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Cyano substituent effects on enol and enethiol acidity and basicity: The protonation and deprotonation of 3-hydroxy-2-propenenitrile and its thio analogue

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Abstract

The gas-phase basicity and acidity of 3-hydroxy-2-propenenitrile (3-hydroxyacrylonitrile) and its sulfur-containing analogue, 3-mercapto-2-propenenitrile, have been determined by means of high-level G3B3 ab initio calculations and, in the case of the latter compound, compared with the experimental values obtained by means of FT-ICR mass spectrometry techniques, and with previous reported values for the N≡C–CH=CH–X (X = CH_3, NH_2, SiH_3, PH_2) analogues. For both compounds the *Z*-isomer is the dominant species in the gas-phase. Protonation takes place in both cases at the cyano group. The loss of the proton from the substituent, was found to be systematically much more favorable than the deprotonation at the HC=CH group. 3-Hydroxy-2-propenenitrile is predicted to be a stronger base by ca. 5 kJ mol^{-1} than its thio analogue, but a weaker acid by 26 kJ mol^{-1}. Both compounds are stronger acids than the corresponding unsubstituted vinyl compounds, because cyano substitution stabilizes much more the deprotonated species than the corresponding neutral compound. There is a clear disagreement between our theoretical estimates for both the gas-phase basicity and the gas-phase acidity of 3-mercapto-2-propenenitrile and the corresponding experimental values, which is consistent with its isomerization to yield isothiazole.

Keywords: Gas-phase basicity and acidity; Cyano substituent effect; Ab initio calculations; Hydroxyacrylonitrile; 3-Mercapto-2-propenenitrile

1. Introduction

The development of gas-phase ion chemistry in the last three decades of the 20th century led to a significant change in our view of chemical reactivity. The absence of solute–solvent and counter-ion interactions revealed the existence of reactivity trends which were very different to those usually accepted and obtained in condensed media. As a consequence, a great deal of effort was concentrated in determining intrinsic reactivities, in particular intrinsic basicities and acidities. Comprehensive compilations of these data, as those carried out by Lias et al. [1–4] were a fundamental tool for the further development of this field. Our research groups have been interested along the last years in measuring and rationalizing the intrinsic basicities and acidities of different series of unsaturated hetero-compounds, containing heteroatoms from the first, second and third row, in an effort to establish basicity and acidity trends and to gain some insight on the peculiarities exhibited by these compounds when the heteroatom belongs to the first row of the periodic table [5–10].

Very recently we undertook the investigation of the gas-phase protonation and deprotonation of acrylonitrile derivatives N≡C–CH=CH–X (X = CH_3, NH_2, PH_2, SiH_3) [10], because, among other things, the cyanoacetylene precursor, a compound detected in the interstellar media, comets and planetary atmospheres [11–13], is supposed to be a good starting material for the formation of new more complex astrochemical species [11]. On the other hand, these robust compounds present particular properties of reactivity and kinetic stability. These studies showed that the presence of the cyano group in acrylonitrile

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derivatives induces dramatic changes with regards to the vinyl compounds from which they can be derived. For example, while vinylamine (H_2C=CH–NH_2) is unstable at −80 °C in the condensed phase, cyanovinylamine is a kinetically stable compound. Also, cyanovinyl derivatives have a significantly stronger gas-phase acidity than that of the corresponding vinyl compounds CH_2=CH–X [10], due to the larger stabilization of the anion with respect to the corresponding neutral compound, triggered by the presence of the cyano group.

The aim of this paper is to extend this investigation to the oxygen and sulfur-containing derivatives, 3-hydroxy-2-propenenitrile (3HPN) (also known as 3-hydroxyacrylonitrile) and 3-mercapto-2-propenenitrile (3MPN), for which there is a complete lack of experimental and theoretical information.

2. Experimental

2.1. Preparation of cyanoacetaldehyde and 3-hydroxy-2-propenenitrile

As already reported [14], the flash vacuum pyrolysis of 5-(*N*-*t*-butyl)-aminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione led, in the condensed phase, to a complex mixture of compounds containing cyanoacetaldehyde and *Z*- and *E*-3-hydroxy-2-propenenitriles. The purification is really difficult and led to an important loss of product. We found that the commercially available isoxazole was a much efficient precursor. The flash vacuum pyrolysis at 770 °C of isoxazole gave a mixture of isoxazole precursor (24%), acetonitrile (41%) and cyanoacetaldehyde (35%). Using a cold trap at −42 °C after the oven, we thus selectively trap the cyanoacetaldehyde which is obtained in pure form in a 32% yield. The aldehyde/alcohol ratio determined by ^{1}H NMR spectroscopy is strongly dependent on the NMR solvent. Since only ^{1}H NMR data have been partially reported in the literature [14], complete ^{1}H and ^{13}C NMR spectra are given below.

