

## A base induced transformation of a 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium salt into $\beta$ -[methyl-(1-adamantyl)amino]acrylonitriles in aliphatic nitriles

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Dedicated to Prof. Anthony J. Arduengo, III on the occasion of his 60th birthday

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### Abstract

A novel 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate has been prepared via the Vilsmeier-Haack reaction of *N*-methyl-*N*-(1-adamantyl)formamide and *N*-methyl-*N*-(1-adamantyl)amine in a mixture of phosphorus oxychloride and benzene. The new formamidinium salt was found to undergo addition-elimination reactions when treated with sodium hydride in acetonitrile or propionitrile solution, thereby forming the corresponding  $\beta$ -[methyl(1-adamantyl)amino]acrylonitriles and *N*-methyl-*N*-(1-adamantyl)amine. The <sup>1</sup>H and <sup>13</sup>C NMR spectra and the single-crystal X-ray structure of the new formamidinium salt have been determined along with those of the related compound 1,3-di-(1-adamantyl)-1-cyanoamidine and the corresponding  $\beta$ -(dialkylamino)acrylonitriles.

**Keywords:** Dimethyldi-(1-adamantyl)formamidinium salt, deprotonation,  $\beta$ -aminoacrylonitriles

### Introduction

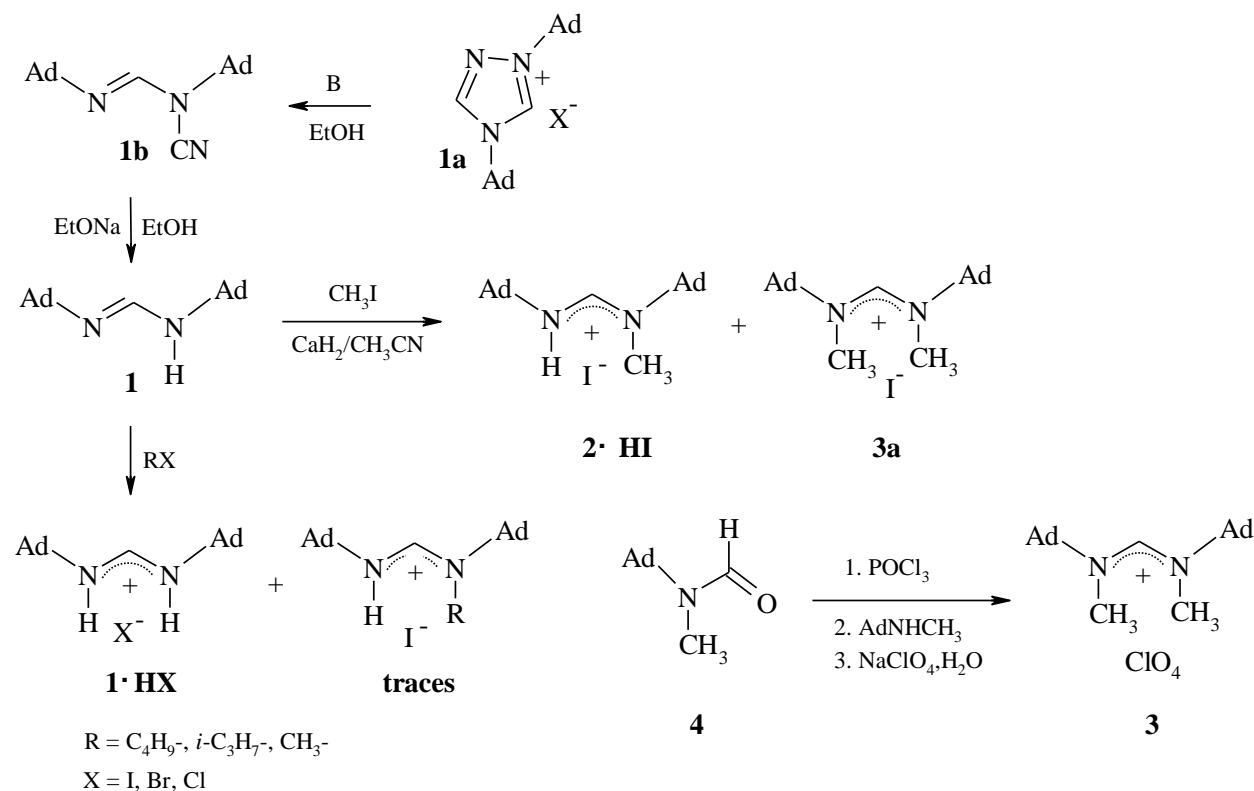
One of the characteristic *in situ* transformations of nucleophilic carbenes involves their C-H bond insertion reactions with ketones, sulfones, nitromethane and nitriles. Reactions of this type were investigated originally by Wanzlick et al.<sup>1-3</sup> and have been reported subsequently by other research groups.<sup>4-5</sup> Furthermore, the corresponding reactions with acetonitrile, dimethylsulfone and acetylenes have been carried out with stable carbenes such as 1,3-dialkylbenzimidazol-2-

ylidenes, 1-alkyl-3,4-diaryl-1,2,4-triazol-5-ylidenes<sup>6-9</sup> and 1,3-dimesitylimidazolin-2-ylidene<sup>10</sup> However, thus far the analogous transformations of highly basic acyclic tetraalkyldiaminocarbenes have not been explored. Such reactions are of considerable potential interest as a source of acyclic diaminomethane derivatives. In earlier work it has been demonstrated that the heterocyclic analogues of these derivatives behave as cryptocarbenes and undergo reactions with both organic and inorganic electrophiles<sup>11, 12</sup> as well as undergoing thermal conversion of the cyanomethylazoline derivative into the free carbene.<sup>8, 9</sup> Given the foregoing, we became interested in exploring the C-H insertion reactions of *in situ* generated tetraalkyldiaminocarbenes in aliphatic nitrile solutions. The sterically encumbered 1,3-di-(1-adamantyl)-substituted formamidinium salt was selected as the precursor for diaminocarbene generation due to its steric stabilization and the likelihood that a crystalline product would be formed.<sup>8, 13</sup>

