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Flash vacuum thermolysis generation and a UV-photoelectron spectroscopy study of the *N*-substituted iminoacetonitriles

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ABSTRACT

Flash vacuum thermolysis of *cis* and *trans* 1-benzyl and 1-allyl-2-cyano-3-phenylzetidines (**1a** and **1b**) at 470 °C resulted in the formation of *E* and *Z* isomers of *N*-benzyl and *N*-allyl iminoacetonitriles **2a** and **2b**, respectively, beside small amounts of products **3a** and **3b** of their [1,3] prototropic shifts. It was found that the thermal fragmentation of the azetidine ring occurred fully regioselectively with a cleavage of the C2–C3 and C4–N bonds, but not the N–C2 and C3–C4 bonds. The UV-photoelectron spectrum of compound **2b** was measured and analyzed with the aid of quantum chemical calculations of ionization energies. The strong modification of the electronic structure of the simplest carbon–nitrogen double bond upon the α,β substitution is due to the combined electron-withdrawing effect of the nitrile group and the donor effect of the allyl group.

1. Introduction

N-Alkyl α-iminoacetonitriles (RN=CHCN), also known as imidoyl cyanides, are particularly interesting compounds, described as a new family by Boyer in 1970.[1,2] Iminonitriles unsubstituted at the nitrogen atom, considered to be covalent dimers of HCN, are of interest as potential interstellar and prebiotic molecules, which via further reaction with HCN can act as building blocks for amino acids, purines and pyrimidines.[3,4] The unstable iminoacetonitrile has been obtained (as *E* and *Z* forms) by several methods such as pyrolysis of *N*,*N*-dimethylcyanamide[5] and photolysis of azidoacetonitrile in an Ar matrix,[6] or by thermal decomposition of the sodium salt of 1-cyanoformamide tosylhydrazone at 200 °C.[7] The products are identified by IR,[6] MS, ^{1}H and ^{13}C NMR spectroscopy,[7] or UV-photoelectron spectroscopy.[8] In contrast to the unsubstituted iminoacetonitrile, its *N*-alkyl analogues are sufficiently stable colourless compounds, so that their full characterization was possible; however, they also decomposed upon handling. Their synthesis was accomplished through a two-step sequence involving N-chlorination of *N*-alkyl aminoacetonitriles with *tert*-butyl or calcium hypochlorite, followed by dehydrochlorination with a base.[1,2,9] The use of *N*-chlorosuccinimide as a chlorinating agent and calcium hydroxide as a base, considerably improved the yield of the reaction.[10] The alternative method of the synthesis of *N*-alkyl iminoacetonitriles based on the oxidation of *N*-alkyl aminoacetonitriles with an aqueous solution of NaOCl was described by Selva.[11] *N*-Alkyl iminoacetonitriles containing a diene system in the *N*-alkyl group were used in hetero-Diels–Alder reactions for the synthesis of several quinolizidines.[12–14] Iminoacetonitrile moieties were incorporated starting from appropriate diene alcohols and using a Mitsunobu coupling reaction with HN(Tf)CH$_2$CN, following base-promoted elimination of trifluoromethanesulfinate.[12]

Simple *N*-methyl iminoacetonitriles were also obtained by flash vacuum thermolysis (FVT) of 1-methyl-2-cyanoaziridine or di(cyanomethyl)amine as well as 1,3,5-tri-cyanomethyl-1,3,5-triazinane.[15] The present paper is aimed at the synthesis of two unstable *N*-alkyl iminoacetonitriles obtained from 2-cyanoazetidines under FVT conditions by regiocontrolled thermal cleavage of the azetidine ring and UV-photoelectron spectroscopic characterization of the obtained products.

