

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231435927>

# Structure of Nitrilimine: Allenic or Propargylic?

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · AUGUST 1993

Impact Factor: 12.11 · DOI: 10.1021/ja00070a019

---

CITATIONS

29

---

READS

10

2 AUTHORS, INCLUDING:



Curt Wentrup

University of Queensland

576 PUBLICATIONS 6,470 CITATIONS

SEE PROFILE

## Structure of Nitrilimine: Allenic or Propargylic?

Ming Wah Wong\* and Curt Wentrup\*

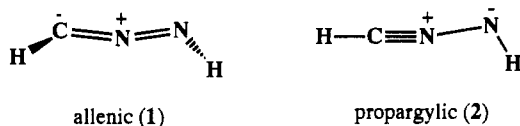
Contribution from the Chemistry Department, The University of Queensland, Brisbane QLD 4072, Australia

Received February 16, 1993

**Abstract:** High-level ab initio molecular orbital calculations, using basis sets up to 6-311+G(2df,2p), with electron correlation incorporated at the quadratic configuration interaction (QCISD) level, have been used to examine the structure of formonitrilimine (HCNNH). In contrast to previous theoretical findings, the lowest energy structure of nitrilimine is predicted to have a nonplanar, allenic geometry. The planar, propargylic structure is not a stable local minimum on the HCNNH potential energy surface at higher levels of theory. On the other hand, the nitrilimine radical cation (HCNNH<sup>•+</sup>) is predicted to have a planar, propargylic structure. The ionization energy and heat of formation ( $\Delta H_f^\circ$ ) of nitrilimine are predicted to be 9.15 eV and 370 kJ mol<sup>-1</sup>, respectively. Calculated IR and UV spectra are also reported.

## Introduction

While nitrilimines are important reagents in organic syntheses, particularly in regioselective 1,3-dipolar cycloadditions,<sup>1</sup> for a long time they could only be observed as transient intermediates in low-temperature matrices.<sup>2</sup> However, recent elegant work by Bertrand and co-workers has shown that, using the right set of substituents, nitrilimines can exist as stable compounds in the crystal or liquid states.<sup>3,4</sup> The structure of the parent molecule, formonitrilimine (HCNNH), has been the subject of several ab initio studies.<sup>5</sup> All calculations to date show that the lowest energy conformation of this simple 1,3-dipole has a planar geometry, corresponding to a propargylic structure (2). Furthermore, Houk et al. have indicated that there exists also another stable, nonplanar, allenic structure (1) of nitrilimine with similar energy.<sup>5c,f</sup>



(1) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565 and 633. (b) Huisgen, R.; Seidel, M.; Wallbillich, G.; Knupfer, H. *Tetrahedron* **1962**, *17*, 3. (c) Caramella, P.; Grunanger, P. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984. (d) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403.

(2) (a) Bock, H.; Dammel, R.; Fischer, S.; Wentrup, C. *Tetrahedron Lett.* **1987**, *28*, 617. (b) Wentrup, C.; Fischer, S.; Maquestiau, A.; Flammang, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 56. (c) Fischer, S.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 502. (d) Meier, H.; Heinzelmann, W.; Heimgartner, H. *Chimia* **1980**, *34*, 504 and 506. (e) Toubro, H.; Holm, A. *J. Am. Chem. Soc.* **1980**, *102*, 2093.

(3) Reau, R.; Veneziani, G.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 439. (b) Arthur, M. P.; Baceiredo, A.; Fischer, J.; Bertrand, G. *Synthesis* **1992**, 43. (c) Castan, F.; Baceiredo, A.; Bigg, D. A.; Bertrand, G. *J. Org. Chem.* **1991**, *56*, 1801. (d) Arthur, M. P.; Goodwin, H. P.; Baceiredo, A.; Dillon, K. B.; Bertrand, G. *Organometallics* **1991**, *10*, 3205. (e) Granier, M.; Baceiredo, A.; Bertrand, G.; Huch, V.; Veith, M. *Inorg. Chem.* **1991**, *30*, 1161. (f) Granier, M.; Baceiredo, A.; Dartiguenave, Y.; Dartiguenave, M.; Menu, M. J.; Bertrand, G. *J. Am. Chem. Soc.* **1990**, *112*, 6277. (g) Castan, F.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1250. (h) Sicard, G.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 2663.

