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Carbenic Nitrile Imines: Properties and Reactivity

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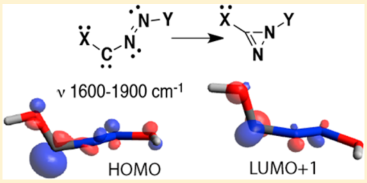
S Supporting Information



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 cm^{-1} have propargylic structures with a CN triple bond ($RCNNSiMe_3$ and $R_2BCNNBR_2$), and those with IR absorptions below ca. 2150 cm^{-1} are allenic (HCNNH, PhCNNH, and HCNNPh). Nitrile imines lacking significant cumulenic IR absorptions at 1900–2200 cm^{-1} are carbenic (R–(C:)–N=N–R′). Electronegative but lone pair-donating groups NR_2, OR, and 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 form azoketenes **21** with CO, to form [2+2] and [2+4] cycloadducts and borane adducts, and 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.[1] Six different structures have been postulated for the non-stabilized 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.[2] 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.[3] Similar results are obtained with all correlated methods.[3−5] However, substituents can have a profound effect on the relative stabilities. Thus, based on the matrix IR spectra and/or calculations[5] we found allenic structures for HCNNH (**1**), MeCNNMe (**2**), PhCNNH (**3**), HCNNPh (**4**), $PhCNNCH_3$ (**5**), and $Ph_3C–CNN–CPh_3$,[6] and propargylic structures, possessing a CN triple bond, for $PhCNNSiMe_3$ (**6**), PhCNNPh (**7**), and diborylnitrile imines exemplified by the model compound $H_2B–CNN–BH_2$ **8** (Chart 2).[7]

Chart 1. Six Fundamental Structures of Nitrile Imines

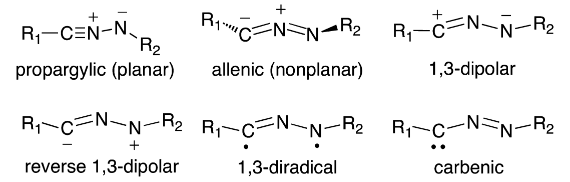


Chart 2. Major Canonical Structures of the Ground States of Nitrile Imines 1–8 Described Previously[5] and the New Nitrile Imines 9–17

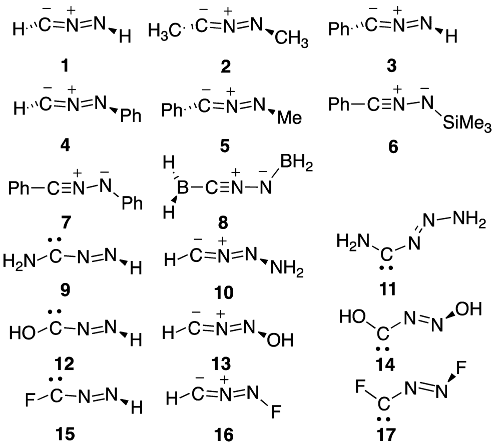


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Table 1. Calculated (CCSD(T)/6-31 G*) Structural Data for Nitrile Imines (R−CNN−R′) and the Transition States for Inversion[a,b]

R,R′ structure[a]	r(R−C)	r(C−N)	r(N−N)	r(N−R′)	∠RCN	∠CNN	∠NNR′	τRCNN	τCNNR′
H,H (**1A**)	1.084	1.213	1.259	1.030	128.1	167.7	108.1	219.4	229.9
H,H (**1P**)[b]	1.063	1.171	1.258	1.024	179.9	172.1	108.9	185.6	180.1
C_6H_5, $Si(CH_3)_3$ (**6P**)[c]	1.420	1.176	1.250	1.763	177.9	175.2	123.2	357.6	181.1
BH_2,BH_2 (**8P**)	1.506	1.189	1.256	1.412	176.6	171.3	128.4	179.7	180.0
NH_2,H (**9C**)	1.364	1.230	1.262	1.033	128.9	159.5	107.0	126.6	149.1
H,NH_2 (**10A**)	1.092	1.229	1.252	1.449	120.4	165.3	110.3	196.6	250.9
H,NH_2 (**10P**)[b]	1.067	1.178	1.279	1.479	179.0	173.5	106.4	307.1	180.1
NH_2,NH_2 (**11C**)	1.326	1.397	1.267	1.397	110.2	117.7	111.4	279.1	178.1
OH,H (**12A**)	1.358	1.237	1.264	1.036	123.6	160.2	107.1	175.8	143.3
H,OH (**13A**)	1.093	1.229	1.250	1.447	120.1	166.3	106.9	158.8	110.8
OH,OH (**14C**)[d]	1.326	1.341	1.230	1.422	111.6	132.4	109.6	245.1	18.8
F,H (**15 A(C)**)	1.340	1.248	1.260	1.035	121.6	157.6	107.6	156.1	114.9
H,F (**16A**)	1.090	1.224	1.255	1.447	122.6	166.6	105.2	151.8	118.3
H,F (**16P**)[b]	1.069	1.180	1.285	1.459	179.1	173.8	102.9	268.7	176.6
F,F (**17A(C)**)	1.330	1.285	1.236	1.442	115.9	154.1	107.1	166.2	103.0

