

# **$\beta$ -Heterosubstituted Acrylonitriles - Electronic Structure Study by UV-Photoelectron Spectroscopy and Quantum Chemical Calculations.**

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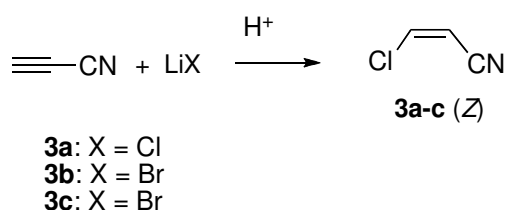
## **Supporting Information (11 pages)**

### **Experimental Section**

**General:** <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer. The NMR samples were prepared using CDCl<sub>3</sub> as solvent. Chemical shifts are given in ppm ( $\delta$ ) relative to tetramethylsilane (<sup>1</sup>H) and solvent (<sup>13</sup>C, CDCl<sub>3</sub>,  $\delta$  77.0 ppm). HRMS (high-resolution mass spectrometry) experiments were performed on a Varian MAT 311 instrument. Photoelectron spectra were recorded with Helectros 0018 spectrometer equipped with a 127° cylindrical analyzer using 21.21 eV He I radiation as photon source and monitored by a microcomputer supplemented with a digital-to-analogue converter. Helium ionization at 4.98 eV and nitrogen ionization at 15.59 and 16.98 eV, respectively, were used for calibration. The spectra contain 2000 points and are accurate to 0.1 eV.

**Materials.** 2-Butenenitrile **5** (*Z*:*E*/62:38) and 3-methoxy-2-propenenitrile **4** (*Z*:*E*/30:70) were purchased from Aldrich and used as received. Cyanoacetylene was prepared by dehydration of the corresponding amide with P<sub>4</sub>O<sub>10</sub> and sea sand.<sup>S1</sup> The 3-halogeno-2-propenenitrile **3a-c** were easily prepared by addition of lithium halide on cyanoacetylene in the presence of acetic acid.<sup>S2</sup> (*Z*+*E*)-3-Amino-2-propenenitrile **1**<sup>S3</sup> and 3-(*t*-butylthio)-2-propenenitrile<sup>S4</sup> were prepared as previously reported.

### Preparation of (*Z*)-3-halogeno-2-propenenitrile (**3a-c**).<sup>S2</sup>



Scheme S1

A mixture of cyanoacetylene (510 mg, 10 mmol), LiX (X = Cl, Br, I, 11 mmol), and acetic acid (10 mL) were introduced in a one-necked cell equipped with a stirring bar and a stopcock. The mixture was cooled at 77 K by a liquid nitrogen bath and evacuated. The cell was closed and allowed to warm to room temperature. The solution was then heated at 70 °C for 24 h under stirring.

The (*Z*)-3-chloro-2-propenenitrile **3a** was purified by distillation *in vacuo* (0.1 mbar) and selective trapping in a cell cooled at -20 °C. bp 78-80 °C (90 mmHg); <sup>S2</sup> <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 5.83 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, CH-CN); 6.98 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, CH-Cl). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 103.5 (<sup>1</sup>J<sub>CH</sub> = 178.3 Hz, CH-CN); 113.9 (CN); 140.1 (<sup>1</sup>J<sub>CH</sub> = 201.6 Hz, CH-Cl).

The crude 3-bromo-2-propenenitrile **3b** was immersed in a cold bath (0 °C) and the solvent was removed *in vacuo* (0.1 mm Hg). Compound **3b** was used without further purification. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 6.25 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, CH-CN); 7.20 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, CH-Br). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 106.7 (<sup>1</sup>J<sub>CH</sub> = 177.5 Hz, CH-CN); 114.6 (CN); 129.2 (<sup>1</sup>J<sub>CH</sub> = 200.0 Hz, CH-Br).

