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Synthesis of aryliminoacetonitriles under FVT conditions or by dehydrogenation of arylaminoacetonitriles: an NMR and UV-photoelectron spectroscopy study

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ABSTRACT

The synthesis of [(*E*)-arylimino]-acetonitriles **3** has been described. It was found that the title compounds can be obtained on the three ways, namely by: (i) dehydrogenation of arylaminoacetonitriles **1**, (ii) thermal fragmentation of 1-aryl-4-cyano-β-lactams **4** and (iii) retro-ene reaction of (allyl-*p*-methoxyphenyl-amino)-acetonitrile (**7a**) under FVT conditions. ^{1}H and ^{13}C NMR spectra of compounds **3**, **5** and **6**, and all their precursors **1** and **4**, were recorded and analysed in detail using chemical shifts δ_H and δ_C [from GIAO DFT B3LYP/6-31(d) calculations] and *J*-couplings predicted at the DFT B3LYP/IGLO-II level. Also, UV-photoelectron spectra of **4a**,**d** and **3a**,**d** were measured and analysed considering the theoretical evaluation of their ionisation potentials.

1. Introduction

Formimidoyl cyanides—RN=CHCN (iminoacetonitriles), are particularly interesting compounds described as a novel family of compounds by Boyer in 1970.[1,2] Iminoacetonitriles unsubstituted at the nitrogen atom, considered to be covalent dimers of hydrogen cyanide (HCN), are of a relevant interest as potential interstellar and prebiotic molecules, which via further reaction with HCN can act as a building block for many amino acids, purines and pyrimidines.[3,4] This unstable compound has been obtained (as *E* and *Z* isomers) by several methods such as: pyrolysis of *N*,*N*-dimethylcyanamide,[5] photolysis of azidoacetonitrile in an Ar matrix with IR spectra identification,[6] by thermal decomposition of the sodium salt of 1-cyanoformamide tosylhydrazone at 200 °C and identified by IR, MS, ^{1}H and ^{13}C NMR techniques,[7] as well as by the UV-photoelectron spectroscopy.[8] In sharp contrast to the parent iminoacetonitrile, its *N*-alkyl analogues are sufficiently stable colourless species, so that their full characterisation was possible; however, they also decomposed upon handling. Their synthesis has been accomplished through a two-step sequence involving initial N-chlorination of *N*-alkylaminoacetonitriles with *tert*-butyl or calcium hypochlorite, followed by dehydrochlorination with an appropriate base.[1,2,9] The use of *N*-chlorosuccinimide as a chlorinating agent and calcium hydroxide as a base considerably improved the yield of this reaction.[10] The alternative method of preparation of *N*-alkyl iminoacetonitriles based on oxidation of *N*-alkyl aminoacetonitriles with aqueous solution of NaOCl was described by Selva.[11] Alkyliminoacetonitriles containing a diene system in the *N*-alkyl group have been used in hetero Diels–Alder reactions for the synthesis of several quinolizidines.[12–14] Iminoacetonitrile moieties were also incorporated starting from appropriate diene alcohols and by a Mitsunobu coupling reaction with HN(Tf)CH_2CN followed by a base-promoted elimination of trifluoromethanesulfinate.[12]

Simple *N*-methyl iminoacetonitriles have also been obtained by the flash vacuum thermolysis (FVT) of 1-methyl-2-cyanoaziridine or di(cyanomethyl)amine as well as 1,3,5-tricyanomethyl-1,3,5-triazinane.[15]

To the best of our knowledge [a through MDL Information Systems GmbH (formerly Beilstein) database], the preparation of aryliminoacetonitrile has not been reported hitherto. The present paper is aimed at the synthesis of this new class of imines, and at a thorough analysis of their ^{1}H, ^{13}C NMR and UV-photoelectron spectra.

2. Results and discussion

2.1. Investigations on the synthesis of aryliminoacetonitriles

As it was mentioned above, the methods for the synthesis of alkyliminoacetonitriles described to date are mostly based on the

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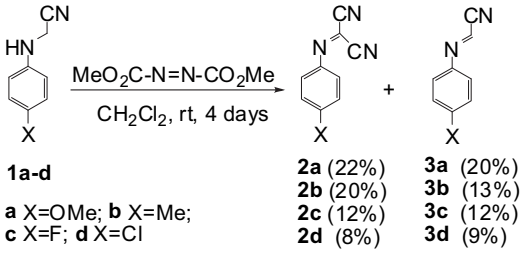
introduction of a double bond C=N in the corresponding alkylaminoacetonitriles, either by their oxidation or by the synthesis of corresponding *N*-chloramine and further elimination of HCl. The fact that the application of these methods to the synthesis of aryliminoacetonitriles had not been previously described suggested to us that they failed in the case of the aromatic amines. In order to verify this tentative assumption, a series of arylaminoacetonitriles, **1a–d**, were synthesised in accordance with the literature procedures. The aminoacetonitriles **1a–d** were subsequently subjected to reactions with chlorinating agents (*N*-chlorosuccimide or calcium hypochlorite) and then elimination of HCl, with the use of $Ca(OH)_2$ as a base. In all these cases, the post-reaction mixture contained only the unreacted starting material. Similarly, attempts to oxidise amines **1a–d** by the Selva method.[11] i.e., with the use of sodium hypochlorite, were unsuccessful. Finally, a very recently reported[16] oxidising procedure based on the application of iodoxybenzoic acid also failed. Fortunately, our attempts to dehydrogenate the amines **1a–d** by using dimethyl azodicarboxylate led to some success. The reactions carried out at room temperature in dichloromethane resulted in obtaining the expected products **3a–d** (Scheme 1).

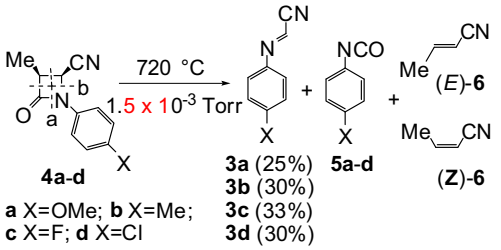


Scheme 1.

However, the yield of these reactions was low and it was not improved despite of our numerous attempts performed at different temperatures, times and reaction stoichiometry. Apart from the target compounds **3a–d**, this process also leads to the dicyano species **2a–d**. Moreover, the post-reaction mixture always contained the substrate **1** beside other numerous unidentifiable products. Compounds **2** and **3** were separated by standard column chromatography on silica gel. The first ones were eluted the species **2** (hexane/CH_2Cl_2 9:1), while the products **3** were eluted with the mixture hexane/CH_2Cl_2 3:1. Furthermore, all the products were purified by recrystallisation from hexane. Immediately after such purification, all cyano compounds **2** and **3** were of analytical purity. The nitriles **3a–d** slowly decompose on storage.