Unfortunately, it was not possible to investigate the gas-phase acidity and basicity of 3-hydroxy-2-propenenitrile, because, as mentioned above, the product obtained is a mixture of the aldehyde and the alcohol, in which the former is the major component. As a matter of fact, our G3B3 calculations predict the aldehyde to be 6.4 kJ mol^{-1} more stable than the alcohol in terms of free energies. Hence, at room temperature, the mixture obtained should contain only 7.2% of 3-hydroxy-2-propenenitrile, and it was not possible to separate the two isomers.

2.2. Cyanoacetaldehyde

^{1}H NMR (CD_3CN) δ 3.75 (d, 2H, $^3J_{HH}$ = 1.0 Hz, CH_2); 9.45 (t, 1H, $^3J_{HH}$ = 1.0 Hz, CH(=O)). ^{13}C NMR (CD_3CN) δ 32.0 (CH_2–CN); 114.0 (s, CN); 190.5 (CH(=O)). 3-Hydroxy-2-propenenitrile. (*Z*) ^{1}H NMR (CD_3CN) δ 4.43 (d, 1H, $^3J_{HH}$ = 6.4 Hz, CH–CN); 7.16 (d, 1H, $^3J_{HH}$ = 6.4 Hz, CH–O) 8.5–9.0 (brd, 1H, OH). ^{13}C NMR (CD_3CN) δ 75.0 (CH–CN); 117.5 (CN); 160.0 (CH–O). (*E*) ^{1}H NMR (CD_3CN) δ 4.80 (d, 1H, $^3J_{HH}$ = 12.7 Hz, CH–CN); 7.37 (d, 1H, $^3J_{HH}$ = 12.7 Hz, CH–O); 8.5–9.0 (brd, 1H, OH). ^{13}C NMR (CD_3CN) δ 72.4 (CH–CN); 118.1 (CN); 162.2 (CH–O).

2.3. Preparation of 3-mercapto-2-propenenitrile

The 3-(*t*-butylthio)-2-propenenitrile [15,16] (200 mg) was vaporized in a vacuum line (10^{-1} mbar) equipped with a short oven heated at 750 °C and two traps. The first trap at room temperature removed the oligomeric products and the thiol was selectively condensed in the second trap cooled at −100 °C. The temperature of −100 °C was determined to trap the kinetically unstable thiol and to avoid the condensation of the isobutene formed in the pyrolysis. This trap was then disconnected from the vacuum line by stopcocks and adapted to the mass spectrometer for ICR experiments. The distillation in vacuo of 3MPN led to an important loss of product, most of the product being decomposed in unidentified oligomeric products before vaporization. To record the NMR spectra, this cell was fitted on a vacuum line equipped with a cold finger (cooled at 77 K) and equipped at the bottom with an NMR tube. The pure thiol was condensed with an NMR solvent ($CDCl_3$, 1 mL) on this cold finger and the solution was then transferred in an NMR tube and kept at low temperature (−50 °C) before analysis. Without distillation, the washing of the cell under nitrogen with an NMR solvent gave a better yield of product. 3-Mercapto-2-propenenitrile was obtained in a 77% yield in an 8:1/*Z*:*E* ratio.

(*Z*) ^{1}H NMR ($CDCl_3$) δ 4.17 (d, 1H, $^3J_{HH}$ = 12.8 Hz, SH); 5.44 (d, 1H, $^3J_{HH}$ = 10.4 Hz, CH–CN); 7.06 (dd, 1H, $^3J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 10.4 Hz, CH–S). ^{13}C NMR ($CDCl_3$) δ 95.3 (d, $^1J_{CH}$ = 180.7 Hz, CH–CN); 115.3 (CN); 143.2 (d, $^1J_{CH}$ = 175.9 Hz, CH–S). (*E*) ^{1}H NMR ($CDCl_3$) δ 3.67 (d, 1H, $^3J_{HH}$ = 11.3 Hz, SH); 5.48 (d, 1H, $^3J_{HH}$ = 15.9 Hz, CH–CN); 7.28 (dd, 1H, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 11.3 Hz, CH–S). ^{13}C NMR ($CDCl_3$) δ 96.5 (d, $^1J_{CH}$ = 179.9 Hz, CH–CN); 116.4 (CN); 144.3 (d, $^1J_{CH}$ = 176.7 Hz, CH–S). IR (film, 77 K) ν (cm^{-1}): 3063 ($\nu_{C=C-H}$), 2546 (ν_{S-H}), 2214 (ν_{CN}), 1633 ($\nu_{C=C}$). HRMS calcd for C_3H_3NS: 84.9986. Found: 84.9993. The half-life of 3MPN (5% diluted in $CDCl_3$) is of the order of about 1 day at room temperature in the presence of small amounts of duroquinone, a radical inhibitor.

