

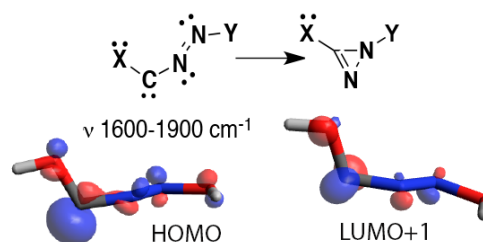
# Carbenic Nitrile Imines: Properties and Reactivity

Didier Bégue\*† and Curt Wentrup\*‡

†Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux, Equipe Chimie Physique, UMR 5254, Université de Pau et des Pays de l'Adour, 64000 Pau, France and

‡School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Queensland 4072, Australia.

E-mail: Didier.Begue@univ-pau.fr; wentrup@uq.edu.au



**Abstract:** Structures and properties of nitrile imines were investigated computationally at B3LYP and CCSD(T) levels. Whereas NBO analysis at the B3LYP DFT level invariably predicts a propargylic electronic structure, CCSD(T) calculations permit a clear distinction between propargylic, allenic, and carbenic structures. Nitrile imines with strong IR absorptions above ca. 2150  $\text{cm}^{-1}$  have propargylic structures with a CN triple bond ( $\text{RCNNSiMe}_3$  and  $\text{R}_2\text{BCNNBR}_2$ ), and those with IR absorptions below ca. 2150  $\text{cm}^{-1}$  are allenic ( $\text{HCNNH}$ ,  $\text{PhCNNH}$ , and  $\text{HCNNPh}$ ). Nitrile imines lacking significant cumulenenic IR absorptions at 1900-2200  $\text{cm}^{-1}$  are carbenic ( $\text{R}-(\text{C}^-)-\text{N}=\text{N}-\text{R}'$ ). Electronegative but lone pair-donating groups  $\text{NR}_2$ ,  $\text{OR}$ , and  $\text{F}$  stabilize the carbenic form of nitrile imines in the same way they

stabilize “normal” singlet carbenes, including *N*-heterocyclic carbenes. NBO analyses at the CCSD(T) level confirm the classification into propargylic, allenic, and carbenic reactivity types. Carbenic nitrile imines are predicted to cyclize to 1*H*-diazirenes of the type **24** in mildly exothermic reactions with activation energies in the range 29-38 kcal/mol. Such reactions will be readily accessible photochemically and thermally, e.g. under the conditions of matrix photolysis and flash vacuum thermolysis.

## Introduction

Nitrile imines (nitrilimines), R-CNN-R', are of continuing interest in synthetic, mechanistic, and theoretical chemistry.<sup>1</sup> Six different structures have been postulated for the nonstabilized nitrile imines, namely propargylic, allenic, 1,3-dipolar and reverse dipolar form, 1,3-diradical, and carbenic as indicated in Chart 1. Each molecule can be described by several canonical structures, which may have different weights, so that the bonding and geometry of each individual molecule may be closer to one of the six alternatives than the other. Calculations at the STO-3G and 4-31G levels indicated that the parent nitrilium betaines are floppy molecules, which may exist in either propargylic or allenic forms with low barriers between them.<sup>2</sup> Further high-level ab initio calculations with configuration interaction and large basis-sets (QCISD/6-311+G(2df,2p)) showed that the parent nitrile imine HCNNH **1** has a nonplanar, allenic geometry, and the propargylic structure with a CN triple bond and a linearized HCN moiety is a transition state for inversion of the allenic form.<sup>3</sup> Similar results are obtained with all correlated methods.<sup>3,4,5</sup> However, substituents can have a profound effect on the relative stabilities. Thus, based on the matrix IR spectra and/or calculations<sup>5</sup> we found allenic structures for HCNNH **1**, MeCNNMe **2**, PhCNNH **3**, HCNNPh **4**, PhCNNCH<sub>3</sub> **5**, and Ph<sub>3</sub>C-CNN-CPh<sub>3</sub>,<sup>6</sup> and propargylic

structures, possessing a CN triple bond, for PhCNNSiMe<sub>3</sub> **6**, PhCNNPh **7**, and diborylnitrile imines exemplified by the model compound H<sub>2</sub>B-CNN-BH<sub>2</sub> **8** (Chart 2).<sup>7</sup>

The importance of the carbenic resonance structures of amino- and fluoro-substituted nitrile imines H<sub>2</sub>N-CNN-NH<sub>2</sub> and F-CNN-F was suggested by a DFT study in combination with natural resonance theory, which concluded that four resonance structures are necessary for a proper description (propargylic, allenic, 1,3-dipolar, and carbenic).<sup>8,9</sup> The carbenic forms would be stabilized by the neighboring lone pairs. Thus, *C,N*-diaminonitrile imine is predicted to be a stable carbene.<sup>9,10,11</sup> However, spin-coupled valence bond calculations for the parent HCNNH **1** using the geometry from a CASSCF(8,6)/cc-pVTZ calculation indicated that both the carbenic and allenic forms are unimportant and that this molecule has a predominantly propargylic electronic structure albeit a bent, non-planar allenic-type geometry.<sup>12</sup> Contributions of 1,3-diradical canonical structures of 1,3-dipoles have also been postulated.<sup>13</sup>

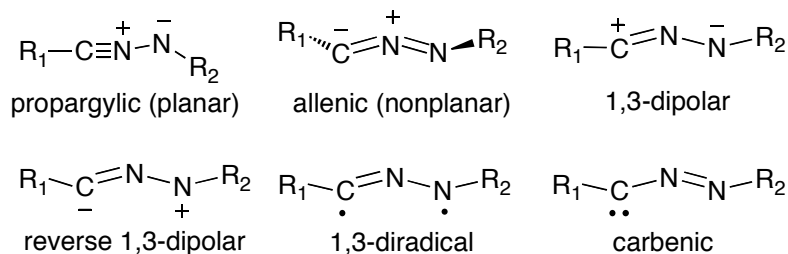
*C,N*-Diarylnitrile imines are formed on thermolysis of 2,5-diaryltetrazoles in the gas phase and in solution. Flash vacuum thermolysis (FVT) of 2,5-diphenyltetrazole causes cyclization of diphenylnitrile imine **7** to 3*H*-3-phenylindazole followed by tautomerization to 3-phenylindazole.<sup>14</sup> The reaction can be described in terms of a carbenic nature of the cyclizing nitrile imine in much the same way that *o*-biphenylcarbene cyclises to fluorene.<sup>14</sup> A C-H insertion of the carbenic nitrile imine is not to be expected.<sup>9b</sup>

Surprisingly, a bent structure of a Zn-coordinated *C,N*-diarylnitrile imine has been reported.<sup>15</sup> The bent structure could be either the 1,3-dipolar (or 1,3-diradicaloid) or the carbenic form. Reaction with water resulted in addition of the OH group to the C atom of the CNN moiety and hence the conclusion that the 1,3-dipolar form R<sup>1</sup>C(+)NN(-)R<sup>2</sup> was the major electronic contributor. This is in sharp contrast to the results of IR spectroscopy of matrix-isolated *C,N*-diphenylnitrile imine **7**, as well

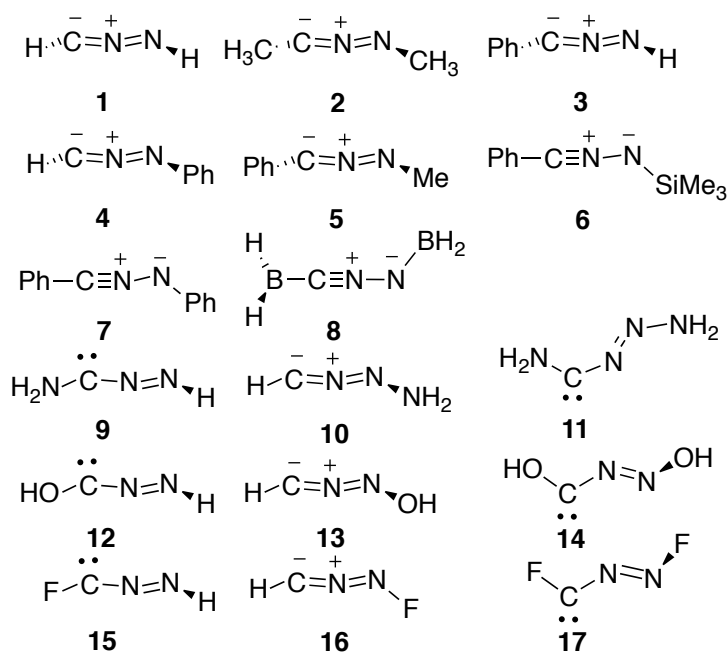
as calculations, which clearly indicate a propargylic ground state structure.<sup>5</sup> It is possible that the crystal lattice of the Zn-coordinated molecule may enforce a bent geometry. In fact, we found two minima for diphenylnitrile imine **7**, the lowest energy structure being propargylic and the other allenic, and the energy difference between them is very small (1.5 kcal/mol at the B3LYP/6-31G\* level).<sup>5</sup> Thus, it is very likely that small environmental effects can influence the preferred structure.