In the present manuscript we describe: (i) the synthesis of the novel sterically encumbered carbenoid 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate, (ii) the unusual addition-elimination reaction pathway for conversion of the amidinium salt into  $\beta$ -(dialkylamino)acrylonitriles when treated with sodium hydride in aliphatic nitrile solutions, (iii) deuterium-exchange evidence for the proposed addition-elimination pathway and (iv) the single-crystal X-ray structures of 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate, 1,3-di-(1-adamantyl)-1-cyanoamidine,  $\beta$ -[methyl(1-adamantyl)amino]acrylonitrile and  $\beta$ -[methyl(1-adamantyl)amino]methacrylonitrile.

## Results and Discussion

**Preparation of 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate.** In principle, the most straightforward route to the desired 1,3-di-(1-adamantyl)-substituted formamidinium salt would appear to be via direct alkylation of 1,3-di-(1-adamantyl)formamidine **1** with alkyl halides. However, this reaction is complicated by deprotonation of the alkylating reagent.<sup>14</sup> We have now found that compound **1** can be prepared in high yields by basic cleavage of the 1,4-di-(1-adamantyl)-1,2,4-triazolium salt **1a** according to the two-step process outlined in Scheme 1.<sup>15</sup> Unfortunately, the subsequent treatment of **1** with a sixfold excess of CH<sub>3</sub>I in the presence of CaH<sub>2</sub>/CH<sub>3</sub>CN resulted in a difficultly separable mixture of *N*-methylformamidinium iodide **2·HI** along with a 15% yield of 1,3-dimethylformamidinium iodide (**3a**). Furthermore, the reaction of **1** with a variety of alkyl halides afforded mixtures of the unsubstituted product (**1·HX**) and the corresponding monosubstituted species.<sup>16</sup>



**Scheme 1.** Preparative pathways for the synthesis of 1,3-dimethyl-1,3-di-(1-adamantyl)-formamidinium salts.

Given the foregoing difficulties, it was decided to investigate the use of the Brederick modification of the Vilsmeier-Haack reaction in an effort to prepare the desired formamidinium salt **3**. This method has been reported earlier by Alder et al.<sup>17</sup> However, this approach has not been employed previously for sterically encumbered systems. The synthetic approach involves the stepwise reaction of *N*-methyl-*N*-(1-adamantyl)formamide **4** with phosphorus oxychloride, followed by the addition of a benzene solution of *N*-methyl-*N*-(1-adamantyl)amine and subsequent anion exchange with an aqueous solution of NaClO<sub>4</sub>. The overall yield for this process is 60% which is superior to the 28% yield reported by Alder et al.<sup>17</sup> for the preparation of the tetraisopropylamidinium salt. The structure and composition of formamidinium salt **3** were established on the basis of elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data and a single-crystal X-ray diffraction study.

A characteristic feature of the <sup>1</sup>H NMR spectrum of **3** is the presence of a singlet corresponding to the *meso*-proton at  $\delta$  7.80 ppm. The *N*-methyl groups of **3** are evidently equivalent since they only exhibit a singlet at  $\delta$  3.19 ppm. Three different resonances attributable to the adamantyl protons were detected in the range  $\delta$  1.66 – 2.16 ppm. An unexpectedly small downfield shift of  $\Delta\delta = 0.03$  ppm was observed for the *meso*-proton of **3** in comparison with that

observed for *N*-methylformamidinium **2**. In the case of the *N*-unsubstituted 1,3-di-(1-adamantyl)-amidinium **1** the change of chemical shift is somewhat larger and in the opposite direction ( $\Delta\delta = -0.14$  ppm). A larger chemical shift change ( $\Delta\delta = -0.24$ ) was found for the cyano-substituted compound **1b**. It is interesting to note that the range of chemical shift changes for the *meso*-protons of aromatic 1,2,4-triazolium salts are significantly larger, the average values being typically  $\Delta\delta = 1.7 - 1.8$  ppm.<sup>18</sup> The foregoing observations imply that there is only modest electronic communication between the amino moiety and the *meso*-carbon atom in the case of amidiniums and their salts.

The <sup>13</sup>C NMR spectrum of **3** exhibits a singlet at  $\delta$  153.7 which falls within the range of 151.1 – 155.8 ppm reported by Alder et al.<sup>19</sup> for other tetraalkyl-substituted formamidinium salts. The signals for the *ipso* carbon of the adamantyl group and the two equivalent N-methyl resonances were detected at  $\delta$  61.6 and 32.7 ppm, respectively.

Single crystals of the amidinium salt **3** and the intermediate cyanoamidinium **1b** were grown from solutions of 2-ethoxyethanol and dimethylformamide, respectively. Selected metrical parameters are presented in Tables 1 and 2, respectively.