3. FT-ICR measurements

The general methodology for gas-phase acidity and basicity measurements [7,17] is very similar to that used in previous works [6,7,9] and is briefly described. Measurements were conducted on an electromagnet Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. As indicated above, for 3HPN, no gas-phase investigations were carried out. For the acidity determination of 3-mercapto-2-propenenitrile, negative ions were generated by proton abstraction from the neutral reactant by tBuO$^-$, which was obtained through dissociative electron capture of tBuONO (partial pressure of about 10^{-5} Pa) at a nominal energy of 0.1 eV. One of the ions Ref$^-$ or [NC–CH=CH–S]$^-$ generated by reaction with tBuO$^-$, was carefully isolated using ejection pulses, and the reformation of the other ion was mon-

Table 1
Bracketing of experimental gas-phase acidity and basicity of HSCH=CHCN (kJ/mol, 298.15 K)

RefH	$\Delta_{acid}G^{\circ}$(RefH)[a]	$\Delta\Delta_{acid}G^{\circ}$[b]	$\Delta_{acid}G^{\circ}$(AH)[c]
Acidity			
2,5-$(CH_3)_2C_6H_3CO_2H$	1391 ± 8.4	<0	1384 ± 16.5
$ClCH_2CO_2H$	1377 ± 8.4	>0	
Ref	**GB(Ref)[a]**	**ΔGB[d]**	**GB(B)[c]**
Basicity			
Pyrrole	843.8 ± 8	>0	851 ± 16.8
2-Methylaniline	859.1 ± 8	<0	

[a] Refs. [3] and [17].
[b] Gibbs energies for the reaction $AH + Ref^- \rightarrow A^- + RefH$ (338 K).
[c] No temperature correction; the indicated uncertainty comprises the uncertainty linked to the bracketing obtained from the standard deviation between the limits of the bracketing, assuming a rectangular distribution, enlarged by a factor of 2, and the uncertainty on the absolute scale.
[d] Gibbs energies for the reaction $BH^+ + Ref \rightarrow B + RefH^+$ (338 K).

itored for several seconds. In all experiments we observed the formation of CN^- and equilibrium was not obtained. The gas-phase acidity was therefore estimated by bracketing. The acidity 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. Bracketing was also used for basicity determination of the thio derivative, but without the use of a reactant gas [10,18]. All FT-ICR measurements were obtained at an ICR cell temperature of 338 K. Literature values of gas-phase acidities and basicities of reference compounds [17] 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, as such corrections were assumed to be minor with respect to other experimental uncertainties. The results of our gas-phase determinations are reported in Table 1.

4. Computational details

Although we did not acquired experimental thermochemical data for the hydroxy derivative, we carried out calculations for both the thio and hydroxy derivatives.

Neutral, protonated and deprotonated forms of (N≡C–CH=CH–XH, X = O, S) were investigated in the framework of the G3 theory, which usually leads to average errors in the calculation of most thermodynamic properties smaller than 4 kJ mol^{-1}. Among the different G3 approaches available, we have chosen the G3B3 formalism, in which B3LYP/6-31G* geometries are used. This usually enhance the good performance of this theoretical scheme, since it provides geometries and vibrational frequencies which are superior [19–24] to those obtained with other correlated formalisms, such as the MP2 method. The B3LYP approach includes the Becke's three parameter non-local hybrid exchange potential [25] and the non-local correlation functional of Lee et al. [26]. Harmonic vibrational frequencies were used to classify the stationary points as local minima or transition states as well as to estimate the corresponding zero point energies (ZPE). All these calculations have been carried out by using the Gaussian-03 series of programs [27]. The proportion in which the different isomers can be found in the gas-phase was obtained assuming a Boltzmann-type distribution and using the G3B3 calculated free energies at 298.2 K.

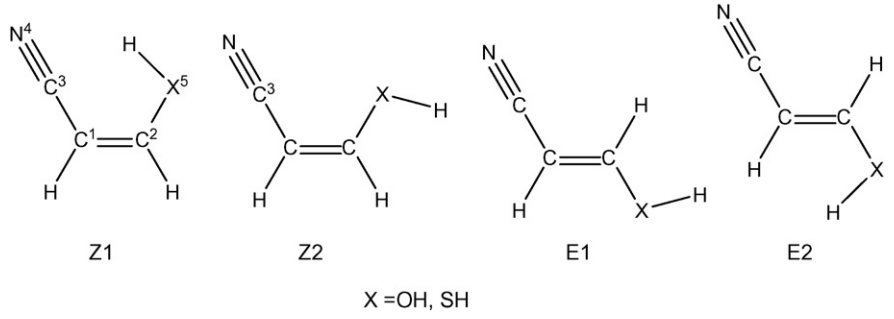
A second order perturbation NBO analysis [28] was carried out in order to analyze the relative stability of the *Z*- and *E*-isomers for each of the two derivatives investigated.

5. Results and discussions

5.1. Structure, relative stability and bonding

Both 3HPN and 3MPN may exist in two different forms, the *Z*- and the *E*-isomer, and each of these two isomers presents, in addition, two different conformations depending on the relative orientation of the O–H or S–H group (see Scheme 1).

The total enthalpies and free energies of all the neutral species investigated are given in Table S1 of the supplementary data. This table also contains similar information for the most stable protonated and deprotonated species. For the sake of clarity, the two isomers of the different structures investigated will be named as XZ and XE where X = O for the oxygen derivative and X = S for the sulfur-containing compound, followed by a number which indicates the stability order of the different conformers. The corresponding protonated and deprotonated species will be designated by inserting H or A in the previous acronyms. For instance, OZH1 and OZA1 will designate the most stable protonated and deprotonated forms, respectively, of the *Z*-isomer of 3-hydroxy-2-propenenitrile. The optimized geometries of all possible conformers of the neutral species have been schematized in Fig. 1, and all of them correspond to local minima of the potential energy surface (PES). For both compounds, and



Scheme 1.