On the other hand, some molecular systems containing the double bond C=N can be obtained by the flash vacuum thermolysis of four-membered rings containing a ring-nitrogen atom.[17] Recently, we showed[18] that such a treatment of 1-benzyl or 1-allyl-2-cyano-3-phenylazetidines leads to the formation of corresponding benzyl- or allyl-iminoacetonitriles. In this work, we intend to present our research results on FVT of *N*-aryl-4-cyano-β-lactams as a potential method of the aryliminoacetonitrile synthesis.

The fragmentation of the β-lactam ring, under FVT conditions, occurs according to a stepwise biradical mechanism and its regiochemistry depends on the substituents present in the system.[17] The 1-aryl-4-cyan-3-methyl-β-lactam substrates **4a–d** were obtained from related 4-formyl-β-lactams. The latter ones were synthesised in line with procedures described in the literature.[17c,19] By subjecting the β-lactams **4a–d** to FVT at 720 °C and 1.0×10^{-3} Torr, it was found that the expected ring fragmentation occurs, and that the regiochemistry of this reaction depends only to a small extent on the substituent in the phenyl ring (Scheme 2).



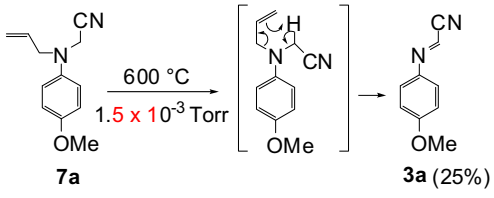
Scheme 2.

In all these cases, we found that aryliminoacetonitriles **3a–d** were formed, even though their yield was not high (~30%). Moreover, the corresponding aryl isocyanate **5** was the main product of the reaction in each case. By analysing the post-reaction mixtures, with the use of ^1H and ^{13}C NMR spectra, it was found that the regiochemistry of the reaction was (path a/path b) 25:75 for **4a**, 33:67 for **4c** and 30:70 for **4b** and **4d**. These results were established on the basis of integrations of selected signals in ^1H NMR spectra, i.e., due to the methyl groups for **3a** and **3b**, or the azomethine proton for **3d**, as well as from the ^{19}F NMR spectrum recorded for **3c**.

The post-reaction mixtures also revealed the presence of corresponding crotonitrile **6** existed as a mixture of its *E*/*Z* isomers. It should be stressed that the total amount of these isomeric species **6** was always smaller than that of related isocyanate **5**. It is interesting to note that an increase in the thermolysis temperature by 50 °C practically leads to the disappearance of **6** in the obtained post-reaction mixtures, while the iminoacetonitrile/isocyanate ratio remains unchanged. In our opinion, this strongly suggests that crotonitrile decomposes under FVT conditions used. The products **3a–d** were easily isolated by applying preparative thin-layer chromatography. Their spectroscopic properties were identical with those previously established for such products synthesised by the dehydrogenation of aminoacetonitriles **1a–d** (vide supra).

The introduction of the second methyl group in the 3-position in the β-lactam ring did not change the regiochemistry of the ring fragmentation. For example, FVT of 4-cyano-3,3-dimethyl-1-*p*-methoxyphenylazetidin-2-one[19b] (**4e**) resulted in the formation of **3a** in 25% yield beside *p*-methoxyphenyl isocyanate (**5a**) (75%) and 3-methyl-but-2-enenitrile (**6e**).

Another attempt to obtain compound **3a** was a retro-ene reaction of [allyl-(*p*-methoxyphenyl)amino]acetonitrile **7a** carried out under FVT conditions. The amine **7a** was obtained by allylation of **1a** under typical conditions.[20] Thermolysis of **7a** led to **3a** in 25% yield (Scheme 3) (on the basis of an integration of the azomethine proton signal in the ^1H NMR spectrum).



Scheme 3.

The yield of **3a** in this FVT reaction was subsequently confirmed after separation of the obtained post-reaction mixture using the preparative thin-layer chromatography. Apart from **3a**, the reaction leads to a great number of by-products, none of them was obtained in the pure form. The spectroscopic data for **3a** were identical with those obtained earlier.

2.2. NMR calculations for the products and their precursors

All iminoacetonitriles **3a**–**d**, related starting materials **1**, **4** and **7a** as well as the obtained by-products **2**, **5** and **6**, were fully characterised by their ^{1}H and ^{13}C NMR spectra. In addition, the calculational DFT-based GIAO[21] method was occasionally used for unambiguous assignments of the signals due to a large complexity of some NMR spectra, especially those achieved for the complicated post-reaction mixtures (see Computational details).

Moreover, all coupling constants $^{n}J_{xH}$s were computed for both unsaturated isomeric nitriles (*E*)-**6** and (*Z*)-**6** using the B3LYP/IGLO-II//B3LYP/6-31(d) approach.[22] The perfect agreement was obtained between the presently measured/predicted and reported[23] J_{HH} values. However, to our large surprise, the four $^{1}J_{CH}$ couplings in =C–H bonds of these stereoisomers were found as erroneously given in Ref. 23, i.e., these *J*-couplings should be mutually replaced within each pair of reported *J* data. Thus, an excellent correlation was found between the calculated and such corrected experimental $^{n}J_{xH}$s (correlation coefficient r=1.000, see Table S1 and Fig. S1 in the Supplementary Data). These findings fully justified a reliability of the B3LYP/6-31(d)-optimised geometries adopted for the differently unsaturated molecules under this study.

Generally, the investigated FVT ring cleavage was found as a highly regioselective process. Indeed, only *E* isomers of all of the acetonitriles **3a**–**d** were NMR spectroscopically observed in $CDCl_3$ solution. Nonetheless, the initial formation of both forms *E* and *Z* under the applied FVT conditions followed by a rapid isomerisation cannot be excluded. As to the simultaneously formed nitriles (*E*)-**6** and (*Z*)-**6**, the former one was found as a prevailing isomer (*E*/*Z*≅3:2, by ^{1}H NMR spectra), in good agreement with the literature data[23] and our calculational gas-phase results ($\Delta G_{298.15}$=0.20 kJ mol^{-1} affording the *E*/*Z* ratio of 52:48).