After removing the solvent *in vacuo* (0.1 mm Hg), the crude (*Z*)-3-iodo-2-propenenitrile **3c** was used without further purification. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 6.77 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.1 Hz, CH-CN); 7.68 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.1 Hz, CH-I). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 103.8 (<sup>1</sup>J<sub>CH</sub> = 196.3 Hz, CH-I); 114.0 (<sup>1</sup>J<sub>CH</sub> = 176.6 Hz, CH-CN); 117.0 (CN).

### Determination of the thermodynamic *Z:E* ratio by flash vacuum thermolysis (FVT).

Crotononitrile **5**, allylcyanide, 3-chloro-2-propenenitrile **3** or methoxy-2-propenenitrile **4** (1 mmol) was vaporized in a vacuum line ( $10^{-1}$  mbar) equipped with a short oven (15 cm) heated to a temperature ranged between 900 to 1200°C. The gaseous flow was then condensed on a cold finger (77 K) equipped at the bottom with an NMR tube. At the end of the thermolysis, a solvent ( $\text{CDCl}_3$ , 700 mL) was added. After disconnection from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen and liquid nitrogen was subsequently removed. The products were collected in the NMR tube and analyzed by  $^1\text{H}$  NMR spectroscopy. No  $Z \rightleftharpoons E$  rearrangement was observed when recording NMR spectra of various stereoisomeric mixtures after some days at room temperature.

**Computational Details.** The calculations were performed using the Gaussian 98<sup>S5</sup> and MOLCAS<sup>S6</sup> (for CASPT2) program packages. The 6-311G(d,p) basis set was used for all calculations since the inclusion of polarization functions is necessary for the accurate description of the neutral molecules containing heteroatom and their cations. Geometry optimizations were carried out at DFT<sup>S7</sup> level of theory with the B3LYP<sup>S8</sup> functional and confirmed as true minima *via* frequency analysis, which was also used to calculate zero-point energies (ZPEs) without scaling. Ionization energies were calculated with  $\Delta\text{SCF}$ -DFT which means that separate SCF calculations are performed to optimize the orbitals of the ground state and the appropriate excited state determinants ( $\text{IE} = E_{\text{cation}} - E_{\text{neut.mol.}}$ ). TDDFT<sup>S9</sup> approach provides a first principles method for the calculation of excitation energies within a density functional context taking into account the low lying ion calculated by  $\Delta\text{SCF}$  method. The vertical ionization energies of the compounds **1-4** were also calculated at the *ab initio* level according to OVGF<sup>S10</sup> method. In this case the effects of electron correlation and reorganization are including beyond the Hartree-Fock approximation and the self-energy part was expanded up to third order. CASPT2<sup>S6</sup> refers to multiconfigurational SCF *ab initio* calculations in which all excitations are taken into account in a certain orbital space (the active space), with second order perturbation corrections added afterwards. To compare the ionization energies resulting from these rigorous methods of calculation, we proceeded also to the currently used estimation of ionization energies. Indeed, recent works<sup>S11</sup> have shown that  $\epsilon_i^{\text{KS}}$  could be linked up to experimental vertical ionization energies ( $\text{IE}_v$ ) by uniform shift  $x = | - \epsilon_i (\text{HOMO}) - \text{IE}_v^{\text{exp}} |$ . This approach gives a remarkable agreement with experimental

values and is justified by the fact that the first calculated vertical ionization potential lies very close to experimental values. Stowasser and Hoffman<sup>S12</sup> have shown that the localizations of KS orbitals are very similar to those obtained after HF calculations.