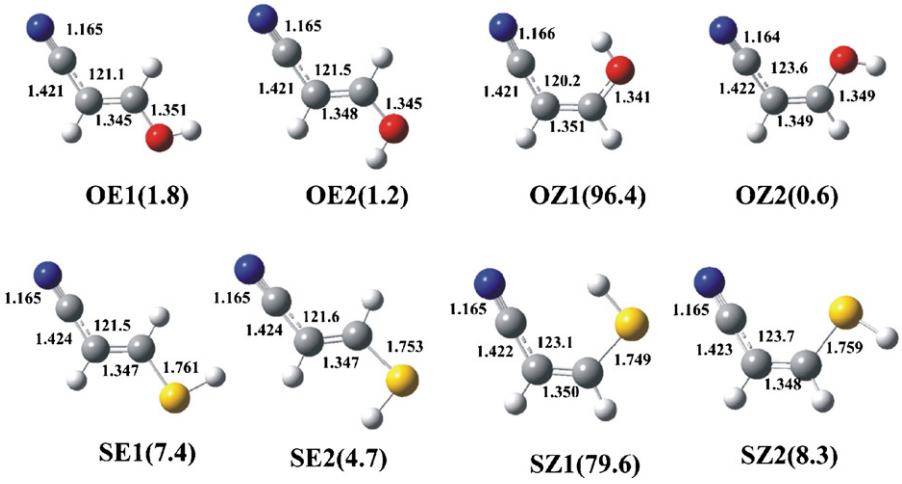


Fig. 1. Optimized geometries of the different isomers of 3-hydroxy-2-propenenitrile (3HPN) and 3-mercapto-2-propenenitrile (3MPN). Bond lengths are in Å and bond angles are in degrees. The number within parenthesis by the acronym of each isomer indicates the percentage of that isomer present in the gas-phase at room temperature (298 K).

similarly to what was found previously for other members of this series, the global minimum of the PES corresponds to a *Z*-isomer, the most stable conformer being that in which the X–H group is *cis* with respect to the cyano group. Similarly to what has been reported for cyanovinylamine [29], the enhanced stability of this conformer is the result of a better conjugation of the heteroatom (O, S) lone-pair with the C=C π-system in the OZ1 or SZ1 isomers, as compared to the other three conformers. As a matter of fact, a NBO second order perturbation analysis shows the existence of an interaction between the O- or S-lone-pair and the C=C π* antibonding orbital. Consistently, the C=C bond length is longer in the OZ1 and SZ1 conformers than in the other three, whereas the C–X (X = OH, SH) bond is shorter, in agreement with a better conjugation between the X lone-pair and the π-system.

It is worth noting however, that there is a significant stability difference between the two *Z*-conformers of both compounds, OZ1 versus OZ2, and SZ1 versus SZ2. The NBO analysis, shows that in the former the interactions between the oxygen (sulfur) lone pairs and the C=C moiety are about 37 kJ mol^{-1} (X = O) and 32 kJ mol^{-1} (X = S) stronger than in the latter. This better conjugation is again reflected in a longer C=C bond and a shorter C–X bond in tautomers OZ1 and SZ1 than in tautomers OZ2 and SZ2, respectively. As a consequence, structures OZ1 and SZ1 are the dominant ones (96.4% and 79.6%, respectively) in the gas-phase. It is worth noting that although for the oxygen derivative the presence of the other conformers is negligibly small, for the sulfur-containing systems, the other three conformers are also present in detectable amounts (see Fig. 1).

5.2. *Protonated species*

As for the other compounds of the series the protonation at the unsaturated carbon atoms is the less favorable processes.