2.3. UV-photoelectron spectroscopy

*2.3.1. cis-4-Cyano-1-(p-methoxyphenyl)-3-methylazetidin-2-one (**4a**).* The photoelectron (PE) spectrum of *cis*-4-cyano-1-(*p*-methoxyphenyl)-3-methylazetidin-2-one (**4a**) (Fig. 1a) displays well distinguished low energy ionisations: the first one at 8.15 eV is followed by the more intense band at 9.4 with a right-side shoulder at 9.7 eV, the third band at 10.15 is narrow and precedes a less intense one at 10.5 eV. The next part of the spectrum constitutes a large massif with a maximum centred at 13.1 eV.

The FVT of **4a** at 840 °C gave a new spectrum (Fig. 1b) with the intensity of several bands particularly changed. The first new ionisation is localised at 8.0 eV, then two maxima at 9.6 and 9.8 eV are followed by a very sharp and intense band at 10.2 eV. Moreover, a small intensity band at 14.0 eV due to the C=O ionisation potential (IE) is distinguished at a broad massif situated at higher energies.

*2.3.2. cis-4-Cyano-1-(p-chlorophenyl)-3-methylazetidin-2-one (**4d**).* The PE spectrum of *cis*-1-(*p*-chlorophenyl)-4-cyano-3-methylazetidin-2-one **4d** is presented in Figure 2a and displays two first broad bands at 8.6 and 9.95 (with a left-side shoulder at 9.75) eV, which are followed by two sharp and intense ones at 10.75 and 11.4 eV. The most intense band of this spectrum is situated on the large massif at 13.3 eV.

The PE spectra of FVT of **4d** at 895 °C are shown in Figure 2b. Several differences concerning, more relative intensity of bands and less their position, should be remarked. The C=O ionisation potential (at 14.0 eV) is well distinguished.

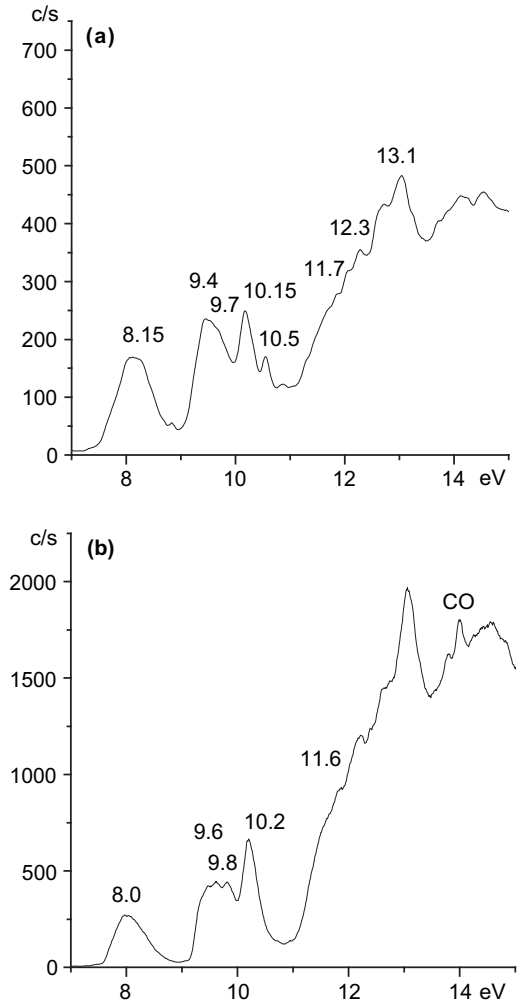


Figure 1. Photoelectron spectra of: (a) *cis*-4-cyano-1-(*p*-methoxyphenyl)-3-methylazetidin-2-one (**4a**); (b) *cis*-4-cyano-1-(*p*-methoxyphenyl)-3-methylazetidin-2-one (**4a**) at 840 °C.

2.4. Theoretical IE evaluation and UV–PE spectra interpretation

*2.4.1. cis-4-Cyano-1-(p-methoxyphenyl)-3-methylazetidin-2-one (**4a**) and cis-1-(p-chlorophenyl)-4-cyano-3-methylazetidin-2-one (**4d**).* The attribution of the PE bands of two starting materials **4a** and **4d** is corroborated by theoretical evaluation of their IEs, which are given with pertinent calculated geometrical parameters in Table S2.

Thus, the PE spectra of *cis*-4-cyano-1-(*p*-methoxyphenyl)-3-methylazetidin-2-one (**4a**) and *cis*-1-(*p*-chlorophenyl)-4-cyano-3-methylazetidin-2-one (**4d**) are interpreted as follow:

- the first band of **4a** at 8.15 eV and that of **4d** at 8.6 eV correspond to the ejection of one electron from the π antibonding interaction of heteroatom lone pairs ($n_{=O}$, n_N, n_O/n_{Cl}) and π_2 aromatic ring, respectively;
- the second IE at 9.4 (**4a**) and 9.75 (**4d**) eV is due to the aromatic ring π_3 ionisation;
- 9.7 (**4a**) and 9.95 (**4d**) eV PE bands are attributed to the MO mainly localised on the σ-oxygen lone pair (of C=O) interacting with two adjacent σ_{CN} and σ_{CC} bonds;
- the band at 10.15 eV for **4a** and at 10.75 eV for **4d** reflects the ionisation of π antibonding interaction of heteroatom lone pairs ($n_{=O}$, n_N, n_O/n_{Cl}) and π_3 aromatic ring, respectively;

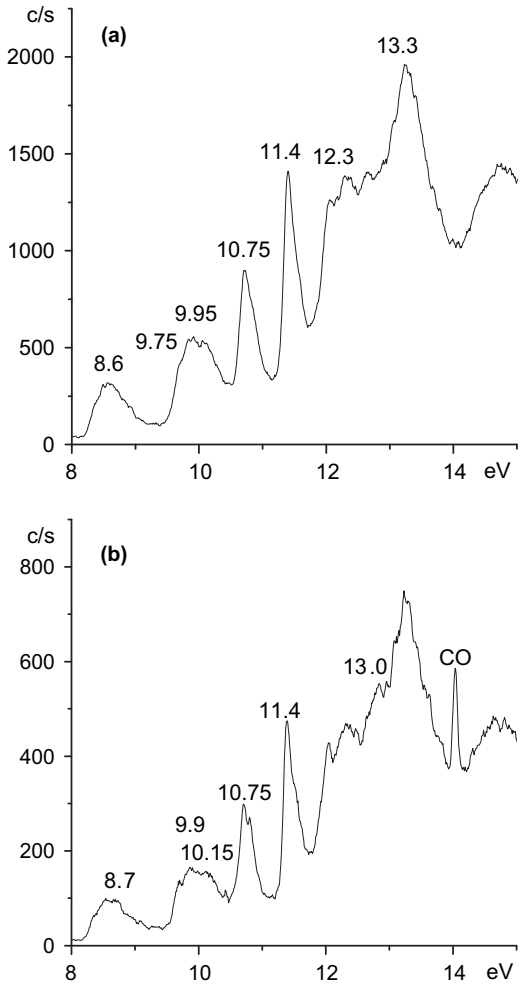


Figure 2. Photoelectron spectra of: (a) *cis*-1-(*p*-chlorophenyl)-4-cyano-3-methylazetidin-2-one (**4d**); (b) *cis*-1-(*p*-chlorophenyl)-4-cyano-3-methylazetidin-2-one (**4d**) at 895 °C.

