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The electronic structure of nitrilimines revisited†

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A combination of density-functional theory and natural resonance theory has been used to show that a complete description of the electronic structure of nitrilimines, R^1CNNR^2, requires four resonance structures (propargylic, allenic, 1,3-dipolar and carbenic); appropriate substituents were shown to enhance the carbene character of nitrilimines to the point where they may be considered stable carbenes.

Nitrilium betaines have been recognized early on to possess some carbene character.[1] Such a concept was later strengthened by the observed competition between 1,1- and 1,3-intramolecular cycloadditions in nitrilimines and nitrile ylides.[2] Further evidence for carbenic behaviour stems from the tendency of nitrilimine to dimerize, forming bis-diazoethylenes (**A** and **B**, Fig. 1) as well as head-to-tail dimers (**D**, Fig. 1) in the absence of other reaction partners.[3] According to Huisgen's original description, based on reactivity, nitrilimines are a combination of 1,3-dipolar **III** and carbenic **IV** resonance structures (Fig. 2).[1,4] However, nitrilimines and other nitrilium betaines are currently described as propargylic **I**/allenic **II** (Fig. 2).[3,5] In order to gain more insight into the electronic structure of nitrilimines we have revisited this issue using a combination of density-functional theory and natural resonance theory (NRT).[6]

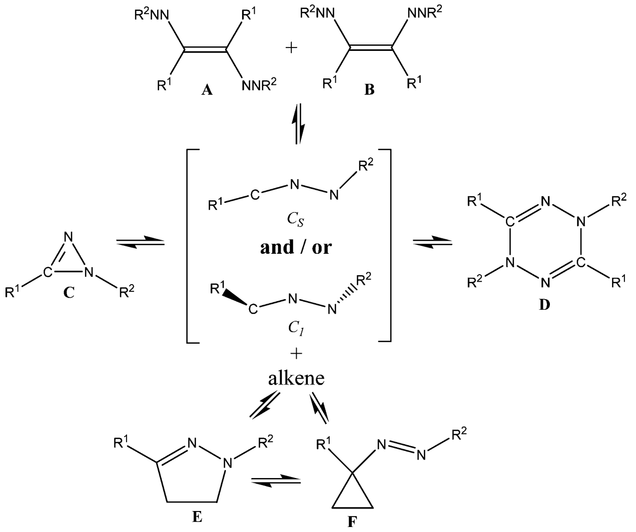

Fig. 1 Possible reactions of nitrilimines (some molecular structures given with connectivity only).

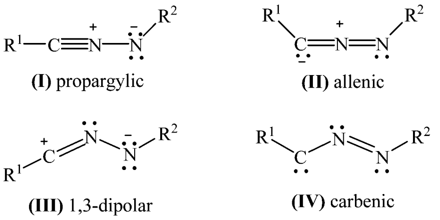
(**I**) propargylic
(**II**) allenic
(**III**) 1,3-dipolar
(**IV**) carbenic

Fig. 2 Major resonance structures of nitrilimines.

The electronic structure of nitrilimines with various substituents (H, BH_2, CH_3, NH_2, OH, F) was calculated with the Perdew–Burke–Ernzerhof (PBE0) functional[7] and the 6–311++G(2df,pd) basis set, as implemented in GAUSSIAN98 (version A.11.4).[8] Three structures were considered: the planar C_s and non-planar C_1 structures to determine the effects of substitution on the "floppiness" of nitrilimine, and the cyclic species (**C**, Fig. 1) since an equilibrium may exist between a carbene and a cyclopropene.[9] The NRT analysis indicates that four main structures (**I**, **II**, **III** and **IV**, Fig. 2) account for 80 to 90% of the electronic structure of all nitrilimines studied, while minor contributors (less than 1% each) account for the remaining 10–20%. The NRT results are given in Table 1 along with relative energies, selected bond angles and absolute chemical shieldings.

For all nitrilimines except **1**, the non-planar C_1 structure is a minimum and the planar C_s structure corresponds to a transition state (TS), whereas the C_s structure is a minimum for **1**. These findings are in qualitative agreement with past studies on **1** and **2**.[3] Previously, the C_s structure was described as propargylic **I** and the C_1 structure as allenic **II**, based on the geometry of the R^1CN moiety. In fact, both **I** and **III** possess a linear R^1CN moiety, while that of **II** and **IV** is bent. Similarly, **I** and **II** describe a linear and **III** and **IV** a bent CNN unit. The sole consideration of the R^1CN and CNN angles in **2** (133 and 170°, respectively) implies that all four resonance structures are required for a proper description of its geometry. Therefore, all four resonance forms are necessary for describing the electronic structure of nitrilimines. This is especially true for **2** where all four resonance forms contribute with nearly equal weights (*cf.* Table 1).