**Table 1.** Selected structural data and calculated bond orders for **3**

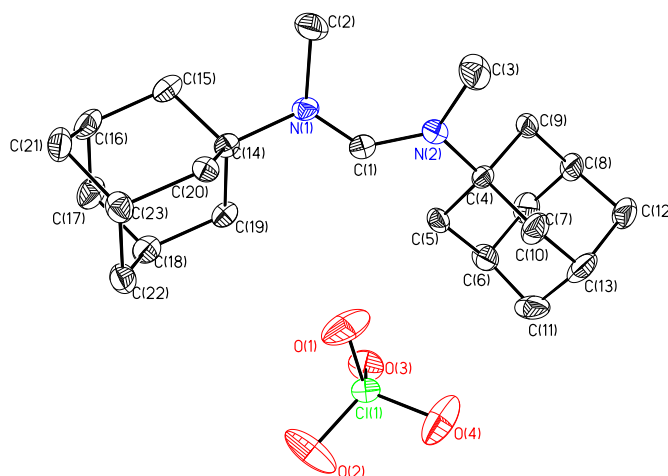
Bond lengths, (Å)		Bond orders, <i>p</i>	Valence angles/torsion angles (°)	
C(1)-N(1)	1.309(3)	1.948	N(1)-C(1)-N(2)	130.5(3)
C(1)-N(2)	1.325(3)	1.856	N(1)-C(1)-H(1)	114.8
C(2)-N(1)	1.480(4)	0.966	N(2)-C(1)-H(1)	114.8
C(3)-N(2)	1.473(4)	1.006	C(1)-N(1)-C(2)	123.1(2)
C(4)-N(2)	1.516(3)	0.759	C(1)-N(2)-C(3)	124.1(2)
C(14)-N(1)	1.516(3)	0.759	C(1)-N(1)-C(14)	120.4(2)
			C(1)-N(2)-C(4)	119.9(2)
			N(2)-C(1)-N(1)-C(2)	12.6(5)
			N(2)-C(1)-N(1)-C(14)	-168.6(3)
			N(1)-C(1)-N(2)-C(3)	13.1(5)
			N(1)-C(1)-N(2)-C(4)	-170.7(3)

As shown in Figure 1, amidinium salt **3** adopts a pseudo-*cis* conformation with respect to the N-C-N framework and an *anti*, *anti* disposition of the substituents relative to the C=N and C-N bonds. The N(2)-N(3) and N(1)-N(2) bond distances are slightly different due to the unsymmetrical location of the perchlorate anion. The values for the dihedral angles N(2)-C(1)-N(1)-C(2), N(1)-C(1)-N(2)-C(3), N(2)-C(1)-N(1)-C(14) and N(1)-C(1)-N(2)-C(4) indicate that the amidinium ion possesses an essentially planar skeletal structure. The bond orders calculated for the C(1)-N(1) and C(1)-N(2) bonds, using the linear dependence of bond lengths and bond orders (*p*) described previously,<sup>20</sup> are 1.968 and 1.856, respectively, thus implying a considerable level of double bonding in the amidinium fragment.

The N(1)-C(1)-N(2) bond angle for cation **3** (130.5°) is larger than that reported by Alder et al.<sup>17</sup> for the neutral tetraisopropylidiamino carbene (121.0°). This difference is due to steric repulsion in conjunction with the strong electron donating effect of the adamantyl groups (for C-N,  $p = 0.759$ ).

**Table 2.** Selected structural data and calculated bond orders for **1b**

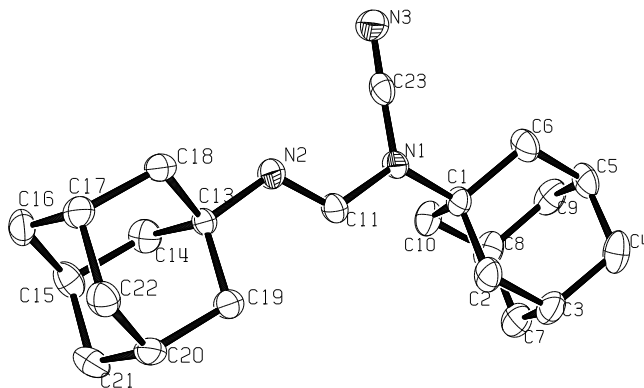
Bond lengths, (Å)	Bond orders, $p$	Valence angles/torsion angles (°)	
C(11)-N(1)	1.408(4)	N(1)-C(11)-H(11)	119.9(2)
C(11)-N(2)	1.266(3)	N(2)-C(11)-H(11)	119.9(2)
C(23)-N(1)	1.353(4)	C(11)-N(1)-C(23)	116.8(2)
C(23)-N(3)	1.141(4)	N(1)-C(23)-N(3)	178.7(3)
C(1)-N(1)	1.513(3)	N(1)-C(11)-N(2)-C(13)	-179.2
C(13)-N(2)	1.476(4)	N(2)-C(11)-N(1)-C(1)	-166.1(3)
		N(2)-C(11)-N(1)-C(23)	-4.8(4)
		N(3)-C(23)-N(1)-C(1)	-21.16(16)
		N(3)-C(23)-N(1)-C(11)	177.0(1)



**Figure 1.** X-ray structure of formamidinium salt **3** showing thermal ellipsoids at 50 % probability.

As illustrated in Figure 2, the cyanoamidine intermediate **1b** also possesses a pseudo-*cis* configuration and an *anti, anti* disposition of the substituents with respect to the C=N and C-N bonds. The overall structure is close to planar as evidenced by the dihedral angle of  $-4.8^\circ$  for N(2)-C(11)-N(1)-C(23). Selected bond lengths are presented in Table 2 along with the calculated bond orders and a listing of pertinent bond and torsion angles. The calculated bond orders are indicative of appreciable conjugation between amino nitrogen N(1) and the cyano carbon C(23)

