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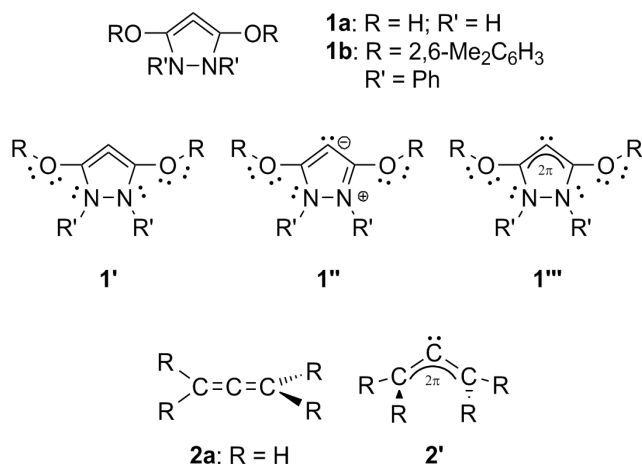
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# Do extremely bent allenes exist?

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*Dedicated to Professor Ronald J. Gillespie on the occasion of his 85<sup>th</sup> birthday.*

In a recently published Communication, Bertrand *et al.* reported the synthesis and ligand properties of a stable five-membered ring allene **1b** containing only first-row main group atoms.<sup>[1]</sup> A correspondence was published soon after by Christl and Engels, who, based on theoretical data for related six-membered cyclic allenes, argued that the compound in question should not be represented as an allene **1'** but rather as a zwitterion **1''**.<sup>[2a]</sup> Bertrand *et al.* issued a response to the critique, defending their point of view with selected experimental and theoretical evidence as well as invoking author's right to name a compound.<sup>[2b]</sup> In the current contribution, we present detailed quantum chemical analyses performed for a set of related molecules, as well as for the model system **1a**, which show how the controversy can be resolved in favor of both parties. In addition, the chemistry of *N*-heterocyclic carbenes (NHCs) is discussed through the prism of the reported findings.



The equilibrium geometry of the parent allene **2a** is linear with orthogonal arrangement of hydrogen atoms ( $D_{2d}$ ).<sup>[3]</sup> It is well known that artificial bending of the molecular framework brings the point group down to  $C_2$  and lifts the degeneracy of the frontier orbitals.<sup>[4]</sup> The HOMO retains its  $\pi$ -type shape with respect to the plane formed by the C–C–C backbone but an increasing amount of s-character is introduced to HOMO–1 as the bond angle becomes more acute. When extremely bent, the HOMO–1 becomes a lone pair orbital localized at the central carbon atom (Figure 1) in agreement with simple hybridization (valence bond) theory based arguments. Hence, bent acyclic singlet allenes eventually adopt an electronic structure which is most conveniently represented using the extended Lewis formula **2'** *i.e.* one  $\sigma$ -symmetric lone pair and two delocalized  $\pi$ -electrons.<sup>[5]</sup> This transformation is illustrated perhaps the best by visualizing the electron localization function (ELF)<sup>[6]</sup> calculated for **2a** at different bond angles (Figure 1), which reveals a monosynaptic, lone pair, valence basin  $V(\text{C}_2)$  at angles below  $120^\circ$ .<sup>[7]</sup> The above conclusion is further supported by atoms in molecules (AIM) analysis<sup>[8]</sup> as well as calculated atomic charges, which reveal an electroneutral central carbon atom with one (3, –3) critical point indicative of a single non-bonded pair of electrons.

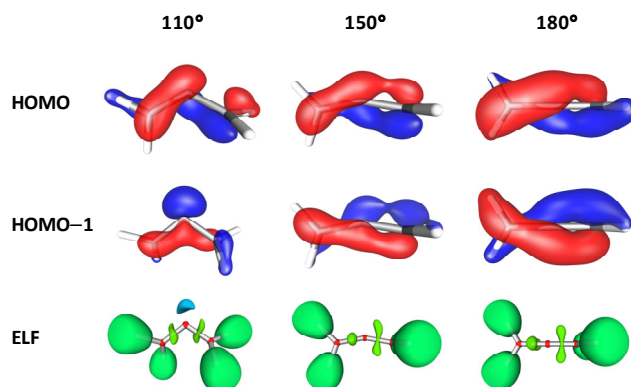


Figure 1. Frontier molecular orbitals and electron localization function of **2a** at different bond angles.