Density functional theory (DFT) has been shown to predict various molecular properties successfully.<sup>S7</sup> The advantages of the most employed method of calculations of the first ionization energies ( $\Delta$ SCF – DFT calculations) have been thoroughly demonstrated.<sup>S13</sup> On the other hand, the frequently used estimation of IEs by “shifting” of calculated Kohn-Sham energies (a not very rigorous process, but nicely working) has also proved its efficiency. Nevertheless, we have to consider that each theoretical method of approaching ionization energies is limited by the calculation procedure. In the  $\Delta$ SCF method we have to take into account that the single-configuration approximation is not valid when several ions of the same symmetry are near in energy. For TDDFT approach, the configuration interaction processes is based on the quality of the evaluation of the low-lying ion described by  $\Delta$ SCF method. In the Outer Valence Green's Function (OVGF) calculation, the quality of the theoretical results depends on the validity of the Hartree-Fock approximation. The limitation of CASPT2 methods is the limit of active space (10 electrons or 9 for the ions in 12 molecular orbitals in our case), so it is reserved for rather small-size molecules.

### Calculated Geometrical Parameters for crotononitrile (2-butenenitrile) (5).

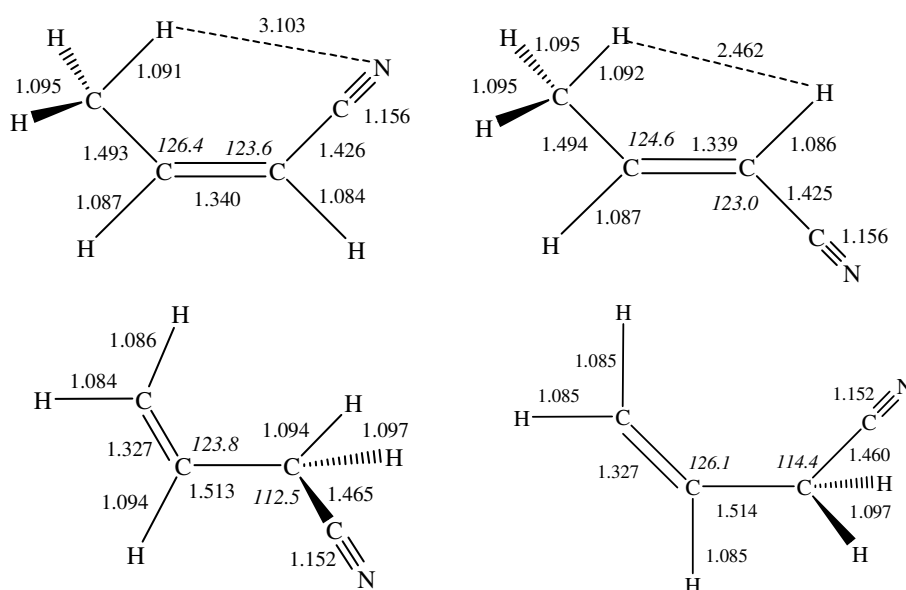


Figure S1. Optimized [B3LYP/6-311G(d,p)] geometrical parameters of *Z* and *E* 2-butenenitriles, anti- and syn-3-butenenitrile (bond lengths in Å, bond angles in degrees).

Table S1. [B3LYP/6-311G(d,p)] calculated total and relative energies of *Z* and *E* crotononitriles, anti- and syn-3-butenenitrile.

Conformer/stereoisomer/transition state	Total energy (Hartree/particle)	Relative energy (kcal/mol)
<i>Z</i> -crotononitrile	-210.212093	0.0
TS1	-210.091961	75.3
syn-3-butenenitrile	-210.20212	6.2
TS2	-210.20199	7.9
anti-3-butenenitrile	-210.20266	5.9
TS3	-210.09059	76.2
<i>E</i> -crotononitrile	-210.133223	0.12

### 3-Mercapto-2-propenenitrile (2).

Table S2. [B3LYP/6-311G(d,p)] calculated total and relative energies of isomers of 3-mercapto-2-propenenitrile **2**, 3-thioxopropanenitrile and corresponding transition states.

Conformer/stereoisomer/transition state	Total energy (Hartree/particle)	Relative energy (kcal/mol)
<i>Z</i> -3-mercapto-2-propenenitrile	-569.049002	0
TS1	-568.961011	55.2
syn-3-thioxopropanenitrile	-569.037533	7.2
TS2	-569.034381	9.2
anti-3-thioxopropanenitrile	-569.038622	6.5
TS3	-568.960237	55.7
<i>E</i> -3-mercapto-2-propenenitrile	-569.047018	1.2

## UV-Photoelectron Spectrum.

Crotononitrile **5**.