We have found that DFT calculations of vibrational frequencies match the experimental IR spectra of several stable and unstable nitrile imines very well.<sup>5</sup> Therefore, it is reasonable to expect a correlation between the DFT-calculated structures and the IR spectra. Furthermore, CCSD(T) and in some cases QCISD calculations predicted IR spectra in excellent agreement with the DFT calculations and with experiment and confirmed the distinction between propargylic and allenic structures based on IR spectroscopy.<sup>5</sup> Thus, IR spectroscopy is an important tool for determining the structures of nitrile imines, especially in the case of unstable compounds, where other spectroscopies are not readily applicable. However, no information on the IR characteristics of carbenic nitrile imines has been published. We have now calculated the structures and IR spectra of a series of nitrile imines **9-17** (Chart 2) substituted with lone-pair carrying heteroatoms (NH<sub>2</sub>, OH, and F), which have the effect of stabilizing the carbenic canonical structures<sup>8,9,10</sup> with the consequence that hardly any IR absorptions are predicted in the normal cumulene region. We will show that, for the carbenic molecules, the absorptions that do occur in the cumulene region are largely due to overtones and combination bands, and the stretchings ascribed to cumulenenic CNN moieties are very weak. Since overtones and combination bands cannot be handled by harmonic frequency calculations, we have, for the first time, carried out high level anharmonic frequency calculations for these compounds.

**Chart 1.** The six fundamental structures of nitrile imines.



**Chart 2.** Major canonical structures of the ground states of nitrile imines **1-8** described previously<sup>5</sup> and the new nitrile imines **9-17**



## Computational Methods

The structures and natural bond orbitals (NBO) of nitrile imines **9-17** were investigated at the CCSD(T)/6-31G\* or CCSD(T)/cc-pVTZ levels (Tables 1 and 2). The previously reported<sup>5</sup> structures of the typical allenic nitrile imine HCNNH **1A**, its propargylic transition state for inversion, **1P**, and the typical propargylic nitrile imines **6P** and **8P** are included in these tables for comparison. Vibrational frequencies in the harmonic approximation were calculated initially

at the B3LYP/6-31G\* level (Table 3). In order to confirm the validity of these frequencies, they were also calculated for the key molecules **1A**, **9aC**, and **14aC** at the CCSD(T)/cc-pVTZ level (Table 3). In conformity with our previous publication,<sup>5</sup> scaling factors of 0.9613 and 0.9676 were used for harmonic and anharmonic wavenumbers, respectively, at the B3LYP/6-31G\* level, and 0.9860 for the anharmonic wavenumbers at the CCSD(T)/cc-pVTZ level. The anharmonic wavenumbers were obtained using the parallel variational multiple window configuration interaction software (P\_VMWCI<sub>2</sub> algorithm).<sup>16,17</sup> These wavenumbers were obtained initially from a variational and perturbation-variation treatment developed to solve the vibrational Schrödinger equation.<sup>18</sup> Relevant wavenumbers in the “cumulenic” region (ca. 1700-2300 cm<sup>-1</sup>) together with the spectroscopic descriptions are listed in Table 3. Potential energy surface calculations at X/B3LYP//Y/6-31G\* levels (X = QCISD or CCSD(T), Y = cc-pVTZ or 6-31G\*) were performed for reference systems by using mathematical procedures reported elsewhere.<sup>19</sup>

## Results and Discussion

For the parent nitrile imine HCNNH **1**, high level calculations predict a bent, allenic ground state ( $\angle\text{HCN} \sim 130^\circ$ ),<sup>3,4,5</sup> and calculations at the B3LYP/6-31G\*, G4MP2, G3MP2B3, CBS-QB3, W1BD and CCSD(T) levels confirm that the allenic form lies 2.5-4.1 kcal/mol below the propargylic form ( $\angle\text{HCN} \sim 180^\circ$ ), which is a transition state for inversion of the allenic structure.<sup>5</sup> Thus, we designate the allenic ground state **1A** for allenic, and the transition state **1P** for propargylic. The matrix IR spectrum<sup>20</sup> is also in good agreement with the anharmonic vibrational data calculated for the allenic structure at B3LYP/6-31G\*, CCSD(T)/6-31G\*, and QCISD/6-31G\* levels.<sup>5,20</sup> Nevertheless, an NBO analysis at the B3LYP/6-31G\* level predicts a

distinctly propargylic *electronic* structure of HCNNH with a CN triple bond, an N-N single bond, and two lone pairs on the NH nitrogen. We find that this is generally the case for all the substituted nitrile imines, including those studied previously,<sup>5</sup> even though the B3LYP method provides excellent agreement with experimental IR spectra of both allenic and propargylic nitrile imines, and with the experimental structures when these are available.<sup>5</sup> Therefore, DFT calculations at the B3LYP level are very useful for structural and IR-spectroscopic information, but they are not reliable as far as the *electronic* structures of nitrile imines are concerned, and it is necessary to perform NBO calculations at the CCSD(T) or QCISD(T) level. The calculated structures, NBO occupancy data and anharmonic vibrational spectral data for the amino-, hydroxy-, and fluoro-substituted nitrile imines **9-17** are presented in Tables 1-3, Figure 1 and Figures 4-11. Several of these molecules can exist in more than one stable conformation. Only the data for the lowest energy conformers are given in Tables 1-3 and Figures 1-11. The full data for all the calculated conformers is presented in the Supporting Information. CCSD(T) data for the allenic HCNNH **1A** and the propargylic transition state **1P** as well as the typical propargylic nitrile imine H<sub>2</sub>BCNNBH<sub>2</sub> **8P**, whose IR spectra were analysed previously,<sup>5</sup> are included for comparison in Tables 1 and 2. PhCNSiMe<sub>3</sub> **6P** has been very well characterized experimentally and is clearly a propargylic ground state molecule;<sup>5</sup> therefore we also include the data for this compound in Tables 1 and 2 although, due to its size, only DFT calculations were possible in this case.

At the CCSD(T) level, the NBO analysis predicts an allenic structure **1A** for the parent compound **1**, H-C(-)=N(+)=N-H with C=N and N=N double bond and a lone pair on C (1.4 electrons) (Tables 1-2 and Figure 1). The two basis sets, 6-31G\* and cc-pVTZ, gave almost identical results. Therefore, the smaller basis set will be used for most compounds discussed

below. The molecular orbitals of **1A** at the CCSD(T)/cc-pVTZ level are depicted in Figure 2a and confirm the allenic C=N=N structure. The MOs at the B3LYP/6-31G\* and CCSD(T)/6-31G\* levels are very similar to those shown in Figure 2. In contrast, the NBO occupancy data and the MOs of the transition state (**1P**) for inversion of **1A** are in keeping with its propargylic structure (Table 2, Figure 2b).

The MOs of MeCNNMe **2** and its transition state for inversion are very similar to those of **1** in keeping with an allenic ground state (Figure S1, Supporting Information). In contrast, PhCNNSiMe<sub>3</sub> **6** is a typically propargylic molecule (**6P**) with a nearly linear CNN moiety, a CN triple bond and two lone pairs on N3 in the ground state (Table 2 and Figure S2). Being propargylic, the TS for inversion (**6TS P**) is also propargylic, and the energy surface is very flat, with only 0.4 kcal/mol energy difference between the two structures (Figure 3b). H<sub>2</sub>BCNN-BH<sub>2</sub> **8** is also clearly a propargylic compound (**8P**) with structural parameters similar to those of **6P**.<sup>5</sup> (Figure S3, Supporting Information).