2. Results and discussion

The thermal reactions of an azetidine ring proceed with the cleavage of two opposite bonds. The regiochemistry of those reactions is determined by substituents present in the system. The previously postulated 1,4-biradical stepwise mechanism for these reactions suggests that the cleavage of the first bond occurs

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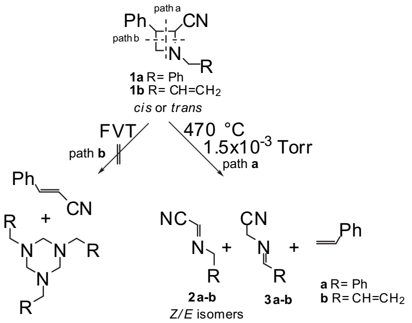
preferentially with the formation of the more efficiently stabilized biradical species depending on the nature of substituents.[16] Accordingly, under FVT conditions, azetidines bearing a cyano group in 2-position and a phenyl substituent in 3-position should preferentially lead to the cleavage of the C(2)–C(3) bond in the first step of the reaction and then follow to C(4)–N bond cleavage with the final formation of iminoacetonitriles and styrene.

2.1. Preparative FVT of 1-benzyl and 1-allyl-2-cyano-3-phenylazetidines (1a and 1b)

Two pairs of *cis* and *trans* 1-benzyl-2-cyano-3-phenylazetidines[17] (**1a**) and 1-allyl-2-cyano-3-phenylazetidines[18] (**1b**) were synthesized for our studies according to the multi-step literature protocol.[17,18] The preparative FVT experiments of **1a** and **1b** were performed at 470 °C under 1.5×10^{-3} Torr, which corresponds to the lowest temperature at which the starting material is not detected in the pyrolysate. The products of the reaction were analyzed directly after the thermolysis using ^{1}H and ^{13}C NMR spectroscopy. It was found that FVT of *trans* **1a** resulted in the formation of equimolar amounts of styrene and *N*-benzyl iminoacetonitrile (**2a**) as the *E*/*Z* isomer mixture accompanied by a small amount of benzylidenecyanomethyl amine **3a** (Scheme 1, path **a**). Since the ^{1}H NMR spectra of compounds **2a**[11] and **3a**[19] were described previously, their identification in the post-reaction mixture was easily accomplished. Directly after thermolysis the ratio of **2a***E*:**2a***Z*:**3a** was 4.5:4.5:1.0, but the products isomerised even when stored in $CDCl_3$ solution at 4–6 °C. After 7 days, this ratio was 3.3:1.4:5.3. Further, at room temperature rapid darkening and decomposition of the products was observed. A similar ratio of the products **2a***E*, **2a***Z* and **3a** (2.0:1.3:5.3) was found directly after the thermolysis, if the reaction temperature was increased to 530 °C.



Scheme 1.

It is likely that the formation of the product **3** proceeds by a [1,3] benzylic/allylic proton shift in **2**.

In the ^{1}H NMR spectrum of a crude mixture, the methylene group in **2a** exhibits signal at 4.99 ppm (d, J=2.5 Hz) for *Z* isomer (5.01 ppm, J=2.5 Hz in Ref. 11), 4.83 ppm (d, J=2.0 Hz) for *E* isomer (4.87 ppm, J=2.0 Hz in Ref. 11), 4.60 (d, J=2.0 Hz) and 8.48 (t, J=1.8 Hz) for **3a** (4.53 ppm, J=2.0 Hz and 8.42 ppm, J=2.0 Hz in Ref. 19). These values are in good agreement with those described in the literature. Unfortunately, signals of protons in the 'aromatic region' were not identifiable because of their overlapping with the strong signals of styrene. The ^{13}C NMR spectrum of the crude pyrolysate shows a methylene group signal at 65.85 ppm for **2a***E*, 63.37 for **2a***Z* and 45.55 ppm for **3a** (45.73 ppm for **3a** in Ref. 19). As above, the aromatic region remained too rich in overlapping signals to allow unequivocal interpretation.

The same results of FVT were obtained starting from *cis* **1a** or a mixture of *cis*/*trans* **1a**, and it shows clearly that the configuration of starting azetidine does not influence the course of the cleavage reaction. Moreover, the total regioselectivity of this reaction was confirmed, since the other regioisomers, i.e., cinnamonitrile and/or 1,3,5-tribenzyl-1,3,5-triazinane (trimer of unstable benzyl-methyl-enamine) (Scheme 1, path **b**), were not detected in the reaction mixture.