( $p = 1.695$ ). A selection of  $p$  values for other bonds of interest is presented in Table 2. It should be noted that only pseudo-*cis*, *syn*, *syn* and pseudo-*trans*-, *anti*, *syn* stable isomers were known earlier for the related formamidinium salts.<sup>21</sup>



**Figure 2.** X-ray structure of cyanoamidinium **1b** showing thermal ellipsoids at 50% probability.

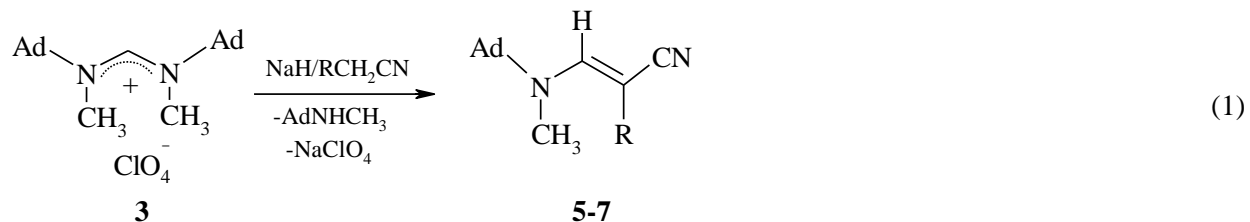
### Interaction of amidinium salt **3** with sodium hydride in aliphatic nitriles

The deprotonation of 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate **3** was investigated in order to explore the possible C-H insertion pathways for the *in situ* generated diaminocarbene in aliphatic nitriles. This objective was accomplished by treatment of **3** with sodium hydride in acetonitrile or propionitrile solution. An additional experiment with deuterated acetonitrile was also carried out with a view establishing whether the reaction pathway involves the free carbene or a carbanion that is formed from the corresponding nitrile.

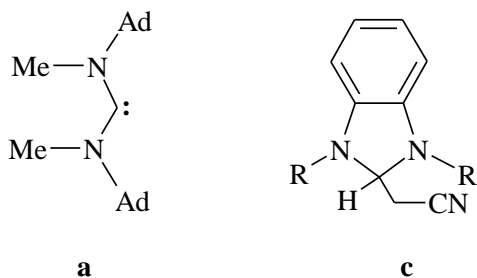
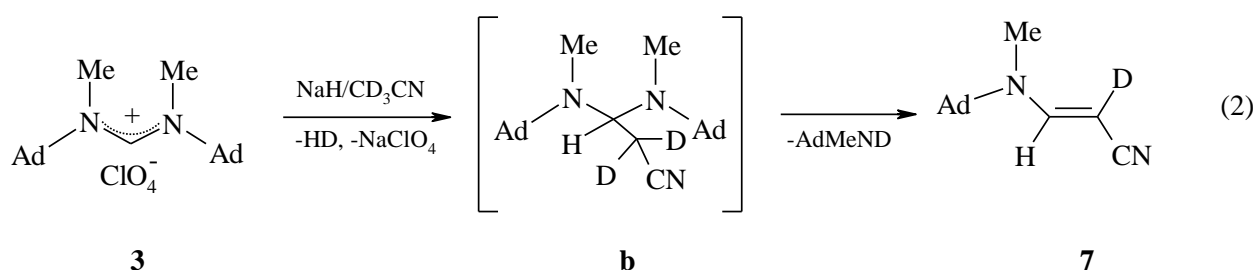
Amidinium salt **3** reacts smoothly when treated with sodium hydride/acetonitrile for 1.5 h at ambient temperature. The corresponding reaction with propionitrile requires more vigorous conditions (45 – 50 °C for 1 h). The latter observation may be due to the lower C-H acidity of propionitrile. Surprisingly, however, cleavage of the N-C-N amidinium linkage was observed in both reactions and the corresponding  $\beta$ -(dialkylamino)acrylonitriles **5** and **6** were isolated in 82 – 83% yields, respectively (Scheme 2, eq. 1). Thus, it was discovered that the initially anticipated products of the insertion of the diaminocarbene into the C-H bonds of nitriles (i.e. the cyanomethyldiaminomethane derivatives) were not observed. However, deprotonation of the related azolium salts under similar conditions afforded high isolated yields of cyanomethylazolines.<sup>6-10</sup>

The <sup>1</sup>H NMR spectrum of aminoacrylonitrile **5** exhibits two doublets for the olefin C-H protons of the cyanoethenyl moiety ( $\delta$  3.55 and 6.95 ppm), with a coupling constant of 13.3 Hz, thus indicating a *trans* geometry for this molecule with respect to the double bond. The signal for the methyl group was detected at  $\delta$  2.0 ppm and three multiplets corresponding to the adamantyl protons were evident in the range  $\delta$  1.12 – 1.74 ppm.

The  $^{13}\text{C}$  NMR spectrum of **5** features signals attributable to the nitrile group ( $\delta$  122.7 ppm), the carbon atoms of the olefin fragment ( $\delta$  148.8 and 60.8 ppm), the N-methyl group ( $\delta$  28.9 ppm) and the adamantyl *ipso*-carbon atoms (57.1 ppm).



