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Are Allenes with Zwitterionic Character Still Allenes? Of Course!**

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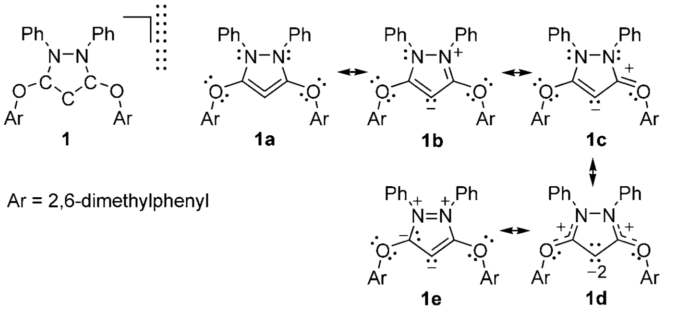
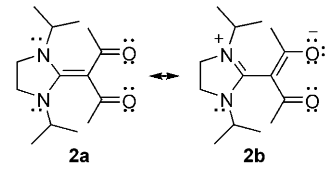
cyclic allenes · donor ligands · heterocycles · pyrazolium ions · strained molecules

In the preceding Correspondence,[1] Christl and Engels have called into question our recent report on cyclic allenes.[2] Their title "*Stable Five-Membered-Ring Allenes with Second-Row Elements Only: Not Allenes, But Zwitterions*", gives the reader the impression that we made an incorrect structural assignment. However, reading their article, one can realize that their issues with our work are only semantic in nature. Their concern is that compound **1** is incorrectly named as an allene and incorrectly represented with Lewis structure **1a**. They argue that the aromatic resonance structure **1b** represents the ground state of **1**, and therefore this compound should be given the very informative designation "*a zwitterion derived from pyrazole*". As we show below, their semantic and scientific arguments are erroneous.



Ar = 2,6-dimethylphenyl

Let's start with the issues of nomenclature and drawing. Arguably, one of the most important uses of a chemical name is to invoke an image for a given molecule. The question now arises as to whether a chemist can draw and name a compound in a way that does not necessarily reflect its ground state. The answer appears to be yes. Are not highly twisted[3] or pyramidalized[4] alkenes still alkenes, and small-ring alkynes[5] still alkynes, despite their unusual geometries and reactivities? Consider the class of push–pull substituted alkenes, such as **2a**.[6] These compounds retain the representation and classification as alkenes despite the fact that they have highly twisted geometries and zwitterionic ground-state configurations without a C–C double bond (**2b**). If this is not a matter of ignorance, then why would any chemist insist on drawing and calling these compounds alkenes rather than zwitterions—it is a simple matter of clarity, convenience, and purpose.



It is in this sense that we chose to use the rather intuitive nomenclature "allene", coupled with representation **1a** in describing compound **1**. Nowhere in our original paper did we state, or even imply, that compound **1** has a ground state similar to that of typical allenes. In fact, when contrasting the geometry of **1** with typical allenes such as 1,2-cyclopentadiene we noted that the "*peculiar features of **1** are all due to the polarization of the allenic π bonds towards the central carbon atom*", clearly implying a ground state differing from that associated with typical allenes, and we even presented the extreme resonance structure **1d**.[2] Note that in earlier work, we and Frenking reported on extremely bent acyclic allenes (also called carbodicarbenes[7]), where it is demonstrated experimentally[8] and theoretically[9] that the push–push substitution pattern induces a severe disruption of the π-system. Although these compounds are bent, the natural bond order (NBO) analysis[9b] reveals that the best Lewis representation is the one with two carbon–carbon double bonds. Therefore, despite the unusual geometry and atypical chemical properties, such as η^1 coordination to metals through the central carbon, the name allene is warranted. The same should be true for cyclic derivatives, such as **1**.

Until our communication appeared, Christl and Engels seemed to agree with our usage of nomenclature, since the

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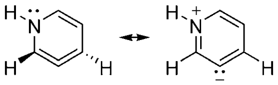
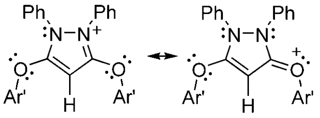
title of one of their papers[10] refers to compound **3** as "1-azacyclohexa-2,3,5-triene", implying allene **3a**, despite the fact that the ground state of this transient compound was already known to be that of 3-dehydropyridinium ylide **3b**.[11] In other work by Engels et al.,[11c] a scheme, which is entitled "Possible Electronic Structures of Cyclic Allenes", shows allene, zwitterion, and diradical forms of a compound. Thus the Christl and Engels recognized that, regardless of the various possible ground states of an allene, it is still appropriate and most convenient to classify the compound as an allene. When a new compound is discovered, are authors to omit naming and representing it for fear of misrepresenting its true ground state? Or are they to draw its skeleton only, but not account for things such as easily delocalized π electrons, as we did in representation **1**?