(4) Bertrand, G.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.*, in press.

(5) (a) Guimon, C.; Khayar, S.; Gracian, F.; Begtrup, M.; Pfister-Guillouzo, G. *Chem. Phys.* **1989**, *138*, 157. (b) Kahn, S. D.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1871. (c) Thomson, C.; Glidewell, C. *J. Comput. Chem.* **1983**, *4*, 1. (d) Moffat, J. B. *J. Mol. Struct.* **1979**, *52*, 275. (e) Caramella, P.; Gandour, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 385. (f) Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397. (g) Houk, K. N.; Sims, J.; Duke, R. E., Jr.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287. (h) Hart, B. T. *Aust. J. Chem.* **1973**, *26*, 461.

In this paper we show, through calculations of the geometry at much higher levels of theory than those previously employed, that nitrilimine has a nonplanar, allenic structure. The planar, propargylic (C<sub>s</sub>) structure (2) does not in fact correspond to a local minimum on the HCNNH potential energy surface at higher levels of theory.

## Theoretical Methods and Results

Standard ab initio molecular orbital calculations<sup>6</sup> were carried out with the GAUSSIAN 92 programs.<sup>7</sup> Optimized geometries and vibrational frequencies for the allenic (C<sub>i</sub>, 1) and propargylic (C<sub>s</sub>, 2) structures of nitrilimine were obtained with a hierarchy of basis sets, namely, STO-3G, 3-21G, 6-31G\*, 6-31G\*\*, 6-31+G\*, 6-311G\*, 6-31G(2d), 6-311G(df), 6-311G(2df), and 6-311+G(2df,2p).<sup>6</sup> Electron correlation was incorporated via second-order Møller–Plesset theory (MP2),<sup>6</sup> complete active space SCF (CASSCF),<sup>8</sup> or quadratic configuration interaction with singles and doubles (QCISD) theory.<sup>9</sup> The vertical transition energies of nitrilimine (1) were calculated via the configuration interaction with the singles (CIS) method<sup>10</sup> using the 6-311-(2+,2+)G(2df,2p) basis set,<sup>11</sup> based on the MP2/6-311+G(2df,2p) geometry. The frozen-core approximation was employed for all correlation calculations. The ionization energies and heat of formation ( $\Delta H_f^\circ$ ) of 1 were computed with the Gaussian-2 (G2) theory.<sup>12</sup>

Calculated total and relative energies are given in Table I. A selection of optimized geometries is shown in Table II. Figure 1 presents the optimized geometries and Mulliken charges of 1 and 2. Vibrational frequencies of allene and nitrilimine are

(6) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(7) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(8) (a) Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795. (b) Eade, R. H. A.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362.

(9) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(10) Foresman, J. B.; Head-Gordon, M.; Pople, J. A. *J. Phys. Chem.* **1992**, *96*, 135.