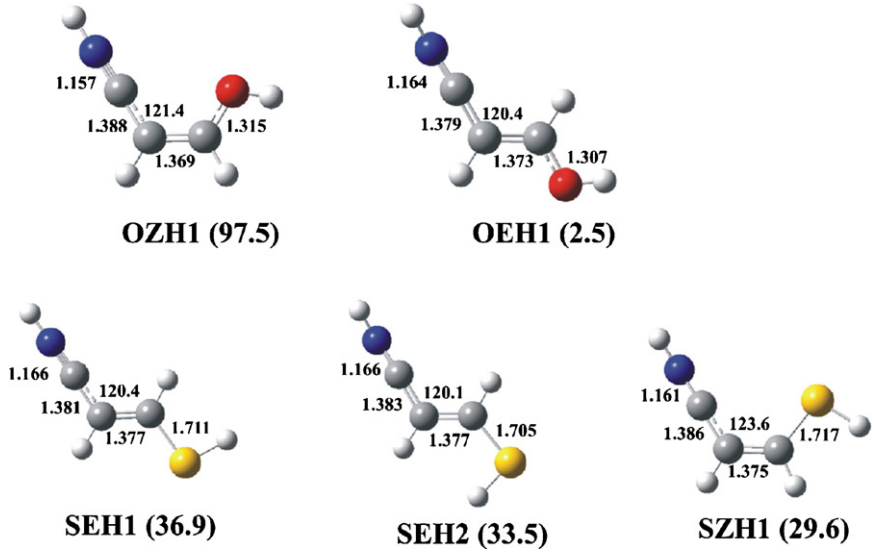
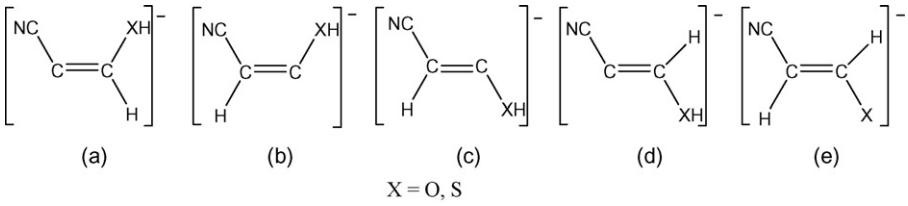


Fig. 2. Optimized geometries of the most stable protonated forms of 3HPN and 3MPN. Bond lengths are in Å and bond angles are in degrees. The number within parenthesis by the acronym of each isomer indicates the percentage of that isomer present in the gas-phase at room temperature (298 K).



Scheme 2.

Also protonation at the oxygen or at the sulfur atom is significantly less favorable than protonation at the nitrogen of the cyano group, which is the most basic site of the system. Interestingly, the behavior of both compounds with respect to protonation is significantly different. For the oxygen-containing compound practically only one protonated species is to be found in the gas-phase (see Fig. 2), and it corresponds to one of the conformers of the *Z*-protonated species. Conversely, for the sulfur derivative, three different protonated forms, two of the *E*-type and one of the *Z*-type, exhibit rather close relative stabilities in terms of both enthalpies and Gibbs free energies, and therefore, three different protonated species in rather similar proportions are predicted to be found in the gas-phase (see Fig. 2).

5.3. Deprotonated species

We have investigated all possible anions (see Scheme 2), whose total energies are summarized in Table S1 of the supporting information. As it has been found before for similar derivatives, the loss of the proton from the substituent, was found to be much more favorable than the deprotonation of the HC=CH group. Furthermore, the Gibbs free energy gap between species **e** and species **a**–**d** is so large, that only species **e** can be found in the gas-phase at room temperature.

On the other hand, when the proton is lost from the substituent, the *E*-conformer is found to be systematically more stable than the *Z*-one (see Fig. 3), the free energy gap being large enough so that practically only the *E*-conformer is expected to be observed in the gas-phase, at room temperature. This implies that, since for the neutrals the *Z*-isomer is the dominant one in the gas-phase, the formation of the most stable deprotonated species requires a rearrangement of the system through an internal rotation around the C=C double bond. However, as it has been shown before using cyanovinylamine as a suitable model compound [10], the required energy (≈60 kJ mol^{-1}) is provided by the strong interactions (hydrogen bonds and ion/dipole) which, under normal experimental conditions, take place between the neutral and the deprotonated bases. These interaction energies are typically between 70 and 125 kJ mol^{-1} and therefore we can safely assume that the anion formed in the deprotonation process of the *Z*-isomer will have enough internal energy as to evolve to the most stable *E*-isomer.

Deprotonation of the XH group triggers significant structural changes, through an enhancement of the conjugation of the oxygen (sulfur) with the C=C moiety. As a matter of fact, a second bond order NBO analysis shows a stronger donation from the oxygen (sulfur) lone pairs to the π^*_{CC} antibonding orbital, which is reflected in a significant lengthening (0.064 Å when X = O, and 0.032 Å when X = S) of the C=C bond. Concomitantly, the C–O and C–S bonds become shorter (0.101 and 0.050 Å, respectively).

5.4. Proton affinities and gas-phase acidities

To calculate the proton affinities and gas-phase acidities of the two compounds under investigation, it is necessary to take into account that under normal experimental conditions the neutral system will be a statistical mixture of the most stable conformers, and that similarly, the protonated and deprotonated products will be also a statistical mixture of the most stable ions. The calculated PAs and $\Delta_{acid}H$ reported in Table 2 were obtained taking this into account. In order to obtain their GBs and the $\Delta_{acid}G$ values, we have also included the corresponding entropy of mixing, evaluated as

$$\Delta_{mix}S = -R\sum x_i \ln x_i$$

where x_i is the mole fraction.