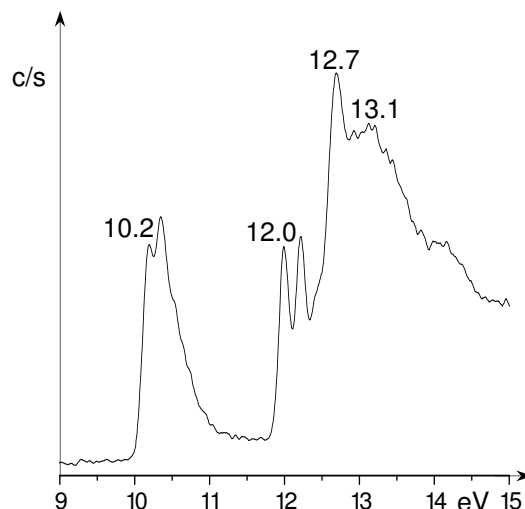


Figure S2. UV-photoelectron spectrum of compound **5**

Figure S2 shows the UV-photoelectron spectrum of crotononitrile **5**. The first intense band with a structural vibration of  $1210\text{ cm}^{-1}$  is found at 10.2 eV. The second one with a structural vibration of *ca.*  $2016\text{ cm}^{-1}$  is located at 12.0 eV. The most intense band is found at 12.7 eV, and is followed by a broad massif at 13.1 eV. Thus, the IEs of this spectrum are very similar to those reported for crotononitrile in the literature<sup>S14</sup> *i.e.* 10.23, 12.11, and 12.82 eV, respectively.

### ***II.1.2.3. Calculated ionization energies for Z and E isomers of crotononitrile, interpretation of theoretical and experimental results.***

Starting from optimized geometrical parameters obtained for *Z* and *E* isomers of crotononitrile, ionization energies (IEs) have been calculated by different methods and are reported in Table S3 with comparison with experimental IEs values.

Table S3: Calculated (B3LYP/6-311G(d,p); OVGF/6-311G(d,p)) and experimental ionization energies (eV) of crotononitrile.

MOs nature	$-\epsilon^{\text{KS}}$		OVGF		TD-DFT		Corrected IEs		IEs. exp.	MOs nature
	<i>Z</i>	<i>E</i>	<i>Z</i>	<i>E</i>	<i>Z</i>	<i>E</i>	<i>Z</i> <small>x=2.53</small>	<i>E</i> <small>x=2.54</small>		
$\pi_{\text{CC}} - \pi_{\text{CN}}$										
$-\pi_{\text{CH}_2}$ (A'')	7.67	7.66	10.12	10.11	10.07 <sup>a</sup>	10.05 <sup>a</sup>	10.2 <sup>b</sup>	10.2 <sup>b</sup>	<b>10.2</b>	
$\pi_{\text{CN}}^{\perp}$ (A')	9.22	9.18	12.10	12.08	11.69	11.67	11.75	11.72	<b>12.0</b>	
$n_{\text{N}}^{\sigma}$ (A')	9.91	9.88	12.98	13.00	12.19	12.15	12.44	12.42	<b>12.7</b>	
$\pi_{\text{CC}} + \pi_{\text{CN}}$										
$-\pi_{\text{CH}_2}$ (A'')	10.23	10.24	13.08	13.12	12.93	12.87	12.76	12.78	<b>13.1</b>	

<sup>a</sup>  $\Delta_{\text{SCF}}$ ; <sup>b</sup> exp. IE.