We now describe the NH<sub>2</sub>-, OH-, and F-substituted nitrile imines **9-17**, which have very different spectroscopic properties. *Carbenic structures are predicted for the two amino-substituted compounds, H<sub>2</sub>N-CNN-H **9**, and H<sub>2</sub>N-CNN-NH<sub>2</sub> **11*** (Tables 1-3 and Figures 3-5). Thus, these compounds are designated **9C** and **11C** to emphasize their carbenic natures. As usual, the NBO analysis at the B3LYP level predicts a propargylic structure for **9**, but CCSD(T) predicts a carbene, H<sub>2</sub>N-C(:)-N=N-H with partial lone pairs on all four heavy atoms (1.85, 1.57, 1.59, and 1.96 electrons, respectively for **9C**), N-C and C-N single bonds and an N=N double bond (Table 2 and Figure 1c). There is an occupancy of 0.59 electron in a ‘vacant’ orbital on C (LP\*), i.e. the vacant p-orbital corresponding to a singlet carbene (Table 2). The calculated, anharmonic vibrational spectrum of **9C** at the B3LYP/6-31G\* level features a rather weak



absorption at  $1903\text{ cm}^{-1}$  (40 km/mol), composed mostly of the CNN antisymmetric stretch (54%), together with a combination of torsion and deformation modes (27%) (Table 3) (we will cite the scaled wavenumbers throughout; see Table 3 for details). The values are very similar at the CCSD(T)/cc-pVTZ level ( $1931\text{ cm}^{-1}$ ), and they are very different from those for “normal” allenic and propargylic nitrile imines, which absorb very strongly in the range  $2000\text{-}2300\text{ cm}^{-1}$ ,<sup>5</sup> e.g. **1A**  $2033\text{ cm}^{-1}$  (177 km/mol) (Table 3).

While carbenic ground state structures are predicted for compound **9C**, the *reactivities* are determined largely by the HOMOs and LUMOs.<sup>2</sup> These are depicted in Figure 4, and they clearly indicate that carbenic reactivity is expected in agreement with earlier observations.<sup>9,10</sup> The HOMO of  $\text{H}_2\text{N-C-NNH}$  **9** has the character of a carbene  $\sigma$  orbital residing in the plane of the molecule ( $\angle\text{NCN} = 133^\circ$ ), and the LUMO+1 has the character of an empty p orbital of the singlet carbene, perpendicular to the molecular plane (Figure 3). (Note that the presence of a carbene-like  $\sigma$ -type orbital in the HOMO is not by itself enough to define a carbenic nature, since allenic and the reverse 1,3-dipolar nitrile imines will also have such an orbital.)

For  $\text{H-CNN-NH}_2$  **10** both B3LYP and CCSD(T) predict a more *allenic*-type ground state structure (**10A**) with C=N and N=N double bonds and lone pairs on C and N3 (1.65 and 1.95 electrons, respectively) and of course also on the terminal  $\text{NH}_2$  group (1.96 electrons). This is in keeping with a relatively intense calculated IR absorption at  $1944\text{ cm}^{-1}$  (115 km/mol), which is largely (85%) due to the CNN stretch (Table 3). Thus, compound **10** is similar to the parent  $\text{HCNNH}$  **1A** (Figure 2). However, the HOMO and LUMO+1 of  $\text{H-CNN-NH}_2$  **10** are similar to those of **9** and thereby indicate that carbenic reactivity may be possible (Figure 4). The transition state **10P** lies 8 kcal/mol above **10A** and is propargylic according to the CCSD(T) NBO analysis

(nearly linear HCN moiety; CN triple bond; IR 2087  $\text{cm}^{-1}$ , 284 km/mol; Tables 2 and 3). As expected, the MOs of **10P** demonstrate a lack of carbenic character (Figure S4).

For  $\text{H}_2\text{N-CNN-NH}_2$  **11** both B3LYP/6-31G\* and CCSD(T)/6-31G\* calculations predict lone-pair donation from the C-NH<sub>2</sub> group, resulting in a structure  $\text{H}_2\text{N}^+=\text{C}^--\text{N}=\text{N}-\text{NH}_2$ . There is no lone pair on the C-amino group (N1), but 1.83 electrons on C, 1.85 on N2, 1.97 on N3, and 1.91 on the terminal N-NH<sub>2</sub> group at the CCSD(T) level for **11** (Table 2). The compound may be described as an aminocarbene, **11C**, having a highly zwitterionic character. The calculated, anharmonic vibrations of **11** indicate a very weak absorption at 1964  $\text{cm}^{-1}$  (3.6 kcal/mol), but this is not a cumulenenic stretching vibration; it is a combination of deformation modes  $\nu_2 + \nu_4 + \nu_5$  (Table 3). The cumulenenic  $\nu_{\text{CNN}}$  vibration is predicted to be very weak and to appear at the extremely low frequency of 1578  $\text{cm}^{-1}$  (68 km/mol in combination with  $\sigma_{\text{NH}_2}$ ) (Table 3).

The HOMO of  $\text{H}_2\text{N-CNN-NH}_2$ , **11** has typical singlet *carbene* character, and the LUMO+1 corresponds to the empty p orbital on C (Figure 5). Thus, *carbenic reactivity* is confirmed, and the compound is designated **11C**.

The structures of the three OH-substituted nitrile imines **12-14** and the relevant molecular orbitals are shown in Figures 6-8. A very low frequency  $\nu_{\text{CNN}}$  absorption at 1882  $\text{cm}^{-1}$  (51 km/mol) is predicted for the lowest energy conformer of **12** at the B3LYP/6-31G\* level (Table 3). The NBO analysis at the CCSD(T)/cc-pVTZ level indicates an *allenic ground state* with a C=N double bond, an N=N double bond, lone pairs on C and N(H), and two lone pairs on O (Figure 7 and Table 2). The 6-31G\* basis set gives basically the same results. The HOMO of **12** features the allenic lone pair on C, but a carbenic p orbital is completely lacking, indicating absence of carbene character (Figure 6). Thus this compounds is designated **12A**.

HCNN-OH **13** is very similar. The predicted  $\nu_{\text{CNN}}$  of the lowest energy conformer is at  $1877 \text{ cm}^{-1}$  (77 km/mol) (Table 3). The NBO analysis at the CCSD(T)/cc-pVTZ level indicates an *allenic* molecule **13A** similar to **12A**. However, the MOs are very similar to those of **9** (see Figures 3 and 7). Thus, although allenic ground states are predicted, *carbenic reactivity* may be possible.

For HO-CNN-OH **14**, apart from OH stretching, the highest calculated harmonic frequency of any significance is  $\nu_9$  at  $1657 \text{ cm}^{-1}$  at the B3LYP/6-31G\* level, or  $1623 \text{ cm}^{-1}$  at the CCSD(T)/cc-pVTZ level (33 km/mol) (Table 3). This frequency is incompatible with a normal cumulene, and it is composed of a combination of  $\nu_{\text{CNN}}$  (77%) and  $2\nu_4$  ( $\nu_{\text{NO}} + \delta_{\text{NNO}}$ ) (17%). Only very weak bands are predicted in the cumulene region at  $1984\text{-}2225 \text{ cm}^{-1}$  (ca. 1 km/mol), and they are all due to combination bands, not to cumulenic stretches. In agreement with this finding, the NBO analysis at the CCSD(T) level indicates a *carbenic ground state* **14C** with O-C, C-N, and N-O single bonds, an N=N double bond, and a lone pair on C (1.90 electrons) as well as an ‘empty’ p orbital on C (housing 0.32 electrons), lone pairs on N2 and N3 and two lone pairs on each O atom (Table 2 and Figure 1d). Compound **14C** has an OCN angle of  $112^\circ$ . The HOMO and LUMO are shown in Figure 8. The carbenic character is clear with a carbenic  $\sigma$  orbital in the HOMO and an orthogonal carbenic p orbital in the LUMO. Accordingly, this molecule is designated **14C**.