The change in the electronic structure of allenes upon bending should by no means be limited to acyclic species. In cyclic systems the allene framework is naturally enforced to deform as the size of the ring becomes smaller.<sup>[4]</sup> The calculated  $\text{C}_1\text{--C}_2\text{--C}_3$

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bond angle for 1,2-cycloheptene **3** and -hexene **4** is 149° and 133°, respectively. The electronic structures of these ring systems are clearly of allene-type as neither MO nor ELF/AIM analysis shows any indication of a distinct  $\sigma$ -lone pair at the central carbon atom (Figure 2). For 1,2-cyclopentadiene **5**, the bond angle drops down to 109°. Consequently, the molecule adopts an electronic structure akin to **2'** and it cannot be considered a classical allene as has been suggested before.<sup>[2,4,9]</sup> However, it turns out that **5** has sufficient singlet diradical character that it cannot be described with only one closed-shell Kohn-Sham determinant.<sup>[4b,9]</sup> Broken-symmetry density functional theory (DFT) and complete active space (CAS) calculations show that the diradical character in **5** leads to transfer of electron density from HOMO-1 and HOMO to LUMO.<sup>[10]</sup> This is also borne out by ELF analysis (Figure 2c) which shows that the  $V(C_2)$  lone pair basin population diminishes roughly by half of an electron when the diradical character is appropriately treated in calculations. Nevertheless, the electronic structure of **5** can still be represented most conveniently using the extended Lewis formula **5'**.

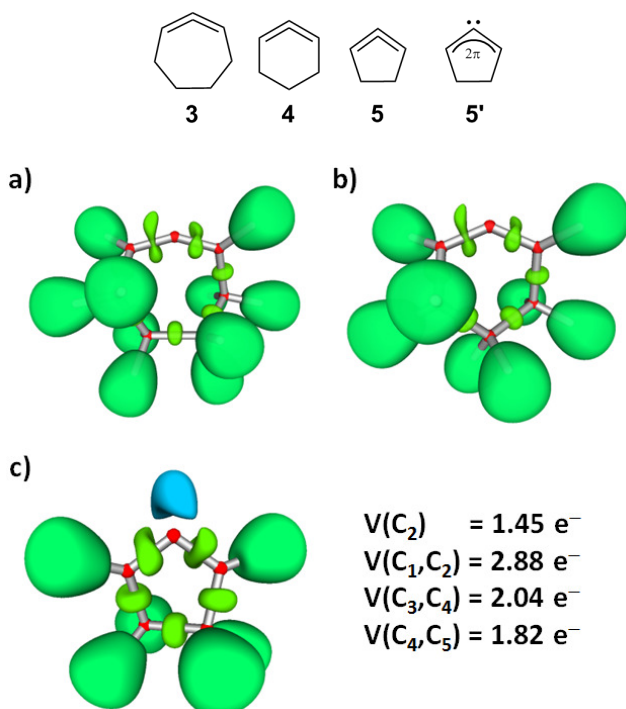


Figure 2. Electron localization functions of **3** (a), **4** (b) and **5** (c). Basin populations are given for **5**.

An in-depth analysis conducted for **1a** reveals that its electronic structure also contains a localized lone-pair of electrons at the middle carbon atom (Figure 3). We note that the optimized geometrical parameters of **1a** are very close to that determined experimentally for **1b** and the use of a model structure incurred only a slight pyramidalization of the nitrogen centers. The HOMO and HOMO-1 orbitals are clearly of  $\sigma$ - and  $\pi$ -type, respectively. In addition, the Kohn-Sham determinant is free of any instability, indicating that **1** has no important singlet diradical character. This is due to the fact that bonding and anti-bonding  $\pi$ -orbitals are well separated in energy: the HOMO→LUMO gap is significantly higher in **1a** (5.0 eV) than in **5** (2.8 eV) and it can be understood why **1b** is an isolable system, whereas **5** is an extremely reactive chemical species. The occupied orbitals in **1a** indicate some  $\pi$ -

type bonding character within C–C, C–N and C–O linkages, in agreement with the determined bond lengths, but the non-planar nature of the molecule prevents true cyclic electron delocalization. The calculated nucleus independent chemical shift<sup>[11]</sup> NICS(1)<sub>zz</sub> index for **1a** is –15 ppm. In comparison, the NICS(1)<sub>zz</sub> index of cyclopentadiene, a true 6 $\pi$ -electron aromatic, is –34 ppm. We note that if the –OH groups in **1a** are replaced by hydrogen atoms, the HOMO→LUMO gap decreases to 3.9 eV and the molecule adopts a near-planar geometry. The NICS(1)<sub>zz</sub> index calculated for such species is –32 ppm, indicating a significant change in the electronic structure towards aromaticity. These results confirm that exocyclic substituents play a more important role to the stability of **1** than cyclic electron delocalization.