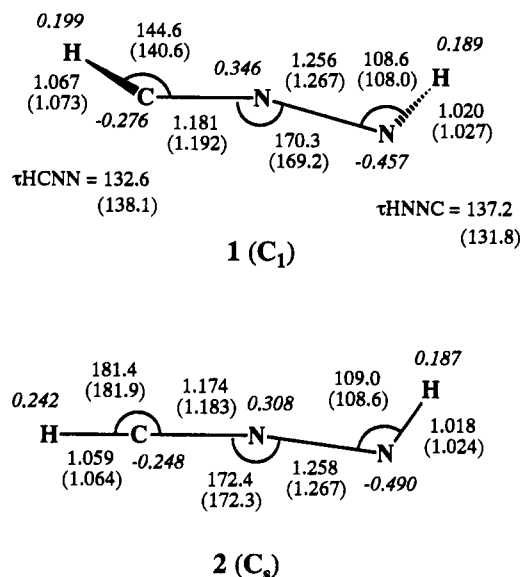
(11) The second set of diffuse functions for C, H, and N atoms are derived by scaling the standard exponent values by 0.3, for example, see: (a) Walters, V. A.; Hadad, C. M.; Thiel, Y.; Wiberg, K. B.; Johnson, P. M.; Foresman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4783. (b) Wiberg, K. B.; Hadad, C. M.; Foresman, J. B.; Chupka, W. A. *J. Phys. Chem.* **1992**, *96*, 10756.

(12) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

**Table I.** Calculated Total Energies (hartrees) and Relative Energies (kJ mol<sup>-1</sup>) for the Allenic and Propargylic Structures of Nitrilimine<sup>a</sup>

level	total energy <sup>b</sup>		rel energy <sup>c</sup>
	allenic (1)	propargylic (2)	
HF/STO-3G	-145.85632(0)	-145.85279(0)	9.3
HF/3-21G <sup>d</sup>	-145.94495(0)	-145.94495(0)	0.0
HF/6-31G*	-147.78838(0)	-147.78700(0)	3.6
HF/6-31G**	-147.79435(0)	-147.79338(0)	2.5
HF/6-31+G*	-147.79461(0)	-147.79373(0)	2.3
HF/6-311G*	-147.82292(0)	-147.82041(1)	6.6
HF/6-31G(2d)	-147.79633(0)	-147.79222(1)	10.8
HF/6-31G(df)	-147.79562(0)	-147.79595(0)	-0.9
HF/6-311+G(2df,2p)	-147.84759(0)	-147.84752(0)	0.2
CASSCF(4,4)/6-31G*	-147.86288(0)	-147.85963(1)	8.5
MP2/6-31G*	-148.25661(0)	-148.25222(1)	11.5
MP2/6-31G**	-148.27411(0)	-148.26977(1)	11.4
MP2/6-31+G*	-148.26811(0)	-148.26423(1)	10.2
MP2/6-311G*	-148.31137(0)	-148.30726(1)	10.8
MP2/6-31G(2d)	-148.29273(0)	-148.28813(1)	12.1
MP2/6-31G(df)	-148.30935(0)	-148.30629(1)	8.0
MP2/6-311G(2df,p)	-148.40735(0)	-148.40429(1)	8.0
MP2/6-311+G(2df,2p)	-148.41823	-148.41584	6.3
QCISD/6-31G*	-148.26759(0)	-148.26028(1)	19.2
QCISD/6-311G**	-148.33769	-148.33093	17.8
QCISD/6-311G(2df,p) <sup>e</sup>	-148.41191	-148.40628	14.8
QCISD(T)/6-311G(2df,p) <sup>e</sup>	-148.44328	-148.43611	18.8
G2	-148.47117	-148.46597	13.7

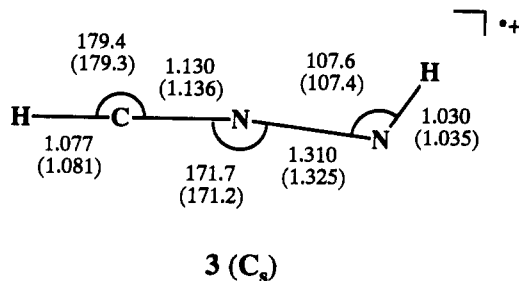
<sup>a</sup> Geometries fully optimized at the level specified, unless otherwise noted. <sup>b</sup> Number of imaginary frequencies in parentheses. <sup>c</sup>  $E(\text{propargylic}) - E(\text{allenic})$ . <sup>d</sup> Only one stable planar structure exists. <sup>e</sup> QCISD/6-311G\*\* optimized structures.