The three F-substituted nitrile imines **15-17** were analyzed in a similar way (Figures 9-11). Neither possesses any true cumulene absorptions according to the frequency calculations. For FCNNH **15** the highest frequencies are  $1807 \text{ cm}^{-1}$  (42 km/mol; a combination of  $\nu_{\text{CNN}}$  and  $\nu_1 + \nu_4$ ) and  $1861 \text{ cm}^{-1}$  (19 km/mol; a combination of  $\nu_1 + \nu_4$  and  $\nu_{\text{CNN}}$ ). Other very weak bands between 1953 and 2299 are all combination bands. The NBO analysis at the CCSD(T)/cc-pVTZ

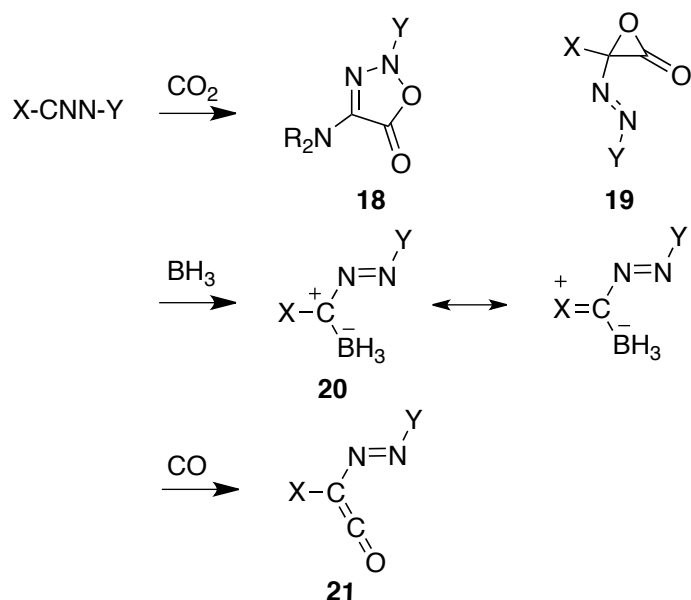
level (Table 2) indicates a typical allenic ground state structure  $\text{F-C}(-)=\text{N}(+)=\text{N-H}$ , **15A**. Nevertheless, the MOs indicate some carbenic character in the HOMO (lone pair on C) and LUMO+1 (vacant p orbital on C) (Figure 10). Therefore, a certain degree of *carbenic reactivity* may be expected as expressed in the description **15A(C)**.

The ground state of HCNNF **16** and the transition state for inversion at C, **16P (TS)**, were examined. The energy difference is 7 kcal/mol (CCSD(T)/6-31G\*). The frequency calculations for **16** at the B3LYP/6-31G\* level indicate a combination band at  $1842\text{ cm}^{-1}$  (60 km/mol;  $\nu_{\text{CNN}}$  (86%) and  $2\nu_4$  (10%); Table 3), and weak absorptions in the range  $2119\text{--}2472\text{ cm}^{-1}$  are all combination bands. The NBO analysis at the CCSD(T)/6-31G\* level indicates a distinctly allenic structure,  $\text{H-C}(-)=\text{N}(+)=\text{N-F}$ , **16A**. The MOs do not support a carbenic character (Figure 10). The transition state for inversion on C, **16P (TS)**, has a linear HCN moiety, a CN triple bond, and a calculated absorption at  $2026\text{ cm}^{-1}$  (93 km/mol; composed largely (67%) of  $\nu_{\text{CNN}}$ ) (Table 3). As expected, **16P** has no carbenic character (Figure S5, Supporting Information).

FCNNF **17** has a calculated absorption at  $1666\text{ cm}^{-1}$  (35 km/mol; composed in part of  $\nu_{\text{CNN}}$  (61%), and there is no truly cumulenic absorption. The NBO analysis at the CCSD(T)/cc-pVRZ level again indicates a clearly allenic structure  $\text{F-C}(-)=\text{N}(+)=\text{N-F}$ , **17A** (Table 2). However, the MOs do suggest *carbenic reactivity*, as there is a large carbene-type  $\sigma$  orbital on C in the HOMO and an orthogonal, vacant p orbital on C in the LUMO+1 (Figure 11). Hence this molecule is designated **17A(C)**.

### Reactivity

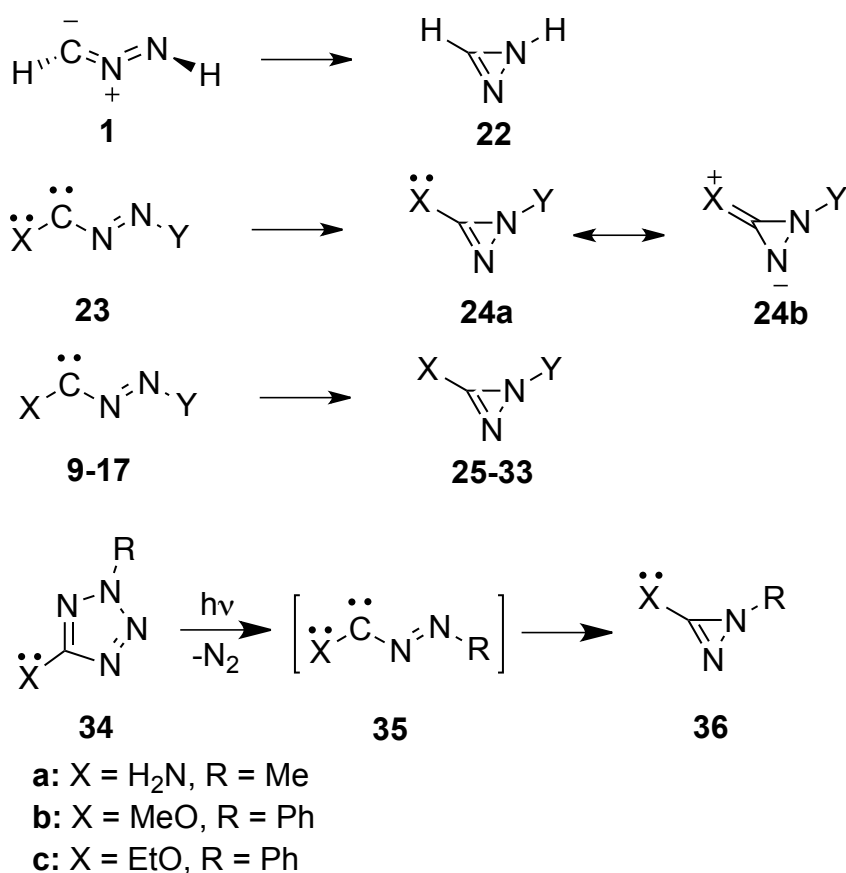
We have outlined above how the three classes of nitrile imines may be distinguished spectroscopically. It is emphasized, however, that all nitrile imines always have canonical structures that correspond to the other two classes. Therefore, it may be difficult to find reactions that are diagnostic for propargylic, allenic, and carbenic nitrile imines. For example, we find that all the nitrile imines discussed here (XCNNX, X = H, NH<sub>2</sub>, OH, or F) are able to undergo “1,3-dipolar” cycloaddition, e.g. with CO<sub>2</sub> to form the respective 1,2,3-oxadiazole-5-ones **18** (Scheme 1). Intriguingly, however, FCNNF is predicted to undergo a facile carbene-type [2+2] cycloaddition to yield an  $\alpha$ -lactone **19**. Conversely, all the nitrile imines are predicted to undergo addition of BH<sub>3</sub> at C, yielding adducts **20** without an activation barrier. This is a typical reaction of *N*-heterocyclic carbenes (NHCs),<sup>21</sup> but it has never been investigated for nitrile imines. Carbenes are known to add to CO to form ketenes. This reaction can also take place with many NHCs, particularly when they are not too electron rich.<sup>22</sup> Here we find that all the nitrile imines (XCNNX, X = H, NH<sub>2</sub>, OH, or F) can in principle form ketenes by addition of CO at C to give **21**. This reaction has the highest barrier for X = H (10 kcal/mol) and very low barriers for X = NH<sub>2</sub> (0.7), OH (3.7), and F (0.7 kcal/mol) at the B3LYP/6-31G\* level. Therefore, trapping with CO may be a versatile reaction of carbenic nitrile imines. Azoketenes of type **21** are very poorly known compounds.<sup>23</sup>