As shown in Table S3, all the methods give only very small differences of IEs (0.01 - 0.06 eV) for *Z* and *E* isomers of crotononitrile. Therefore, the stereoisomers cannot be clearly distinguished by UV-photoelectron spectroscopy. The interpretation of the experimental spectrum is done as follow:

- the first band is associated with the ejection of an electron from the totally antibonding molecular orbital A'' [ $(\pi_{\text{CC}} - \pi_{\text{CN}}) - \pi_{\text{CH}_2}$ ],
- the second band is assigned to the orbital localized mainly on the CN moiety (orthogonal  $\pi$  system of cyano functional group :  $\pi_{\text{CN}}^{\perp}$ , A'),
- the third band corresponds to the ionization of the nitrogen lone pair of the nitrile function ( $n_{\text{N}}^{\sigma}$ , A'),
- The last one reflects the totally bonding interaction of  $(\pi_{\text{CC}} + \pi_{\text{CN}})$  and pseudo  $\pi_{\text{CH}_2}$  (A'') systems.

In this case, rather good agreement between calculated and experimental data for crotononitrile was observed, except for the third TDDFT IE which gives a 0.51 eV under-estimation.

The Figure S3 displays the correlation diagram of the experimental ionization energies of ethylene, propene, acrylonitrile, and crotononitrile.

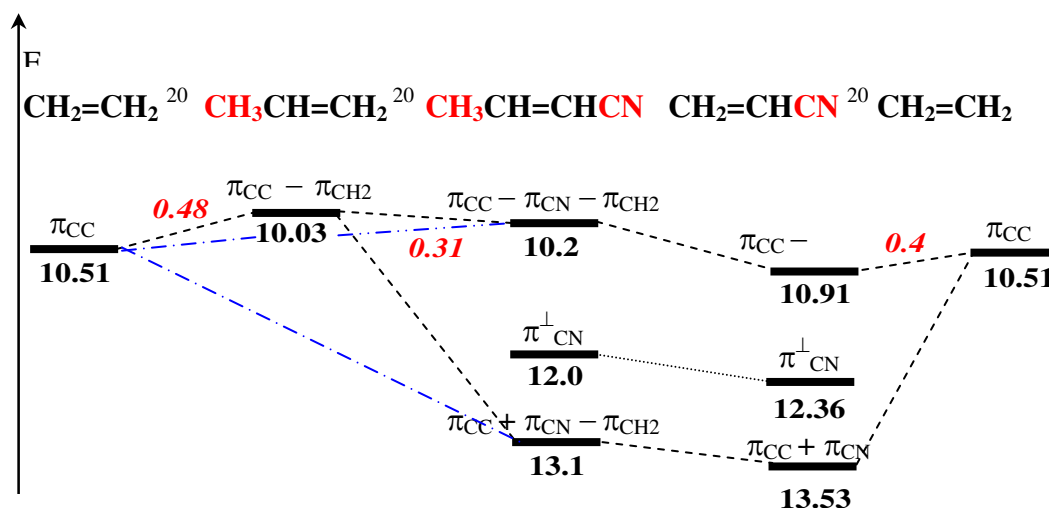


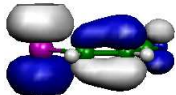
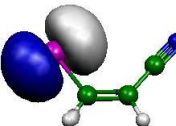
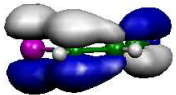
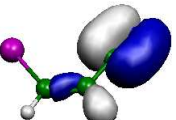
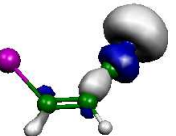

Figure S3: Correlation diagram of the characteristic experimental potentials of the "naked" carbon-carbon double bond, CH<sub>3</sub> and CN mono- and di-substituted ethylene (eV).

The introduction of the methyl group on the carbon-carbon double bond induces a 0.48 eV  $\pi$ -system destabilization while the nitrile group stabilizes the system by about 0.4 eV. Thus, in comparison with the "naked" system, these two opposite effects under (Z)  $\alpha,\beta$ -disubstitution causes 0.31 eV destabilization. The latter becomes even stronger if compared to the acrylonitrile (0.71 eV). This is an experimental visualization of nearly equivalent CH<sub>3</sub>  $\pi$ -donor (pseudo- $\pi_{CH_2}$ ) and CN  $\pi$ -acceptor effects and that can be associated with a push-pull system.



