituent. The results obtained at the G3B3 level are summarized in Table 4, and indicate that the CN group stabilizes both the neutral and the anionic species; however, the latter effect is much larger than the former, leading to a significant acidity enhancement. Notably, this enhancement is greater for first-row than for second-row substituents.

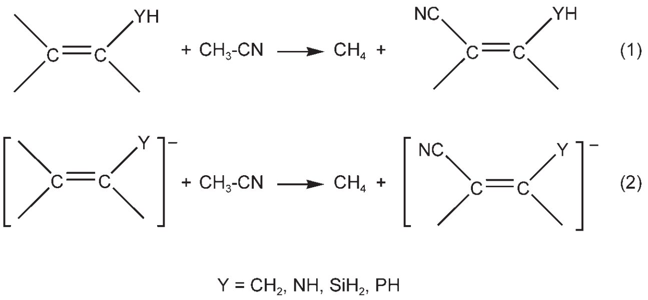


Table 4. Calculated enthalpy (ΔH^0) for the isodesmic reactions (1) and (2), as well as the calculated acidity strengthening triggered by cyano substitution. All values are in kJ mol^{-1}.

Substituent	Calculated enthalpy Reaction (1)	 Reaction (2)	Acidity strengthening
CH_3	20	152	132
NH_2	36	147	111
SiH_3	15	88	73
PH_2	13	113	100

Conclusion

The neutral cyanovinyl derivatives ($N{\equiv}C{-}CH{=}CH{-}X$, $X = CH_3, NH_2, SiH_3, PH_2$) may exist in two forms: the *Z* isomer and the *E* isomer. From the results of our study, we can conclude that the *Z* isomer is more stable in energy than the *E* isomer in all cases, although the percentage of *E* isomer at room temperature can be significant. The situation is completely different as far as the most stable protonated and deprotonated species are concerned. In all cases, the loss of the proton from the substituent X was much more favorable than deprotonation of the HC=CH group, with the *E* conformer being much more stable than its *Z* isomer so that only the former should exist in the gas phase at room temperature. The most significant structural changes upon deprotonation are observed for the methyl and amino derivatives because, in both cases, deprotonation of the substituent leads to a significant charge delocalization in the corresponding anion, which is particularly important in the case of the methyl derivative. Protonation takes place systematically at the cyano group, whereby the *E* conformer is again more stable than its *Z* isomer. The fact that aminoacrylonitrile protonates preferentially at the cyano group may be considered surprising, but this can be rationalized on the basis of an electronic "push–pull" effect that leads to strong stabilization by resonance of the corresponding protonated species. This is reflected in the relatively high basicity of this derivative with respect to the other members of the series we examined. In fact, all compounds, with the exception of aminoacrylonitrile, exhibit rather similar gas-phase basicities, indicating that the different nature of the substituents has a weak effect on the intrinsic basicity of the cyano group.

The cyanovinyl derivatives have a stronger gas-phase acidity than the corresponding $CH_2{=}CH{-}X$ vinyl compounds. This acidity enhancement reflects the fact that cyano substitution stabilizes the anion much more than the corresponding neutral compound.

Experimental Section

Materials: Crotononitrile (2-butenenitrile) was purchased from Aldrich. Aminoacrylonitrile (3-amino-2-propenenitrile) was synthesized from cyanoacetylene, which was obtained by treatment of the corresponding amide with P_4O_{10},[26] as reported.[16] 3-Phosphino-2-propenenitrile and 3-silyl-2-propenenitrile were prepared as reported.[8] Only analytical samples of the crude products were obtained, with acrylonitrile, cyanoacetylene, and hydrogen cyanide as impurities. These crude mixtures, as well as pure samples of 3-amino-2-propenenitrile or crotononitrile, were thermolyzed at 750 °C in vacuum (10^{-1} mbar) (flash vacuum pyrolysis (FVP)) to determine experimentally the thermodynamic *E*/*Z* ratio. For this purpose, the nitrile (10 mg) was vaporized in a vacuum line (10^{-1} mbar) equipped with a short oven (15 cm) heated to 750 °C. The products were collected on a cold finger (77 K), and an NMR solvent ($CDCl_3$, 1 mL) was added. The mixture was transferred to a cooled NMR tube (77 K) and kept at this temperature. Analysis was performed at −50 °C and then at RT. The same *E*/*Z* ratios were obtained at both temperatures for all samples. Tertiary butyl nitrite and reference acids and bases were commercial compounds (Aldrich, Fluka) of the best available purity, and were used as supplied, apart from several freeze-pump-thaw cycles in the spectrometer inlet to remove gases and volatile impurities.