- 10.5 (**4a**) and 11.4 eV IE correspond to the σ-oxygen lone pair of OCH_3 and σ-chlorine lone pair ionisations, respectively;
- higher energy PE bands are due to the two $\pi_{C\equiv N}$ ionisations and other, mainly sigma bonds ionisations.

The comparison of these two spectra shows the similarity of two lactams **4a** and **4d**, which are different only by the substituent in *para* position of the aromatic ring. However, the π-donor effect of OCH_3 is clearly evidenced as the more efficient than that of the chlorine one and visualised by the shift of corresponding IE to the lower energies.

*2.4.2. Calculated geometries for isomers E and Z of iminoacetonitriles **3a** and **3d**.* The calculated structures of aryliminoacetonitriles **3a** and **3d** are displayed in Figures 3 and 4, whereas the optimised geometrical parameters of their *E* and *Z* isomers are summarised in Table 1. Considering the calculated geometries of *E* and *Z* isomers of aryliminoacetonitriles **3a** and **3d**, the nitrogen–carbon double bond ($N^2{=}C^2$) in both isomers of imine **3a** is slightly longer than those of imine **3d**. For both (*E*)-iminoacetonitriles, the C(2)–C(1) distance is shorter than for their *Z* isomers.

Sterical hindrance and electronic repulsions between the phenyl and nitrile groups make the angles C(1)C(2)N(2) and C(3)N(2)C(2) biggest in *Z* than in *E* forms. This is also probably the reason of '*gauche*' phenyl ring orientation and out-of-plane position (by 2°) of the C≡N unit, clearly observed for both *Z* isomers. Thus, the non-planar structure and not fully conjugated system are main characteristics of the geometrical structures of these aryliminoacetonitriles.

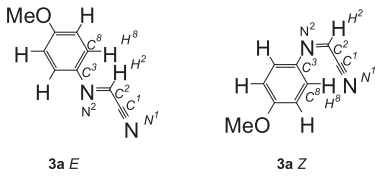


Figure 3. *E* and *Z* isomers of (*p*-methoxyphenyl)iminoacetonitrile **3a**.

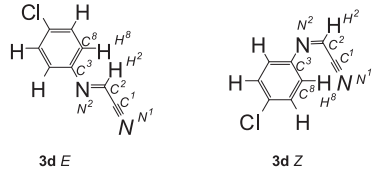


Figure 4. *E* and *Z* isomers of (*p*-chlorophenyl)iminoacetonitrile **3a**.

Table 1
Optimised [B3LYP/6-311G(d,p)] geometrical parameters of *E* and *Z* isomers of aryliminoacetonitriles **3a** and **3d**, distances in Å, angles in degrees

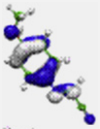
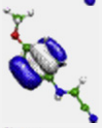
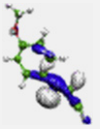
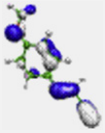
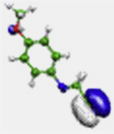
Parameters	(*E*)-**3a**	(*Z*)-**3a**	(*E*)-**3d**	(*Z*)-**3d**
N(2)–C(2)	1.277	1.278	1.275	1.275
C(2)–C(1)	1.434	1.442	1.435	1.444
C(1)–N(1)	1.155	1.156	1.155	1.159
N(2)–C(3)	1.401	1.398	1.404	1.403
N(1)–H(8)		2.739		2.942
H(2)–H(8)	2.215		2.288	
C(3)–N(2)–C(2)	121.3	126.8	120.5	124.7
N(2)–C(2)–C(1)	120.1	128.7	120.2	128.0
N(2)–C(2)–H(2)	124.7	117.5	124.5	117.8
H(2)–C(2)–C(1)	115.2	113.8	115.3	114.2
C(2)–C(1)–N(1)	177.2	176.6	177.2	176.2
C(1)–C(2)–N(2)–C(3)	178.0	2.9	177.8	3.7
C(2)–N(2)–C(3)–C(8)	−25.4	−23.7	−32.6	−37.5
N(2)–C(2)–C(1)–N(1)	179.9	164.5	179.8	164.5

*2.4.3. Theoretical and experimental IEs for E and Z isomers of iminoacetonitriles **3a** and **3d**.* The application of the FVT in tandem with UV–PES is considerably different from preparative FVT in terms of vacuum and temperature (10^{-7} Torr, 840 °C for **4a** and 895 °C for **4d**). Thus, the presence of the very characteristic CO ionisation (sharp band at 14.0 eV) in the spectra of Figures 1b and 2b suggests that even if isocyanates **5a** and **5b** are formed, they decompose instantly. Moreover, considering the calculated values of IEs for **5a** and **5b** (given in the Supplementary Data), the expected bands are not clearly distinguished. Tables 2 and 3 display IEs calculated by different methods for *E* and *Z* isomers of iminoacetonitriles **3a** and **3d** in comparison with their experimental values.