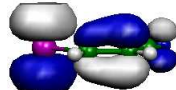
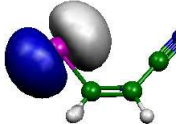
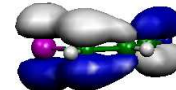
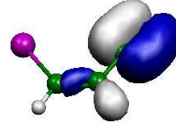
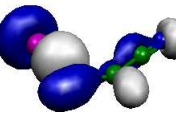
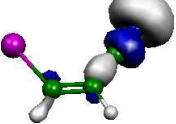
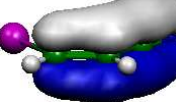
### 3-Halogeno-2-propenenitriles (3a-c)

Table S4. Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] IEs of the Z and E isomers of 3-bromo-2-propenenitrile **3b** in comparison with experimental data (eV).

MOs nature	$-\varepsilon^{\text{KS}}$	OVGF	TD-DFT	Corrected IEs $\times 2.55$	IEs exp.	MOs nature
$(\pi_{\text{CC}} - \pi_{\text{CN}})$ $- n^{\pi}_{\text{Br}} (A'')$	7.75	10.08	10.06 <sup>a</sup>	10.3 <sup>b</sup>	<b>10.3</b>	
$n^{\sigma}_{\text{Br}} (A')$	8.61	11.15	11.79	11.16	<b>11.4</b>	
$(\pi_{\text{CC}} - \pi_{\text{CN}})$ $+ n^{\pi}_{\text{Br}} (A'')$	9.58	12.12	12.25	12.13	<b>12.4</b>	
$\pi^{\perp}_{\text{CN}} (A')$	9.58	12.30	12.29	12.13	<b>12.4</b>	
$n^{\sigma}_{\text{N}(\equiv\text{C})} (A')$	10.27	13.65	13.50	12.82	<b>13.0</b>	
$(\pi_{\text{CC}} + \pi_{\text{CN}})$ $+ n^{\pi}_{\text{Br}} (A'')$	11.07	13.70	13.85	13.62	<b>13.8</b>	

<sup>a</sup>  $\Delta_{\text{SCF}}$ ; <sup>b</sup> exp IE

Table S5. Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] IEs of the Z and E isomers of 3-iodo-2-propenenitrile **3c** in comparison with experimental data (eV).

MOs nature	$-\epsilon^{\text{KS}}$	OVGF	TD-DFT	Corrected IEs $x=2.36$	IEs exp.	MOs nature
$(\pi_{\text{CC}} - \pi_{\text{CN}})$ $- n_{\text{I}}^{\pi}(\text{A}'')$	7.44	9.32	9.69 <sup>a</sup>	9.8 <sup>b</sup>	<b>9.8</b>	
$n_{\text{I}}^{\sigma}(\text{A}')$	7.87	9.91	10.26	10.23	<b>10.5</b>	
$(\pi_{\text{CC}} - \pi_{\text{CN}})$ $+ n_{\text{I}}^{\pi}(\text{A}'')$	9.07	11.24	11.57	11.43	<b>11.7</b>	
$\pi_{\text{CN}}^{\perp}(\text{A}')$	9.62	12.10	11.61	11.98	<b>12.3</b>	
$\sigma_{\text{C-I}}(\text{A}')$	10.10	12.71	11.90	12.46	<b>12.55</b>	
$n_{\text{N}(\equiv\text{C})}^{\sigma}(\text{A}')$	10.81	12.89	13.08	13.17	<b>13.0</b>	
$\pi_{\text{CC}} + \pi_{\text{CN}}$ $(\text{A}'')$	10.93	13.43	13.09	13.29	<b>13.4</b>	

<sup>a</sup>  $\Delta_{\text{SCF}}$ ; <sup>b</sup> exp IE

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