**Figure 1.** Optimized structures (MP2/6-311+G(2df,2p), with MP2/6-31G\* values in parentheses) and Mulliken charges (HF/6-311+G(2df,2p)) of allenic (1) and propargylic (2) forms of nitrilimine (in *italic*).

summarized in Tables III and IV, respectively. The optimized geometry of the nitrilimine radical cation (HCNNH<sup>•+</sup>, 3) is shown in Figure 2. Finally, the calculated transition energies for the first ten excited states of 1 are given in Table V.

## Results and Discussion

**Relative Energies.** The calculated energy difference between the nonplanar, allenic structure (1) and the planar, propargylic form (2) is quite dependent on the theoretical level employed (Table I). As noted previously,<sup>5c</sup> 1 is more stable than 2 by 9 kJ mol<sup>-1</sup> at the HF/STO-3G level. However, with the split-valence 3-21G basis set, the planar propargylic structure (2) is the only stable minimum on the HCNNH potential energy surface. At the HF/6-31G\* level, both 1 and 2 lie close in energy, with

**Figure 2.** Optimized structure of the nitrilimine radical cation (3) (MP2/6-311+G(2df,2p), with MP2/6-31G\* values in parentheses).

1 slightly favored by 4 kJ mol<sup>-1</sup>, and both are true local minima (with all real frequencies). To explore further the effect of basis set on the relative energies, we have optimized 1 and 2 systematically at the Hartree-Fock level with a hierarchy of basis sets, including 6-31G\*\*, 6-311G\*, 6-31+G\*, 6-31G(2d), 6-31G(df), and 6-311+G(2df,2p).<sup>6</sup> From Table I, it can be seen that an expansion of the basis set from double- $\zeta$  valence to triple- $\zeta$  valence (6-31G\*  $\rightarrow$  6-311G\*) and from one set of d-polarization functions to two (6-31G\*  $\rightarrow$  6-31G(2d)) strongly favors the allenic structure (1). In fact, the planar propargylic structure (2) is no longer a local minimum on the HCNNH potential energy surface at these levels of theory. On the other hand, inclusion of f functions on heavy atoms (6-31G\*  $\rightarrow$  6-31G(df)) favors the propargylic structure. At the HF/6-31G(df) level, 2 is more stable than 1 by 1 kJ mol<sup>-1</sup>. Inclusion of p-polarization functions on hydrogens (6-31G\*  $\rightarrow$  6-31G\*\*) and inclusion of diffuse sp function on heavy atoms (6-31G\*  $\rightarrow$  6-31+G\*) have little effect on the relative energies. With the largest 6-311+G(2df,2p) basis set, the energy difference between 1 and 2 is just 0.2 kJ mol<sup>-1</sup>. Interestingly, the effect of multiple d-polarization functions (6-31G\*  $\rightarrow$  6-31G(2d)) is significantly smaller at the MP2 level than at the HF level.

We have investigated the effect of electron correlation on the relative energy with three different levels of theory, MP2, CASSCF, and QCISD. It is evident from Table I that *all correlation calculations lower the energy of the allenic conformation more than that of the propargylic form*. At the MP2/6-31G\* level, the allenic structure is favored over the propargylic one by 12 kJ mol<sup>-1</sup>. The preference for the allenic structure is more pronounced at higher levels of electron correlation treatment (QCISD). The planar propargylic structure (2) is predicted to be a first-order saddle point at all correlated levels considered, even with the 6-31G(df) basis set. Rearrangement of 2 along the normal coordinates representing the imaginary frequency leads to 1 without an energy barrier. At the QCISD/6-311G(2df,p) level, 1 is more stable than 2 by 19 kJ mol<sup>-1</sup>. Inclusion of triple substitution in the QCISD theory reduces the energy difference by 4 kcal mol<sup>-1</sup>. At our best level of theory, Gaussian-2 (corresponds effectively to QCISD(T)/6-311+G(3df,2p) with zero-point vibrational and isogyric corrections),<sup>12</sup> the allenic structure (1) is favored over the propargylic one by 14 kJ mol<sup>-1</sup>. In summary, *the nonplanar allenic structure is the only stable minimum of nitrilimine at higher levels of theory*. Incorporation of electron correlation is essential for the proper description of this 1,3-dipolar molecule.