The analysis and interpretation of FVT UV–PE spectra of iminoacetonitriles **3a** and **3d** have been done, as for their precursors **4**, in conjunction with theoretical evaluation of ionisation energies as a main support:

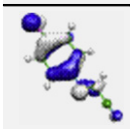
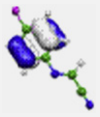
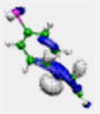
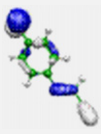
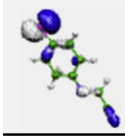
- two first ionisations expected for **3a** and **3d** (at 8.0 and 9.6 eV for **3a**; at 8.7 and 9.9 eV for **3d**) are attributed to the π_2 and π_3 ionisations of the aromatic ring. The lower values of the first one reflect an antibonding interaction of its orbitals with the heteroatom π lone pair. As remarked for the precursors, a more efficient donor effect is noted for the OCH_3 substituent versus the chlorine one;

Table 2
Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] and experimental ionisation energies (IEs) for *Z* and *E* isomers of (*p*-metoxyphenyl)iminoacetonitrile **3a** (all values in eV)

Nature of MO	$-\varepsilon^{KS}$		TD-DFT		OVGF		'Corrected' IE		IE exp.
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z*, *x*=1.66	*E*, *x*=1.58	
	6.34	6.42	8.13[a]	8.19[a]	8.00	8.09	8.00[b]	8.00[b]	**8.0**
	7.47	7.60	9.35	9.47	9.25	9.39	9.13	9.18	**9.6**
	7.87	8.06	9.65	9.80	10.94	10.99	9.35	9.64	**9.8**
	8.67	8.68	10.46	10.43	10.16	10.39	10.33	10.27	**10.2**
	9.32	9.45	10.97	11.31	11.97	12.13	10.99	11.03	**11.6**

[a] Value of ΔSCF.
[b] Experimental value.

Table 3
Calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] and experimental ionisation energies (IEs) for *Z* and *E* isomers of (*p*-chlorophenyl)iminoacetonitrile **3d** (all values in eV)

Nature of MO	$-\varepsilon^{KS}$		TD-DFT		OVGF		'corrected' IE		IE exp.
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z*, *x*=1.74	*E*, *x*=1.61	
	6.96	7.09	8.77[a]	8.87[a]	8.65	8.94	8.70[b]	8.70[b]	**8.7**
	7.83	7.99	9.71	9.85	9.74	9.89	9.57	9.60	**9.9**
	8.47	8.54	10.33	10.32	11.33	11.38	10.21	10.15	**10.15**
	8.99	9.09	10.97	10.98	11.17	11.11	10.73	10.70	**10.75**
	9.32	9.80	11.45	11.38	12.49	12.48	11.64	11.41	**11.4**

[a] Value of ΔSCF.
[b] Experimental value.

- the imino nitrogen lone pair is localised at slightly lower energies for **3a** versus **3d** iminoacetonitrile (9.8 and 10.15 eV, respectively);
- the antibonding interaction between the C=N and C≡N systems is more affected by the presence of the methoxy substituent than by the chlorine one (10.20 and 10.75 eV, respectively);
- the CH_3–CH=C=O PE bands are not very clearly evidenced in the FVT spectra because of their low intensity and the superposition with other bands;
- the high temperature of these FVT processes shows the high stability of lactams under study.

3. Conclusion

We have presented three possible methods of preparing the aryliminoacetonitriles, namely via: (i) dehydrogenation of arylaminoacetonitriles **1**, (ii) thermal fragmentation of 1-aryl-4-cyano-β-lactams **4** and (iii) retro-ene reaction of [allyl-(*p*-methoxyphenyl)amino]-acetonitrile **7a** under FVT conditions. In our opinion, the first and second methods are the most useful. Even though all of these reactions proceed with a similar yield, the problem with the last method is such that [allyl-(*p*-methoxyphenyl)amino]acetonitrile applied as a starting material is less stable in comparing to related β-lactam or (*p*-methoxyphenyl)aminoacetonitrile.

The cycloreversion reaction applied to 4-cyano-azetidin-2-ones **4a**–**d** under FVT conditions has allowed the synthesis of two iminoacetonitriles **2** and their full ^1H, ^{13}C NMR, as well as UV–PES spectroscopic characterisation.

As remarked previously,[24] introduction of the cyano group at the C atom of methaneimine provokes the 1 eV imino-nitrogen lone pair stabilisation (in the antibonding interaction with $\pi^{\perp}_{C\equiv N}$), while the C=N double bond (in the antibonding interaction with $\pi_{C\equiv N}$) is slightly stabilised, by 0.09 eV. Full destabilisation of π and σ iminoacetonitrile system is achieved under N-electron-donor substitution. Thus, electronic properties of two iminoacetonitriles **3** in comparison with methaneimine and iminoacetonitrile can be resumed by the $\pi_{C=N}$–$\pi_{C\equiv N}$ level of experimental IEs (Table 4).

Table 4
Experimental ionisation energies (IEs) for selected imines

Compound	IE, eV	Assignment
H_2C=NH	12.43	$\pi_{C=N}$
N≡C–CH=NH	12.34	$\pi_{C=N}$–$\pi_{C\equiv N}$
N≡C–CH=N–C_6H_4Cl-*p* (**3d**)	10.75	$\pi_{C=N}$–$\pi_{C\equiv N}$
N≡C–CH=N–C_6H_4OMe-*p* (**3a**)	10.20	$\pi_{C=N}$–$\pi_{C\equiv N}$

On the whole, if the N-electron donation effect is strong then bigger IE destabilisation is found and corresponds to the more electronically rich structure. For iminoacetonitriles **3** under this study, such a push–pull effect is really played by electron-donating *p*-methoxy- and *p*-chlorophenyl groups, and a strongly electron-withdrawing CN substituent.

As to theoretical evaluation of IEs experimentally measured for products **3** in the gaseous phase, the in vacuo TD-DFT predictions are evidently the best. However, it is not possible to use these results for an unequivocal distinction between two isomeric forms, owing to similarity of their IEs. Nonetheless, the (*E*) isomer seems to be generally favoured (especially for **3a**), in full agreement with NMR data for $CDCl_3$ solution.

4. Experimental

4.1. General

The ^1H, ^{13}C and ^{19}F NMR spectra were recorded at ca. 21 °C with a *Varian Gemini 200 BB VT* instrument, operating at 200.11, 50.33 and 188.14 MHz for ^1H, ^{13}C and ^{19}F nuclei, respectively. $CDCl_3$ was used as a solvent. Chemical shifts δ_xs are expressed in parts per million [against internal tetramethylsilane (TMS) or external trifluoroacetic acid (TFA)], while coupling constants *J*s determined by first-order analysis are in hertz. Signals are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or p (pseudo). For majority of the spectra, the assignments of NMR signals were achieved by selective decouplings or performing the ATP, DEPT or HETCOR experiments. IR spectra were recorded in KBr pellets on a *Thermo-Nicolet Nexus FT-IR* spectrometer. Electrospray ionisation (ESI) mass spectra were taken on a *Varian 500-MS Ion Trap* mass spectrometer operating in positive- or negative-ion mode (ESI^+ or ESI^-). Melting points (uncorrected) were determined on a *Boëtius* hot-plate apparatus. Normal column chromatography was performed with silica gel (*Merck type 60*, 63–200 microns). Analytical thin-layer chromatography (TLC) was carried out on standard *Merck 5554* aluminium-backed SiO_2 plates. Preparative TLC was performed using the glass plates with a 1.5-mm layer of *Merck silica gel 60 PF_{254}*. The products were visualised by UV light (254 nm).

