

# The electronic structure of nitrilimine: absence of the carbenic form†

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Received (in Cambridge, UK) 1st December 2005, Accepted 4th January 2006

First published as an Advance Article on the web 24th January 2006

DOI: 10.1039/b517030c

The electronic structure of nitrilimine HCNNH is shown to essentially be propargylic by CASSCF and Spin-Coupled (modern VB) calculations; in contrast to a recent claim, the carbenic resonance form is absent.

Since the first report by Huisgen,<sup>1</sup> nitrilimine cycloadditions to a variety of dipolarophiles represent the choice method in the synthesis of variously substituted azoles.<sup>2</sup> A huge number of examples deal with the typical reactivity of the nitrilimine intermediate as a genuine 1,3-dipole able to provide the [3] moiety in the overall [3 + 2] process.<sup>3</sup> However, a recent application<sup>4</sup> of natural resonance theory<sup>5</sup> to HCNNH led to the statement that the singlet ground electronic state of HCNNH in its minimal-energy geometry comprises four major resonance forms with similar weights, namely the propargylic (I), allenic (II), allylic (III), and (singlet) carbenic (IV) forms (Fig. 1). Those authors claimed that the carbenic behaviour of nitrilimines is operating in the case of *N*-(2-vinylphenyl)-substituted nitrilimines, which cyclise to 1,2-benzodiazepine and/or cyclopropa[*c*]cinnolines.<sup>6</sup> However, it has been demonstrated that the mechanism of these transformations involves a 1,7-electrocyclic reaction as the key step<sup>7</sup> and “does not necessitate carbenic reactivity”.<sup>8</sup> Furthermore, scrupulous searches for azacarbene-derived products in the reaction between *C*-methoxycarbonyl-*N*-aryl-nitrilimines and allylic<sup>9</sup> or homo-allylic<sup>10</sup> alcohols did not give any positive result, since only the usual pyrazoles due to the [3 + 2] cycloaddition were found in the

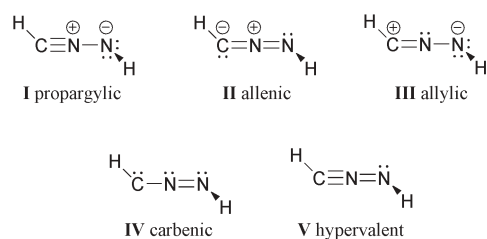


Fig. 1 Resonance forms for nitrilimine in its minimum-energy structure.

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† Electronic supplementary information (ESI) available: Pictures of the starting and converged spin-coupled orbitals; overlap and spin-coupling matrices, Chirgwin–Coulson and Kotani occupation numbers of spin-coupled calculations. See DOI: 10.1039/b517030c

reaction mixtures together with trivial side-products. From the experimental point of view, it seems that there is no evidence for the carbenic behaviour of nitrilimines. Given that the claim that nitrilimine has a large carbenic character<sup>4</sup> is in contrast with a large body of organic synthesis literature and with previous valence bond (VB)<sup>11</sup> and molecular orbital (MO)<sup>12,13</sup> computational results, we were prompted to investigate the electronic structure of HCNNH by means of Complete Active Space Self-Consistent Field (CASSCF) and Spin-Coupled (SC) calculations.

The geometry of singlet ground-state HCNNH was optimised at the CASSCF(8,6)/cc-pVTZ level and characterised by harmonic analysis. All  $\pi$ -bonding and non-bonding electrons are active so that we are confident that the wavefunction has proper variational freedom. SC(8)/cc-pVTZ//CASSCF(8,6)/cc-pVTZ calculations have been carried out with 8 active electrons as for CASSCF calculations, *i.e.* core and  $\sigma$ -bond electrons are frozen, using Hartree–Fock MOs and the full singlet spin space (14 configurations). In order to make a proper comparison with the SC(8) energy, a CASSCF(8,8) calculation was also performed keeping fixed the inactive (doubly occupied) orbitals, imported from restricted Hartree–Fock (RHF) calculations. We also considered four idealised molecular structures, which were optimised at the CASSCF(8,6)/cc-pVTZ level under the following constraints: collinear HCN moiety (A); collinear CNN moiety and HCN–NNH dihedral angle = 90° (B); collinear HCN moiety and CNN angle = 120° (C); NNH and CNN angles = 120° (D) (Fig. 2). CASSCF calculations have been performed by Gaussian98<sup>14</sup> and GAMESS<sup>15</sup> packages. SC calculations were performed using a locally written program.<sup>16</sup> The main computational results are collected in Tables 1 and 2.