Aside from geometrical considerations, the interplay of the resonance structures also accounts for the observed stabilities of the stationary points. The C_s stationary points are primarily described by resonance structures **I** and **III** while the C_1 species mainly consist of **II** and **IV**. As a matter of fact, variations in the sums of the **I**+**III** and **II**+**IV** contributions correlate with relative stabilities. For example, **1** has a C_s minimum and a total **I**+**III** contribution of 75% while the **I**+**III** contribution for **2** approximately equals that of **II**+**IV**, resulting in two stationary points that are nearly isoenergetic. This trend is seen in all nitrilimines investigated. However, the total **I**+**III** contribution for **5** is 5% smaller than for **4**, but the C_s transition state is much higher in energy with respect to the C_1 minimum than for **4**. This inconsistency may be correlated to singlet–triplet energy gaps.[10]

The most fascinating finding in this work is the dramatic increase in % carbene character, **IV**, going from **1** to **5**, which is accompanied by a reduction in the contributions of all other resonance structures. Note that the allenic resonance structure **II** only has a small consistent contribution to the electronic structure, despite it being considered as one of the major nitrilimine descriptors.[3,5] The carbon lone pair character is obvious in the highest occupied molecular orbital (HOMO) of **2**–**5** (*cf.* Table 1) and is consistent with the observed carbene character. Caramella and Houk stated early on that nitrile ylide orbitals "have an uncanny

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† Electronic supplementary information (ESI) available: Optimized structures and absolute energies of all stationary points. See http://www.rsc.org/suppdata/cc/b4/b407302a/

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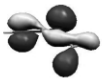
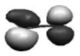
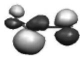
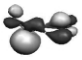
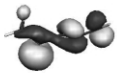
Table 1 Relative energies, selected bond angles, % resonance structure contribution, carbon absolute chemical shielding, and HOMO for nitrilimines **1**–**5**[a]

	H–CNN–BH_2 **1**	H–CNN–H **2**	F–CNN–H **3**	F–CNN–F **4**	H_2N–CNN–NH_2 **5**
Δ*E*					
C_1	6[b]	0	0	0	0
C_s	0	1.7 (TS)	14.5 (TS)	25 (TS)	12 (TS)
C	15	11	−7	50	56
θ_{R^1CN}	177	133	123	117	117
θ_{CNN}	174	170	163	159	132
% Contribution[c]					
I	30 (24)	22 (20)	13 (11)	8 (7)	4 (3)
II	16 (14)	18 (16)	20 (18)	18 (15)	10 (9)
III	45 (36)	33 (29)	24 (22)	17 (14)	16 (15)
IV	9 (7)	27 (23)	43 (39)	57 (47)	70 (62)
σ_{iso}	124	122	76	−11	−53
HOMO					

[a] Zero-point-energy corrected relative energies (Δ*E*) in kcal mol^{-1}, bond angles *θ* in degrees, absolute chemical shieldings σ_{iso} in ppm. [b] Not a stationary point. [c] Normalized values (absolute values in parenthesis).

resemblance to the HOMO… of singlet carbene”.[11] Yet, the idea that substituted nitrilimines could be carbenes has since been ignored, despite the fact that the synthesis of stable carbenes has taken this class of compounds from transient intermediates to viable synthetic targets.[12]

The increase in carbene character is accompanied by a decrease in the R^1CN bond angle (*cf.* Table 1), resulting in values for **4** and **5** that are typical of singlet carbenes. This increase is also mirrored by the stability of the cyclic structure (**C**, Fig. 1), such that for **3** the cyclic minimum is more stable than the C_1 minimum, in line with the proposed equilibrium between a carbene and its cyclopropene analog.[9] Nitrilimines **4** and **5**, however, do not follow this trend, with the cyclic minimum **C** being less stable by over 50 kcal mol^{-1}. Carbon absolute chemical shieldings, σ_{iso}, which have been shown to provide information on the nature of carbenes,[12] actually bring further support for the stability of **4** and **5**. Carbenes in general possess negative absolute chemical shielding values, as do **4** and **5**, consistent with the observed bond angles at carbon typical of carbenes. In fact, the value of −53 ppm for **5** (*cf.* Table 1) compares with that for stable carbenes such as the diamino prototype $C(NH_2)_2$, which has a value of −62 ppm.[13] This suggests that the destabilization of **C** for **4** and **5** corresponds to an increase in carbene stability.

In conclusion, we have reported a preliminary characterization of the electronic structure of nitrilimines with a combination of density-functional theory and natural resonance theory. Our results unambiguously show that a complete description of the electronic structure of nitrilimines requires all four resonance structures (propargylic, allenic, 1,3-dipolar and carbenic), and not just two as previously postulated.[1,3] Furthermore, appropriate substituents enhance the carbene character of nitrilimine to the point where it may be considered a stable carbene. Not only do these findings imply that it may be possible to use nitrilimines as a template for generating new stable carbene species, but they shed new light on the reactivity of nitrilimines,[14,15] which may be much more varied and complex than previously thought.

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