4.2. Starting materials

Arylaminoacetonitriles **1a**–**d** were prepared according to literature: **1a**,[25] **1b**[26] and **1d**.[27] Compound **1c** was prepared in 12% yield using the procedure reported for **1b**.[26] ^1H NMR: 3.75 (s, 1H), 4.05 (s, 2H), 6.50–6.72 (m, 2H), 7.08–7.32 (m, 2H). [Allyl-(4-methoxyphenyl)amino]-acetonitrile **7a** was prepared in 82% yield by allylation of **1a**.[20] IR (KBr, cm^{-1}): 3079, 3001, 2954, 2935, 2910, 2835, 2235, 1643, 1612, 1582, 1514, 1464, 1443, 1420, 1244, 1182, 1044, 1031, 935, 820. ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 3.70–3.90 (m, 2H), 3.75 (s, 3H), 4.04 (s, 2H), 5.15–5.48 (m, 2H), 5.62–6.12 (m, 1H), 6.60–7.05 (m, 4H).

New 4-cyano-β-lactams **4a**–**d** were prepared by treatment of related 4-formylazetidin-2-ones with hydroxylamine hydrochloride in formic acid.[28] For the synthesis of 4-formyl-β-lactams used in this work, see Supplementary data.

*4.2.1. cis-4-Cyano-3-methyl-1-(p-methoxyphenyl)azetidin-2-one (**4a**).* Yield 242 mg (56%), colourless solid. Mp 119–120 °C (hexane/CH_2Cl_2). IR (KBr, cm^{-1}): 2243ν_{CN}, 1755ν_{CO}. ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 1.58 (d, *J* 7.5 Hz, 3H), 3.71 (dq, *J* 7.5, 5.5 Hz, 1H), 3.80 (s, 3H), 4.69 (d, *J* 5.5 Hz, 1H), 6.85–6.95 (m, 2H), 7.30–7.40 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 11.44, 44.86, 48.35, 55.53, 114.70, 115.00, 118.04, 129.85, 157.02, 164.56. Anal. Calcd for $C_{12}H_{12}N_2O_2$ (216.24): C, 66.65; H, 5.59; N, 12.95%. Found: C, 66.48; H, 5.71; N, 12.81%.

*4.2.2. cis-4-Cyano-3-methyl-1-(p-tolyl)azetidin-2-one (**4b**).* Yield 208 mg (52%), colourless solid. Mp 91–93 °C (hexane/CH_2Cl_2). IR (KBr, cm^{-1}): 2243ν_{CN}, 1750$\nu_{C=O}$. ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 1.53 (d, *J* 7.5 Hz, 3H), 2.31 (s, 3H), 3.64 (dq, *J* 7.5, 5.6 Hz, 1H), 4.67 (d, *J* 5.6 Hz, 1H), 7.10–7.18 (m, 2H), 7.27–7.37 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 11.36, 20.93, 44.64, 48.23, 115.14, 116.50, 130.08, 134.13, 135.05, 165.02. Anal. Calcd for $C_{12}H_{12}N_2O$ (200.24): C, 71.98; H, 6.04; N, 13.99%. Found: C, 71.80; H, 6.07; N, 13.83%.

*4.2.3. cis-1-(p-Fluorophenyl)-4-cyano-3-methylazetidin-2-one (**4c**).* Yield 166 mg (40%), colourless solid. Mp 112–115 °C (hexane/CH_2Cl_2). IR (KBr, cm^{-1}): 2250ν_{CN}, 1757ν_{CO}. ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 1.61 (d, *J* 7.5 Hz, 3H), 3.76 (dq, *J* 7.5, 5.6 Hz, 1H), 4.73 (d, *J* 5.6 Hz, 1H), 7.05–7.18(m, 2H), 7.38–7.47(m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 11.41, 44.88, 48.64, 114.68, 116.44 (d, *J* 23.0 Hz), 118.11 (d, *J* 8.1 Hz), 132.63 (d, *J* 2.8 Hz); 159.79 (d, *J* 245.3 Hz), 164.70. ^{19}F NMR (188 MHz, $CDCl_3$,

TFA_{ext}=0 ppm): δ −39.4 (m). Anal. Calcd for $C_{11}H_9FN_2O$ (204.20): C, 64.70; H, 4.44; N, 13.72%. Found: C, 64.57; H, 4.57; N, 13.58%.

*4.2.4. cis-1-(p-Chlorophenyl)-4-cyano-3-methylazetidin-2-one (**4d**).* Yield 203 mg (46%), colourless solid. Mp 130–132 °C (hexane/CH_2Cl_2). IR (KBr, cm^{-1}): 2248ν_{CN}, 1763ν_{CO}. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 1.60 (d, *J* 7.5 Hz, 3H), 3.76 (dq, *J* 7.5, 5.6 Hz, 1H), 4.72 (d, *J* 5.6 Hz, 1H), 7.36 (s, 4H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 11.38, 44.72, 48.68, 114.53, 117.66, 129.63, 130.43, 134.86, 164.78. Anal. Calcd for $C_{11}H_9ClN_2O$ (220.66): C, 59.88; H, 4.11; N, 12.70%. Found: C, 59.74; H, 4.17; N, 12.58%.

4.3. Dehydrogenation of acetonitriles 1a–d with dimethyl azodicaboxylate (DMAD)

To a solution of 3 mmol of **1a–d** in 1 mL of CH_2Cl_2, 0.632 g (4.2 mmol) of DMAD was added. The mixture was stirred for 4 days at rt. The solvent was removed in vacuum and products were separated chromatographically (silica gel, hexane/CH_2Cl_2).

*4.3.1. 2-(p-Methoxyphenyl)iminomalononitrile **2a**.* Yellow solid (hexane/CH_2Cl_2 80:20), 57 mg (20% from 2:1 stoichiometry). After recrystallisation from hexane mp 95–97 °C, lit.[29] mp 97 °C. R_f (hexane/AcOEt, 4:1) 0.54. IR (KBr, cm^{-1}): 2228ν_{CN}, 2211ν_{CN}, 1605$\nu_{C=N}$, 1507, 1265, 1169, 1160, 1026, 845. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 3.92 (s, 3H), 6.96–7.08 (m, 2H), 7.72–7.82 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 56.08, 110.65, 113.54, 114.78, 115.42, 128.09, 138.98, 164.86.