**Geometrical Structures.** Most of the previous ab initio calculations on nitrilimine were carried out with split-valence basis set.<sup>5</sup> As far as we are aware, the highest-level geometry optimization on nitrilimine is the SCF calculation by Kahn et al.,<sup>5b</sup> using the 6-31G\* basis set and with the assumption of a planar geometry. Here, we have calculated the molecular structure of 1 using basis sets up to 6-311+G(2df,2p), with electron correlation incorporated at the MP2 and QCISD levels (Table II). The CNN and HNN bond angles are predicted to be approximately 169° and 108°, respectively, at all levels of theory.

Table II. Optimized Parameters for the Allenic Structure of Nitrilimine (1)<sup>a</sup>

level	parameter								
	r(C-H)	r(C-N)	r(N-N)	r(N-H)	∠HCN	∠CNN	∠HNN	τHCNN	τHNNC
HF/6-31G*	1.069	1.179	1.223	1.009	127.5	171.5	108.7	140.2	130.1
MP2/6-31G*	1.073	1.192	1.267	1.027	140.6	169.2	108.0	138.1	131.8
CASSCF/6-31G* <sup>b</sup>	1.063	1.182	1.246	1.006	136.9	169.7	108.2	142.4	128.2
QCISD/6-31G*	1.082	1.207	1.254	1.028	128.2	168.5	108.2	140.8	129.9
MP2/6-31+G*	1.074	1.191	1.269	1.027	141.9	169.5	108.5	134.3	135.3
MP2/6-311G*	1.073	1.189	1.258	1.021	140.2	169.5	108.6	136.6	133.2
MP2/6-31G(2d)	1.078	1.189	1.261	1.027	138.7	169.2	107.9	138.7	131.5
MP2/6-31G(df)	1.068	1.187	1.261	1.021	142.9	169.5	108.5	135.8	133.7
MP2/6-311+G(2df,2p)	1.067	1.181	1.256	1.020	144.6	170.3	108.6	132.6	137.2
QCISD/6-31+G*	1.082	1.206	1.256	1.028	128.9	168.6	108.4	137.6	133.2
QCISD/6-31G(2d)	1.087	1.206	1.246	1.028	125.9	168.8	108.3	140.7	130.0
QCISD/6-31G(df)	1.075	1.200	1.249	1.022	130.2	168.8	108.5	140.1	130.5
QCISD/6-311G**	1.081	1.204	1.244	1.022	128.9	169.1	107.1	140.2	130.6

<sup>a</sup> Bond lengths in Å and bond angles in deg. <sup>b</sup> Complete active space SCF calculation (four electrons in four active orbitals).

Table III. Calculated and Experimental Frequencies (cm<sup>-1</sup>) of Allene

symmetry	calcd <sup>a</sup>		exptl <sup>b</sup>
	direct <sup>c</sup>	scaled <sup>d</sup>	
e	3262 (0.95)	3099	3086
a <sub>1</sub>	3171 (0.95)	3013	3015
b <sub>2</sub>	3171 (0.95)	3013	3007
b <sub>2</sub>	2046 (0.96)	1944	1957
a <sub>1</sub>	1487 (0.97)	1442	1443
b <sub>2</sub>	1434 (0.97)	1391	1398
a <sub>1</sub>	1100 (0.98)	1067	1073
e	1018 (0.98)	988	999
b <sub>1</sub>	898 (0.96)	871	865
e	867 (0.97)	841	841
e	365 (0.97)	354	355

<sup>a</sup> MP2/6-311G(2df,p) values. <sup>b</sup> From ref 14. <sup>c</sup> Calculated/experimental ratios in parentheses. <sup>d</sup> Scaled by 0.95 if over 2000 cm<sup>-1</sup> and 0.97 if under 2000 cm<sup>-1</sup>.