[a] Bond lengths in angstroms and angles in degrees. Major canonical structures denoted as follows: A allenic; P propargylic; C carbenic. [b] Transition state. [c] B3LYP/6-31G* calculation. [d] CCSD(T)/cc-pVTZ calculation.

The importance of the carbenic resonance structures of amino- and fluoro-substituted nitrile imines $H_2N{-}CNN{-}NH_2$ 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).[8,9] The carbenic forms would be stabilized by the neighboring lone pairs. Thus, *C*,*N*-diaminonitrile imine is predicted to be a stable carbene.[9−11] 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, nonplanar allenic-type geometry.[12] Contributions of 1,3-diradical canonical structures of 1,3-dipoles have also been postulated.[13]

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.[14] The reaction can be described in terms of a carbenic nature of the cyclizing nitrile imine in much the same way that *o*-biphenylylcarbene cyclizes to fluorene.[14] A C−H insertion of the carbenic nitrile imine is not to be expected.[9b]

Surprisingly, a bent structure of a Zn-coordinated *C*,*N*-diarylnitrile imine has been reported.[15] 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 $R^1C(+)NN(-)R^2$ 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.[5] 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).[5] 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.[5] 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.[5] 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_2, OH, and F), which have the effect of stabilizing the carbenic canonical structures[8−10] 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 cumulenic 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.

■ 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[5] 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,[5] scaling factors of 0.9613 and 0.9676

Table 2. NBO Occupancy Data for X–C1N2N3–Y[a]

	BD			LP			LP*	
compd/NBO	X–C1	C1–N2	N2–N3	N3–Y	C1	N2	N3	C1
H,H (**1A**)[a]	1.99	1.99 1.98	2.00 1.99	1.96	1.37	none	1.93	none
H,H (**1P**)[d]	1.99	2.00 2.00 1.99	1.99	1.96	none	none	1.84 1.56	none
C_6H_5, $Si(CH_3)_3$ (**6P**)[b]	1.97	1.99 1.98 1.94	1.99	1.86	none	none	1.78 1.53	none
BH_2,BH_2 (**8P**)[c]	1.98	1.99 1.98 1.93	1.99	1.82	none	none	1.70	none
NH_2,H (**9C**)[c]	1.98	1.99	1.99 1.99	1.98	1.57	1.59	1.96	0.59
H,NH_2 (**10A**)[c]	1.92	1.99 1.97	1.99 1.98	1.98	1.65	none	1.95	none
H,NH_2 (**10P**)[c,d]	1.99	2.00 1.99 1.98	1.99	1.97	none	none	1.94 1.60	none
NH_2,NH_2 (**11C**)[c]	1.99 1.98	1.98	1.99 1.98	1.99	1.83	1.85	1.97	none
OH,H (**12A**)[c]	1.98	1.99 1.98	2.00 1.98	1.98	1.68	none	1.96	none
H,OH (**13A**)[c]	1.91	1.99 1.96	1.99 1.99	1.98	1.66	none	1.97	none
OH,OH (**14C**)[a]	1.99	1.99	1.99 1.98	1.99	1.90	1.81	1.98	0.32
F,H (**15A(C)**)[c]	1.98	1.99 1.98	2.00 1.98	1.97	1.73	none	1.96	none
H,F **16A**[c]	1.91	1.99 1.95	1.99 1.99	1.98	1.61	none	1.97	none
H,F (**16P**)[c,d]	1.99	2.00 1.99 1.97	1.99	1.98	none	none	1.96 1.61	none
F,F (**17A(C)**)[c]	1.98	1.99 1.92	1.99 1.98	1.99	1.81	none	1.98	none

[a] NBO occupancy (number of electrons) at the CCSD(T)/pVTZ level unless indicated otherwise (CCSD(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. [b] B3LYP/6-31G* calculations. [c] CCSD(T)/6-31G* calculations. [d] Transition state.