It can be observed that both compounds exhibit rather similar calculated intrinsic basicities (protonation of the cyano group, GB(O) = 781 kJ mol^{-1}, GB(S) = 776 kJ mol^{-1}), which in turn are also rather close to those of other members of the same family of compounds, such as N≡C–CH=CH–X (X = CH_3, SiH_3, PH_2) (GBs: 780, 769 and 776 kJ mol^{-1}, respectively). This seems to indicate that the influence of the substituent on the intrinsic basicity of the cyano group is rather small. These compounds constitute another example of the influence

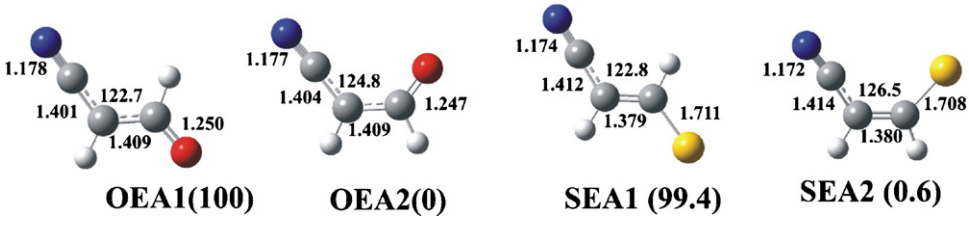


Fig. 3. Optimized geometries of the most stable deprotonated structures of 3HPN and 3MPN Bond lengths are in Å and bond angles are in degrees.

Table 2
Calculated gas-phase basicities (enthalpy, PA; Gibbs free energy, GB) and gas-phase acidities (enthalpies, $\Delta_{acid}H^{\circ}$, Gibbs free energies, $\Delta_{acid}G^{\circ}$), all values[a] in kJ mol^{-1}

	PA	PA_{aver}	GB	GB_{aver}	$\Delta_{acid}H$	$(\Delta_{acid}H)_{aver}$	$\Delta_{acid}G$	$(\Delta_{acid}G)_{aver}$	%
OE1	825.7	**812.5**	797.9	**781.4**	1376.2	**1389.3**	1345.8	**1358.0**	1.8
OE2	812.1		785.3		1389.7		1358.4		1.2
OZ1	823.5		796.0		1378.3		1347.8		96.4
OZ2	822.0		795.0		1379.8		1348.7		0.6
SE1	804.9	**806.4**	775.0	**776.2**	1364.0	**1362.5**	1333.6	**1332.4**	7.4
SE2	812.3		782.0		1356.6		1326.6		4.7
SZ1	813.0		780.9		1355.9		1327.8		79.6
SZ2	811.7		780.6		1357.1		1328.0		8.3

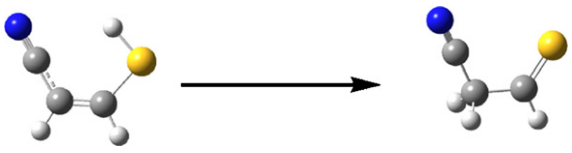
The last column gives the percentage (%) of each isomer in the gas-phase at 298.15 K.
[a] Values calculated at the G3B3 level of theory. Average PAs and GBs values were obtained taking into account the Boltzman distribution at 298.15 K for the different neutral and protonated isomers. Average gas-phase acidities take only into account the distribution of the different neutral isomers, since all anions are exclusively in the *E* form. Free energies include the entropy of mixing contribution.

of the cationic resonance in the corresponding conjugate acids on the gas-phase basicity as pointed out before in the literature [30,31].

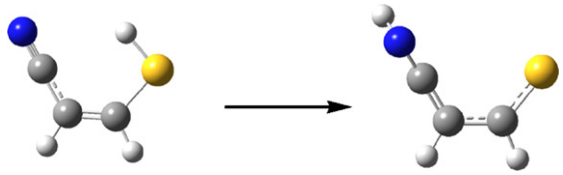
Unfortunately, we did not have the possibility to investigate experimentally the gas-phase properties of 3-hydroxy-2-propenenitrile. For 3-mercapto-2-propenenitrile, the experimental GB range is quite large (851 ± 17 kJ mol^{-1}) but the lower limit is quite above our theoretical estimates (776 kJ mol^{-1}). It should be mentioned that our G3B3 calculations reproduced very well the PA of NC–CH=CH–CH_3, but they predict it to have almost the same PA as NC–CH=CH–SH, while the experimental basicity of NC–CH=CH–SH was found to be at least 70 kJ mol^{-1} larger than that of NC–CH=CH–CH_3. A similar disagreement between experiment and theory appears again when dealing with the intrinsic acidity of this compound. As a matter of fact, the G3B3 calculated values for NC–CH=CH–SH are 52 kJ mol^{-1} lower than the experimental ICR value. In other words, theory predicts 3-mercapto-2-propenenitrile to be a stronger acid than suggested by experimental methods.

Our first attempt to reconcile theoretical and experimental values was to carry out the calculations at the highest level we can afford. For this purpose the final energies of the enethiol NC–CH=CH–SH and its protonated and deprotonated species were obtained at the CCSD(T)/aug-ccQZ level of theory, but the values obtained differed from those calculated at the G3B3 level by no more than 1.3 kJ mol^{-1}, and therefore the disagreement theory/experiment remained.

Another possibility can be associated with some isomerization processes which may take place under normal experimental conditions, so that species that undergoes protonation and deprotonation is not 3MPN, but a different isomer. The most obvious isomerization process is that leading to the corresponding thioaldehyde (see Scheme 3).