**Scheme 1.** Addition of CO<sub>2</sub>, BH<sub>3</sub>, and CO to Nitrile Imines

Most importantly, we find that the carbenic nitrile imines are able to cyclize to *1H*-diazirenes of the type **24** (Scheme 2). A cyclization of HCNNH **1** to the formally antiaromatic *1H*-diazirene **22** is endothermic by 11 kcal/mol, and it has an activation barrier of 56 kcal/mol (Table 4), so this reaction is not likely to take place. Similarly, calculations indicate that the cyclization of *N*-phenylnitrile imine PhNNCH to the corresponding diazirene is endothermic by 17 kcal/mol and has a barrier of 48 kcal/mol.<sup>24</sup> In contrast, among the nitrile imines **9-17** considered in this paper, **9**, **11**, **12**, **14**, **15**, and **17** form diazirenes in mildly exothermic reactions (by -1 to -6 kcal/mol) and with activation barriers of the order of 28 to 36 kcal/mol (Scheme 2 and Table 4). The relative stabilities of the resulting diazirenes **25**, **27**, **28**, **30**, **31**, and **33** can be ascribed to resonance stabilization as expressed in the canonical structure **24b**, which serves to remove the antiaromatic character. Obviously, this can only happen when X is a lone pair-carrying substituent like NH<sub>2</sub>, OH and F. With the exception of HCNNF **16**, the potential cyclizations of all the nitrile imines with X = H are endothermic (Table 4). Most likely, cyclizations of carbenic-type nitrile imines to *1H*-diazirenes have already taken place in matrix

photolyses of tetrazoles **34** (Scheme 2). Photolysis of 2,5-disubstituted tetrazoles is expected to generate nitrile imines,<sup>5</sup> but no nitrile imines **35** were reported in the matrix photolyses of **34**.<sup>25</sup> Instead, evidence for the formation of diazirenes **36** was adduced by IR spectroscopy. It seems very likely that carbenic nitrile imines were formed but cyclized to the diazirenes under the reaction conditions. The energy calculations confirm that the cyclization of **34a** to **36a** is mildly exothermic with a modest activation energy of 31 kcal/mol (Table 4). We now envisage intensive investigation of the formation and chemistry of 1*H*-diazirenes.

**Scheme 2.** Formation of 1*H*-Diazirenes



## Conclusion

Usually, there are two types of nitrile imines, (i) planar, propargylic, nitrile-like structures with short CN triple bonds, N-N single bonds, and strong IR frequencies in the high range, ca. 2150-2300  $\text{cm}^{-1}$  range, and (ii) non-planar, allenic structures with longer CN bonds, shorter NN bonds, and strong IR absorptions below ca. 2150  $\text{cm}^{-1}$ .<sup>5</sup> A third class of nitrile imines with significant carbenic character is characterized by very weak absorptions at very low frequencies in the 1600-1900  $\text{cm}^{-1}$  range, which have very little cumulene character. This IR-spectroscopic analysis of the three types of nitrile imines – propargylic, allenic, and carbenic – will aid the experimental differentiation. The nitrile imines **9-17** carry highly electronegative but lone pair-donating substituents,  $\text{NH}_2$ , OH, and F. NBO calculations at the CCSD(T) level are in agreement with the existence of either allenic or carbenic structures for these compounds and absence of propargylic structures except for transition states with linearized X-CN moieties. The carbenic character is particularly noticeable in  $\text{H}_2\text{N-C}(\cdot)\text{NN-H}$ ,  $\text{H}_2\text{N-C}(\cdot)\text{NN-NH}_2$ ,  $\text{HO-C}(\cdot)\text{NN-OH}$ , and  $\text{F-C}(\cdot)\text{NN-F}$ . These carbenic nitrile imines have much in common with *N*-heterocyclic carbenes and analogous open-chain lone pair-stabilized carbenes, i.e. they can be considered as amino(azo)carbenes, e.g.  $\text{H}_2\text{N-C}(\cdot)\text{-N=N-Y}$ , etc. Carbenic nitrile imines are predicted to cyclize to 1*H*-diazirenes of the type **24** in mildly exothermic reactions with activation energies in the range 29-38 kcal/mol. Such reactions will be readily accessible both photochemically and thermally, e.g. under the conditions of matrix photolysis and flash vacuum thermolysis.

---



**Table 1. Calculated (CCSD(T)/6-31 G\*) Structural Data for Nitrile Imines (R-CNN-R') and the Transition States for Inversion.<sup>a,b</sup>**

R,R' structure <sup>a</sup>	r(R-C)	r(C-N)	r(N-N)	r(N-R')	∠RCN	∠CNN	∠NNR'	τRCNN	τCNNR'
H,H <b>1A</b>	1.084	1.213	1.259	1.030	128.1	167.7	108.1	219.4	229.9
H,H <b>1P<sup>b</sup></b>	1.063	1.171	1.258	1.024	179.9	172.1	108.9	185.6	180.1
C <sub>6</sub> H <sub>5</sub> , Si(CH <sub>3</sub> ) <sub>3</sub> <b>6P<sup>c</sup></b>	1.420	1.176	1.250	1.763	177.9	175.2	123.2	357.6	181.1
BH <sub>2</sub> ,BH <sub>2</sub> <b>8P</b>	1.506	1.189	1.256	1.412	176.6	171.3	128.4	179.7	180.0
NH <sub>2</sub> ,H <b>9C</b>	1.364	1.230	1.262	1.033	128.9	159.5	107.0	126.6	149.1
H,NH <sub>2</sub> <b>10A</b>	1.092	1.229	1.252	1.449	120.4	165.3	110.3	196.6	250.9
H,NH <sub>2</sub> <b>10P<sup>b</sup></b>	1.067	1.178	1.279	1.479	179.0	173.5	106.4	307.1	180.1
NH <sub>2</sub> ,NH <sub>2</sub> <b>11C</b>	1.326	1.397	1.267	1.397	110.2	117.7	111.4	279.1	178.1
OH,H <b>12A</b>	1.358	1.237	1.264	1.036	123.6	160.2	107.1	175.8	143.3
H,OH <b>13A</b>	1.093	1.229	1.250	1.447	120.1	166.3	106.9	158.8	110.8
OH,OH <b>14C<sup>d</sup></b>	1.326	1.341	1.230	1.422	111.6	132.4	109.6	245.1	18.8
F,H <b>15 A(C)</b>	1.340	1.248	1.260	1.035	121.6	157.6	107.6	156.1	114.9
H,F <b>16A</b>	1.090	1.224	1.255	1.447	122.6	166.6	105.2	151.8	118.3
H,F <b>16P<sup>b</sup></b>	1.069	1.180	1.285	1.459	179.1	173.8	102.9	268.7	176.6
F,F <b>17A(C)</b>	1.330	1.285	1.236	1.442	115.9	154.1	107.1	166.2	103.0

<sup>a</sup>Bond lengths in Å and angles in degrees. Major canonical structures denoted by A allenic; P propargylic; C carbenic. <sup>b</sup>Transition state. <sup>c</sup>B3LYP/6-31G\* calculation. <sup>d</sup>CCSD(T)/cc-pVTZ calculation.

**Table 2. NBO Occupancy Data for X-C1N2N3-Y<sup>a</sup>**

Compound/NB O	BD				LP			LP*
	X- C1	C1-N2	N2-N3	N3-Y	C1	N2	N3	C1
H,H <b>1A<sup>a</sup></b>	1.99	1.99 1.98	2.00 1.99	1.96	1.37	none	1.93	None
H,H <b>1P<sup>d</sup></b>	1.99	2.00 2.00 1.99	1.99	1.96	none	none	1.84 1.56	None
C <sub>6</sub> H <sub>5</sub> , Si(CH <sub>3</sub> ) <sub>3</sub> <b>6P<sup>b</sup></b>	1.97	1.99 1.98 1.94	1.99	1.86	none	none	178 1.53	None
BH <sub>2</sub> ,BH <sub>2</sub> <b>8P<sup>c</sup></b>	1.98	1.99 1.98 1.93	1.99	1.82	none	none	1.70	None
NH <sub>2</sub> ,H <b>9C<sup>c</sup></b>	1.98	1.99	1.99 1.99	1.98	1.57	1.59	1.96	0.59
H,NH <sub>2</sub> <b>10A<sup>c</sup></b>	1.92	1.99 1.97	1.99 1.98	1.98	1.65	none	1.95	None
H,NH <sub>2</sub> <b>10P<sup>c,d</sup></b>	1.99	2.00 1.99 1.98	1.99	1.97	none	none	1.94 1.60	None
NH <sub>2</sub> ,NH <sub>2</sub> <b>11C<sup>c</sup></b>	1.99 1.98	1.98	1.99 1.98	1.99	1.83	1.85	1.97	None
OH,H <b>12A<sup>c</sup></b>	1.98	1.99 1.98	2.00 1.98	1.98	1.68	none	1.96	None
H,OH <b>13A<sup>c</sup></b>	1.91	1.99 1.96	1.99 1.99	1.98	1.66	none	1.97	None
OH,OH <b>14C<sup>a</sup></b>	1.99	1.99	1.99 1.98	1.99	1.90	1.81	1.98	0.32
F,H <b>15 A(C)<sup>c</sup></b>	1.98	1.99 1.98	2.00 1.98	1.97	1.73	none	1.96	None
H,F <b>16A<sup>c</sup></b>	1.91	1.99 1.95	1.99 1.99	1.98	1.61	none	1.97	None
H,F <b>16P<sup>c,d</sup></b>	1.99	2.00 1.99 1.97	1.99	1.98	none	none	1.96 1.61	None
F,F <b>17 A(C)<sup>c</sup></b>	1.98	1.99 1.92	1.99 1.98	1.99	1.81	none	1.98	None