The minimum-energy structure of HCNNH at the CASSCF(8,6)/cc-pVTZ level turned out to be very similar to previous computational results.<sup>13</sup> The CNN moiety is slightly bent (167.6°) and thus defines a plane which approximately bisects the HCN–NNH dihedral = –94.3°. The HCN and NNH angles are 130.1° and 110.1°, respectively. This geometry is close to that expected for an allenic type molecule. In the CASSCF

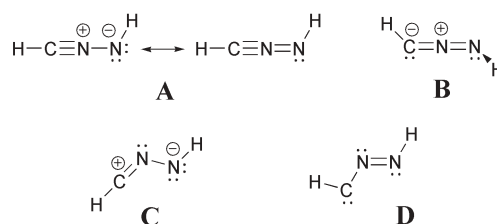


Fig. 2 Limit structures of nitrilimine with the corresponding favoured resonance forms.

**Table 1** Energies (in atomic units) of HCNNH at the CASSCF(8,6) optimised geometry. All calculations use the cc-pVTZ basis set

Method	$E$	$10^3(E - E_{\text{RHF}})$
RHF	-147.8491	—
CASSCF(8,6)	-147.9430	-93.9
CASSCF(8,8) <sup>a</sup>	-147.9579	-108.8
SC(8)	-147.9332	-84.1

<sup>a</sup> The inactive orbitals are frozen HF MOs.

wavefunction the configuration with double occupancy of the four lowest MOs has a coefficient of 0.945 in the active space CI expansion, whereas the excited configurations have coefficients lower than 0.13 (absolute values). The populations of the first four active MOs are all larger than 1.9. As such, it appears that a multi-determinant wavefunction is not essential to describe HCNNH, although the mixing in of excited configurations does of course lead to energy lowering ( $E_{\text{CASSCF}(8,6)} - E_{\text{RHF}} = -94$  millihartree,  $E_{\text{CASSCF}(8,8)} - E_{\text{RHF}} = -133$  millihartree). Since CASSCF spatial orbitals are not uniquely defined, we turned our attention to the single-configuration SC method which provides a sound basis to discuss the relative importance of the resonance forms because of the explicit spin-pairing schemes and the uniqueness of its spatial orbitals.

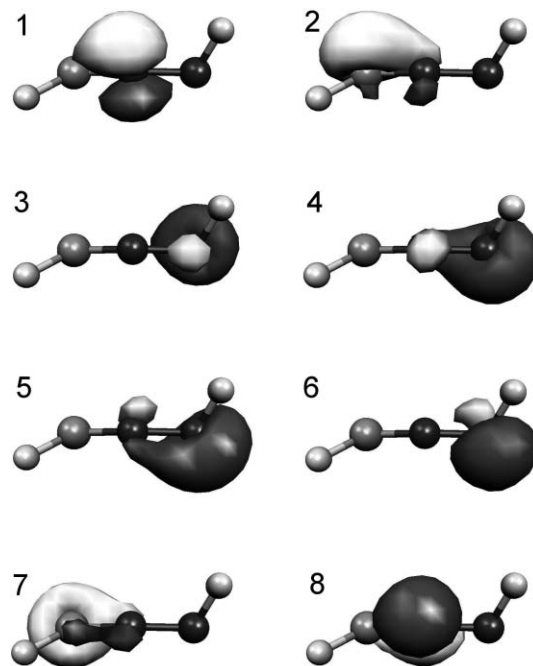
The SC wavefunction of singlet HCNNH at the CASSCF(8,6) optimised geometry, using localised HF orbitals as the basis set (see Supplementary Material†), recovers 77% of the correlation energy recovered by the corresponding CASSCF(8,8) calculation. The unique SC orbitals are depicted in Fig. 3. All of the orbitals essentially have atomic character, though some of them feature a distortion already observed for other 1,3-dipoles.<sup>17</sup> There are 2, 2 and 4 occupied orbitals on the carbon, central nitrogen and terminal nitrogen atoms, respectively. Since in the SC wavefunction each orbital accommodates a single electron, an electron has been transferred from the central to the terminal nitrogen atom, consistent with a propargylic electronic structure. However, the chemical interpretation of the SC wavefunction comes from the following analysis of the electron spin coupling scheme.