**5:** R = H; **6:** R = CH<sub>3</sub>; **7:** R = D

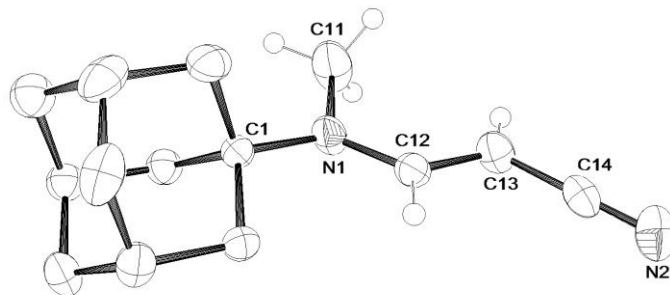


**Scheme 2.** Reaction of formamidinium salt **3** with sodium hydride in aliphatic nitrile solutions.

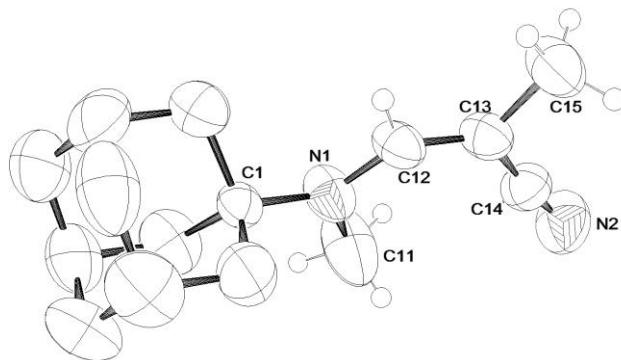
In contrast to **5**, the aminomethacrylonitrile **6** exhibits downfield proton chemical shifts for the N-bonded signals. The adamantyl protons of **6** are also downfield shifted ( $\Delta\delta$  0.38 – 0.53 ppm) and comprise a set of multiplets. Akin to compound **3**, the multiplets fall in the range  $\delta$  1.65 – 2.16 ppm. The N-CH<sub>3</sub> signal of **6** is also shifted downfield by 1.1 ppm with respect to that of **5**. By contrast, the CH signal of **6** is shifted by 0.36 ppm in comparison with that of **5**. Collectively, the foregoing NMR data are indicative of different structures for **5** and **6**. Interestingly, however the  $^{13}\text{C}$  NMR data for **6** were found to be less sensitive to structural change (see Experimental Section).

The distinctive structural features of **5** and **6** were confirmed by single-crystal X-ray diffraction. As shown in Figures 3 and 4, compound **5** adopts a *pseudo-cis* configuration about the N-C=C fragment and an *anti, trans* arrangement with respect to the C-N and C=C bonds. By contrast, **6** possesses a *pseudo-trans* geometry with reference to the N-C=C fragment and hence

adopts an *anti, cis* orientation with respect to the C-N and C=C bonds. The foregoing structural differences between **5** and **6** presumably stem from the variations in the steric interactions between the alkyl substituents of the amidinium ion and the methyl group of propionitrile. It is clear from the calculated bond orders (Tables 3 and 4) that the structure of **5** is more polarized toward the nitrile group in comparison with that of **6**.



**Figure 3.** X-ray structure of  $\beta$ -[methyl(1-adamantyl)amino]acrylonitrile **5** showing thermal ellipsoids at 50% probability.



**Figure 4.** X-ray structure of  $\beta$ -[methyl(1-adamantyl)amino]methacrylonitrile **6** showing thermal ellipsoids at 50% probability.

**Table 3.** Selected structural data and calculated bond orders for **5**

Bond lengths, ( $\text{\AA}$ )		Bond orders, $p$	Valence angles/torsion angles ( $^\circ$ )	
C(1)-N(1)	1.495(3)	0.879	C(1)-N(1)-C(12)	123.68(17)
C(11)-N(1)	1.461(3)	1.075	C(1)-N(1)-C(11)	118.48(17)
C(12)-C(13)	1.358(3)	1.893	N(1)-C(12)-C(13)	127.4(2)
C(12)-N(1)	1.335(3)	1.799	C(12)-C(13)-C(14)	120.1(2)
C(13)-C(14)	1.411(3)	1.624	C(13)-C(14)-N(2)	179.4(3)
C(14)-N(2)	1.156(3)	2.828	C(11)-N(1)-C(12)-C(13)	-7.8(3)
			C(1)-N(1)-C(12)-C(13)	-174.1(2)
			C(14)-C(13)-C(12)-N(1)	-179.6(2)



In an effort to elucidate the reaction mechanism, the formamidinium salt **3** (Scheme 1) was allowed to react with CD<sub>3</sub>CN. It was found that the resulting β-aminoacrylonitrile was monodeuterated in the α position with respect to the cyano substituent (Scheme 2, eq. 2.). This conclusion is based on the disappearance of the resonance at δ 3.55 ppm for **7** which is assigned to the CH(CN) proton and the presence of the CHN proton resonance at δ 6.95 ppm. The <sup>13</sup>C NMR spectrum of **7** features resonances at δ 60.8 (C 13) and 148.8 ppm (C 12). Of these, the former resonance splits into two components upon deuteration with a *J*<sub>CD</sub> coupling constant of 16.8 Hz. The foregoing observations imply that the latter process is initiated by proton (deuteron) elimination from the acidic α-CH(D) bonds of the nitriles rather than the amidinium ion to form carbene **a**.