Scheme 3.



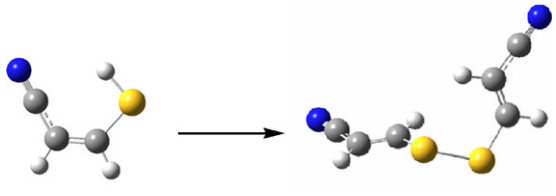
Scheme 4.

As it has been found for 3MPN, the corresponding thioaldehyde undergoes protonation preferentially at the N atom, but the G3B3 calculated GB is even lower (741 kJ mol^{-1}) than that of 3MPN. This isomerization does not explain either the disagreement as far as the intrinsic acidity is concerned because the thioaldehyde is still a stronger acid ($\Delta_{acid}G^{\circ} = 1305$ kJ mol^{-1}) than the corresponding enethiol. Besides, the isomerization barrier associated with the necessary 1,3-H shift is very large as to expect that this isomerization will take place in significant amount.

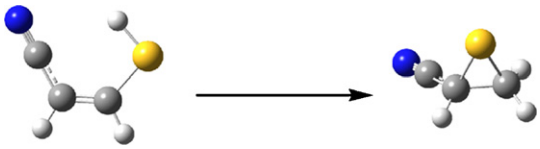
Another possible isomerization is the one leading to the corresponding allenimine (see Scheme 4).

The allenimine form protonates preferentially at the S atom yielding the two most stable protonated forms SEH1 and SEH2 but even though its estimated GB is higher than that of 3MPN (810 kJ mol^{-1}) is still 33–49 kJ mol^{-1} lower than the experimental values. Its gas-phase acidity ($\Delta_{acid}G^{\circ} = 1262$ kJ mol^{-1}) is, in contrast, even stronger than that of the corresponding thioaldehyde, and therefore much larger than that of 3MPN.

Taken into account that enethiols can be easily oxidized through the formation of S–S linkages we have also considered as a third alternative the possible formation of the disulfide, shown in Scheme 5, that may interfere in the proton transfer measurements.



Scheme 5.



Scheme 6.

However, both the intrinsic basicity and the intrinsic acidity of this form (GB = 780 kJ mol^{-1}, $\Delta_{acid}G^{\circ}$ = 1332 kJ mol^{-1}) differ very little from that of 3MPN, and therefore are still quite far from the experimental values.

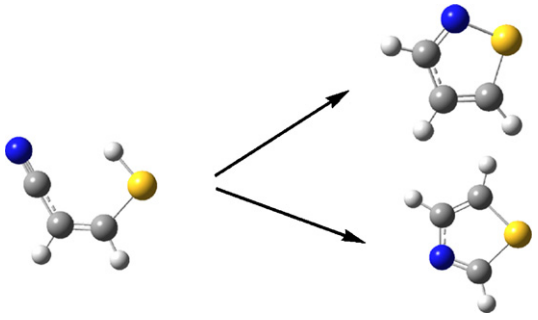
We have also explored the possibility of cyclization of the system as illustrated in Scheme 6, even though this isomerization process seems a priory very unlikely.

The three-membered ring shown in Scheme 6 is indeed a local minimum of the PES, which lies 22.5 kJ mol^{-1} above SZ1 (see Fig. 1). A proton loss from the CH_2 group leads to the most stable anion SEA1 (see Fig. 3), and the estimated $\Delta_{acid}G$ is 1308 kJ mol^{-1}, clearly much smaller than the experimental value. A proton loss from the CH(CN) group leads to a much less cyclic anion, so that the predicted $\Delta_{acid}G$ is 1491 kJ mol^{-1}, much higher than the experimental value.

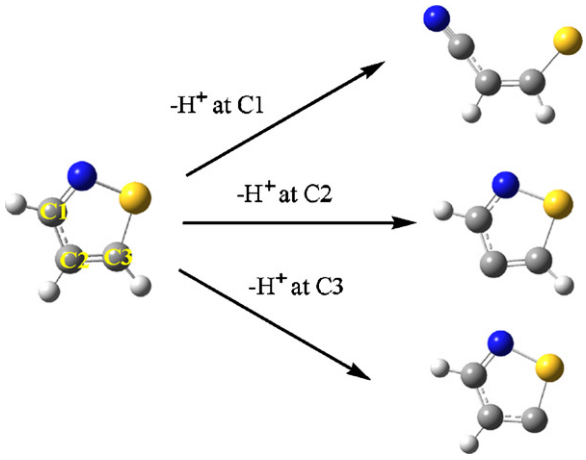
It could also be possible the isomerization of 3MPN to yield thiazole or isothiazole (see Scheme 7).