*4.3.2. 2-(p-Tolyl)iminomalononitrile **2b**.* Light yellow solid (hexane/CH_2Cl_2 80:20), 56 mg (22% from 2:1 stoichiometry). Mp 92–93 °C (hexane), lit.[30] 98–100 °C. R_f (hexane/AcOEt, 4:1) 0.72. IR (KBr, cm^{-1}): 2236ν_{CN}, 2219ν_{CN}, 1605$\nu_{C=N}$, 1530, 1215, 1173, 1154, 818. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.46 (s, 3H), 7.30–7.38 (m, 2H), 7.47–7.55 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 21.80, 107.92, 109.59, 112.79, 123.95, 130.67, 143.32, 145.06.

*4.3.3. 2-(p-Fluorophenyl)iminomalononitrile **2c**.* Light yellow solid (hexane/CH_2Cl_2 80:20), 31 mg (12% from 2:1 stoichiometry). Mp 93.5–94.5 °C (hexane). R_f (hexane/AcOEt, 4:1) 0.71. IR (KBr, cm^{-1}): 2238ν_{CN}, 2226ν_{CN}, 1602$\nu_{C=N}$, 1587, 1541, 1499, 1243, 1161, 851. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 7.20–7.32 (m, 2H), 7.61–7.70 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 108.94 (d, *J* 3.0 Hz), 109.26, 112.47 (d, *J* 1.1 Hz) 117.41, (d, *J* 23.4 Hz), 126.43 (d, *J* 9.5 Hz), 141.68 (d, *J* 3.3 Hz), 165.30 (d, *J* 258.5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$, TFA_{ext}=0 ppm): δ −27.4 (m). ESI(−)-MS (*m*/*z*): 173.0 [M]. Anal. Calcd for $C_9H_4FN_2$ (173.15): C, 62.43; H, 2.33; N, 24.27%. Found: C, 62.51; H, 2.24; N, 24.29%.

*4.3.4. 2-(p-Chlorophenyl)iminomalononitrile **2d**.* Light yellow solid (hexane/CH_2Cl_2 80:20), 22 mg (8% from 2:1 stoichiometry). Mp 132–134 °C (hexane), lit.[30] 136–138 °C. R_f (hexane/AcOEt, 4:1) 0.72. IR (KBr, cm^{-1}): 2238ν_{CN}, 2222ν_{CN}, 1594$\nu_{C=N}$, 1544, 1533, 1473, 1208, 1163, 1092, 1011, 839, 818. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 7.45–7.58 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 108.97, 110.19, 112.31, 124.66, 130.41, 139.42, 143.80.

*4.3.5. (p-Methoxyphenyl)iminoacetonitrile **3a**.* Light yellow solid (hexane/CH_2Cl_2 70:30), 98 mg (20%). Mp 55–57 °C (hexane). R_f (hexane/AcOEt, 3:1) 0.48. IR (KBr, cm^{-1}): 2223ν_{CN}, 1608$\nu_{C=N}$, 1562, 1505, 1457, 1432, 1298, 1258, 1177, 1164, 1020, 831. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 3.85 (s, 3H), 6.90–7.00 (m, 2H), 7.28–7.37 (m, 2H), 7.54 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 55.63, 114.49, 114.79, 123.54, 128.53, 141.06, 161.64. ESI(+)-MS (*m*/*z*): 161.0 [M+1]. Anal. Calcd for $C_9H_8N_2O$ (160.18): C, 67.49; H, 5.03; N, 17.49%. Found: C, 67.74; H, 5.17; N, 12.33%.

*4.3.6. (p-Tolyl)iminoacetonitrile **3b**.* Light yellow solid (hexane/CH_2Cl_2 70:30), 56 mg (13%). Mp 66–68 °C (hexane). R_f (hexane/AcOEt, 3:1) 0.64. IR (KBr, cm^{-1}): 2229ν_{CN}, 1608$\nu_{C=N}$, 1573, 1505, 1492, 1340, 1208, 1171, 823. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.39 (s, 3H), 7.14–7.28 (m, 4H), 7.54 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 21.28, 115.48, 121.45, 130.31, 131.02, 140.87, 145.82. ESI(+)-MS (*m*/*z*): 145.0 [M+1]. Anal. Calcd for $C_9H_8N_2$ (144.18): C, 74.98; H, 5.59; N, 19.43%. Found: C, 74.87; H, 5.63; N, 19.37%.

*4.3.7. (p-Fluorophenyl)iminoacetonitrile **3c**.* Light yellow solid (hexane/CH_2Cl_2 70:30), 53 mg (12%). Mp 73–76 °C (hexane). R_f (hexane/AcOEt, 3:1) 0.62. IR (KBr, cm^{-1}); 2230ν_{CN}, 1609$\nu_{C=N}$, 1597, 1578, 1503, 1486, 1330, 1235, 1161, 841, 782. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 7.08–7.21 (m, 2H), 7.25–7.35 (m, 2H), 7.55 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 115.20, 116.78 (d, *J* 23.1 Hz), 123.50 (d, *J* 8.9 Hz), 131.84 (d, *J* 2.2 Hz), 144.40 (d, *J* 3.2 Hz), 163.76 (d, *J* 251.7 Hz). ^{19}F NMR (188 MHz, $CDCl_3$, TFA_{ext}=0 ppm): δ −33.9 (m). ESI(+)-MS (*m*/*z*): 149.0 [M+1]. Anal. Calcd for $C_8H_5FN_2$ (148.14): C, 64.86; H, 3.40; N, 18.91%. Found: C, 64.77; H, 3.29; N, 18.93%.

*4.3.8. (p-Chlorophenyl)iminoacetonitrile **3d**.* Light yellow solid (hexane/CH_2Cl_2 70:30), 44 mg (9%). Mp 62–64 °C (hexane). R_f (hexane/AcOEt, 3:1) 0.66. IR (KBr, cm^{-1}): 2231ν_{CN}, 1605$\nu_{C=N}$, 1580, 1572, 1481, 1330, 1093, 832. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 7.18–7.27 (m, 2H), 7.38–7.46 (m, 2H), 7.55 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ 114.98, 122.63, 129.87, 132.67, 136.03, 146.59. ESI(+)-MS (*m*/*z*): 164.0 [M+1]. Anal. Calcd for $C_8H_5ClN_2$ (164.60): C, 58.38; H, 3.06; N, 17.02%. Found: C, 58.31; H, 3.01; N, 17.11%.