**Table 4.** Selected structural data and calculated bond orders for **6**

Bond lengths, (Å)		Bond orders, <i>p</i>	Valence angles/torsion angles (°)	
C(1)-N(1)	1.496(4)	0.874	C(1)-N(1)-C(12)	119.8(3)
C(11)-N(1)	1.444(5)	1.172	C(1)-N(1)-C(11)	120.9(3)
C(12)-N(1)	1.353(4)	1.695	C(11)-N(1)-C(12)	117.7(3)
C(12)-C(13)	1.334(5)	2.015	C(12)-C(13)-C(14)	125.7(3)
C(13)-C(14)	1.422(5)	1.569	C(12)-C(13)-C(15)	121.1(3)
C(13)-C(15)	1.522(5)	1.061	C(13)-C(14)-N(2)	173.9(4)
C(14)-N(2)	1.152(4)	2.851	C(14)-C(13)-C(15)	113.1(3)
			C(1)-N(1)-C(12)-C(13)	167.2(3)
			C(11)-N(1)-C(12)-C(13)	1.5(6)
			N(1)-C(12)-C(13)-C(15)	176.7(4)
			N(1)-C(12)-C(13)-C(14)	-7.0(6)

In a previous study, Clemens et al.<sup>22</sup> described two plausible pathways for the trans-formations of the related dialkyl-diaryl-substituted formamidinium salts in the presence of basic reagents. In the cases of secondary amines, phenyllithium, alkoxides and sodium hydride the addition of these nucleophiles to the *meso*-carbon atom resulted in the formation of relatively stable aminomethane derivatives, namely the orthoformamides, benzaldianilines, alkoxydiaminomethanes and methylenedianilines, respectively. Furthermore, treatment of the amidinium salt with mercaptide anions and primary amines in the presence of sodium hydride resulted in the substitution of the arylalkylamine with dimercapto or imino groups. These authors postulated that the most likely reaction pathway involves the elimination of *N*-methylaniline from the orthoformamide that was formed at the beginning of the reaction. However, this process was not investigated experimentally.

In order to gain additional insight into the proposed mechanism, a series of DFT B3LYP5 (6-31 G) calculations were carried out by us using the PC GAMESS 7.1 program. These calculations indicated that the reaction **3** + NaH + CH<sub>3</sub>CN → **5** + MeAdNH is exothermic by 19.5 Kcal/mol and thus thermodynamically favorable. However, the computed geometry of **b**

features elongated and unequal bond distances (1.535 and 1.573 Å) for the NCN moiety. Likewise, the computed bond distances for the N-C(1-adamantyl) moiety were found to be unequal (1.506 and 1.600 Å). Moreover, the NCCH<sub>2</sub>-C<sup>2</sup> bond distance of 1.576 Å was computed to be even longer than that determined by single-crystal X-ray diffraction for the sterically congested molecule 1,3-di-(1-adamantyl)-2-cyanomethyl-2H-benzimidazoline.<sup>8,23</sup> The asymmetry of the foregoing molecules indicated by the theoretical calculations suggests the possibility of facile C-N bond cleavage and easy elimination of *N*-methyl-*N*-(1-adamantyl)amine. It is plausible that the initial addition of the cyanomethanide anion to the amidinium cation induces a significant elongation of the C-N bond in the NCN amidinium linkage in the course of forming the sterically encumbered methane derivative **b**. The latter step is followed by further cleavage to form β-dialkylaminoacrylonitrile (**7**) and *N*-methyl-*N*-(1-adamantyl)amine.

The decisive factor in terms of defining the pathway for the reaction of aliphatic nitriles with carbenoid amidinium and related azolium compounds that contain a carbenoid N-C-N link is the ratio of the CH-acidities of the reactants. In the case of benzimidazolium and 1,2,4-triazolium salts, a carbene mechanism is observed<sup>7,8</sup> because of the higher acidities of these carbenoids relative to those of aliphatic nitriles.<sup>24</sup> The carbenes that are formed by treatment with sodium hydride react further with acetonitrile via C-H insertion to afford cyanomethyl-substituted azolines of type **c**. The amidinium salts have lower acidities<sup>25</sup> than those of the aliphatic nitriles that were employed here hence the addition of the cyanomethanide anion to the formamidinium cation becomes the preferred reaction pathway. This process is also facilitated by an unusually easy Hofmann cleavage of the intermediate diaminomethane **b** by a stepwise or (more likely) a concerted mechanism. Finally, we note that the transformation **3** + NaH + RCH(D)<sub>2</sub>CN → **5-7** + MeAdNH somewhat resembles the substitution of a phosphonio group in aminophosphonio-carbenes when treated with nucleophiles.<sup>26</sup> However in this case the reaction proceeds by a different mechanism. A related reaction has also been reported by Alder<sup>27</sup> and comprises the interaction of formamidinium salts with dimsyl sodium to form β-aminovinylsulfoxides. However, no experimental data were provided.