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$_2$ algorithm).[16,17] These wavenumbers were obtained initially from a variational and perturbation-variation treatment developed to solve the vibrational Schrödinger equation.[18] Relevant wavenumbers in the "cumulenic" region (ca. 1700–2300 cm^{-1}) 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.[19]

■ RESULTS AND DISCUSSION

For the parent nitrile imine HCNNH **1**, high-level calculations predict a bent, allenic ground state (∠HCN ~130°),[3−5] 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 (∠HCN ~180°), which is a transition state for inversion of the allenic structure.[5] Thus, we designate the allenic ground state **1A** for allenic and the transition state **1P** for propargylic. The matrix IR spectrum[20] 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.[5,20] 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 of the substituted nitrile imines, including those studied previously,[5] 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.[5] 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

Table 3. Harmonic and Anharmonic Calculated Wavenumbers (cm^{-1}) of the CNN Moiety in Nitrile Imines RCNNR′ and Their Transitions States for Inversion[a]

substituents	IR				
R,R′ structure[a]	calcd harmonic wavenumber	calcd anharmonic wavenumber	calcd intensities[g]	% wave function	mode description
H,H (**1A**)		1878	7.4	50	$\nu_3 + \nu_5$
				28	ν_7
		1917	1.5	26	$3\nu_3$
				25	$\nu_2 + \nu_3$
				16	$\nu_2 + 2\nu_3$
	2147 (2065)[b] *2080*[e]	2101 (2033)[b,c] *2062*[e] *(2033)*[e,f]	177.1	64	$\nu_7\ \nu_{CNN}$
		2296	4.5	46	$\nu_3 + 2\nu_4$
				18	$\nu_2 + 2\nu_4$
H,H (**1P**)		2143	1.8	87	$2\nu_6$
		2156	8.3	88	$\nu_3 + \nu_8$
	2302 (2213)[b]	2246 (2173)[b]	756.8	87	$\nu_{10}\ \nu_{CNN}$
		2293	8.1	69	$2\nu_1 + \nu_9$
H_2N,H (**9C**)	2063 (1983)[b]	1967 (1903)[b] *1958*[e] *(1931)*[e,f]	39.7	54	$\nu_9\ \nu_{CNN}$
				27	$\nu_2 + \nu_7$
		2030	26.0	51	$\nu_2 + \nu_7$
				35	$\nu_9\ \nu_{CNN}$
				11	$\nu_1 + \nu_7$
		2122	16.6	54	$\nu_2 + \nu_3$ τ and δ
				21	$2\nu_3$
				10	$\nu_6\ \delta_{NH}$
H,NH_2 (**10A**)	2049 (1971)[b]	2009 (1944)[b]	114.5	85	$\nu_9\ \nu_{CNN} + (\nu_{NN})$
		2081	2.5	82	$\nu_2 + \nu_7$
		2096	1.6	81	$\nu_4 + \nu_6$
H,NH_2 (**10P**)	2233 (2147)[b]	2157 (2087)[b]	284.2	85	$\nu_9\ \nu_{CNN} + (\nu_{NN})$
NH_2,NH_2 (**11C**)	1650 (1586)[b]	1631 (1578)[b]	68.3	66	$\nu_{11}\ \nu_{CNN} + \sigma_{NH2}$
				20	ν_{12}
		1964	3.6	86	$\nu_2 + \nu_4 + \nu_5$
HO,H (**12A**)	2023 (1945)[b]	1945 (1882)[b]	50.5	87	$\nu_7\ \nu_{CNN}$
H,OH (**13A(C)**)	2017 (1939)[b]	1940 (1877)[b]	77.1	84	$\nu_7\ \nu_{CNN}$
HO,OH (**14C**)	1748 (1680)[b] *(1642)*[e]	1712 (1657)[b] *(1623)*[e,f]	32.7	77	$\nu_9\ \nu_{CNN}$
				17	$2\nu_4$
F,H (**15A(C)**)	1968 (1892)[b]	1867 (1807)[b]	41.9	50	$\nu_6\ \nu_{CNN}$
				45	$\nu_1 + \nu_4$
		1923 (1861)[b]	19.1	50	$\nu_1 + \nu_4$
				45	ν_6
		1953	4.0	90	$2\nu_3$
		2299	3.8	83	$\nu_3 + \nu_4$
				10	$\nu_3 + \nu_5$
H,F (**16A**)	1978 (1901)[b]	1904 (1842)[b]	59.5	86	$\nu_7\ \nu_{CNN}$
				10	$2\nu_4$
H,F (**16P**)[d]	2178 (2094)[b]	2094 (2026)[b]	92.5	67	$\nu_6\ \nu_{CNN}$
				17	ν_5
		2235	6.4	64	$2\nu_5$
				23	ν_6
F,F (**17A(C)**)	1772 (1703)[b]	1722 (1666)[b]	35.0	61	$\nu_8\ \nu_{CNN}$
				18	$\nu_2 + \nu_7$

