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β-Heterosubstituted Acrylonitriles − Electronic Structure Study by UV-Photoelectron Spectroscopy and Quantum Chemical Calculations

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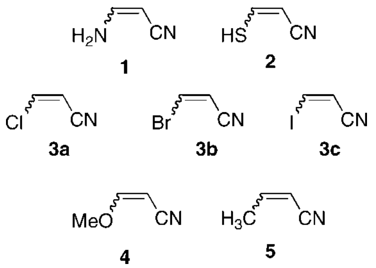
β-Heterosubstituted acrylonitriles correspond to the formal addition of nucleophiles on cyanoacetylene. Acrylonitriles substituted with an amino, methoxy, mercapto group, or halogeno atom have been synthesized. Rearrangements between *Z* and *E* stereoisomers or tautomerizations have been studied by NMR spectroscopy and by quantum calculations. The photoelectron spectra were recorded and analyzed with the aid of a time-dependent density functional theory, ab initio OVGF, and so-called "corrected" ionization energy calculations. The electronic structure of the studied species was determined, and strong differences between *β*-heterosubstituted acrylonitriles and the corresponding nitrile-free heteroalkenes were clearly documented. A "push−pull" effect was noticed, due to the combined donor effect of the substituent on one side of the carbon−carbon double bond and the electron-withdrawing effect of the nitrile group on the other side. Thus, the presence of a nitrile group strongly stabilizes the electronic structure. The efficient *π*-donor contribution of the NH$_2$ and SH groups was evidenced.

Introduction

β-Heterosubstituted acrylonitriles are constituted by a carbon−carbon double bond, a carbonitrile group, and a heterosubstituent on the *β*-position. With such a complex association of functional groups, the physicochemical properties of these compounds are often very different from those of the corresponding nitrile-free derivatives. These *β*-heterosubstituted acrylonitriles are formally the primary adducts of a nucleophile on the cyanoacetylene, a compound observed in the interstellar medium, the atmosphere of Titan, or formed in electric discharge reactions designed to simulate events on the primitive Earth.[1−7] Some of these adducts, isolated or generated in situ, were used to prepare, in very short sequences, several building blocks of life such as diaminopyrimidine, cytosine, uracil, asparagine, or aspartic acid.[8−10] A better understanding of the physicochemical properties of these unsaturated nitriles is a key step in the evaluation of the possible roles of such compounds in various areas of astrobiology.

Among the particular properties, the higher thermodynamic stability of the *Z* isomer as compared to the *E* isomer has been reported for several substituted acrylonitriles bearing a methyl, chlorine, or thioalkyl substituent.[11] In the case of 3-amino-2-propenenitrile **1**, the gas-phase isomerization occurs when heated by a C=C torsion. This also happens for many substituted acrylonitriles. Tautomerization, a well-known property of vinylamines, only occurs in basic media.[12] For this compound also, the *Z* isomer is also thermodynamically more stable than the *E* one, and both stereoisomers are more stable than the corresponding imine stereoisomers. In contrast to conformations of vinylamine, the most stable conformer of 3-amino-2-propenenitrile **1**[13] has almost a planar structure. For 3-amino-2-propenenitrile **1**[13] and 3-mercapto-2-propenenitrile **2**,[14] a hydrogen connected to the heteroatom has some interaction with the nitrile group. In the gaseous phase, the protonation of such heteroacrylonitriles takes place systematically at the cyano group (even for the amine **1**), and these compounds present rather similar gas-phase basicity. This indicates that the nature of the substituent has only a weak effect on the intrinsic basicity of the cyano group.[15,16] Among these derivatives, the 3-hydroxy-2-propenenitrile (HO−CH=CH−CN) possesses a thermodynamically more stable tautomer, the cyanoacetaldehyde (NCCH$_2$CH(=O)), and thus has strong similarities to the unsubstituted derivative, the ethenol.[16,17]

CHART 1



To investigate the electronic structure and reactivity of these compounds, we chose UV-photoelectron spectroscopy (UV-PES) as the most valuable spectroscopic technique able to give a direct experimental access to the ionization band patterns as "molecular fingerprints" of studied systems. The introduction of a carbonitrile substituent on simple compounds like vinylamine or vinylthiol should lead to dramatic modifications of

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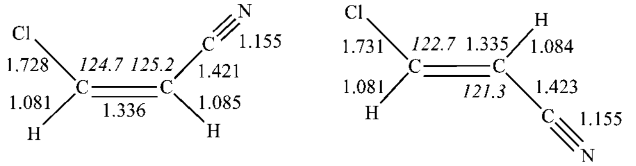


Figure 1. Optimized [B3LYP/6-311G(d,p)] geometrical parameters of (*Z*)- and (*E*)-3-chloro-2-propenenitrile **3a** (bond lengths in angstroms, bond angles in degrees).

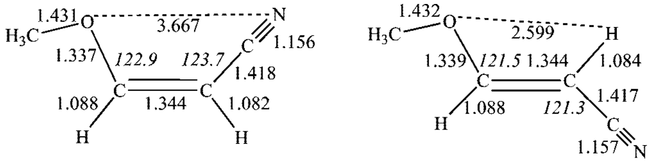


Figure 2. Optimized [B3LYP/6-311G(d,p)] geometrical parameters of *Z*- and *E*-3-methoxy-2-propenenitrile **4** (bond lengths in angstroms, bond angles in degrees).

the frontier orbitals and consequently of the bands observed on the PE spectra.

In this Article, we report a theoretical and UV-photoelectron study devoted to 3-amino- **1**, 3-mercapto- **2**, 3-chloro- **3a**, 3-bromo- **3b**, and 3-iodo-2-propenenitrile **3c**. To complete the series with a nonenolizable oxygenated derivative, the 3-methoxy-2-propenenitrile **4** is added to the list. The PE spectra of **1**−**4** are also compared to those of the corresponding extensively studied nitrile-free derivatives, and the crotononitrile (2-butenenitrile) **5** is considered as a reference (Chart 1). We first discuss the thermodynamic stability and *E*/*Z* isomerization of the studied compounds, then describe the UV-photoelectron spectra and attribute the bands with the support of theoretical evaluation of ionization energies. Finally, we analyze the consequences of the simultaneous presence of the nitrile group and another functional group on the physicochemical properties of such systems.

Results

Structures. The *Z*:*E* ratio of each compound is dependent on the preparation method used. In this study, the samples have the following ratios: **1**, *Z*:*E*/95:5; **2**, *Z*:*E*/88:12; **3a**−**c**, *Z*:*E* > 99:1;[18] **4**, *Z*:*E*/30:70; **5**, *Z*:*E*/62:38 (see the experimental procedure in the Supporting Information).

Several studies have been reported on the $E \leftrightarrows Z$ isomerization and thermodynamic stability of stereoisomers of compounds **1**, **3a**−**5**.[11−15] Because of the lack of a hydrogen in the substituent (compounds **3a**−**c**, **4**), this process can only occur via a direct isomerization, which implies a C=C torsion.