<sup>a</sup> NBO occupancy (number of electrons) at the CCSD(T)/pVTZ level unless indicated otherwise (CCD(T)/6-31G\* or B3LYP/6-31G\* as noted). BD = two-center bond; LP = lone pair; LP\* = vacant "lone pair", i.e. the empty p orbital of a carbene.

<sup>b</sup> B3LYP/6-31G\* calculations. <sup>c</sup> CCSD(T)/6-31G\* calculations. <sup>d</sup> Transition state.

**Table 3. Harmonic and Anharmonic Calculated Wavenumbers (cm<sup>-1</sup>) of the CNN Moiety in Nitrile Imines RCNNR' and Their Transitions States for Inversion.<sup>a</sup>**

Substituents	IR				
R,R' structure <sup>a</sup>	calc harmonic wavenumber	calc anharmonic wavenumber	calc Intensities <sup>g</sup>	% wavefunction	mode description
H,H <b>1A</b>		1878	7.4	50 28	$\nu_3+\nu_5$ $\nu_7$
		1917	1.5	26 25 16	$3\nu_3$ $\nu_2+\nu_3$ $\nu_2+2\nu_3$
	2147 (2065) <sup>b</sup> 2080 <sup>e</sup>	2101 (2033) <sup>b,c</sup> 2062 <sup>e</sup> (2033) <sup>e,f</sup>	177.1	64	$\nu_7 \nu_{\text{CNN}}$
		2296	4.5	46 18	$\nu_3+2\nu_4$ $\nu_2+2\nu_4$
H,H <b>1P</b>		2143	1.8	87	$2\nu_6$
		2156	8.3	88	$\nu_3+\nu_8$
	2302 (2213) <sup>b</sup>	2246 (2173) <sup>b</sup>	756.8	87	$\nu_{10} \nu_{\text{CNN}}$
		2293	8.1	69 15	$2\nu_1+\nu_9$
H <sub>2</sub> N,H <b>9C</b>	2063 (1983) <sup>b</sup>	1967 (1903) <sup>b</sup> 1958 <sup>e</sup> (1931) <sup>e,f</sup>	39.7	54 27	$\nu_9 \nu_{\text{CNN}}$ $\nu_2 + \nu_7$
		2030	26.0	51 35 11	$\nu_2 + \nu_7$ $\nu_9$ $\nu_1 + \nu_7$
		2122	16.6	54 21 10	$\nu_2 + \nu_3$ $2\nu_3$ $\nu_6$
H,NH <sub>2</sub> <b>10A</b>	2049 (1971) <sup>b</sup>	2009 (1944) <sup>b</sup>	114.5	85	$\nu_9 \nu_{\text{CNN}} + (\nu_{\text{NN}})$
		2081	2.5	82	$\nu_2 + \nu_7$
		2096	1.6	81	$\nu_4 + \nu_6$
H,NH <sub>2</sub> <b>10P</b>	2233 (2147) <sup>b</sup>	2157 (2087) <sup>b</sup>	284.2	85	$\nu_9 \nu_{\text{CNN}} + (\nu_{\text{NN}})$
NH <sub>2</sub> ,NH <sub>2</sub> <b>11C</b>	1650 (1586) <sup>b</sup>	1631 (1578) <sup>b</sup>	68.3	66 20	$\nu_{11} \nu_{\text{CNN}} + \sigma_{\text{NH}_2}$ $\nu_{12}$
		1964	3.6	86	$\nu_2 + \nu_4 + \nu_5$
HO,H <b>12A</b>	2023 (1945) <sup>b</sup>	1945 (1882) <sup>b</sup>	50.5	87	$\nu_7 \nu_{\text{CNN}}$
H,OH <b>13A(C)</b>	2017 (1939) <sup>b</sup>	1940 (1877) <sup>b</sup>	77.1	84	$\nu_7 \nu_{\text{CNN}}$

HO,OH <b>14C</b>	1748 (1680) <sup>b</sup> (1642) <sup>e</sup>	1712 (1657) <sup>b</sup> (1623) <sup>e,f</sup>	32.7	77 17	$\nu_9$ $2\nu_4$
F,H <b>15A(C)</b>	1968 (1892) <sup>b</sup>	1867 (1807) <sup>b</sup>	41.9	50 45	$\nu_6$ $\nu_{\text{CNN}}$ $\nu_1 + \nu_4$
		1923 (1861) <sup>b</sup>	19.1	50 45	$\nu_1 + \nu_4$ $\nu_6$
		1953	4.0	90	$2\nu_3$
		2299	3.8	83 10	$\nu_3 + \nu_4$ $\nu_3 + \nu_5$
H,F <b>16A</b>	1978 (1901) <sup>b</sup>	1904 (1842) <sup>b</sup>	59.5	86 10	$\nu_7$ $\nu_{\text{CNN}}$ $2\nu_4$
H,F <b>16P<sup>d</sup></b>	2178 (2094) <sup>b</sup>	2094 (2026) <sup>b</sup>	92.5	67 17	$\nu_6$ $\nu_{\text{CNN}}$ $\nu_5$
		2235	6.4	64 23	$2\nu_5$ $\nu_6$
F,F <b>17A(C)</b>	1772 (1703) <sup>b</sup>	1722 (1666) <sup>b</sup>	35.0	61 18	$\nu_8$ $\nu_{\text{CNN}}$ $\nu_2 + \nu_7$

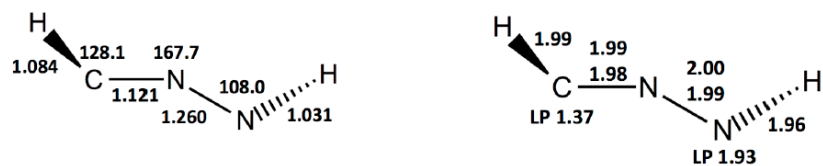
<sup>a</sup> B3LYP/6-31G\* calculations except when indicated otherwise. The major canonical structures are denoted by A (allenic), P (propargylic), C (carbenic). The spectroscopic descriptions are indicated beneath each compound table. <sup>b</sup> Scaled values in parentheses; scaling factor 0.9613 for calculated harmonic wavenumbers and 0.9676 for the corresponding anharmonic calculations.<sup>5</sup> <sup>c</sup> Experimental value for **1A** (ref 20): 2033 cm<sup>-1</sup>. <sup>d</sup> Transition state. <sup>e</sup> Values in italics are at the CCSD(T)/cc-pVTZ level. <sup>f</sup> Scaling factor 0.986 for calculated anharmonic CCSD(T)/cc-pVTZ wavenumbers. <sup>g</sup> I > 1 km/mol at the B3LYP/6-31G\* level except when indicated otherwise. <sup>h</sup>value by purely variational calculation due to presence of strong resonance.