[a] 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 in Table S3, Supporting Information. [b] Scaled values in parentheses; scaling factor 0.9613 for calculated harmonic wavenumbers and 0.9676 for the corresponding anharmonic calculations.[5] [c] Experimental value for **1A** (ref 20): 2033 cm^{-1}. [d] Transition state. [e] Values in italics are at the CCSD(T)/cc-pVTZ level. [f] Scaling factor 0.986 for calculated anharmonic CCSD(T)/cc-pVTZ wavenumbers. [g] $I > 1$ km/mol at the B3LYP/6-31G* level except when indicated otherwise.

amino-, hydroxy-, and fluoro-substituted nitrile imines **9−17** are presented in Tables 1−3 and Figures 1 and 2. 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 and 2. The full data for all the calculated conformers is presented in the Supporting Information (Figure S1−S22 and Tables S1−S3). CCSD(T) data for the allenic HCNNH (**1A**) and the propargylic transition state **1P** as well as the typical propargylic nitrile imine $H_2BCNNBH_2$ (**8P**), whose IR spectra were analyzed previously,[5] are included for comparison in Tables 1 and 2. $PhCNNSiMe_3$ (**6P**) has been very well characterized

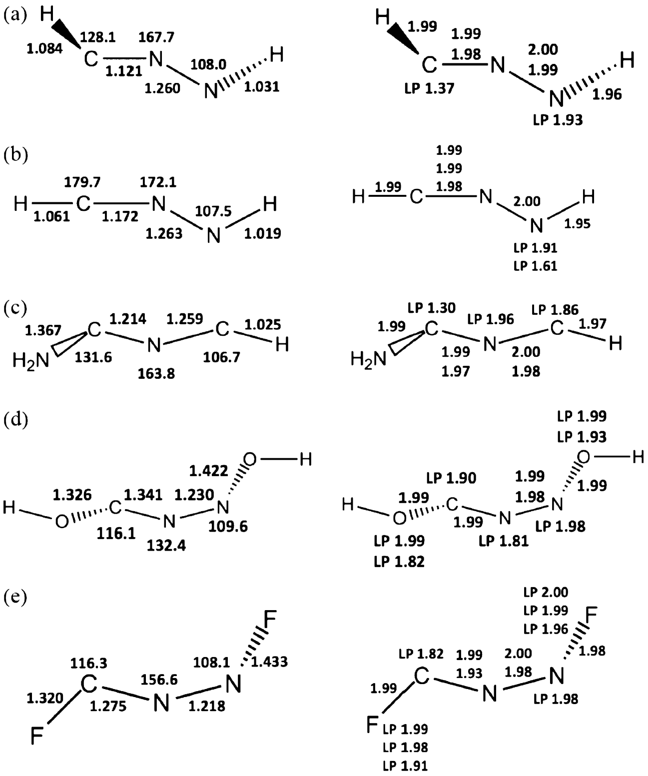
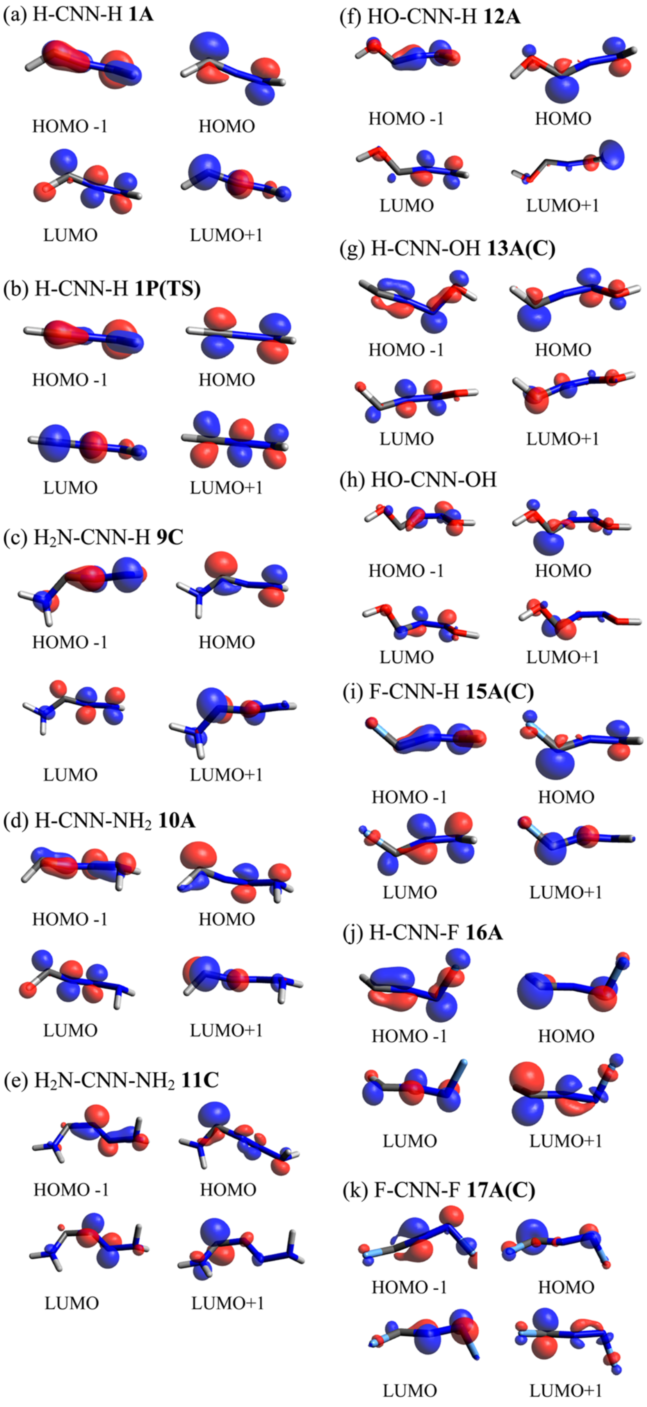


Figure 1. Calculated structures (angstroms and degrees) and NBO bond and lone pair occupancies of (a) HCNNH (**1A**), (b) the transition state HCNNH (**1P(TS)**), (c) H_2N−CNN−H (**9C**), (d) HO−CNN−OH (**14C**), and (e) F−CNN−F (**17A(C)**), all at the CCSD(T)/cc-pVTZ level.

experimentally and is clearly a propargylic ground state molecule;[5] 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 and 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, $PhCNNSiMe_3$ **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 S3, Supporting Information). Being propargylic, the TS for inversion (**6P(TS)**) is also propargylic, and the energy surface is very flat, with only 0.4 kcal/mol energy difference between the two structures (Figure S4, Supporting Information). $H_2BCNN−BH_2$ **8** is also clearly a propargylic compound (**8P**) with structural parameters similar to those of **6P**[5] (Figure S2, Supporting Information).