FT-ICR measurements: The general methodology for gas-phase acidity and basicity measurements[15,27] is very similar to that used in previous work[11,12,14] and is described briefly. Measurements were conducted by using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. For acidity determinations, negative ions were generated by proton abstraction from the neutral reactant by $t\mathrm{BuO}^-$, which was obtained through dissociative electron capture of *t*BuONO (partial pressure $\approx 10^{-5}$ Pa) at a nominal energy of 0.1 eV. Aminoacrylonitrile decomposed in the spectrometer inlet that was heated to a temperature necessary to obtain a significant signal. This decomposition generated a large excess of ammonia. As the partial pressure of the compound could not be determined, it was not possible to determine the proton-transfer equilibrium. The gas-phase acidity was estimated from bracketing experiments. Ammonia did not interfere in bracketing experiments, owing to its very weak acidity. A mixture of $NC{-}CH{=}CH{-}NH_2$ and a reference acid (RefH) were introduced into the FT-ICR spectrometer at pressures between 10^{-5} and 10^{-4} Pa. One of the ions, Ref^- or $[NC{-}CH{=}CH{-}NH]^-$, generated by reaction with $t\mathrm{BuO}^-$, was isolated carefully by means of ejection pulses, and the reformation of the other ion was monitored for several seconds. A qualitative acidity order, given in Table 1, was obtained from the disappearance of the selected ion and the appearance of its competitor, or from the absence of significant proton transfer. In the case of $NC{-}CH{=}CH{-}CH_3$, equilibrium conditions could not be reached either, due to the formation of CN^-, and a similar bracketing method was applied for this compound too. For basicity measurements on aminoacrylonitrile, the presence of a large proportion of ammonia in the vapors introduced in the spectrometer hampered the determination of equilibrium constants, because of NH_4^+ formation. Nevertheless, the mass spectra recorded after a delay of several seconds, to allow for ion/molecule reactions, showed a persistent signal for protonated aminoacrylonitrile. This observation led us to conclude that this compound was a somewhat weaker base than ammonia (although probably of similar basicity), which places an upper limit of 819.0 kJ mol^{-1} for GB(aminoacrylonitrile). Determination of crotononitrile basicity was possible by determination of accurate proton-transfer equilibrium constants with five reference bases. Variable pressure ratios between the nitrile and the reference compound were used (three to five experiments for each reference), with total pressures (read by using a Bayard–Alpert ion gauge) in the range of 10^{-5} to 10^{-4} Pa. The five relative basicities were combined with the absolute GB values,[15] leading to five values that are in good agreement. A detailed description of the methodology used for gas-phase basicity determinations is given in a recent paper.[28]

Computational details: The geometries of the neutral, protonated, and deprotonated forms of substituted acrylonitrile ($N{\equiv}C{-}CH{=}CH{-}X$, X = CH_3, NH_2, SiH_3, PH_2) derivatives were optimized by using the B3LYP density functional theory (DFT) approach, together with a 6-31G(d) basis-set expansion. The good performance of this theoretical scheme in obtaining reliable geometries and vibrational frequencies is well documented.[29–36] Harmonic vibrational frequencies were obtained at the same level of theory to classify the stationary points as local minima or as transition states and to estimate the corresponding zero-point energies (ZPE). The B3LYP approach includes Becke's three-parameter nonlocal hybrid-exchange potential[37] and the nonlocal correlation functional of Lee, Yang, and Parr.[38] Final energies were obtained by using the G3B3 approach[36] that employs the aforementioned optimized geometries and frequencies and assures good accuracy, with a mean absolute deviation from the experimental value of 6.0 kJ mol^{-1}. All these calculations were carried out by using the Gaussian 03 series of programs.[39] The proportion in which the different isomers are present in the gas phase was obtained by assuming a Boltzmann-type distribution and by using the Gibbs free energies at 298.15 K, calculated at the G3B3 level.

A second-order perturbation NBO analysis[40] was carried out to analyze the relative stabilities of the *Z* and *E* isomers of each of the derivatives investigated. This analysis was complemented with that performed in terms of the atoms in molecules (AIM) theory.[41] For this purpose, we located the corresponding bond critical points (bcps), whose electron density is a good measure of the strength of the linkage.

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