The geometrical parameters of the two stereoisomers of 3-chloro-2-propenenitrile **3a**, chosen as an example of a halogenous derivative, are given in Figure 1. They have a C_s symmetry [B3LYP/6-311G(d,p)], the *E* isomer being slightly more stable than the *Z* one (0.68 kcal/mol). In the case of the G2 calculation, this difference of stability is even smaller (0.11 kcal/mol). Nevertheless, the application of B3LYP in conjunction with 6-31G(d) basis set allowed one to reverse this relative stability (*Z* isomer is calculated to be 1.38 kcal/mol more stable than the *E* one, and the $E \leftrightarrows Z$ isomerization barrier is of 54.34 kcal/mol via a biradical state with a 90° torsion). This last result is consistent with the previously reported experimental data.[11a] The flash vacuum thermolysis (FVT) of the pure *Z* isomer was carried out until a temperature of 1200 °C without formation of decomposition products. The analysis was performed via ^{1}H NMR spectroscopy. The *Z*:*E* ratio decreases with increasing temperature: 59.6:40.4 and 58.1:41.9, respectively, at 1100 and 1200 °C. Considering the calculated isomerization barrier, the result obtained at 1200 °C corresponds probably to the equilibrium between both forms.

The comparison of calculated geometrical parameters shows that the ClCC and CC(CN) bond angles are bigger in the *Z* isomer than in the *E* one (124.7° and 125.2°, 122.7° and 121.3°, respectively). This result can be explained by the steric and electronic repulsions between the nitrile group and chlorine atom. Considering stabilizing interactions (negative hyperconjugation effect) derived from Natural Bond Orbital analysis of these two isomers, the chlorine atom lone pair delocalization into $\pi^*_{C=C}$ seems more important in the *Z* isomer than in the *E* one (19.2 versus 17.6 kcal/mol, respectively) and is correlated with the shortening of the Cl−C bond length in the *Z* isomer in comparison with the *E* one (1.728 versus 1.731 Å, respectively). Moreover, the comparison of total energy stabilization (NBO) shows a larger value by about 10 kcal/mol for the *Z* isomer (*Z*, 237.0 kcal/mol; and *E*, 227.4 kcal/mol).

The geometrical parameters of 3-methoxy-2-propenenitrile **4** are represented in Figure 2. The two isomers of 3-methoxy-2-propenenitrile **4** are calculated to have C_s symmetry, the *E* isomer being only 0.77 kcal/mol more stable than the *Z* one. The calculated CCO and C=C−C bond angles are slightly bigger in the *Z* isomer as compared to the *E* one. This can be explained, as previously, by the steric and electronic repulsions between nitrile and methoxy groups.

The determination of the most stable stereoisomer by FVT is difficult: starting from the commercially available mixture (30% *Z*), the flash vacuum thermolysis at 900 °C gave huge amounts of acrylonitrile and acetonitrile and a 44:56/*Z*:*E* ratio of compound **4**. At a higher temperature of thermolysis, only traces of **4** were detected.

On the other hand, the case of enolizable compounds is of particular interest: in the presence of one or more hydrogens on the atom connected to the CC double bond (**1**, **2**, and formally **5**), another reaction pathway $Z \leftrightarrows E$ involving a bis 1,3-sigmatropic rearrangement can be considered. For amine **1**[12] and thiol **2**, this process corresponds to a tautomerization.

In the case of the crotononitrile **5**, the *Z*−*E* isomerization was studied by MP2 and MP4[19] or G3B3 calculations[15] and showed a higher stability for the *Z* isomer.

Two different isomerization mechanisms can be envisaged for going from the *E*- to the *Z*-form of crotononitrile **5**. The first one corresponds to a direct isomerization by a C=C torsion. The second one (which seems much less favorable than the first one) would imply, as a first step, a rearrangement from the *E*-crotononitrile to the corresponding allyl cyanide (Figure 3), followed by a rearrangement from the allyl cyanide to the corresponding *Z*-crotononitrile.

The optimized structures of both stereoisomers of 2- and 3-butenenitrile are reported in the Supporting Information (Figure S1 and Table S1). [B3LYP/6-311G(d,p)] calculations show that the unexpected bis-sigmatropic rearrangement via the allyl cyanide implies an activation barrier of 17.4 kcal mol^{-1} higher than that corresponding to the C=C torsion. This directly connects *Z* and *E* isomers of crotononitrile **5** (75.3 versus 57.9 kcal/mol). These data are close to those calculated for the amine **1** (62.3 and 50.5 kcal/mol, respectively).[12]

The FVT of crotononitrile (*Z*:*E*/62:38) gave an interesting result: at 1200 °C, a mixture with a *Z*:*E*/55.7:44.3 ratio was obtained, but allyl cyanide was also formed at this temperature (16% yield). On the other hand, the FVT of allyl cyanide at 1200 °C gave a mixture of isomers containing about 30% of

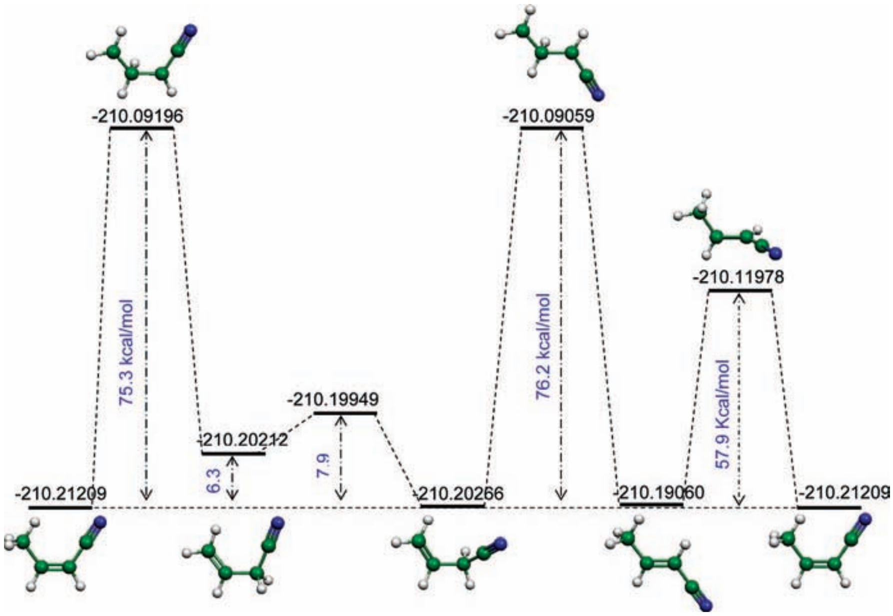


Figure 3. [B3LYP/6-311G(d,p)] calculated $E \leftrightarrows Z$ isomerization pathways of crotononitrile via an allyl cyanide and via a biradical (total and relative energies in au and kcal/mol, respectively).