As might be anticipated from the corresponding CASSCF description, there is a dominant spin configuration which accounts for most of the SC(8) wavefunction (Kotani population: 92%). In this leading configuration the electron coupling scheme is 1–2, 3–4, 5–6, 7–8. Referring to Fig. 3, one can easily see that there are two  $\pi$  C–N bonds (1–2 and 7–8) and two lone pairs on the terminal N atom (3–4 and 5–6). Therefore, the electronic structure of singlet HCNNH in its minimum energy geometry is essentially propargylic, featuring a C=N triple bond and two lone pairs on the terminal nitrogen atom. Orbital distortion suggests that the allenic and the hypervalent forms might contribute to the

electronic structure. More importantly, these results show that singlet HCNNH has little, if any, carbenic or allylic character. Indeed, the two orbitals on the central nitrogen (1 and 8) have high overlap, even larger than the 1–2 overlap, but the associated electrons do not couple to each other, the expectation value of the squared sum of the spins of electrons 1 and 8 being 1.38, very close to the value of 3/2 that is the characteristic of totally uncoupled spins. Hence, a lone pair on the central nitrogen, a distinguishing feature of resonance forms **III** and **IV**, is not present in HCNNH. Moreover, the fact that the C–N bond is at least a full double bond, speaks against form **IV**.

SC(8) calculations were also attempted using a frozen-core taken from the CASSCF(8,6) description, but the orbital overlap matrix became nearly-singular and so the calculations did not properly converge. However, it turns out that the calculations do converge normally if a single constraint is applied to the degree of mixing between two of the SC active orbitals. The resulting description is qualitatively very similar to the one we have described here, albeit with a modest further lowering of the total energy (see Supplementary Material†).

Even if the SC results and their interpretation is rather clear cut, we were puzzled by the apparent contradiction between the propargylic electronic structure and the allenic geometrical



**Fig. 3** Spin-coupled orbitals from frozen-core calculations based on Hartree-Fock MOs

**Table 2** RHF and CASSCF(8,6) energies (in atomic units) of the minimum-energy and idealized structures optimised at the CASSCF(8,6) level. All calculations use the cc-pVTZ basis set

Structure	$E_{\text{RHF}}$	$E_{\text{RHF}}(\mathbf{X}) - E_{\text{RHF}}(\text{min})^a$	$E_{\text{CASSCF}}$	$E_{\text{CASSCF}}(\mathbf{X}) - E_{\text{CASSCF}}(\text{min})^a$
Minimum -energy	-147.8491	—	-147.9430	—
<b>A</b>	-147.8469	6	-147.9347	22...
<b>B</b>	-147.8480	3	-147.9400	8
<b>C</b>	-147.7840	171	-147.8711	189
<b>D</b>	-147.7634	225	-147.8703	191

<sup>a</sup> Energy difference ( $\text{kJ mol}^{-1}$ ) between the minimum energy and the limit structures ( $\mathbf{X} = \mathbf{A}, \mathbf{B}, \mathbf{C}, \mathbf{D}$ ).

structure. In order to obtain further insight and to strengthen our conclusions, CASSCF calculations have been carried out for the idealised structures **A–D** (see Table 2). The molecular geometries imposed on **A–D** could enforce orbital hybridisations of the heavy atoms favouring one resonance form in each idealised structure, as can be seen by comparing Fig. 1 with Fig. 2. Unexpectedly, the results are rather insensitive to the investigated geometrical structures. The energy differences between the minimum-energy and these idealised structures are reported in Table 2. Structure **B** is only slightly destabilised with respect to the minimum. Such a difference is comparable to the thermal energy at room temperature ( $\sim 2.5 \text{ kJ mol}^{-1}$ ). A little higher in energy lies structure **A**, the ideal propargylic geometry. It seems that HCNNH is thus a flexible molecule, its electronic structure essentially consisting of a  $\text{C}\equiv\text{N}$  triple bond and two lone pairs on the terminal nitrogen, irrespective of moderate deformations from the idealised molecular geometry.

In conclusion, consideration of molecular structure and energetics and of wavefunction composition from CASSCF and SC calculations provides compelling evidence that HCNNH has predominantly a propargylic electronic structure with four  $\pi$ -bonding and four non-bonding electrons; minor contributions may come from the hypervalent and allenic forms. All of the evidence is against significant contribution from the allylic and carbenic resonance forms with two  $\pi$ -bonding and six non-bonding electrons. These conclusions are consistent with the main body of knowledge about 1,3-dipolar cycloadditions to nitrilimines.

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