The FVT of **1b** performed under the same conditions, regardless of the configuration (*cis* or *trans* or *cis*/*trans* mixture) gave the mixture **2b***E*, **2b***Z* and **3b** with the same ratio as from **1a**. In the ^{1}H NMR spectrum the methylene group exhibits a multiplet pattern at 4.40–4.50 ppm for **2b***Z*, a multiplet pattern at 4.20–4.38 ppm for **2b***E* and signals at 4.48 ppm (dd J=1.2, J=0.5 Hz) and 8.08 ppm (dt J=8.7, J=1.5 Hz) for **3b** (4.52 and 8.12 ppm for **3b** in Ref. 20). In the ^{13}C NMR spectrum of the crude pyrolysate the signals of the methylene group are visible at 64.25 ppm for **2b***E*, 61.78 ppm for **2b***Z* and 45.27 ppm for **3b** (45.4 ppm for **3b** given in Ref. 20). Unfortunately, similarly as above, the signals of olefinic protons in the 'aromatic region' were not identifiable.

2.2. UV-photoelectron spectroscopy

The course of the thermolysis reaction of 1-allyl-2-cyano-3-phenylazetidine (**1b**) was also studied by UV-photoelectron spectroscopy, and the spectra were analyzed with the aid of TDDFTC (Time Dependent Density Functional Theory[21]) [B3LYP[22]/6-311G(d,p)] and Outer Valence Green's Function[23] [6-311G(d,p)] calculations. As we have discussed previously,[24] these methods offer quite a reasonable compromise between the quality of the results and the cost associated with calculations of this type.

The photoelectron spectrum of **1b** (Fig. 1**a**) exhibits the first broad band centred at 9.3 eV with the left-side shoulders at 8.8 and 9.0 eV, and the second one at 10.0 eV, which is followed by the two very intense and large massifs with maxima at 12.5 and 14.8 eV.

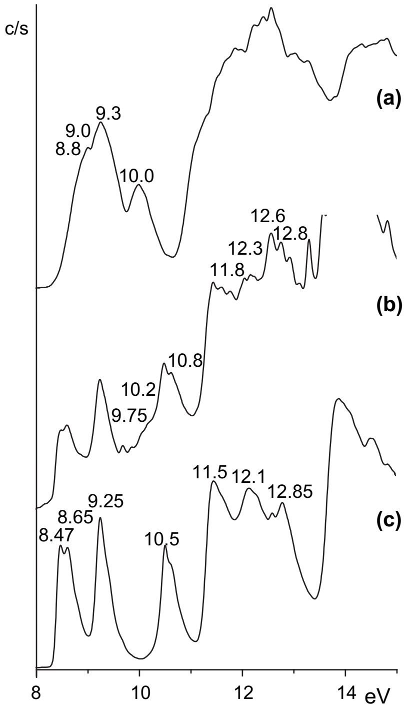


Figure 1. Photoelectron spectra of 1-allyl-2-cyano-3-phenylazetidine (**1b**) (**a**), its decomposition products at 650 °C (**b**) and of styrene (**c**).

The attribution of these PE bands was corroborated by theoretical evaluation of ionization energies (see Supplementary data Table, SI1). The first band at 8.8 eV is associated with the ejection of one electron from the nitrogen lone pair of the azetidine ring. The second IE at 9.0 eV and the third one at 9.3 eV are due to the π_2 and π_3 aromatic ring ionizations, respectively, while the fourth PE band at 10.0 eV corresponds mainly to $\pi_{C=C}$ allyl group ionization.

At 510 °C of FVT, the precursor spectrum started changing, and at 650 °C (Fig. 1**b**) characteristic ionizations of styrene (Fig. 1**c**) are easily discernible. This observation clearly indicates that a thermal cleavage of the azetidine ring took place. The new spectrum (Fig. 1**b**) is completely different from that of the precursor, and all main ionizations of styrene (8.47, 8.65, 9.25, 10.5, 11.5, 12.1, 12.85, 14.0 eV) are present. They are accompanied by those ascribed to the new product at 9.75, 10.2, 10.8, 11.8, 12.3, 12.6 and 12.8 eV.