On the other hand, the HCN bond angle and the HCNN and HNCC torsional angles are sensitive to the effect of electron correlation and basis set (in particular, the inclusion of diffuse sp and f functions on heavy atoms). For the C-N and N-N bond lengths, high-level treatment of electron correlation (QCISD) favors a more delocalized cumulative double bond, while improvement of basis set (6-311+G(2df,2p)) favors a more propargylic character (i.e. localized C≡N bond). Note that the effect of expanding the 6-31G\* basis, to 6-311G\*, 6-31+G\*, and 6-31G(df), at the QCISD level is similar to that at the MP2 level (Table II). At the MP2/6-311+G(2df,2p) level, the calculated C-N (1.181 Å) and N-N (1.256 Å) bond lengths and CNN (170.3°) bond angle are in very good agreement with the structural information on bis(triphenylmethyl)nitrilimine [*r*(C-N) = 1.173 Å, *r*(N-N) = 1.262 Å, and ∠CNN = 169.4].<sup>3a</sup> It may be concluded that no major steric and electronic effects are operating in this molecule. Note that the calculated N-N bond distance (1.256 Å) is comparable to the experimental N=N bond length of 1.252 Å in diazene (H-N=N-H).<sup>13</sup> This rather short N-N bond length reflects the -C<sup>-</sup>=N<sup>+</sup>=N- cumulenenic skeleton in nitrilimine (1).

We have examined the charge distributions of both 1 and 2 (Figure 1). The calculated Mulliken charges (HF/6-311+G(2df,2p)/MP2/6-311+G(2df,2p)) are consistent with the expectation from the resonance structure: the electron population of the carbon atom is significantly greater in 1 than in 2, while stronger negative charge is calculated for the terminal nitrogen atom in the propargylic form (2). Thus, one would expect an electron-withdrawing substituent to have a stronger electronic effect at the N-terminus than at the C-terminus. The calculated

dipole moments at the MP2/6-311+G(2df,2p) level are 2.43 and 2.82 D for 1 and 2, respectively.

**IR and UV Spectra.** IR and UV spectroscopy represent the most important experimental techniques for studying nitrilimines.<sup>2</sup> Unsubstituted formonitrilimine has not yet been observed.<sup>1,4</sup> To facilitate future characterization of this reactive intermediate, we report the calculated IR and UV spectra of 1. To provide an estimate of the likely accuracy of our computed vibrational frequencies at the MP2/6-311G(2df,p) level, we have determined the vibrational frequencies of allene (CH<sub>2</sub>=C=CH<sub>2</sub>), which also has a cumulative double bond structure, and compared them with the experimental values<sup>14</sup> (Table III). There is good agreement between theory and experiment. The calculated frequencies are 2–5% higher than the experimental values. This suggests that scaling factors of 0.95 (>2000 cm<sup>-1</sup>) and 0.97 (≤2000 cm<sup>-1</sup>) may be suitable for this level of theory. The mean absolute error of the scaled frequencies is just 6 cm<sup>-1</sup> with a maximum error of 13 cm<sup>-1</sup>. This lends confidence to our prediction of the vibrational frequencies for nitrilimine. As can be seen in Table IV, the characteristic features of the IR spectrum of 1 are the strong absorption bands of the CNN stretching (*ν*<sub>3</sub> and *ν*<sub>5</sub>) and CH bending (*ν*<sub>7</sub>) modes. The calculated (scaled) CNN stretching frequency, 2228 cm<sup>-1</sup>, is in good accord with the characteristic IR absorption between 2040 and 2259 cm<sup>-1</sup> for a large number of substituted nitrilimines.<sup>2–4</sup> Note that the CNN symmetric stretching mode (*ν*<sub>3</sub>) is dominated by the C≡N stretch and coupled with CH and NH stretches.