3a **3b**

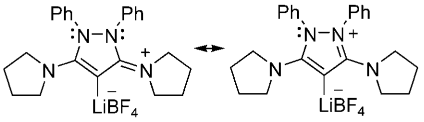
Let's now look at the scientific arguments of Christl and Engels. As scientists, we were hesitant to predict the ground-state configuration of allene **1** without the aid of further experimental or theoretical studies. In contrast, Christl and Engels readily state that the aromatic zwitterionic resonance form **1b** is the best representation for **1**. The crystallographically observed pyramidalization of the nitrogen centers (sum of angles being 347.1° and 351.0°) in **1** seems to contradict an aromatic zwitterion. This is dismissed by Christl and Engels by stating "*Because of the mutual steric hindrance of the phenyl groups, the nitrogen atoms accept a slight pyramidalization, which should hardly disturb the aromatic state*"[1] of **1b**. We carried out preliminary calculations on the parent compound **1′** (H at N and O), at the B3LYP/6-311+G(d,p) level of theory.[12] The optimized geometry matched very closely that determined crystallographically for **1**, but for this discussion, the most relevant observation is that the nitrogen atoms in **1′** are strongly pyramidalized (sum of angles being 337.5°), even in the gas phase. Moreover, we found that the structure with planar nitrogen centers is higher in energy (4.05 kcal mol^{-1}) than the structure with pyramidal nitrogen atoms and represents a second-order saddle point on the potential energy surface of **1′**. We decided to look for experimental evidence as to whether or not the steric repulsion between the phenyl rings prohibits the planarization of the nitrogen centers. The answer is no. As can be seen in Figure 1,[12] the nitrogen atoms of a related pyrazolium precursor **4**[SnCl$_3$] are in a perfectly planar environment (sum of angles being 359.9° and 360.0°).

The influence of the exocyclic π-donating substituents in **1** (see **1c**) and even **4** (see **4b**) should not be underestimated, since we observe by X-ray crystallography that in our reported lithium salt adduct **5**[2] the exocyclic amino groups are nearly planar (356.0°, 357.2°) while the endocyclic nitrogen atoms are strongly pyramidalized (337.7°, 335.9°). This result suggests that a disruption of the electron delocalization within the ring (as in **5a**), and that aromaticity (as in **5b**) is not needed to explain the stability of these compounds. As to the true nature of the ground state of **1**, for now this must be left an open question, which awaits further detailed scientific exploration. Of particular interest, one can wonder if there is any diradical contribution?



4a **4b**

Ar' = 2,6-diisopropylphenyl



5a **5b**

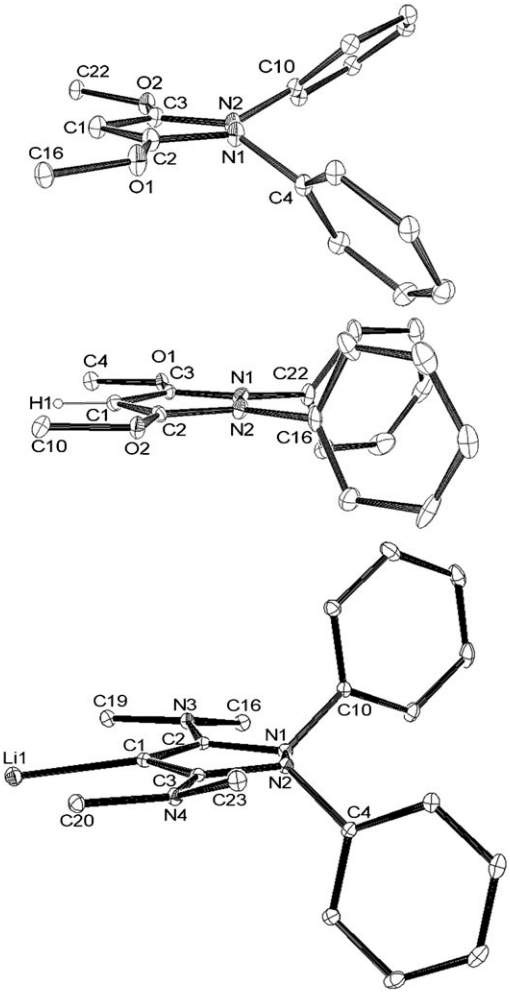


Figure 1. Perspective view of the core in **1** (top), **4**-[SnCl$_3$] (middle), and **5** (bottom) as determined by X-ray crystallography. Thermal ellipsoids are set at 10% probability.

Since undergraduate students might read the preceding Correspondence, we feel obligated to warn them of the improbability of resonance form **1e**, which appears in it. Moreover, the presumption of Christl and Engels that resonance form **1d** has a smaller weight than **1e** "*because of the presence of two negative charges at C4*" contradicts the existence of the long-known carbodiphosphoranes (R$_3$PCPR$_3$).[13]

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