2.3. Theoretical IE evaluation and UV-PE spectral interpretation

Theoretical calculations were carried out on **2b** and **3b** in order to assist in the assignment of the PE spectrum obtained from **1b** thermolysed at 650 °C. Geometry optimizations of *E* and *Z* isomers for iminoacetonitrile **2b**, and azabutadiene **3b** were carried out at the B3LYP/6-311G(d,p) level of theory and the results are summarized in Figure 2 (see also Supplementary data, Tables SI2 and SI3).

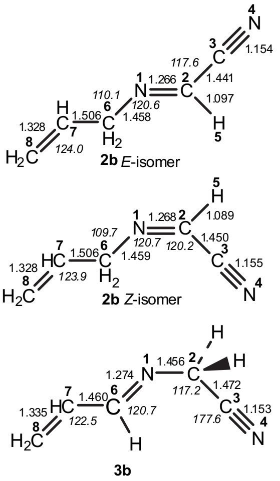


Figure 2. Selected calculated geometrical parameters for *Z* and *E* isomers of the *N*-allyliminoacetonitrile (**2b**) and 1-cyanomethyl-1-aza-1,3-butadiene (**3b**) (bond lengths in Å, angles in degrees).

Considering calculated geometrical parameters obtained for *E* and *Z* isomers of *N*-allyliminoacetonitrile (**2b**), it should be noted that the nitrogen–carbon double bond for isomer Z is slightly longer than the corresponding one for isomer *E*. The two bond angles $C_6N_1{=}C_2$ and $N_1{=}C_2C_3$ of *Z* are larger than those calculated for *E*. This fact is mainly due to the repulsions in the *Z* configuration. Also, for *E* iminoacetonitrile, the C_2–C_3 distance is shorter than for *Z* iminoacetonitrile. In the case of *s-trans* azabutadiene **3b**, the conjugated system of two double bonds ($C_8{=}C_7$ and $C_6{=}N_1$) shows the usual lengthening of these bonds, while the C_2–C_3 distance is longer compared to **2b**.

The *E* form iminoacetonitrile **2b** is predicted to be lower in energy than the *Z* one by only 0.18 kcal/mol, which is insignificant. The most stable conformer of azabutadiene **3b** is ∼8 kcal/mol more stable than both isomers of *N*-allyliminoacetonitrile (**2b**) (see Fig. SI-1 in Supplementary data).

Calculations of ionization energies for *Z* and *E* *N*-allyliminoacetonitrile (**2b**), as well as for 1-cyanomethyl-1-aza-1,3-butadiene (**3b**) are presented in Tables 1 and 2.

The comparison of calculated (*Z* and *E* isomers) IEs of cyanoimine **2b** (Table 1) shows quite similar theoretical evaluation for the two stereoisomers; the difference between the two calculated values is rather small, and their unambiguous differentiation by PES is not possible.

A second point deals with the first ionization potential at 9.75 eV, which corresponds to the ejection of one electron from the carbon–carbon double bond. Compared to the ethylene first IE (10.55 eV),[25] 0.8 eV destabilization of $\pi_{C=C}$ is due to a slight 'pseudo π' donor effect of the CH_2 group.

Third, the ionization of the imino-nitrogen lone pair is located at 10.2 eV. This position should be compared to the simplest homologue methanimine $H_2C{=}NH$ nitrogen lone pair for which the experimental value of 10.62 eV[26] has been reported. In the case of the cyanoimine molecule,[8] the nitrogen lone pair is in interaction with the π cyano group in the same plane, and two IEs have to be considered: $n_N-\pi^{\perp}_{C\equiv N}$ at 11.6 eV and $n_N+\pi^{\perp}_{C\equiv N}$ at 13.09 eV. Thus, the 1.4 eV shift corresponds to the strong donor effect of the allyl substituent.