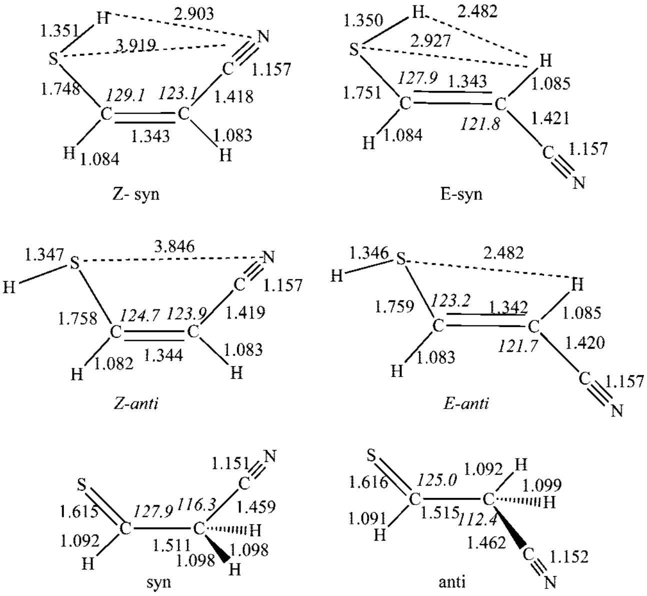


Figure 4. Optimized [B3LYP/6-311G(d,p)] geometrical parameters of syn and anti rotamers of (*Z*)- and (*E*)-3-mercapto-2-propenenitrile **2**, and syn and anti rotamers of 3-thioxopropanenitrile (bond lengths in angstroms, bond angles in degrees).

crotononitrile in a *Z*:*E*/54.5:45.5 ratio, confirming also the highest thermodynamic stability of the *Z* derivative. Thus, the bis-sigmatropic rearrangement could be partly the cause of the $Z \leftrightarrows E$ isomerization at this temperature.

For the thiol **2**, the FVT at 800 °C of the *t*-butylsulfide derivative gave the 3-mercapto-2-propenitrile **2** in a 88:12/*Z*:*E* ratio.[14] The thioaldehyde tautomer was never observed in the condensed phase. Theoretical calculations predict that each of the *Z* and the *E* forms have two "stable" planar rotameric forms with the H−S−C═C link of atoms in either a synperiplanar or an antiperiplanar conformation. The synperiplanar form of the *Z* isomer has the global minimum energy.[14] By [B3LYP/6-311G(d,p)] calculations, we found also that the *Z* isomer of the enethiol is the most stable stereoisomer (ΔE_{E-Z}: 1.2 kcal/mol), whereas the syn- and antithioaldehyde tautomers are less stable isomers (ΔE: 7.2 and 6.5 kcal/mol, respectively). This is shown in Figure 4, and the calculated total and relative energies are summarized in Table S2 in the Supporting Information. Such results are consistent with the nature of the thermolysis products and the *Z*:*E* ratio observed for **2**.

The two different isomerization mechanisms described above for the crotononitrile can be envisaged on going from the *E* to the *Z* form of compound **2** (Figure 5). It can proceed via a suprafacial or antarafacial pathway with activation barriers of 55.2 and 54.5 kcal/mol, respectively. The $Z \leftrightarrows E$ isomerization of **2** can also occur by a C═C bond torsion via a biradical with a smaller activation barrier of 51.7 kcal/mol.

Thus, for all compounds **1**−**5**, the isomerization occurs via a C═C torsion. The differences between both reaction pathways for the enolizable compounds **1**, **2**, and **5** are, respectively, 11.8, 3.5, and 17.4 kcal/mol.

UV-Photoelectron Spectra. The UV-PE spectra of compounds **1**−**5** have been recorded, and those of compounds **1**−**4** are reported in Figure 6 (the PE spectrum of crotononitrile **5** and the attribution of the corresponding ionizations are reported in the Supporting Information and are used as a reference system (Figures S1 and S2, Table S3)). The interpretation has been supported by theoretical evaluation of vertical ionization energies (IE). First, vertical ionization energies were calculated with ΔSCF-DFT, which means that separate SCF calculations are performed to optimize the orbitals of the ground state and the appropriate excited-state determinants ($\mathrm{IE} = E_{\mathrm{cation}} - E_{\mathrm{neut.mol.}}$). The experimental data were then compared to the time-dependent density functional theory (TD-DFT) as well as ab initio estimated by Outer Valence Green's Function (OVGF) IE calculations, and so-called "corrected" IE (the less rigorous "shifting" of Kohn−Sham energies ($\varepsilon_i^{\mathrm{KS}}$) directly linked up to experimental vertical ionization energies ($\mathrm{IE_v}$) by uniform shift $x = |-\varepsilon_i(\mathrm{HOMO}) - \mathrm{IE_v}^{\mathrm{exp}}|$) (see Computational Details in the Supporting Information).

The UV-photoelectron spectrum of the 3-amino-2-propenenitrile **1** with 95:5/*Z*:*E* ratio displays a first large and intense band at 8.95 eV. The second and third bands are located at 11.95 and 12.15 eV; they are followed by the two others at 12.5 and

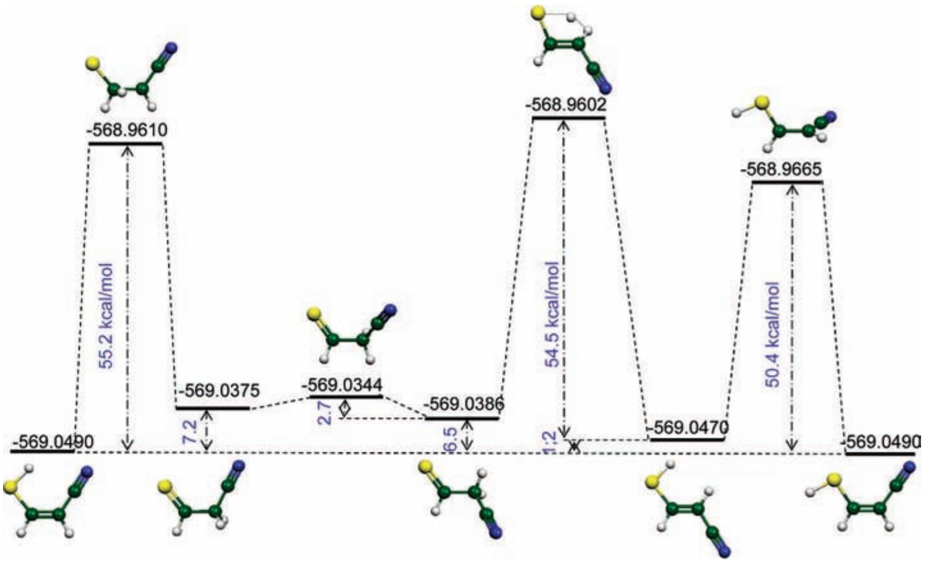


Figure 5. [B3LYP/6-311G(d,p)] calculated *E*⇆*Z* isomerization pathways of 3-mercaptoprop-2-enenitrile **2** via 3-thioxopropanenitrile and via a biradical (total and relative energies in au and kcal/mol, respectively).