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

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

(c) H_2N-CNN-H **9C**

(d) H-CNN-NH_2 **10A**

(e) H_2N-CNN-NH_2 **11C**

(f) HO-CNN-H **12A**

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

(h) HO-CNN-OH

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

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

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

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

We now describe the NH_2-, 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_2N−CNN−H* **9**, *and H_2N−CNN−NH_2* **11** (Tables 1−3 and Figure2c,e). 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_2N−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 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 cm^{-1}), and they are very different from those for "normal" allenic and propargylic nitrile imines, which absorb very strongly in the range 2000−2300 cm^{-1},[5] e.g., **1A** 2033 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.[2] These are depicted in Figure 2c, and they clearly indicate that carbenic reactivity is expected in agreement with earlier observations.[9,10] The HOMO of H_2N−CNN−H **9** has the character of a carbene σ orbital residing in the plane of the molecule (∠NCN = 133°), and the LUMO+1 has the character of an empty p orbital of the singlet carbene, perpendicular to the molecular plane . (Note that the presence of a carbene-like σ-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 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 NH_2 group (1.96 electrons). This is in keeping with a relatively intense calculated IR absorption at 1944 cm^{-1} (115 km/mol), which is largely (85%) due to the CNN stretch (Table 3). Thus, compound **10** is similar to the parent HCNNH (**1A**) (Figure 2). However, the HOMO and LUMO +1 of H−CNN−NH_2 **10** are similar to those of **9** and thereby indicate that carbenic reactivity may be possible (Figure 2d). 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 cm^{-1}, 284 km/mol; Tables 2 and 3). As expected, the MOs of **10P** demonstrate a lack of carbenic character (Figure S10, , Supporting Information).