As a fourth point, the IEs at 10.8 and 12.8 eV correspond to the antibonding and bonding interaction of the two multiple carbon–nitrogen bonds ($\pi_{C=N}-\pi_{C\equiv N}$; $\pi_{C=N}+\pi_{C\equiv N}$), respectively. The intensity of this interaction (2.0 eV) is of the same order of magnitude that in the parent cyanoimine[8] (2.17 eV).

Considering that in the products of FVT of 1-allyl-2-cyano-3-phenylazetidine (**1b**) (Scheme 1), formation of *s-trans* 1-cyanomethyl-1-aza-1,3-butadiene (**3b**) has also been detected (10% yield), the experimental and theoretical evaluation of IEs of this compound was necessary for the reliable interpretation of the FVT-PES results. Thus, *N*,*N*-diallyl-*N*-cyanomethylamine[27] **4** was used as a precursor of 1-cyanomethyl-1-aza-1,3-butadiene (**3b**) and thermolysed at 550 °C (Scheme 2, Fig. 3).

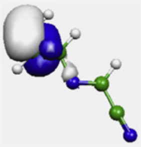
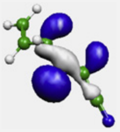
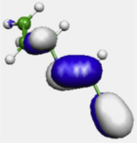
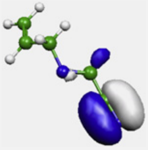
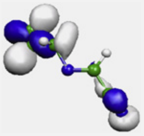
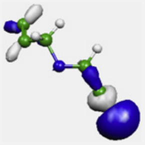
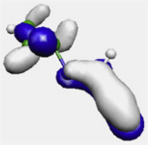
The interpretation of the UV-PE spectrum of *N*,*N*-diallyl-*N*-cyanomethylamine (Fig. 3**a**) is done by analogy with tri-methylamine (n_N IE 8.54 eV),[28] propene ($\pi_{C=C}$ IE 10.03 eV)[25] and acetonitrile ($\pi_{C\equiv N}$ IE 12.56; n_N 13.14 eV).[25] Considering the withdrawing character of three substituents on the amino-nitrogen atom, its lone pair is shifted to higher energies and located at 9.9 eV, the carbon–carbon double bond IE appears at 10.1–10.4 eV, the carbon–nitrogen triple bond at 12.15 eV, and the nitrile nitrogen lone pair at 13.0 eV. Upon FVT at 550 °C the spectrum of this amine has completely changed, and the propene ionizations at 10.0 and 12.3 eV confirm the previously described[27] elimination reaction (Scheme 2). Thus, the band located at 9.9 eV of azabutadiene **3b** corresponds to the antibonding interaction of two conjugated double bonds ($\pi_{C=C}-\pi_{C=N}$). The second one at 10.2 eV is attributed to the imino-nitrogen lone pair ionization. The two nitrile group ($\pi_{C\equiv N}$ and $\pi^{\perp}_{C\equiv N}$) ionizations are visible at 12.2 eV, while the next bands ($\pi_{C=C}+\pi_{C=N}$; $\pi_{C\equiv N}$ and $n_{N(\equiv N)}$, respectively) are centred at 12.5 eV.

A minor presence of 1-cyanomethyl-1-aza-1,3-butadiene (**3b**) formed as a rearranged product cannot be excluded since in the spectrum of 1-allyl-2-cyano-3-phenylazetidine (**1b**) thermolysed at 650 °C the bands corresponding to azabutadiene **3b** could be obscured by those of iminoacetonitrile **2b** and styrene.

Thermolysis of the 2-cyano-3-phenylazetidine (**1b**) was carried out in conjunction with the direct analysis of decomposition products using the UV-photoelectron spectroscopy. Thus, these real-time gas phase measurements have provided ionization energies, which constitute the starting point in our studies of the electron structure of cyanoimine **2b** in comparison to the previously described methanimine and cyanomethanimine.[8] Figure 4 presents a correlation diagram of the characteristic experimental ionization energies of these three molecules. First, it should be noted that the position of the imino-nitrogen lone pair changes by ∼1 eV when the cyano group is located on the carbon atom (comparison of $H_2C{=}NH$ and $NCCH{=}NH$). This important stabilization is due to the antibonding interaction between the nitrogen