4.4. Preparative flash vacuum thermolysis

The FVT was carried out in a 30×2.5 cm electrically heated horizontal quartz tube packed with quartz rings, at 1.5×10^{-3} Torr. All precursors **4a–d** or **7a** (1 mmol) were slowly sublimed from a flask held at 50–60 °C into the thermolysis tube preheated to 720 °C for **4–d** or 600 °C for **7a**. The products were collected in a CO_2/acetone trap. After thermolysis, the whole system was brought to atmospheric pressure, allowing a slow warming up to rt, and the products were dissolved either in $CDCl_3$ for ^{1}H NMR measurement or in Et_2O for their separation with the use of preparative TLC (SiO_2, hexane/AcOEt 2:1).

All products **3a–d** obtained in this way had spectroscopic data identical with those prepared by dehydrogenation of amines **1a–d**.

The yields of separated compounds: **3a** 40 mg (25%), **3b** 44 mg (30%), **3c** 48 mg (33%), **3d** 50 mg (30%), **3a** (from **7a**) 40 mg (25%).

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

The PE 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 analyser (Omicron). The spectrometer is operating at constant analyser energy mode and is monitored by the microcomputer supplemented with a digital-analogue converter. Spectral results of the single scans are built with 2048 points and are accurate within 0.05 eV. They are calibrated against the autoionisation of xenon at 12.13 and 13.45 eV, and nitrogen at 15.59 eV and 16.98 eV. Sample manipulations were carried out in a thermolysis oven attached directly to an inlet probe; a distance between the oven exit and the ionisation head does not exceed 1 cm. Precursors **4a** and **4d** were slowly vaporised under low pressure (10^{-7} Torr in the ionisation chamber) directly in

an oven, and the formed gaseous thermolysate was analysed continuously.

4.6. Computational details

A full conformational analysis of selected compounds **1**–**6** was initially performed for their isolated molecules with a force-field searching protocol, by using PCMODEL V 8.5.[31] The resulting MMX models were applied as trial input configurations in a further geometry refinement using the PM3 hamiltonian of HyperChem.[32] Final in vacuo energy minimisation was carried out applying a double-ζ plus polarisation basis set 6–31G(d) (with six, not five d wave functions used for all heavy atoms) in conjunction with the HF-DFT hybrid exchange-correlation B3LYP[33] functional as implemented in the Gaussian 98 code,[34] by a force gradient method using the Berny algorithm. All of the energy minima were found by optimising the equilibrium geometries.[35]

Some attempts to evaluate the solvent influence on the molecular structures and properties were also made using the integral equation formalism model (IEF-PCM).[36] Default value of the relative permittivity, ε=4.90, was applied at 298.15 K for $CHCl_3$ as a solvent.

The vibrational wavenumbers were also calculated for selected molecules in a rigid-rotor harmonic-oscillator (RRHO) approximation, by using analytical second derivatives at the same B3LYP/6-31G(d) level of theory. These data were applied to check the nature of all located critical points as correct minima on the Born–Oppenheimer potential energy surfaces (N_{imag}=0) and to determine relative differences in the standard Gibbs free energy, $\Delta G^{o}_{298.15}$.[35] Related zero-point vibrational energies (ZPVEs) were computed from the pertinent vibrational frequencies scaled with a uniform factor of 0.96,[37] to bring them into a better agreement with experiment.

Single-point gauge-including atomic orbital (GIAO)[21] in vacuo calculations of isotropic nuclear magnetic shieldings (σ_Xs) were executed at the B3LYP/6-31G(d) level with standard routines in Gaussian 98 on fully relaxed B3LYP/6-31G(d) structures. The relative chemical shift δ_X of a given nucleus X in each molecule was defined as δ_X^{calcd} [ppm]=$\sigma_X^{ref}-\sigma_X^{calcd}$ In the case of the ^{1}H and ^{13}C NMR spectra, σ_X^{ref} was equal to 32.1821 and 189.7710 ppm, respectively, as was analogously evaluated for the B3LYP/6–31G(d) model of the dual-reference δ_X standard (TMS, T_d point group, opt=tight).[35] Moreover, indirect isotropic spin–spin couplings, J_{HH} and J_{CH}, in nitriles (*E*)-**6** and (*Z*)-**6** were predicted for $CHCl_3$ solution by the B3LYP/IGLO-II//B3LYP/6-31(d) method[22] employing the IEF-PCM model[36] within Gaussian 03[38] (Table S1).

All geometry optimisations before ionisation potential (IE) theoretical evaluations were carried out at the higher B3LYP/6-311G(d,p) level, and were again followed by frequency calculations in order to verify that new stationary points obtained were true energy minima (Tables 1, and S2–S4).

To calculate the first ionic states, a time-dependent density functional theory (TD-DFT)[39] was used. This calculation is based on an evaluation of electronic spectrum of the low lying ion, described by the ΔSCF corresponding to the first vertical ionisation potential, IE_V^{cal}, calculated as the difference $E_{cation}-E_{neutral\ molecule}$. Vertical IEs were also calculated at the ab initio level employing the outer-valence Green's function (OVGF)[40] method, which includes the electron correlation and electron relaxation effects. Finally, the so-called 'corrected' IEs were evaluated applying a uniform shift, $x=-IE_V^{exp}-\varepsilon^{KS}{}_{HOMO}$, where $\varepsilon^{KS}{}_{HOMO}$ is the B3LYP/6-311G(d,p) Kohn–Sham energy of the highest occupied MO of the molecule in the ground state and IE_V^{exp} is the lowest experimental IE energy of this species, as was suggested previously by Stowasser and Hoffman[41] and in our studies on different methods for the calculation of IEs.[42]

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Supplementary Data

This material (10 pages) contains: Synthesis of 4-formyl-β-lactams. A full assignment of the NMR signals for **3a** and **4e**. Couplings J_{HH} and J_{CH} in (*E*)-**6** and (*Z*)-**6** measured in $CDCl_3$ versus B3LYP/IGLO-II//B3LYP/6-31(d)-calculated for the PCM/$CHCl_3$ model. Optimised [B3LYP/6-311G(d,p)] geometrical parameters of **4a** and **4d**, calculated [B3LYP/6-311G(d,p); OVGF/6-311G(d,p)] and experimental ionisation energies (IEs) for **4a** and **4d**; calculated [B3LYP/6-311G(d,p)] ionisation energies for **5a** and **5d**; calculated [B3LYP/6-311G(d,p)] scheme of fragmentation by the stepwise singlet biradical mechanism of the **4d** β-lactam ring. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2009.10.080.

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