13.3 eV. The theoretical evaluations of ionization energies in comparison with the experimental values are reported in Table 1.

These results lead to the attribution of the bands of the experimental spectrum: the first IE is linked with the ejection of an electron from the molecular orbital corresponding mainly to the total antibonding interaction of the π system $[(\pi_{CC} - \pi_{CN}) - n^{\pi}_{N(H2)}]$. The second PE band reflects the $\pi_{C\equiv N}$ bond ionization (in the σ-plane). The third IE is due to the antibonding interaction between the $\pi_{C\equiv N}$ and (pseudo) $\pi_{N=C}$ system. Next, the ionization of the nitrogen lone pair of the nitrile group and the total bonding interaction of the π system $[(\pi_{CC} + \pi_{CN}) + n^{\pi}_{N(H2)}]$ are attributed to the bands located at 12.5 and 13.3 eV, respectively.

The calculated IEs for the *Z* isomer fit slightly better with the experimental values, but the difference between two calculated values is rather small, and their unambiguous differentiation by PES seems unsubstantiated. However, because the *Z*:*E* ratio is 95:5, the same before and after distillation, the spectrum corresponds mainly to the *Z* isomer, and the bands of the *E* isomer cannot be easily differentiated. OVGF calculated IEs are in good agreement with experimental data, except for the first one; TD-DFT values are systematically underestimated.

The UV-PES-FVT has been applied in tandem to the generation and characterization of 3-mercapto-2-propenenitrile **2** (Figure 6b). On the starting 3-*t*-butylthio-2-propenenitrile spectrum, the first very sharp and intense band at 8.55 eV has been attributed to the sulfur atom lone pair ionization. Upon thermolysis at 650 °C, the new bands at 9.20, 11.60, 11.70, 12.45, 12.9, and 13.20 eV are present together with ionizations at 9.45 and 11.81 eV corresponding to the isobutene molecule, a byproduct. Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] and experimental IEs of the *Z* and *E* isomers of thiol **2** are reported in Table 2.

These calculated data allow the attribution of the observed bands. The first IE at 9.20 eV is linked with the ejection of an electron from the molecular orbital corresponding mainly to $[(\pi_{CC} - \pi_{CN}) - n^{\pi}_{S}]$. The second band at 11.60 eV corresponds to the antibonding interaction between the π_{SC} and π_{CN} (A″) system. The third band at 11.70 eV is attributed to the orthogonal π system of $[\pi^{\perp}_{CN}]$ of the cyano group. The forth and fifth bands correspond to the ionization of the nitrogen lone pair of the nitrile (12.45 eV n^{σ}_{N}, A′) and of sulfur (12.90 eV n^{σ}_{S}, A′). The sixth one of symmetry A″ at 13.20 eV is the total bonding combination of the $[(\pi_{CC} + \pi_{CN}) + n^{\pi}_{S}]$ system. This theoretical evaluation of ionization energies is in good agreement with the experimental data, except for the OVGF calculated third, fourth, and fifth values, for which the overestimation is close to 0.4 eV. The energetic gap of 4 eV between the first and the sixth IEs, corresponding to the total antibonding and total bonding π-systems, reflects the strong interaction between these systems. Once again, the difference in the calculated IEs of *E* and *Z* isomers is not large enough to differentiate both systems. With a 88:12/*Z*:*E* ratio in the thermolyzed products for **2**,[14] only the *Z* isomer is unambiguously identified in the PE spectrum.

The UV-photoelectron spectrum of the 3-methoxy-2-propenenitrile **4** (Figure 6c) displays a first intense band at 9.6 eV, which is followed by the most intense massif with a maximum at 12.6 eV and well-distinguished shoulders: left side at 12.0 eV and right side at 12.9 and 13.4 eV.

Because the UV-PE spectrum of **4** corresponds to a mixture of both isomers and the calculated IEs (Table 3) have differences between each EI of *Z* and *E* isomers even smaller than in the case of **1**, the unambiguous differentiation by this technique seems again difficult. However, OVGF and “corrected” IEs are rather uniform and in good agreement with experimental data. Once again, TD-DFT values are underestimated. The first IE at 9.6 eV corresponds to the ejection of one electron of the total antibonding interaction of π bond system $[(\pi_{CC} - \pi_{CN}) - n^{\pi}_{O}]$ of A″ symmetry. The second band at 12.0 eV is due to the ionization of the π orthogonal lone pair of the nitrile group ($\pi^{\perp}_{CN}$, A′). The third one at 12.6 eV contains two ionizations: the one of $[(\pi_{CN} - \pi_{CO}) + \pi_{CH2}]$ system of A″ symmetry and the one of the nitrile nitrogen lone pair (n^{σ}_{N}, A′). The next one at 12.9 eV corresponds mainly to the ionization of the oxygen lone pair (A′), whereas the bonding interaction between ($\pi_{CC} + \pi_{CN}$) and the ($n^{\pi}_{O} - \pi_{CH2}$) system (A″) appears at 13.4 eV.

The HeI UV-photoelectron spectrum of the 3-chloro-2-propenenitrile **3a** (Figure 6d) displays a first intense band at 10.45 eV. The most intense and very sharp second band at 12.15 eV has a right sideband at 12.4 eV, which is clearly distinguished in the HeII spectrum. The following ionizations are located at 12.55, 12.9 (with a vibrational progression spacing of 1210 cm^{-1}), and 14.1 eV.