The study of isotopic substitutions may provide a more definitive assignment of the vibrational spectrum of nitrilimine. The calculated <sup>13</sup>C and <sup>15</sup>N isotopic shifts of 1 are listed in Table IV. Introduction of <sup>13</sup>C and <sup>15</sup>N (both central and terminal N positions) isotopes in 1 gives rise to significant frequency shifts in *ν*<sub>2</sub>, *ν*<sub>3</sub>, and *ν*<sub>5</sub>. In particular, both <sup>13</sup>C and <sup>15</sup>N (central N) substitutions lead to a lower CNN stretching (*ν*<sub>3</sub>) frequency (Δ*ν* = -24 and -46 cm<sup>-1</sup> for <sup>13</sup>C and <sup>15</sup>N isotopomers, respectively). The calculated <sup>15</sup>N frequency shift for *ν*<sub>3</sub> in 1 compares favorably with the experimental <sup>15</sup>N isotopomer shift (Δ*ν* = -33 cm<sup>-1</sup>) for diphenylnitrilimine.<sup>2e</sup> This result provides additional support for the assignment of the CNN stretching vibrational frequency of diphenylnitrilimine. Note that the changes in intensity due to isotopic substitutions are small (Table IV).

The first ten transition energies of nitrilimine (1) were calculated by using the configuration interaction including the all singly excited configurations (CIS) approach,<sup>10</sup> with the 6-311-(2+,2+)G(2df,2p) basis set. The calculated UV spectrum (Table V) shows a strong absorption at 231 nm (T<sub>2</sub>), which corresponds to a π → π\* transition. This value is in close agreement with the observed UV absorption values (244–275 nm) of several substituted nitrilimines in pentane solution.<sup>3c</sup> The longer wavelengths

(13) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. L.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619.

(14) Tanabe, K.; Sachi, S. *Bull. Chem. Soc. Jpn.* 1974, 47, 1847.

**Table IV.** Calculated IR Spectrum of Nitrilimine (1) and Its Isotopomers<sup>a</sup>

mode	frequency (cm <sup>-1</sup> ) <sup>b</sup>				intensity (km mol <sup>-1</sup> )				assign
	HCNNH	H <sup>13</sup> CNNH <sup>c</sup>	HC <sup>15</sup> NNH <sup>c</sup>	HCN <sup>15</sup> NH <sup>c</sup>	HCNNH	H <sup>13</sup> CNNH <sup>d</sup>	HC <sup>15</sup> NNH <sup>d</sup>	HCN <sup>15</sup> NH <sup>d</sup>	
$\nu_1$	3296	0	0	-7	34	1	0	-2	NH stretch
$\nu_2$	3236	-15	-1	0	95	-5	-2	0	CH stretch
$\nu_3$	2228	-24	-46	-3	194	1	-9	-4	CNN sym stretch
$\nu_4$	1253	-8	-2	-6	28	13	-1	10	NH bend
$\nu_5$	1158	-8	-3	-21	133	-14	2	-13	CNN antisym stretch
$\nu_6$	696	-3	0	0	46	0	0	0	CH + NH rock
$\nu_7$	620	-6	-3	0	191	2	6	1	CH bend
$\nu_8$	527	-1	-9	-2	36	-4	-7	0	CNN bend
$\nu_9$	503	-2	-9	-2	6	0	0	0	CNN torsion

<sup>a</sup> MP2/6-311G(2df,p) values. <sup>b</sup> Scaled by 0.95 if over 2000 cm<sup>-1</sup> and 0.97 if under 2000 cm<sup>-1</sup>. <sup>c</sup> Isotopomer frequency shifts. <sup>d</sup> Intensity changes due to isotopic substitutions.