Table 1

Calculated [B3LYP/6-311G(d,p), OVGF/6-311G(d,p)] and experimental ionization energies (IEs) for *Z* and *E* of *N*-allyliminoacetonitrile (**2b**) (all values in eV)

MO's nature	$-\varepsilon^{KS}$		OVGF		TD-DFT		'Corrected'		Exp
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z*, $x=2.06$	*E*, $x=1.95$	
	7.69	7.80	10.23	10.34	9.95[a]	10.03[a]	9.75[b]	9.75[b]	**9.75**
	8.06	8.16	10.19	10.12	10.24	10.32	10.12	10.11	**10.2**
	8.80	8.73	10.52	10.46	10.65	10.48	10.86	10.68	**10.8**
	9.81	9.70	12.53	12.54	11.50	11.23	11.87	11.64	**11.8**
	10.09	10.13	12.83	12.90	12.27	11.86	12.15	12.08	**12.3**
	10.63	10.40	13.56	13.56	12.18	12.23	12.69	12.35	**12.6**
	10.83	10.85	13.87	13.56	12.74	12.75	12.89	12.79	**12.8**

[a] ΔSCF value.

[b] Exp. value, *x*—empirical energy correction, see Computational details.

lone pair n_N and $\pi^{\perp}{}_{C\equiv N}$. However, the introduction of the allyl substituent on the nitrogen atom reverses this tendency and gives 0.42 eV destabilization (comparison of $H_2C{=}NH$ and $NCCH{=}NCH_2{-}CH{=}CH_2$). Secondly, the influence of this CN group on the imine function causes a very slight destabilization (0.15 eV; $\pi_{C=N}{-}\pi_{C\equiv N}$) in the case of cyanomethanimine, but a very strong one in *N*-allylcyanoimine (**2b**) (1.69 eV; $\pi_{C=N}{-}\pi_{C\equiv N}$).

Thus, upon α,β substitution, the simplest carbon–nitrogen double bond experiences an important electronic structure modification, which can be associated with a 'push–pull' effect due to the combined donor effect of the allyl group on the nitrogen atom on the one hand, and the acceptor effect of the nitrile group on the carbon atom, on the other.

3. Conclusions

The cycloreversion reaction applied to 2-cyano-3-phenylazetidines (**1a**) and (**1b**) under FVT conditions has allowed the synthesis of two iminoacetonitriles **2a** and **2b** and their ^1H and ^{13}C NMR characterization. It was found that a thermal cleavage reaction proceeded fully regioselectively with the formation of the expected iminoacetonitriles **2a** and **2b**.

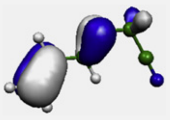
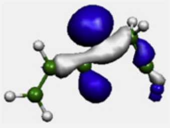
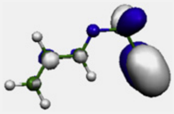
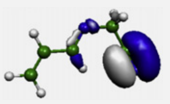
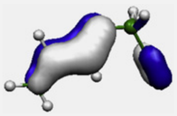
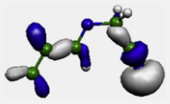
4. Experimental

4.1. General

The ^1H and ^{13}C NMR spectra were recorded at ca. 21° with a Varian Gemini 200 BB VT instrument, operating at 200.11 and 50.33 MHz for ^1H and ^{13}C nuclei, respectively. $CDCl_3$ was used as a solvent; chemical shifts in ppm (TMS). Coupling constants (*J*) in hertz. The majority of spectra were assigned with ATP and DEPT experiments and/or using the values of δ_Xs (X=H and, especially, C) predicted by a gauge independent atomic orbital (GIAO) method at the DFT B3LYP/6-31G*//B3LYP/6-31G* level of theory.