For H_2N−CNN−NH_2 (**11**)both B3LYP/6-31G* and CCSD(T)/6-31G* calculations predict lone-pair donation from the *C*-NH_2 group, resulting in a structure $H_2N(^+)$═$C(^-)$−N═N−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_2 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 cm^{-1} (3.6 kcal/mol), but this is not a cumulenic stretching vibration; it is a combination of deformation modes $\nu_2 + \nu_4 + \nu_5$ (Table 3). The cumulenic ν_{CNN} vibration is predicted to be very weak and to appear at the extremely low frequency of 1578 cm^{-1} (68 km/mol in combination with σ_{NH2}) (Table 3).

The HOMO of H_2N−CNN−NH_2, **11** has typical singlet *carbene* character, and the LUMO+1 corresponds to the empty p orbital on C (Figure 2e). 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 2f−h. A very low frequency ν_{CNN} absorption at 1882 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 2f). Thus, this compounds is designated **12A**.

HCNN−OH (**13**) is very similar. The predicted ν_{CNN} of the lowest energy conformer is at 1877 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** (Figure 2g). 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 ν_9 at 1657 cm^{-1} at the B3LYP/6-31G* level, or 1623 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 ν_{CNN} (77%) and $2\nu_4$ (ν_{NO} + δ_{NNO}) (17%). Only very weak bands are predicted in the cumulene region at 1984−2225 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°. The HOMO and LUMO are shown in Figure 2h. The carbenic character is clear with a carbenic σ orbital in the HOMO and an orthogonal carbenic p orbital in the LUMO. Accordingly, this molecules are designated **14C**.

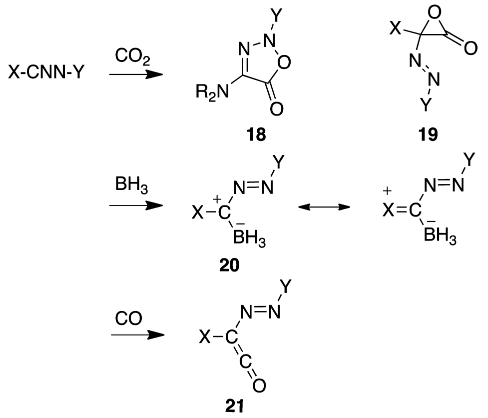
The three F-substituted nitrile imines **15**−**17** were analyzed in a similar way (Figures 2i-k). Neither possesses any true cumulene absorptions according to the frequency calculations. For FCNNH **15** the highest frequencies are 1807 cm^{-1} (42 km/mol; a combination of ν_{CNN} and $\nu_1 + \nu_4$) and 1861 cm^{-1} (19 km/mol; a combination of $\nu_1 + \nu_4$ and ν_{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 F−C(−)═N(+)═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 2i). 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 cm^{-1} (60 km/mol; ν_{CNN} (86%) and $2\nu_4$ (10%); Table 3), and weak absorptions in the range 2119−2472 cm^{-1} are all combination bands. The NBO analysis at the CCSD(T)/6-31G* level indicates a distinctly allenic structure, H−$C(^-)$═$N(^+)$═N−F, **16A**. The MOs do not support a carbenic character (Figure 2j). The transition state for inversion on C, **16P** (**TS**), has a linear HCN moiety, a CN triple bond, and a calculated absorption at 2026 cm^{-1} (93 km/mol; composed largely (67%) of ν_{CNN}) (Table 3). As expected, **16P** has no carbenic character (Figure S21, Supporting Information).