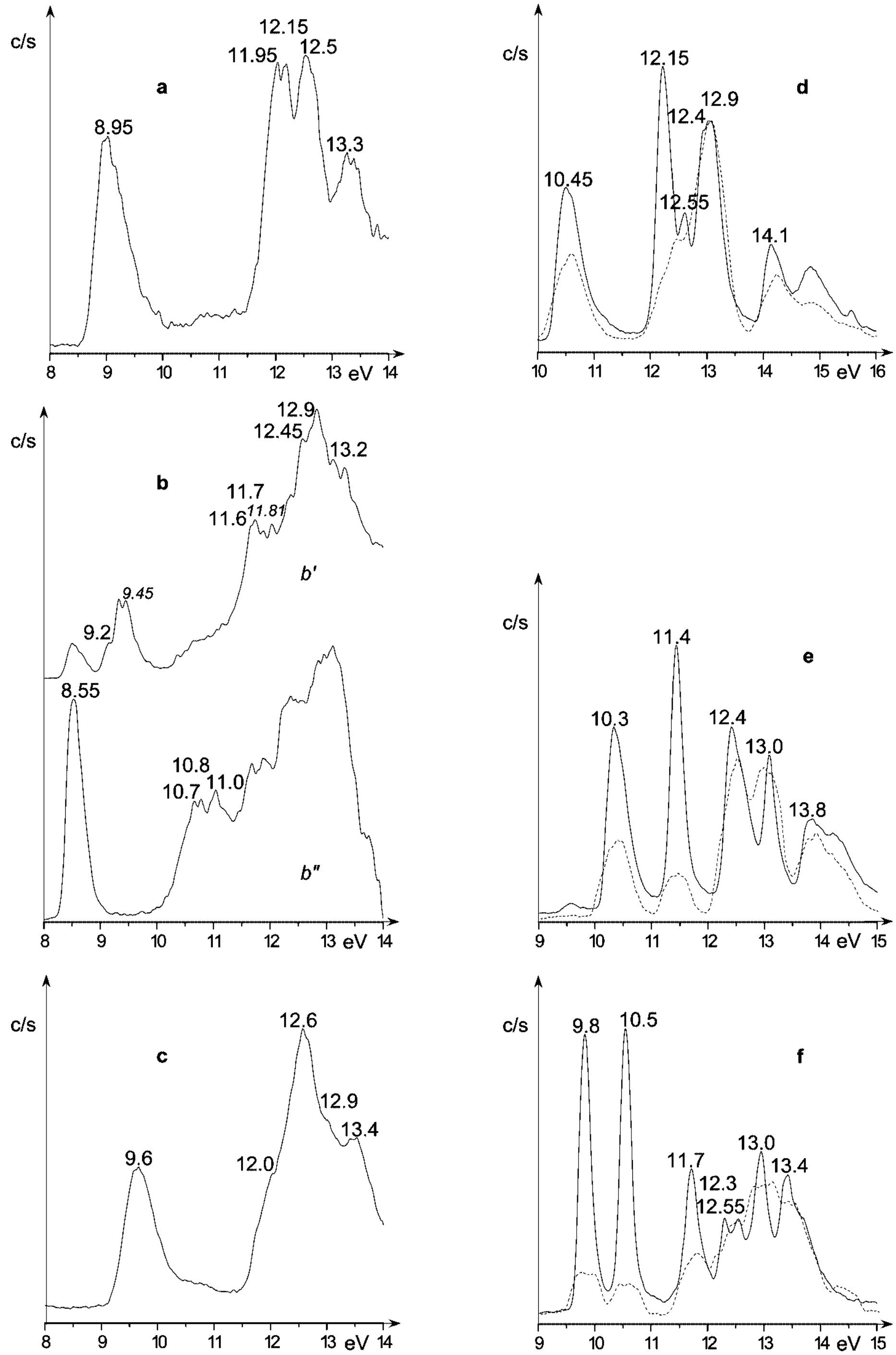


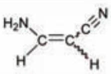
Figure 6. UV-photoelectron spectra of compounds **1**–**4** (IE in eV): (a) **1**, (b) **2** ((b″) 3-(*t*-butylthio)-2-propenenitrile, (b′) 3-(*t*-butylthio)-2-propenenitrile themolyzed at 650 °C), (c) **4**, (d) **3a**, (e) **3b**, (f) **3c** (HeI and HeII (dashed line)).

The comparison of experimental and calculated (*Z* and *E* isomers) IEs of chloropropenenitrile **3a** (Table 4) shows quite similar theoretical evaluation for the two stereoisomers. In the synthesis giving exclusively the *Z* isomer, the UV-PES spectrum corresponds unambiguously to this one.

The comparison of the calculated ionization energies for 3-chloro-2-propenenitrile **3a** by three different methods with experimental data seems satisfactory. However, the 0.44 eV overestimation of the fifth IE by OVGF and 0.37 eV underestimation of the second TD-DFT IE have to be noted.

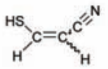
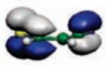
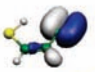
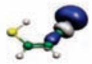
The first PE band at 10.45 eV corresponds to the ionization of the molecular orbital of A″ symmetry [$(\pi_{CC} - \pi_{CN}) - n^{\pi}_{Cl}$], while the second IE results in the ejection of one electron of the chlorine lone pair n^{σ}_{Cl} (A′). The third one at 12.4 eV is attributed to the nitrile group ($\pi^{\perp}_{CN}$) of A′ symmetry. The nature of the fourth IE at 12.55 eV is associated with the MO corresponding to the antibonding interaction between the π chlorine atom lone pair and the π_{CN} system (A″). The ejection of one electron of the nitrile nitrogen lone pair (A′) has an IE of 12.9 eV, whereas the band at 14.1 eV (A″) describes the total bonding interaction between ($\pi_{CC} + \pi_{CN}$) and the chlorine atom lone pair n^{π}_{Cl}. The energy gap between the first (total antibonding) and the sixth (total bonding) ionization energies is quite big (3.65 eV) and corresponds to the strongly interacting π systems. To evaluate the order of magnitude of this type of interaction, the PE spectra of the bromo- and iodo- derivatives

TABLE 1: Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] IEs of the *Z* and *E* Isomers of 3-Amino-2-propenenitrile (1) in Comparison with Experimental Data (eV)

Molecular orbital	$-\varepsilon^{KS}$		OVGF		TD-DFT		"Corrected"		IE (exp.)	
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z* x=2.66	*E* x=2.65		
$(\pi_{CC}-\pi_{CN})-n^{\pi}_{N(H2)}$ (A")	6.29	6.30	8.41	8.42	8.71[a]	8.68[a]	8.95[b]	8.95[b]	**8.95**	
$\pi^{\perp}_{CN}$ (A')	8.87	8.68	11.77	11.59	11.22	11.03	11.53	11.33	**11.95**	
$\pi_{N=C}-\pi_{CN}$ (A")	9.29	9.29	11.97	11.99	11.74	11.55	11.95	11.94	**12.15**	
$n^{\sigma}_{N(\equiv C)}$ (A')	9.56	9.39	12.54	12.39	11.79	11.83	12.22	12.04	**12.50**	
$\pi_{CC}+\pi_{CN}+n^{\pi}_{N(H2)}$ (A")	10.76	10.76	13.34	13.33	13.21	13.17	13.42	13.41	**13.30**	

[a] Δ_{SCF}. [b] IE (exp.).

TABLE 2: Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] IEs of the *Z* and *E* Isomers of 3-Mercapto-2-propenenitrile (2) in Comparison with Experimental Data (eV)

Molecular orbital	$-\varepsilon^{KS}$		OVGF		TD-DFT		Corrected IE		IE (exp.)	
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z* x=2.26	*E* x=2.14		
$\pi_{CC}-\pi_{CN}-n^{\pi}_{S}$ **(A")**	7.04	7.06	9.18	9.20	9.32[a]	9,28[a]	9.20[b]	9.20[b]	**9.20**	
$(\pi_{SC}-\pi_{CN})$ **(A")**	9.27	9.32	11.66	11.75	11.62	11.39	11.43	11.46	**11.60**	
$\pi^{\perp}_{CN}$ **(A')**	9.49	9.34	12.19	12.16	11.78	11.83	11.65	11.48	**11.70**	
n^{σ}_{N} **(A')**	10.17	9.96	12.90	13.00	12.14	11.88	12.33	12.10	**12.45**	
n^{σ}_{S} **(A')**	10.44	10.74	13.30	13.30	12.94	13.12	12.60	12.88	**12.90**	
$\pi_{CC}+\pi_{CN}+n^{\pi}_{S}$ **(A")**	10.86	10.80	13.46	13.39	13.18	13.14	13.02	12.94	**13.20**	

[a] Δ_{SCF}. [b] IE (exp.).

have been also recorded. HeI and HeII PE spectra of these halogeno compounds are reported in Figure 6e and f.