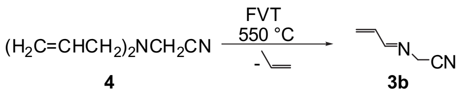
Table 2

Calculated [B3LYP/6-311G(d,p), OVGF/6-311G(d,p)] and experimental ionization energies (IEs) for *s-trans N*-cyanomethyl-1-aza-1,3-butadiene (**3b**) (all values in eV)

MO's nature	$-\varepsilon^{KS}$	OVGF	TD-DFT	'Corrected' x=2.34	Exp
	7.56	9.86	10.06[a]	9.9[b]	9.9
	7.78	10.19	11.04	10.12	10.2
	9.31	12.15	11.30	11.65	12.2
	9.53	12.45	11.98	11.87	
	10.06	12.63	12.30	12.40	12.5
	10.19	13.11	12.53	12.53	

[a] ΔSCF value.

[b] Exp. value, x—empirical energy correction, see Computational details.



Scheme 2.

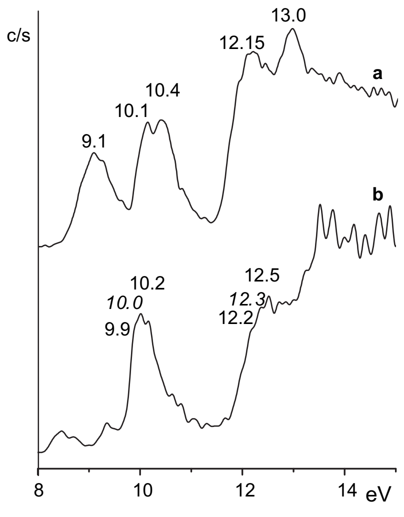


Figure 3. Photoelectron spectra of *N*,*N*-diallyl-*N*-cyanomethylamine **4** (**a**) and its decomposition products at 550 °C (**b**) (propene IEs, in italics).

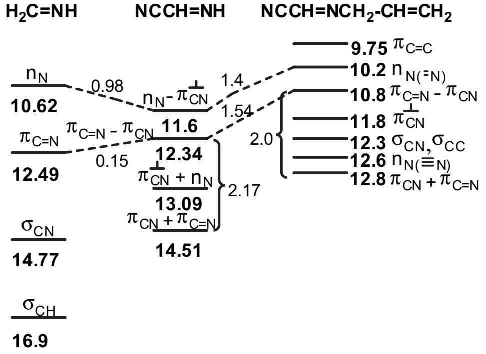


Figure 4. Correlation diagram of the characteristic experimental ionization energies of methanimine, cyanomethanimine[8] and *N*-allylcyanomethanimine (**2b**) (eV).

4.2. Starting materials

The *cis* and *trans* isomers of 1-benzyl-2-cyano-3-phenylazetidines (**1a**) and 1-allyl-2-cyano-3-phenylazetidines (**1b**) were synthesized according to the multi-step literature protocol.[17,18]

4.3. Preparative flash vacuum thermolysis

The flash vacuum thermolysis was carried out in a 30×2.5 cm electrically heated horizontal quartz tube packed with quartz rings at 1.5×10^{-3} Torr. The starting compounds **1a**–**b** (0.5 mmol) were slowly introduced from a flask held at 30–40 °C into the thermolysis tube preheated to 470 °C. The products were collected in a solid CO_2–acetone cold trap. After thermolysis, the system was brought to atmospheric pressure, allowing slow warming to rt and the products were dissolved in $CDCl_3$. The ^1H and ^{13}C NMR spectra were recorded directly.

4.3.1. Thermolysis of **1a**

*4.3.1.1. (E)-N-Benzyliminoacetonitrile[11] (**2a**E).* Only selected diagnostic signals: ^1H NMR ($CDCl_3$) δ 4.83 ppm (d, J=2.0 Hz). ^{13}C NMR ($CDCl_3$) δ 65.85 ppm (CH_2).

*4.3.1.2. (Z)-N-Benzyliminoacetonitrile[11] (**2a**Z).* Only selected diagnostic signals: ^1H NMR ($CDCl_3$) δ 4.99 ppm (d, J=2.5 Hz). ^{13}C NMR ($CDCl_3$) δ 63.37 ppm (CH_2).