## Conclusions

In summary, we have synthesized a novel carbenoid formamidinium salt with bulky 1-adamantyl substituents and a pseudo-*cis*, *anti*, *anti*-structure. The new compound was characterized on the basis of <sup>1</sup>H, <sup>13</sup>C NMR and X-ray crystallographic data. It was found that the interaction of this salt with sodium hydride in aliphatic nitriles resulted in the cleavage of the NCN amidinium linkage of the substrate thereby affording β-(dialkylamino)acrylonitriles **5** and **6** and *N*-methyl-*N*-(1-adamantyl)amine. The outcome of the transformation of 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate **3** in deuterated acetonitrile implies that the reaction involves an addition-elimination process initiated by nucleophilic attack of the generated

cyanomethanide anion to produce an intermediate cyanomethyldiaminomethane **b** that eliminates *N*-methyl-*N*-(1-adamantyl)amine, thereby affording  $\beta$ -(dialkylamino)acrylonitriles. X-ray diffraction studies of the  $\beta$ -(dialkylamino)acrylonitriles **5** and **6** revealed a *pseudo-cis* configuration for the NCC fragment of **5** and an *anti, trans* arrangement of the N-C and C=C bonds. In the case of the methylsubstituted derivative **6** the NCC fragment adopts a *pseudo-trans* configuration and an *anti, cis* arrangement of the N-C and C=C bonds.

## Experimental Section

**General.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance II 400 spectrometer (400 MHz for  $^1\text{H}$  NMR spectra and 100 MHz for  $^{13}\text{C}$  NMR spectra) in DMSO-*d*<sub>6</sub>, C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> solution. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts are reported relative to tetramethylsilane as the internal standard. X-Ray analyses were performed on a Nonius-Kappa CCD diffractometer [ $\lambda$  0.71069 – 0.71073 Å; temperature 153(2) K] with no corrections for absorption. All structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ . Mass spectra were measured on an Agilent 1100 Series chromatomass spectrometer (APCI, 3 kV). The chromatography was carried out on a Zorbax SB C18 column using a 95.5% acetonitrile mixture that contained 0.1% of formic acid. Thin-layer chromatography was performed on silica gel with chloroform or a 10:1 mixture of chloroform and methanol as eluent, followed by development with iodine. Elemental analyses were carried out at the Analytical Laboratory of the Litvinenko Institute of Physical Organic and Coal Chemistry. The quantum chemical calculations were performed with the help of the PC GAMESS 7.1 program.

**1,3-Dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate (3).** A solution of phosphorus oxychloride (0.047 mL, 5.18 mmol) in benzene (2.5 mL) was added dropwise to a solution of *N*-methyl-*N*-(1-adamantyl)formamide (1 g, 5.18 mmol) in benzene (2.5 mL) over a period of 10 min and allowed to stir for a further 40 min at room temperature. A solution of *N*-methyl-*N*-(1-adamantyl)amine (0.85 g, 5.18 mmol) in benzene (3 mL) was added and the reaction mixture was left at room temperature for 16 h followed by refluxing for 4 h. The benzene was evaporated, and the resulting residue was dried in vacuum at 90 °C for 1 h, then washed with small volumes of hexanes. The product was dissolved in boiling water (50 mL), to which a small amount of charcoal was added. Following filtration of the hot solution, perchlorate **3** was precipitated with an excess of sodium perchlorate, filtered off and dried. Yield: 1.37 g, 60%, mp 229 – 231 °C (from 2-ethoxyethanol). Found: C, 62.4; H, 8.6; Cl, 8.1; N, 6.4. Calc. for C<sub>23</sub>H<sub>37</sub>ClN<sub>2</sub>O<sub>4</sub>: C, 62.6; H, 8.5; Cl, 8.0; N, 6.4%.  $\delta_{\text{H}}$  (400 MHz, DMSO-*d*<sub>6</sub>, Me<sub>4</sub>Si): 1.66 (12H, m), 1.96 (12H, m), 2.16 (6H, m) (Ad), 3.19 (6H, s, CH<sub>3</sub>), 7.80 (1H, s, CHN);  $\delta_{\text{C}}$  (100 MHz, DMSO-*d*<sub>6</sub>, Me<sub>4</sub>Si):  $\delta$  32.7 (CH<sub>3</sub>), 28.7, 34.5, 39.1, 61.6 (Ad), 153.7 (CHN).

**Alkylation of 1,3-di-(1-adamantyl)formamidine with methyl iodide in the presence of calcium hydride.** Calcium hydride (1.34 g, 32 mmol) was added to a solution of 1,3-di-(1-

adamantyl)formamidine (1 g, 3.2 mmol) in acetonitrile, followed by dropwise addition of a solution of methyl iodide (1 mL, 16 mmol) in acetonitrile (4 mL) upon stirring for 2 h. The reaction mixture was allowed to stand at room temperature for 3 h following which a solution of methyl iodide (0.4 mL, 6.4 mmol) in acetonitrile (2 mL) was added. After the reaction mixture had been stirred for 2 h, the solution was filtered and the residual inorganic precipitate was washed with small amounts of acetonitrile. The solvent was evaporated in vacuo and the resulting precipitate was washed with diethyl ether, filtered off and dried. Yield 1.03 g. According to  $^1\text{H}$  NMR spectroscopic data the alkylation product includes approximately 15% of 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium iodide. The other product is 1-methyl-1,3-di-(1-adamantyl)formamidinium hydroiodide. Following treatment of the resulting mixture with sodium hydroxide (0.27 g, 6.8 mmol) in a stirred two phase system of benzene (10 mL) and water (2 mL), the benzene phase was separated and dried over anhydrous sodium sulfate. Evaporation of the solvent resulted in the isolation of 0.67 g, 64% of 1-methyl-1,3-di-(1-adamantyl)formamidine. Mp 168 – 170 °C (from acetonitrile). Found: C, 81.2; H, 10.3; N, 8.5. Calc. for  $\text{C}_{22}\text{H}_{34}\text{N}_2$ : C, 80.9; H, 10.5; N, 8.6%.  $\delta_{\text{H}}$  (400 MHz,  $\text{DMSO}-d_6$ ,  $\text{Me}_4\text{Si}$ ): 1.66 (6H, m), 1.60 – 1.64 (18H, m), 1.82 (6H, m), 2.03 – 2.10 (6H, m) (Ad), 2.72 (3H, s,  $\text{CH}_3$ ), 7.77 (1H, s, CHN).