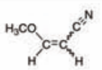
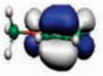
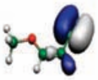
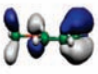
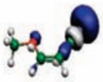
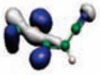
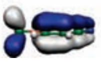
Going from the HeI (21.2 eV) to the HeII (40.8 eV) energy of photons, the intensity of bands has changed considerably. The intensities of photoelectron bands are most conveniently described in terms of specific differential cross sections, which are a function of the incident photon energy and which are the measure of the probability of photoionization from a specific molecular orbital. The attribution of the PE bands of the *Z* and *E* isomers of 3-bromo-2-propenenitrile **3b** and 3-iodo-2-propenenitrile **3c** was made by comparison of calculated IEs (see Tables S4 and S5 in the Supporting Information) with the corresponding HeI and HeII experimental data. The attribution of the PE bands is similar to **3a**, except for the third and fourth IEs of **3b** and **3c**, which are inverted with respect to **3a**. The position of $\pi^{\perp}_{CN}$ and $n^{\sigma}_{N(\equiv C)}$ IEs in the three cases remains constant (12.3−12.4; 12.9−13.0 eV, respectively). The lowering of the IE's values with halogen atom participation is observed in series Cl, Br, and I and, in principle, should be linked to the decrease of the electronegativity and the increase of the polarizability of these atoms.

Discussion

The PE spectra reported above are discussed successively to document the general rule correlated to the presence of the nitrile group. Considering experimental IEs, the first diagram (Figure 7) shows the modification of the electronic structure of the carbon−carbon double bond under mono- NH_2 or CN, and α,β-disubstitution for 3-amino-2-propenenitrile **1**.[20,21]

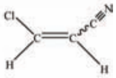
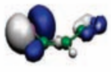
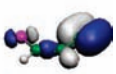
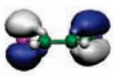
The introduction of the amino function on the carbon−carbon double bond induces a 1.87 eV π-system destabilization, while

TABLE 3: Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] IEs of the *Z* and *E* Isomers of 3-Methoxy-2-propenenitrile (4) in Comparison with Experimental Data (eV)

Molecular orbital	$-\varepsilon^{KS}$		OVGF		TD-DFT		Corrected IE		IE (exp.)	
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z* x=2.73	*E* x=2.71		
$(\pi_{CC}-\pi_{CN})-n^{\pi}_{O}$ (A″)	6.87	6.89	9.13	9.12	9.20[a]	9.20[a]	9.6[b]	9.6[b]	**9.6**	
$\pi^{\perp}_{CN}$ (A′)	8.88	9.01	11.78	11.91	11.20	11.34	11.61	11.72	**12.0**	
$(\pi_{CN}-\pi_{CO})+\pi_{CH2}$ (A″)	9.50	9.65	12.28	12.44	11.73	11.86	12.23	12.36	**12.6**	
n^{σ}_{NC} (A′)	9.59	9.71	12.81	12.69	11.94	12.09	12.32	12.42	**12.6**	
$\sigma_{CC}, \sigma_{CO,}$ (A′)	10.12	10.16	12.86	13.11	12.23	12.25	12.85	12.87	**12.9**	
$(\pi_{CC}+\pi_{CN})+n^{\pi}_{O}-\pi_{CH2}$ (A″)	10.77	10.82	13.63	13.67	13.06	13.11	13.5	13.53	**13.4**	

[a] Δ_{SCF}. [b] IE (exp.).

TABLE 4: Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] IEs of the *Z* and *E* Isomers of 3-Chloro-2-propenenitrile (3a) in Comparison with Experimental Data (eV)

Molecular orbital	$-\varepsilon^{KS}$		OVGF		TD-DFT		Corrected IE		IE (exp.)	
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z* x=2.5	*E* x=2.49		
$(\pi_{CC}-\pi_{CN})-n^{\pi}_{Cl}$ (A″)	7.95	7.96	10.32	10.33	10.32[a]	10.31[a]	10.45[b]	10.45[b]	**10.45**	
$n^{\sigma}_{Cl}-\pi^{\perp}_{CN}$ (A′)	9.40	9.53	12.14	12.26	11.78	11.85	11.90	12.02	**12.15**	
$\pi^{\perp}_{CN}+n^{\sigma}_{Cl}$ (A′)	9.62	9.72	12.23	12.3	11.9	12.0	12.1	12.21	**12.40**	
$n^{\pi}_{Cl}-\pi_{CN}$ (A″)	10.1	10.2	12.76	12.9	12.4	12.4	12.6	12.75	**12.55**	
$n^{\sigma}_{N(\equiv C)}$ (A′)	10.3	10.3	13.34	13.3	12.79	12.9	12.8	12.85	**12.90**	
$\pi_{CC}+\pi_{CN}+n^{\pi}_{Cl}$ (A″)	11.4	11.4	14.04	14.0	13.96	13.9	13.9	13.93	**14.10**	

[a] Δ_{SCF}. [b] IE (exp.).

the nitrile group stabilizes the system by about 0.4 eV. Thus, in comparison with the "naked" system, these two opposite effects under (*Z*) α,β-disubstitution cause 1.56 eV destabilization. The latter becomes even stronger if compared to the acrylonitrile (1.96 eV). The contribution of the CN group versus vinylamine is only 0.31 eV stabilization. This is an experimental visualization of strong NH_2 π-donor and rather weak CN π-acceptor effects that can be associated with a push−pull system.

In Figure 8, a similar comparison was performed for the 3-mercapto-2-propenenitrile **2**. In this case, the very close position of the $\pi_{C=C}$ and the sulfur atom lone pair (10.51 and 10.48 eV)[20] leads to the strong interaction between these two systems and induces 1.59 eV destabilization of carbon−carbon double bond as observed for vinylthiol.[22] A 1.31 eV $\pi_{C=C}$ destabilization is observed under (*Z*) α,β-disubstitution by SH and CN, but if the acrylonitrile is substituted in β-position by a thiol function, the 1.71 eV destabilization reflects its strong π-donor effect.

The contribution of the methoxy group to the carbon−carbon double bond electronic structure modification is shown in Figure 9.[20,23] The π-donating effect is weaker than that observed for SH and corresponds to the 1.38 eV shift to the lower energies of the

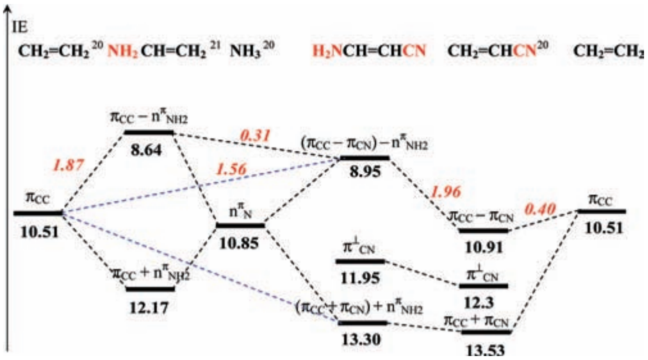


Figure 7. Correlation diagram of the ionization potentials of the carbon−carbon double bond, in ethylene, NH_2, and CN mono- and disubstituted ethylenes (eV).