*4.3.1.3. Benzylidenecyanomethyl amine[19] (**3a**).* Only selected diagnostic signals: ^1H NMR ($CDCl_3$) δ 4.60 (d, J=2.0 Hz), 8.48 (t, J=1.8 Hz). ^{13}C NMR ($CDCl_3$) δ 45.55 ppm (CH_2).

*4.3.2. Thermolysis of **1b**.* (*E*)-*N*-Allyliminoacetonitrile (2**b***E*). Only selected diagnostic signals: ^1H NMR ($CDCl_3$) δ 4.20–4.38 ppm (m). ^{13}C NMR ($CDCl_3$) δ 64.25 ppm (CH_2).

*4.3.2.1. (Z)-N-Allyliminoacetonitrile (2**b**Z).* Only selected diagnostic signals: ^1H NMR ($CDCl_3$) δ 4.40–4.50 ppm (m). ^{13}C NMR ($CDCl_3$) δ 61.78 ppm (CH_2).

*4.3.2.2. (E)-2-Propenylidene glycinnitrile[20] (**3b**).* Only selected diagnostic signals: ^1H NMR ($CDCl_3$) δ 4.48 (dd, J=1.2 Hz, J=0.5 Hz), 8.08 (dt, J=8.7, J=1.5 Hz). ^{13}C NMR ($CDCl_3$) δ 45.27 ppm (CH_2).

4.4. Flash vacuum thermolysis in tandem with UV-photoelectron spectroscopy

The UV-PES spectra were recorded on a home-built, three-part spectrometer equipped with a main body device (Meca2000), He–I radiation source (Focus) and a spherical analyzer (Omicron). The spectrometer works at constant analyzer energy and is monitored by a microcomputer supplemented by a digital–analogue converter. The spectra resulting from a single scan are built from 2048 points and are accurate within 0.05 eV. They are calibrated against the autoionization of xenon at 12.13 and 13.45 eV, and nitrogen at 15.59 and 16.98 eV. Compound **1b** was slowly vaporized at low pressure (10^{-7} mmHg), and the gaseous flow was directly passing to the internal, progressively heated, FVT quartz furnace (furnace length 20 cm) built into the PE spectrometer. The in situ generated compounds were then directly conducted to the ionization chamber (the distance between the oven exit and the ionization head does not exceed 5 cm) and analyzed.

4.5. Computational details

The calculations were performed using the Gaussian 98[29] program package. 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[30] level of theory with the B3LYP[22] 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 ΔSCF−DFT, which means that separate SCF calculations were performed to optimize the orbitals of the ground state and the appropriate excited state determinants ($IE=E_{cation}-E_{neut.mol.}$). TDDFT[21] approach provides a first principle method for the calculation of excitation energies within a density functional context taking into account the low lying ion calculated by ΔSCF method. The vertical ionization energies of the compounds **1**–**4** were also calculated at the ab initio level according to OVGF[23] method. In this case the effects of electron correlation and reorganization are included beyond the Hartree–Fock approximation, and the self-energy part was expanded up to third order. To compare the ionization energies resulting from these rigorous methods of calculation, we also used a current estimation of ionization energies. Indeed, it has been shown[31] that ε_i^{KS} could be correlated with experimental vertical ionization energies (IE_v) by a uniform shift $x=|-\varepsilon_i\ (HOMO)-IE_v^{exp}|$. 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[32] have shown that the localizations of KS orbitals are very similar to those obtained after HF calculations. The advantages of the most employed method of calculations of the first ionization energies (ΔSCF−DFT calculations) have been thoroughly demonstrated.[24,33]

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Supplementary data

Calculated and experimental values of ionization energies for *N*-allyl-2-cyano-3-phenylazetidine (**1a**), calculated geometrical parameters for the isomers of *N*-allyliminoacetonitrile (**2b**), and the rotamers of *N*-cyanomethyl-1-aza-1,3-butadiene (**3b**), calculated total energies of iminoacetonitrile **2b** and the rotamers of azabutadiene **3b**, calculated (*E*)- and (*Z*)-iminonitrile **2b** isomerization pathways to *s-cis* and *s-trans N*-cyanomethyl-1-aza-1,3-butadiene (**3a**). Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.09.008.

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