**$\beta$ -[Methyl(1-adamantyl)amino]acrylonitrile (5).** A mixture of 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate (0.6 g, 1.36 mmol) and a 55 % mineral oil suspension of sodium hydride (0.06 g, 1.36 mmol) in acetonitrile (10 mL) was stirred for 1.5 h at room temperature during which time the evolution of hydrogen had ceased. The resulting precipitate was washed with small amounts (2 – 3 mL) of acetonitrile and dried in vacuo at 50 °C for 40 min. Yield: 0.24 g (82%), mp 114 – 116 °C (from hexanes). Found: C, 77.5; H, 9.6; N, 12.9. Calc. for  $\text{C}_{14}\text{H}_{20}\text{N}_2$ : C, 77.7; H, 9.3; N, 13.0%.  $\delta_{\text{H}}$  (400 MHz, benzene- $d_6$ ,  $\text{Me}_4\text{Si}$ ): 1.12 (6H, m), 1.30 (6H, m), 1.74 (3H, m) (Ad), 2.00 (3H, s,  $\text{CH}_3\text{N}$ ), 3.55 (1H, d, CHCN), 6.95 (1H, d, CHN) ( $J^3_{\text{trans}}$  13.3 Hz).  $\delta_{\text{C}}$  (100 MHz, benzene- $d_6$ ,  $\text{Me}_4\text{Si}$ ): 28.9 ( $\text{CH}_3\text{N}$ ), 29.6, 35.8, 40.4, 57.1 (Ad), 60.8 ( $\text{CH}=\text{C}$ ), 122.7 ( $\text{C}\equiv\text{N}$ ), 148.8 (CHN).  $m/z$  (APCI): Calc. for  $\text{C}_{14}\text{H}_{21}\text{N}_2$  ( $\text{MH}^+$ ) 217; found 217 (100%).

**$\beta$ -[Methyl(1-adamantyl)amino]methacrylonitrile (6).** A mixture of 1,3-dimethyl-1,3-di-(1-adamantyl)formamidinium perchlorate (0.6 g, 1.36 mmol) and a 55% mineral oil suspension of sodium hydride (0.06 g, 1.36 mmol) in propionitrile (7 mL) was stirred for 2 h at 45 °C. After the evolution of hydrogen had ceased, the reaction mixture was cooled and the resulting precipitate was filtered off, washed with small amounts of acetonitrile (2 – 3 mL) and dried in vacuo at 80 °C for 30 min. Yield: 0.26 g (83%), mp 135 °C (from hexanes). Found: C, 78.0, H, 10.0; N, 12.0. Calc. for  $\text{C}_{15}\text{H}_{22}\text{N}_2$ : C, 78.2; H, 9.6; N, 12.2%.  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ): 1.65 (6H, m), 1.78 (6H, m), 2.16 (3H, m) (Ad), 1.83 (3H, s,  $\text{CH}_3\text{C}$ ), 3.11 (3H, s,  $\text{CH}_3\text{N}$ ), 6.59 (1H, s, CHN);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ): 19.8 ( $\text{CH}_3\text{C}$ ), 29.8, 36.2, 41.1, 57.8 (Ad), 31.4 ( $\text{CH}_3\text{N}$ ), 65.8 ( $\text{CH}_3\text{C}$ ), 124.4 ( $\text{C}\equiv\text{N}$ ), 144.7 (CHN).

**$\beta$ -[Methyl(1-adamantyl)amino]monodeuteroacrylonitrile (7).** This compound was synthesized according to the method described above for  $\beta$ -[methyl(1-adamantyl)amino]acrylonitrile 5.

However, deuterioacetonitrile was used instead of acetonitrile. Yield: 0.2 g, 67%, mp 115 – 116 °C (from hexanes). Found: C, 77.7; H/D, 9.5; N, 12.8. Calc. for C<sub>14</sub>H<sub>19</sub>DN<sub>2</sub>: C, 77.4; H, 8.8; D, 0.9; N, 12.9%.  $\delta_{\text{H}}$  (400 MHz, benzene-*d*<sub>6</sub>, Me<sub>4</sub>Si)  $\delta$ : 1.07 (6H, m), 1.26 (6H, m), 1.70 (3H, m), (Ad), 1.92 (3H, s, CH<sub>3</sub>N), 6.95 (1H, s, CHN);  $\delta_{\text{C}}$  (400 MHz, benzene-*d*<sub>6</sub>, Me<sub>4</sub>Si)  $\delta$ : 28.9 (CH<sub>3</sub>N), 29.6, 35.8, 40.4, 57.2 (Ad), 60.8 (CD=)(*J*<sub>C-D</sub> 16.8 Hz), 122.7 (C≡N), 148.8 (CHN).

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## Supporting information

The supplementary crystallographic data for this paper (ORTEP drawings and tables of crystallographic data for **1b**, **3**, **5** and **6** can be obtained free of charge from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data-request/cif](http://www.ccdc.cam.ac.uk/data-request/cif) (the deposit numbers are 836123, 836669, 835725, and 835724, respectively).

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