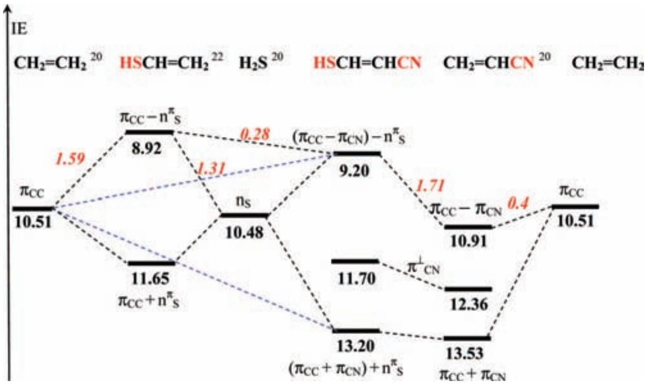


Figure 8. Correlation diagram of the characteristic experimental potentials of ethylene, SH−, and CN− mono- and disubstituted ethylene (eV).

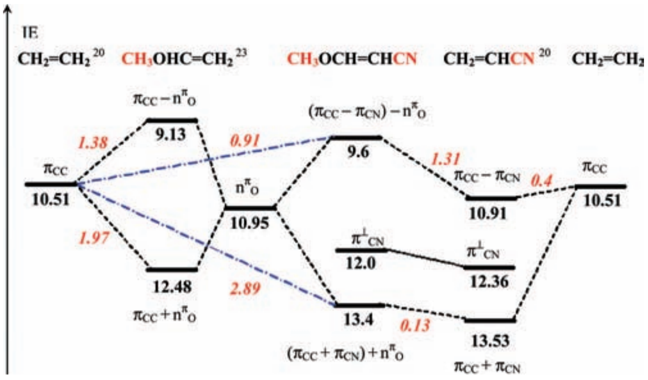


Figure 9. Correlation diagram of the characteristic experimental potentials of ethylene, OCH_3−, and CN− mono- and disubstituted ethylene (eV).

first IE in comparison to the ethylene molecule. The α,β-simultaneous introduction of both methoxy and nitrile groups causes a less pronounced, global π-system destabilization (0.91 eV).

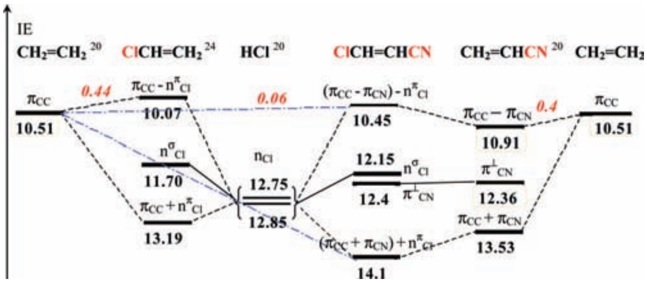


Figure 10. Correlation diagram of the characteristic experimental potentials of the ethylene, Cl−, and CN− mono- and disubstituted ethylene (eV).

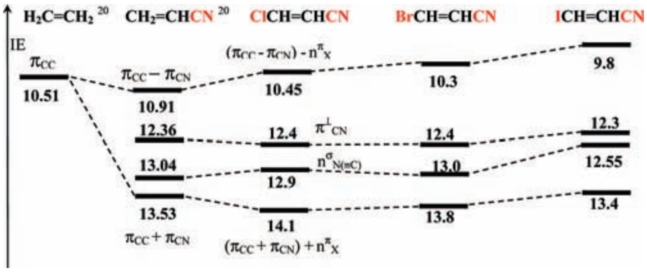


Figure 11. Comparison of experimental IEs (eV) of *Z*-acrylonitriles substituted in β-position by a chlorine, bromine, or iodine atom.

The study on chloropropenenitrile **3a** is reported in Figure 10.[20,24] The first and third IEs of vinyl chloride[22] are located at 10.07 and 13.19 eV and correspond to the antibonding and bonding interaction of the π_{CC} system and chlorine atom lone pair (n^{π}_{Cl}, A″), respectively. This interaction is less important than that previously observed for OCH_3 (3.35 eV) in compound **4**: the energetic gap is smaller (2.96 eV), and the π-donating effect of chlorine destabilizes the $\pi_{C=C}$ system by 0.44 eV. Chlorine atom lone pair ionization (n^{σ}_{Cl}, A′) is situated as the second IE at 11.70 eV. However, the corresponding IE of β-chloroacrylonitrile (12.15 eV) indicates clearly a 0.45 eV σ-acceptor (stabilizing) effect of the nitrile group in the α,β-disubstituted compound. On the other hand, the comparison of the IEs corresponding to the ethylene and acrylonitrile shows a 0.4 eV stabilization of the π-system due to the CN mesomeric acceptor effect. The effect of α,β-substitution by Cl and CN groups leads by their compensation to a slight $\pi_{C=C}$ electronic structure modification (0.06 eV destabilization).

The same type of reasoning has been applied to the (*Z*)-bromo- and (*Z*)-iodo-acrylonitriles (Figure 11). The introduction of the halogen atom in the β-position of the acrylonitrile affects principally the π-system of the molecule and is reflected by the global shift of the first IE to the lower energies (see Tables S4 and S5 in the Supporting Information). The strongest destabilizing effect is evidenced under iodine atom substitution (1.11 eV) and results not only in the most efficient π-donation, but also in the most important repulsions between the biggest halogen atom and the nitrile group in the *Z* isomer. The energetic gap between the IEs of total antibonding $[(\pi_{CC} - \pi_{CN}) - n^{\pi}_{X}]$ and total bonding $[(\pi_{CC} + \pi_{CN}) + n^{\pi}_{X}]$ π-systems is nearly the same for the three halogen derivatives (Cl 3.65, Br 3.5, I 3.6) and corresponds to the strongly interacting π_{CC}, π_{CN}, and n^{π}_{X} systems. The modification of the electronic structure of ethylene molecule (IE of π_{CC} 10.51 eV), under (*Z*) α,β-substitution, is expressed by the global destabilizing perturbation and should be followed by an increased reactivity of the β-iodoacrylonitrile as compared to β-bromoacrylonitrile, β-chloroacrylonitrile, ethylene, and acrylonitrile.

The following conclusions can be drawn from this study concerning the introduction in the last step of the cyano group or the other substituent (Figure 12).[25]

Independently of the nature of the substituent (alkyl, halogen, NH_2, OCH_3, or SH), the introduction of the nitrile group induces a stabilization of the carbon−carbon double bond system.