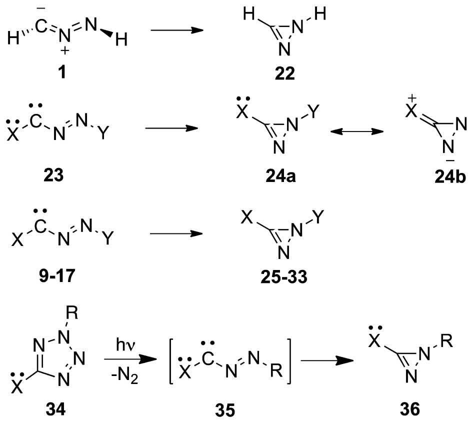
FCNNF (**17**) has a calculated absorption at 1666 cm^{-1} (35 km/mol; composed in part of ν_{CNN} (61%), and there is no truly cumulenic absorption. The NBO analysis at the CCSD(T)/cc-pVRZ level again indicates a clearly allenic structure F−C(−)═N(+)═N−F, **17A** (Table 2). However, the MOs do suggest *carbenic reactivity*, as there is a large carbene-type σ orbital on C in the HOMO and an orthogonal, vacant p orbital on C in the LUMO+1 (Figure 2k). 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_2, OH, or F) are able to undergo "1,3-dipolar" cycloaddition, e.g. with CO_2 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 α-lactone **19**. Conversely, all the nitrile imines are predicted to undergo addition of BH_3 at C, yielding adducts **20** without an activation barrier. This is a typical reaction of *N*-heterocyclic carbenes (NHCs),[21] 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.[22] Here we find that all the nitrile imines (XCNNX, X = H, NH_2, 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_2 (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.[23]

Scheme 1. Addition of CO_2, BH_3, and CO to Nitrile Imines



Scheme 2. Formation of 1*H*-Diazirenes



a: X = H_2N, R = Me
b: X = MeO, R = Ph
c: X = EtO, R = Ph

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

nitrile imine	E_a	azirene	E_R
HCNNH (**1**)	56.1	**22**	10.7
H_2NCNNH (**9**)	33.8	**25**	−1.0
$HCNNNH_2$ (**10**)	33.1	**26**	1.6
$H_2NCNNNH_2$ (**11**)	25.6	**27**	−0.5
HOCNNH (**12**)	36.1	**28**	−3.7
HCNNOH (**13**)	41.2	**29**	0.8
HOCNNOH (**14**)	28.5	**30**	−3.3
FCNNH (**15**)	36.9	**31**	−6.3
HCNNF (**16**)	43.9	**32**	−1.1
FCNNF (**17**)	32.8	**33**	−5.6
$H_2NCNNMe$ (**35**)	30.9	**36**	−1.0

[a]Calculations at the B3LYP/6-31G* level, corrected for zero-point vibrational energies.

Most importantly, we find that the carbenic nitrile imines are able to cyclize to 1*H*-diazirenes of the type **24** (Scheme 2). A cyclization of HCNNH (**1**) to the formally antiaromatic 1*H*-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.[24] 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_2, 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 1*H*-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,[5] but no nitrile imines **35** were reported in the matrix photolyses of **34**.[25] 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.

■ 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 cm^{-1} range, and (ii) nonplanar, allenic structures with longer CN bonds, shorter NN bonds, and strong IR absorptions below ca. 2150 cm^{-1}.[5] A third class of nitrile imines with significant carbenic character is characterized by very weak absorptions at very low frequencies in the 1600−1900 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, 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 $H_2N{-}C(:)NN{-}H$, $H_2N{-}C(:)NN{-}NH_2$, HO−C(:)NN−OH, and F−C(:)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., $H_2N{-}C(:){-}N{=}N{-}Y$, etc. Carbenic nitrile imines are predicted to form [2+4] or [2+2] cycloadducts **18** and **19** with CO_2, borane adducts **20**, and azoketenes **21** with CO, and 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.

■ ASSOCIATED CONTENT

Supporting Information

Figures showing the molecular orbitals of **2A**, **6P**, **6P**(**TS**), 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 http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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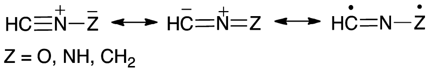

$$\mathrm{HC{\equiv}\overset{+}{N}{-}\overset{-}{Z}} \longleftrightarrow \mathrm{H\overset{-}{C}{=}\overset{+}{N}{=}Z} \longleftrightarrow \mathrm{H\overset{\bullet}{C}{=}N{-}\overset{\bullet}{Z}}$$

Z = O, NH, CH_2

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