**Table V.** Calculated Vertical Transition Energies (TE) of Nitrilimine (1)<sup>a</sup>

	TE		$f^b$
	nm	eV	
T1	276	4.49	0.049
T2	231	5.36	0.146
T3	215	5.76	0.006
T4	207	6.00	0.004
T5	182	6.82	0.030
T6	173	7.16	0.055
T7	171	7.25	0.002
T8	164	7.57	0.013
T9	158	7.85	0.007
T10	158	7.86	0.015

<sup>a</sup> CIS/6-311(2+,2+)G(2df,2p)//MP2/6-311+G(2df,2p) values.

<sup>b</sup> Oscillator strength.

(310–383 nm) observed for phenyl-substituted nitrilimines<sup>2c,d</sup> can be attributed to conjugation with the phenyl group.

**Ionization Energies and Heat of Formation.** We have calculated both adiabatic (IE<sub>a</sub>) and vertical (IE<sub>v</sub>) ionization energies of nitrilimine (1) at the G2 level of theory, which is able in general to reproduce ionization energies to within 0.1 eV.<sup>12,15</sup> The calculated IE<sub>a</sub> and IE<sub>v</sub> of 1 are 9.15 and 9.43 eV, respectively.<sup>16</sup> Interestingly, the nitrilimine cation is predicted to have a planar propargylic structure (3, Figure 2), in contrast to the nonplanar, allenic structure of the corresponding neutral. Indeed, compared to the neutral propargylic structure (2), a stronger propargylic

character is calculated for the radical cation (3): the C–N bond length is significantly shorter (by 0.044 Å) while the N–N bond length is significantly longer (by 0.052 Å) at the MP2/6-311+G-(2df,2p) level.

The heat of formation ( $\Delta H_f^\circ$ ) of nitrilimine (1) can be estimated from the calculated G2 heat of atomization reaction,



in conjunction with accurate literature  $\Delta H_f^\circ$  values for atomic C, N, and H.<sup>17</sup> This approach is shown to be capable of reproducing experimental values to within 10 kJ mol<sup>-1</sup>.<sup>15e</sup> The predicted  $\Delta H_f^\circ$  and  $\Delta H_f^\circ$  values for 1 are 376 and 370 kJ mol<sup>-1</sup>, respectively.

## Concluding Remarks

High-level ab initio calculations predict that the parent nitrilimine prefers a nonplanar, allenic geometry, rather than the previously accepted planar, propargylic structure. Correction for electron correlation is essential for a proper description of the structure of this 1,3-dipolar species. Note that recent X-ray crystallographic studies have demonstrated that nitrilimines always have a bent, nonplanar, allenic type of structure, but appropriate electron-withdrawing substituents can induce geometrical changes in the direction of propargylic structures.<sup>3,4</sup> A comprehensive theoretical investigation of the substituent effects on nitrilimine is underway.<sup>18</sup>

**Acknowledgment.** We are grateful for financial support of this research by the Australian Research Council (ARC). M. W. Wong thanks the ARC for an Australian Research Fellowship. We thank the University of Queensland, the Queensland Supercomputing Laboratories, and the Australian National University Supercomputing Facility for generous allocations of computing time.

(18) Wong, M. W.; Wentrup, C. To be published.

(15) (a) Curtiss, L. A.; Kock, D.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 4040. (b) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1991**, *95*, 10549. (c) Ma, N. L.; Smith, B. J.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1991**, *113*, 7903. (d) Curtiss, L. A.; Nobes, R. H.; Pople, J. A.; Radom, L. *J. Chem. Phys.* **1992**, *97*, 6766. (e) Wong, M. W.; Radom, L. To be published.

(16) The calculated G2 energies for nitrilimine radical cation are -148.13348 (adiabatic) and -148.12471 (vertical) hartrees, respectively.

(17) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.