The destabilization of the acrylonitrile π-system upon *Z*-β-disubstitution is extremely important in the case of NH_2 (1.96 eV) and HS (1.71 eV) groups, a little bit weaker effect is noticed upon OCH_3 (1.31 eV) and I (1.11 eV) substitution, and a much less pronounced one is observed with the Cl atom (0.46 eV).

The substituent effect can be associated with the modification of the electronic structure of the studied systems. The scale of

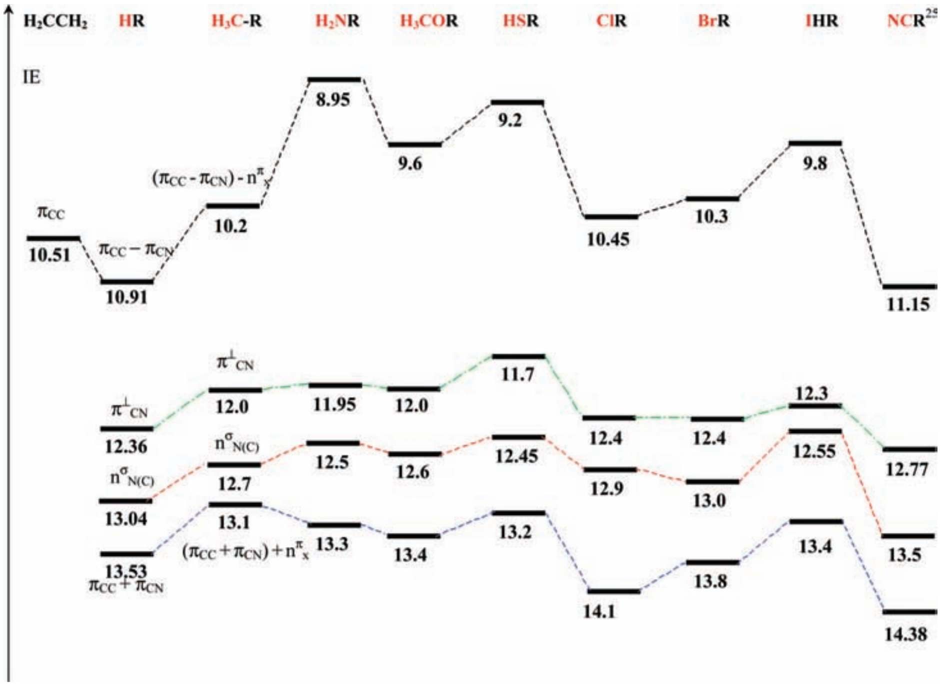
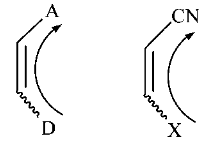


Figure 12. Experimental ionization energies (eV) comparison of *Z* isomers of differently substituted β-acrylonitriles (R = −CH=CH−CN).

SCHEME 1



X= CH_3, NH_2, OH, OCH_3, SH, Cl, Br, I

the electronic properties of substituents starting from the stronger π-donor effect up to the weaker one is drawn as follows:

$$NH_2 > SH > OCH_3 > I > CH_3 > Br > Cl \tag{1}$$

The presence of the nitrile group leads to a "push−pull" effect due to the donor effect on one side of the CC bond and the electron-withdrawing effect on the other side. The relative reactivity of each compound can be considered as a compromise between the strengths of the donor and acceptor effects (Scheme 1).

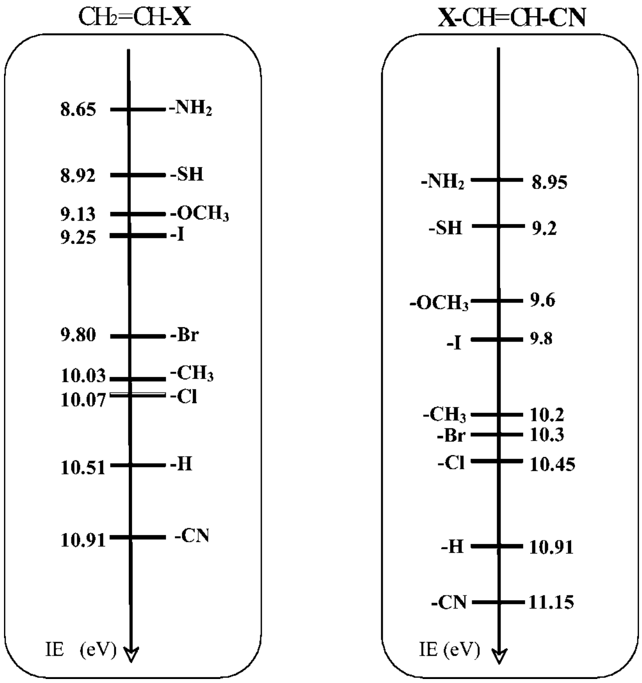


Figure 13. "Thermometer drawing style" of the first IE (eV) experimental value of β-substituted ethenes and acrylonitriles.

The electronic properties of heterosubstituted ethenes and propenenitriles with heterosubstituents bearing a heteroatom of the columns 14−17 of the Periodic Table can be quantified considering the first IE experimental value and represented in a "thermometer drawing style" (Figure 13).

The electronic structure modification of the carbon−carbon double bond under the nitrile group introduction is clearly visualized as a stabilizing effect (IEs shift to the larger values). The presence of the first nitrile group leads to a 0.4 eV $\pi_{C=C}$ stabilization, but the introduction of the second CN in the β-position causes a less pronounced effect (0.24 eV). This electronic structure modification is also particularly significant in the case of methoxy, bromo, and iodo derivatives, while a weaker influence is conferred to the amino, thio, chloro, and then methyl derivatives.

Conclusion

Several β-heterosubstituted acrylonitriles have been synthesized, and their UV-PE spectra have been recorded to determine the first ionization energies of the title species and to make a systematic comparison of their electronic structure. The PE spectra were analyzed with the aid of time-dependent density functional theory as well as the ab initio OVGF calculations. This study shows the particular properties of the (*Z*) α,β-disubstituted ethylenes due to the presence of the nitrile group and sheds light on the relative influence/contribution of each group. The presence of both substituents leads to a "push−pull" effect due to the combined donor effect of the substituent of the carbon−carbon double bond on one side, and the electron-withdrawing effect of the nitrile on the other side. The stabilization of the electronic structure by the nitrile group introduction is clearly documented. Similarly, the particularly efficient π-donor contribution of the NH_2 and SH groups is demonstrated.

Thus, the presence of the nitrile group on the CC double bond gives to these compounds physicochemical properties dramatically different from those of the unsubstituted vinylamine, vinylthiol, or vinyl halide. The particular role already observed for some of them in organic chemistry can be directly correlated to the presence of a push−pull effect.

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Supporting Information Available: Details on the preparation of compounds **1**,**3a**−**c** and spectroscopic characterization, computational details, optimized geometrical parameters, calculated energies, PE spectrum of **5**, and correlation diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

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