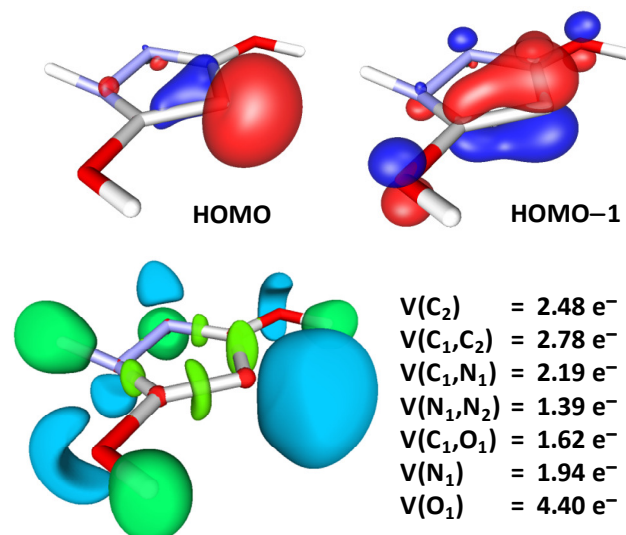
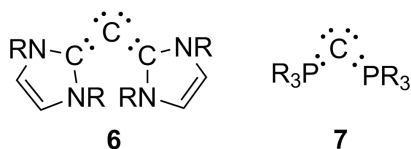


Figure 3. Frontier molecular orbitals (top) and electron localization function (bottom) of **1a**.

The IUPAC Gold Book<sup>[12]</sup> defines allenes as “hydrocarbons (and by extension, derivatives formed by substitution) having two double bonds from one carbon atom to two others,  $R_2C=C=CR_2$ ”. In light of results presented herein, an extremely bent allene appears to be an oxymoron. On the other hand, NHCs are widely accepted as carbenes even though their electronic structure differs from the IUPAC definition.<sup>[12]</sup> In addition, as far as the general electronic structure is concerned, **1b** is as close to an extremely bent allene **5** as can possibly be. Thus, considering **1b** formally as an allene is convenient since it is derived from allenes. However, representing its electronic structure with either **1'** or **1''** is misleading as they both point to inaccurate ground state configuration. Based on the theoretical analyses presented herein, a more appropriate representation of the electronic structure of **1b** is given by the extended Lewis formula **1'''**, analogous to **2'** and **5'**. This is also the best single Lewis-type structure assigned to **1a** by natural bond orbital (NBO) analysis.<sup>[13]</sup> Alternatively, **1'''** can be decomposed to two localized, zwitterionic, Lewis structures. However, the main contribution comes from  $C^+-C=C \leftrightarrow C=C-C^+$  resonance as evidenced by both calculated atomic charges and NBO analyses using Lewis-structures restricted to 2-center-2-electron bonds. Nevertheless, it should be remembered that **1'''** only represents the leading contribution in the wave function and a more accurate representation of reality requires the structure to be drawn as a resonance hybrid.<sup>[14]</sup>

In light of the true electronic structure of **1b**, its chemical properties appear anything but peculiar.<sup>[1]</sup> In particular, it can be

readily explained why it coordinates to metal centers using  $\eta^1$  mode instead of  $\eta^2$  typically observed for allenes.<sup>[3]</sup> In many respects **1b** resembles NHCs,<sup>[15]</sup> for which zwitterionic Lewis structures can also be drawn, and can therefore be considered a carbenoid *i.e.* a complexed carbene-like entity that displays the reactivity characteristics of carbenes.<sup>[12]</sup> However, the shape of the HOMO-1 orbital implies that  $\pi$ -electrons might be more readily accessible for bond formation in **1b** than in NHCs. Hence, as has been suggested before,<sup>[1,2b]</sup> **1b** could display hidden divalent carbon(0) character akin to carbodicarbenes **6**.<sup>[16–18]</sup>