Although the isomerization to yield thiazole is unlikely to occur, because it would require a previous nitrile–isonitrile rearrangement, the isomerizaton to yield isothiazole can be readily produced by a simple 1,3-H shift. Nevertheless, we have investigated the basicity and the acidity of both compounds. In both cases three different protonation and deprotonation processes can be envisaged. Thiazole is predicted to be much less acidic than 3MPN. The values of $\Delta_{acid}G$ calculated for the three possible deprotonation processes (1495, 1597, and 1540 kJ mol^{-1}) are much higher than those calculated for 3MPN, and therefore much higher than the experimental value. Our calculations show that, as expected, protonation takes place at the nitrogen atom, the calculated GB (870.4 kJ/mol) being in very good agreement with the experimental value (872.1) [17], but much higher than the one measure in the present work for 3MPN.

The situation is different as far as isothiazole is concerned. The first conspicuous fact is that deprotonation at the C1 position (see Scheme 8) triggers an opening of the cycle, so the corresponding anion is identical to the one produced by deprotonation of 3MPN.



Scheme 7.



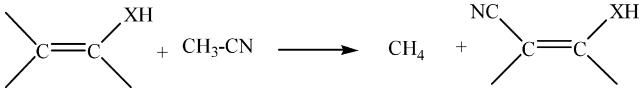
Scheme 8.

The other two deprotonation processes maintain the cyclic structure of the system but are much less favorable from the energetic point of view. Since 3MPN and isothiazole yield the same anion upon deprotonation, the $\Delta_{acid}G$ of the latter is larger by the amount of the stabilization energy of isothiazole relative to its isomer 3MPN. The consequence is that the predicted value for $\Delta_{acid}G$ is 1379 kJ mol^{-1}, now in quite good agreement with the value obtained in our ICR measurements (see Table 1).

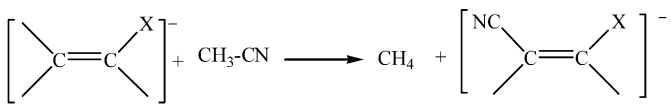
Protonation of isothiazole takes place as in thiazole preferentially at the N atom. The calculated GB (850 kJ mol^{-1}) is also in extremely good agreement with the GB measured for 3MPN. Hence, these results point out to a 3MPN → isothiazole isomerization as the explanation of the disagreement between theory and experiment as far as acidity and basicity of 3MPN are concerned.

5.5. Cyano substituent effects on acidity

As it has been found for other cyanovinyl derivatives, both 3HPN and 3MPN are more acidic than the corresponding unsubstituted vinyl compounds. The following isodesmic reactions:



(1)



X =O, S

(2)

provide a good way to understand the origin of this acidity enhancement. Reactions (1) and (2) measure the effect of the CN substituent on the relative stability of the neutral and the anionic species produced by the most favorable deprotonation

Table 3
Calculated enthalpy (ΔH°) for the isodesmic reactions (1) and (2) and calculated acidity strengthening triggered by cyano substitution

Substituent	Calculated enthalpy		Acidity strengthening
	Reaction (1)	Reaction (2)	
OH	31	132	101
SH	15	102	87

All values in kJ mol^{-1}.

process of the former, respectively. The results obtained at the G3B3 level (see Table 3) show that although the CN group stabilizes both the neutral and the anionic species, the latter effect is much larger than the former, leading to the observed acidity enhancement. The strong acidifier character of the cyano groups when attached to planar π-systems was pointed out before in the literature for other kind of systems and has been used to designing neutral organic superacids [32,33].

6. Conclusions

In the gas-phase, both 3HPN and 3MPN should exist as an equilibrium mixture of the two conformers of their *Z*- and the *E*-isomers, although in both cases the XZ1 (X = O, S) structure is the dominant one. The situation is completely different as far as the most stable protonated and deprotonated species are concerned. Protonation takes place systematically at the cyano group, and while for the sulfur-containing compound the two conformers of the *E*-isomer and one of the conformers of the *Z*-isomer should coexist in similar proportions in the gas-phase, for the oxygen derivative, the *Z*-isomer is clearly dominant. The calculated GBs for both compounds are rather similar to other members of the series, N≡C–CH=CH–X (X = CH_3, NH_2, SiH_3, PH_2) that indicates that the nature of the X substituent has a small influence on the intrinsic basicity of the cyano group. Conversely, both compounds are predicted to be from 20 to 117 kJ mol^{-1} more acidic than the C-, N-, Si- and P-containing analogues. As in these compounds, the deprotonation of the OH and SH groups is the most favorable process, and practically only the corresponding *E* isomer should be found in the gas-phase at room temperature.

Both 3HPN and 3MPN have gas-phase acidities significantly larger than those of the corresponding unsubstituted vinyl compounds, because the cyano group stabilizes much more the deprotonated anion than the corresponding neutral compound.

There is a significant disagreement between our theoretical estimates for both the gas-phase basicity and the gas-phase acidity of N≡C–CH=CH–SH derivative and the corresponding experimental values, obtained by bracketing. This disagreement points out to a possible isomerization of the system under the normal ICR conditions. One of these isomerizations leads to isothiazole. The notably good agreement between the measured and calculated $\Delta_{acid}G$ and GB for this compound allows us to conclude that very likely the N≡C–CH=CH–SH → isothiazole isomerization is taking place.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2007.02.021.

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