**Table 4. Activation Energies ( $E_a$ ) and Energies of Reaction ( $E_R$ ) for Cyclization of Nitrile Imines to 1*H*-Diazirenes (kcal/mol)<sup>a</sup>**

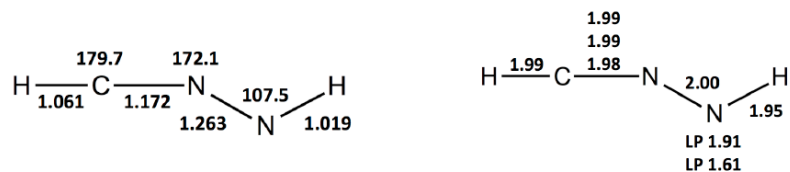
Nitrile imine	$E_a$	Azirene	$E_R$
HCNNH <b>1</b>	56.1	<b>22</b>	10.7
H <sub>2</sub> NCNNH <b>9</b>	33.8	<b>25</b>	-1.0
HCNNH <sub>2</sub> <b>10</b>	33.1	<b>26</b>	1.6
H <sub>2</sub> NCNNH <sub>2</sub> <b>11</b>	25.6	<b>27</b>	-0.5
HOCNNH <b>12</b>	36.1	<b>28</b>	-3.7
HCNNOH <b>13</b>	41.2	<b>29</b>	0.8
HOCNNOH <b>14</b>	28.5	<b>30</b>	-3.3
FCNNH <b>15</b>	36.9	<b>31</b>	-6.3
HCNNF <b>16</b>	43.9	<b>32</b>	-1.1
FCNNF <b>17</b>	32.8	<b>33</b>	-5.6
H <sub>2</sub> NCNNMe <b>35</b>	30.9	<b>36</b>	-1.0

<sup>a</sup> Calculations at the B3LYP/6-31G\* level, corrected for zero-point vibrational energies

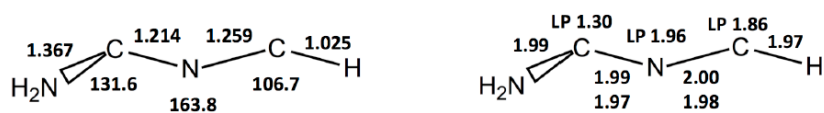
(a)



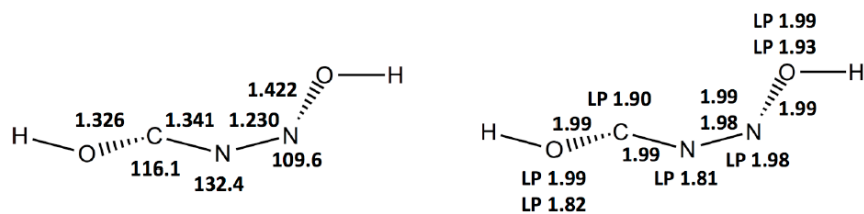
(b)



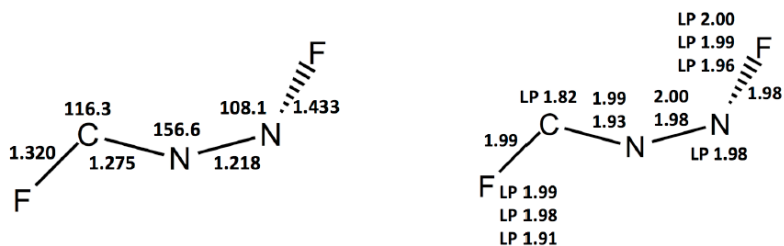
(c)



(d)

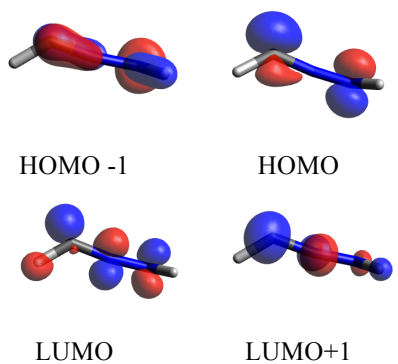


(e)

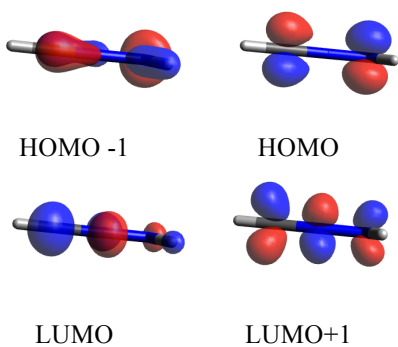
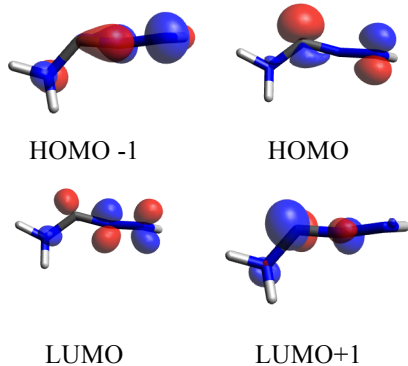
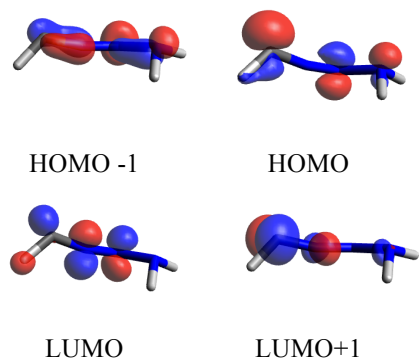
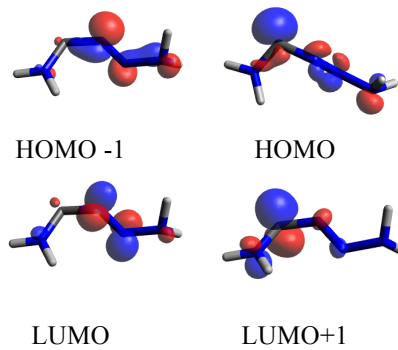


**Figure 1.** Calculated structure (Å and degree), double bonds and NBO lone pairs of (a) H-CNN-H **1A**, (b) the transition state HCNNH **1P(TS)**, (c) H<sub>2</sub>N-CNN-H **9C**, (d) HO-CNN-OH **14C**, and (e) F-CNN-F **17A(C)**, all at the CCSD(T)/cc-pVTZ level.

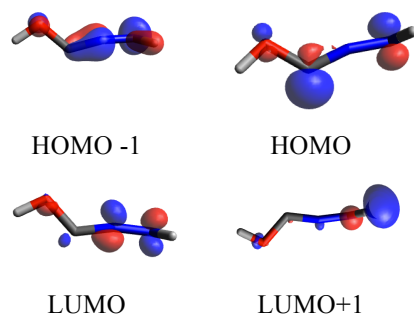
a) H-CNN-H **1A**



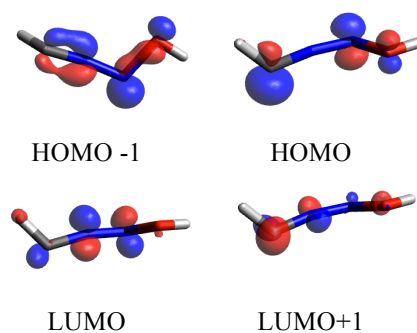
(b) H-CNN-H 1P(TS)

(c) H<sub>2</sub>N-CNN-H 9C(d) H-CNN-NH<sub>2</sub> 10A(e) H-CNN-NH<sub>2</sub> 11C

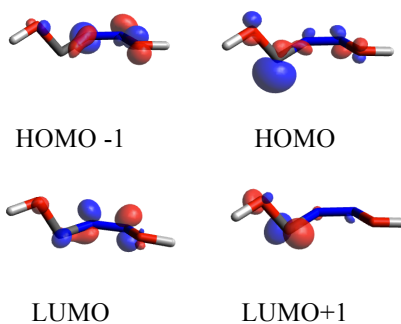
(f) HO-CNN-H 12A



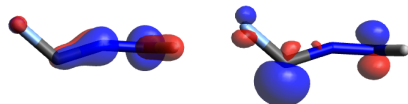
(g) H-CNN-OH 13A(C)



(h) HO-CNN-OH

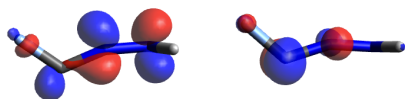


## (i) F-CNN-H 15A(C)



HOMO -1

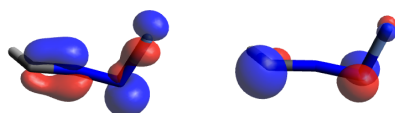
HOMO



LUMO

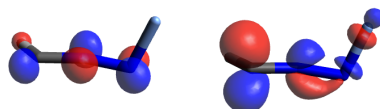
LUMO+1

## (j) H-CNN-F 16A



HOMO -1

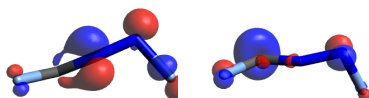
HOMO



LUMO

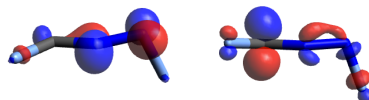
LUMO+1

## (k) F-CNN-F 17A(C)



HOMO -1

HOMO



LUMO

LUMO+1

Figure 2. Molecular Orbitals for the ground states of nitrile imines X-CNN-Y computed at CCSD(T)/6-31G\* level of theory.