Carbodicarbenes can formally be considered bent allenes but detailed AIM<sup>[16b]</sup> and molecular electrostatic potential (MESP)<sup>[19]</sup> analyses have revealed one (3, –3) critical point indicative of (at least) one non-bonded pair of electrons located at the central carbon atom.<sup>[20]</sup> However, strong Lewis acids can bring to fore their divalent carbon(0) nature.<sup>[16,18]</sup> The chemical behavior of carbodicarbenes can be rationalized by the shape of their  $\sigma$ - and  $\pi$ -type frontier MOs which are localized on the central carbon atom.<sup>[16]</sup> Accordingly, push-push substitution in **6** induces a flow of electrons to the central carbon atom in an analogous manner to what artificial bending does for **2a**.<sup>[22]</sup> Consequently, the electronic structure of carbodicarbenes resides in between that of tetravalent carbon(0) and divalent carbon(0), though much closer to the latter, and only a modest energetic perturbation is required to transform their bonding characteristics.<sup>[16,18]</sup> These results can be contrasted to data reported for carbodiphosphoranes **7** which, even as isolated molecules, appear as true divalent carbon(0) compounds.<sup>[19,23,24]</sup>

A comparison of **1a** to data reported for imidazol-2-ylidene<sup>[16,25]</sup> and carbodicarbenes<sup>[16]</sup> reveals that, as an isolated entity, its electronic structure has more in common with the former. Hence, it can be expected that systems **1** function as two electron donors unless extremely strong electrophiles are used. In good agreement, theoretical calculations demonstrate that the first and second proton affinities of **1a** are 1200 and 370 kJ mol<sup>–1</sup>, respectively (*cf.* 1180 and 634 kJ mol<sup>–1</sup> for *N*-Me substituted carbodicarbene and 1064 and 200 kJ mol<sup>–1</sup> for parent NHC).<sup>[16b]</sup> Consequently, coordination of two BH<sub>3</sub> ligands to **1a** does not give a chemically stable species but leads to a transition state with respect to ligand exchange. However, the aluminum analogue **1a**·(AlH<sub>3</sub>)<sub>2</sub> is a stable minimum with a calculated dissociation energy of approximately 50 kJ mol<sup>–1</sup> with respect to **1a**·AlH<sub>3</sub> and AlH<sub>3</sub>. We note that real-life synthetic attempts towards **1b**·(AlH<sub>3</sub>)<sub>2</sub>, or any related systems, might be thwarted by *e.g.* the steric bulk of the substituents attached to oxygen atoms.

In summary, the results reported herein unambiguously demonstrate that extremely bent allenes, be they cyclic or acyclic, only bear a formal relationship with classical allenes. In particular, the five-membered ring systems **1** and **5** both possess a lone pair of electrons at the C<sub>2</sub> carbon. It has been demonstrated that **1b** acts as a strong  $\sigma$ -donor and thus shares many of the properties associated with carbenes. Hence, it is best described as a carbenoid. Depending on the emphasis, its electronic structure can be represented using either localized (zwitterionic) or delocalized (carbene-like) Lewis structures. Thus, **1b** bridges the gap between classical allenes and carbodicarbenes. When combined with

extremely electrophilic metal fragments, the  $\pi$ -electrons in **1b** can, at least in principle, be used for bonding and the ligand acts as a four electron donor. By analogy, it seems reasonable that, via appropriate modification of the electronic structure, one could design NHCs that could be classified as carbenes as isolated species, but would nevertheless display bonding to electrophilic metals using four electrons. Similar behavior has already been demonstrated for the heavier group 14 analogues of NHCs which contain a bipyridyl backbone.<sup>[25,26]</sup> Surprisingly, theoretical calculations show that AlH<sub>3</sub> forms a marginally stable (15 kJ mol<sup>–1</sup>) 2:1 complex even with the parent imidazol-2-ylidene. Such systems are currently under active computational investigation by our group.

## Experimental Section

The theoretical calculations were performed with Turbomole 5.10<sup>[27]</sup> and Gaussian 03 program packages.<sup>[28]</sup> The geometries were optimized using density functional theory. A combination of B3LYP hybrid functional<sup>[29]</sup> and Ahlrich's def2-TZVP basis sets<sup>[30]</sup> was employed. The nature of all stationary points found was assessed by performing frequency analyses. Complete active space calculations for **5** used the DFT optimized geometry and an active space in which four highest electrons and orbitals were correlated *i.e.* CAS(4,4). NICS values were determined at 1 Å above the molecular plane and only the component of the magnetic shielding tensor perpendicular to the plane (*zz*) was used in the analysis. ELF, AIM and NBO analyses were performed with programs TopMod,<sup>[31]</sup> Bubble<sup>[32]</sup> and NBO 5.0,<sup>[33]</sup> respectively, whereas program gOpenMol was used for all visualizations.<sup>[34]</sup>

## Acknowledgements

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