## ASSOCIATED CONTENT

**Supporting Information Available:** Figures showing the molecular orbitals of **2A** and **8P** and several conformers of **9-17**; Cartesian coordinates and energies of calculated ground states and transition states, details of NBO calculations for compounds **1**, **2**, **6**, **8**, and **9-17**. This material is available free of charge via the Internet at [www.pubs.acs.org](http://www.pubs.acs.org).

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [didier.begue@univ-pau.fr](mailto:didier.begue@univ-pau.fr) (D.B.); [wentrup@uq.edu.au](mailto:wentrup@uq.edu.au) (C.W.).

### Notes

The authors declare no competing financial interest.

**Acknowledgments:** This work was supported by The University of Queensland and the Australian Research Council. Computer time for this study was provided by the computing facilities at the Mésocentre de Calcul Intensif Aquitain of the Université de Bordeaux and at the Université de Pau et des Pays de l'Adour.

## References and Notes

- 
- 1 (a) Kanemasa, S. Product Class 2: Nitrile Imines. *Science of Synthesis* **2004**, *19*, 41-52. (b) Sharp, J. T. Nitrile Ylides and Nitrile Imines. In *The Chemistry of Heterocyclic Compounds 59: Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Padwa, A., Pearson, W. H., Eds.; John Wiley & Sons: New York, 2002. (c) Bertrand, G.; Wentrup, C. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 527. (d) Shawali, A. S. *Chem. Rev.* **1993**, *93*, 2731. (e) *1,3-Dipolar Cycloaddition Chemistry*, Padwa, A., Ed.; Wiley

---

Interscience: New York, 1984.

2 Caramella, P.; Houk, K. N., *J. Am. Chem. Soc.* **1976**, *98*, 6397.

3 Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1993**, *115*, 7743.

4 (a) Puzzarini, C.; Gambi, A. *Theor. Chem. Acc.* **2012**, *31*, 1135. (b) Kawauchi, S.; Tachibana, A.; Mori, M.; Shibusa, Y.; Yamabe, T. *J. Mol Struct. (Theochem)*, **1994**, *310*, 255.

5 Bégué, D.; Qiao, G. G.; Wentrup, C. *J. Am. Chem. Soc.* **2012**, *134*, 5339.

6 The allenic structure of Ph<sub>3</sub>C-CNN-CPh<sub>3</sub> has also been demonstrated by X-ray crystallography and chemical reactivity: Fauré, J.-L.; Réau, R.; Wong, M. W.; Koch, R.; Wentrup, C.; Bertrand, G. *J. Am. Chem. Soc.* **1997**, *119*, 2819.

7 A propargylic structure has been demonstrated by X-ray crystallography for bis(dialkylamino) derivatives (R<sub>2</sub>N)<sub>2</sub>B-CNN-B(R<sub>2</sub>N)<sub>2</sub>: Arthur, M. P.; Baceiredo, A.; Fischer, J.; De Cian, A.; Bertrand, G. *Synthesis* **1992**, 43.

8 Mawhinney, R. C.; Muchall, H. M.; Peslherbe, G. H. *Chem. Comm*, **2004**, 1862-1063.

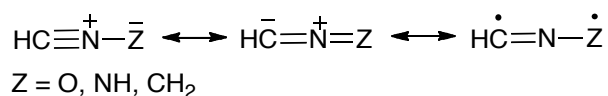
9 (a) Mawhinney, R. C.; Peslherbe, G. H.; Muchall, H. M. *J. Phys. Chem. B* **2008**, *112*, 650-655.  
(b) Muchall, H. M. *J. Phys. Chem. A* **2011**, *115*, 13694

10 Mawhinney, R. C.; Muchall, H. M.; Peslherbe, G. H. *Can. J. Chem.* **2005**, *83*, 1615-25.

11 Related DFT calculations on carbenic and non-carbenic nitrile imines have been reported: Lucero, P. L.; Pelaez, W. J.; Riedl, Z.; Hajos, G.; Moyano, E. L.; Yranzo, G. I. *Tetrahedron* **2012**, *68*, 1299.

12 Cargnoni, F.; Molteni, G.; Cooper, D. L.; Raimondi, M.; Ponti, A. *Chem. Comm.* **2006**, 1030.

13 Using the breathing-orbital valence bond ab initio method Hiberty et al. have described 1,3-dipoles as linear combinations of three valence bond structures, two zwitterionic and one diradical,



By this method, the ground states of the nitrile imines were found to have approximately equal contributions from propargylic and allenic VB structures (38 and 36 %, respectively), with a little less diradical character (26 %), but carbenic structures were not considered to be important:

Braida, B.; Walter, C.; Engels, B.; Hiberty, P. C. *J. Am. Chem. Soc.* **2010**, *132*, 7631-7637.

14 (a) Wentrup, C.; Damerius, A.; Reichen, W. *J. Org. Chem.* **1978**, *43*, 2037. (b) Wentrup, C.; Benedikt, J. *J. Org. Chem.*, **1980**, *45*, 1407.

15 Zheng, S.-L.; Wang, Y. W.; Coppens, P. *J. Am. Chem. Soc.* **2009**, *131*, 18036-18037.

16 Bégué, D.; Baraille, I.; Garrain, P. A.; Dargelos, A.; Tassaing, T. *J. Chem. Phys.* **2010**, *133*, 034102.

17 Gohaud, N.; Bégué, D.; Darrigan, C.; Pouchan, C. *J. Comput. Chem.* **2005**, *26*, 743-754.

18 Bégué, D.; Gohaud, N.; Pouchan, C.; Cassam-Chenaï, P.; Lievin, J. *J. Chem. Phys.* **2007**, *127*, 164115.

19 (a) Gohaud, N.; Bégué, D.; Pouchan, C. *Int. J. Quantum. Chem.* **2005**, *104*, 773. (b) Bégué, D.; Pouchan, C.; Guillemin, J.C.; Benidar, A. *Theor. Chem. Acc.* **2012**, *132*, 1122.

20 Maier, G.; Eckwert, J.; Bothur, A.; Reisenauer, H. P.; Schmidt, C. *Liebigs Ann.* **1996**, 1041.

<sup>21</sup> Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **200**, *100*, 39-91.

<sup>22</sup> (a) Goedecke, C.; Leibold, M.; Siemeling, U.; Frenking, G. *J. Am. Chem. Soc.* **2011**, *133*, 3557-3569 and references therein. (b) David Martin, Michele Soleilhavoup and Guy Bertrand, *Chem. Sci.* **2011**, *2*, 389-399.

<sup>23</sup> Tidwell, T. T. *Ketenes*. 2<sup>nd</sup> Ed, Wiley Interscience, Hoboken, N.J., 2006.

- 
- <sup>24</sup> Veedu, R. N.; Kvaskoff, D.; Wentrup, C. *Aust. J. Chem.* **2014**, *67*. Published online, [dx.doi.org/10.1071/CH13536](https://doi.org/10.1071/CH13536)
- <sup>25</sup> (a) Gomez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L.; Fausto, R. *J. Phys. Chem. A* **2005**, *109*, 7967. (b) Gomez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L. S.; Fausto, R. *J. Photochem. Photobiol. A: Chemistry* **2006**, *180*, 175. (c) Frija, L.; Reva, I. D.; Gomez-Zavaglia, A.; Cristiano, M. L. S.; Fausto, R. *J. Phys. Chem. A* **2007**, *111*, 2879.