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A Stable Carbene as π-Acceptor
Electrochemical Reduction to the Radical Anion

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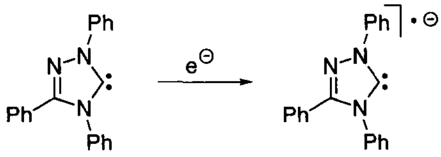
Abstract: The electrochemical reduction of the carbene **1** reversibly yielded the corresponding radical anion **2**, which was characterized by ESR measurements. *Ab initio* calculations provided a better understanding of its structure and stability. © 1997 Elsevier Science Ltd.

In the recent past, there has been a major renaissance of the chemistry of nucleophilic carbenes, which was initiated by the discovery of some stable Wanzlick-type carbenes by Arduengo.[1] Recently, a few studies concerning the oxidation of related Wanzlick-dimers (2,2'-diimidazolinylidenes) and the reduction of the corresponding diimidazolium salts were reported.[2] However, the electrochemical reduction of a stable carbene has not yet been described.

In 1995, we contributed an extraordinarily stable triazol-5-ylidene **1** to the small group of stable carbenes.[3] A number of authors theoretically investigated the underlying reasons for the stability of these Wanzlick-type systems.[4] Their obvious reluctance to dimerize prompted us to attempt the preparation of the radical anion **2** derived from the carbene **1**.



1 **2**

Therefore we carried out some cyclic voltammetry studies with the carbene **1**. After some initial sweeps, we found one reversible wave for the electrochemical reduction of the carbene in the cyclic voltammetry (CV), implying a clean one electron reduction yielding the radical anion **2** (Figure 1).

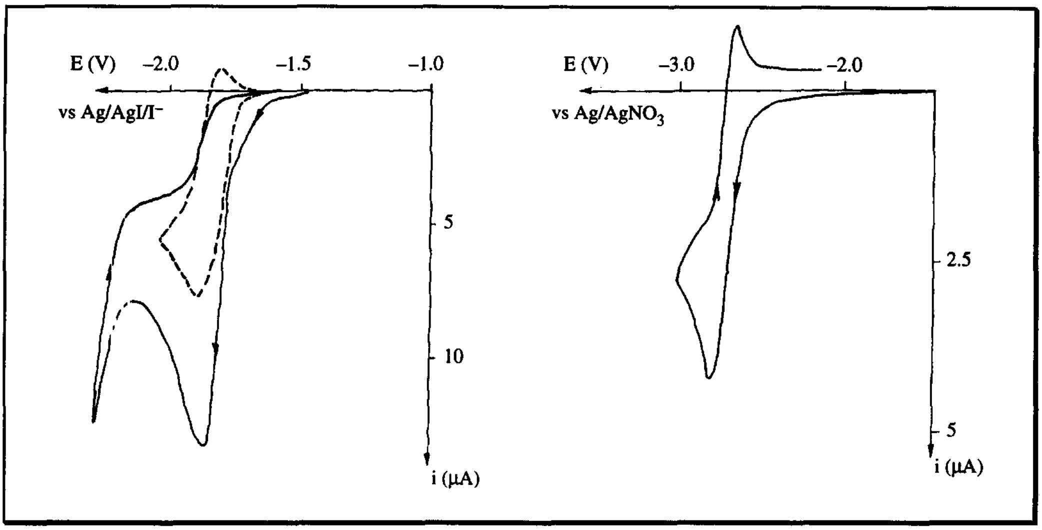


Figure 1: Cyclic voltammetries of carbene **1** at room temperature [CV on the left: concentration $2\cdot10^{-3}$ M in DMF containing $n\mathrm{Bu_4NBF_4}$ (0.1 M)] and −40°C [CV on the right: concentration $3\cdot10^{-3}$ M in acetonitrile containing $n\mathrm{Bu_4NBF_4}$ (0.1 M)]. Cathode: mercury microelectrode; sweep rate: 0.5 $\mathrm{Vs^{-1}}$. Full line: first sweep in dry DMF; broken line: CV recorded after several sweeps.[5]

In order to characterize the radical anion formed in the electrochemical reaction the solution resulting from the cyclic voltammetry was subjected to ESR measurements. The clean ESR spectrum obtained could be simulated assuming three different couplings with hydrogen atoms and one coupling with a nitrogen atom (Figure 2).

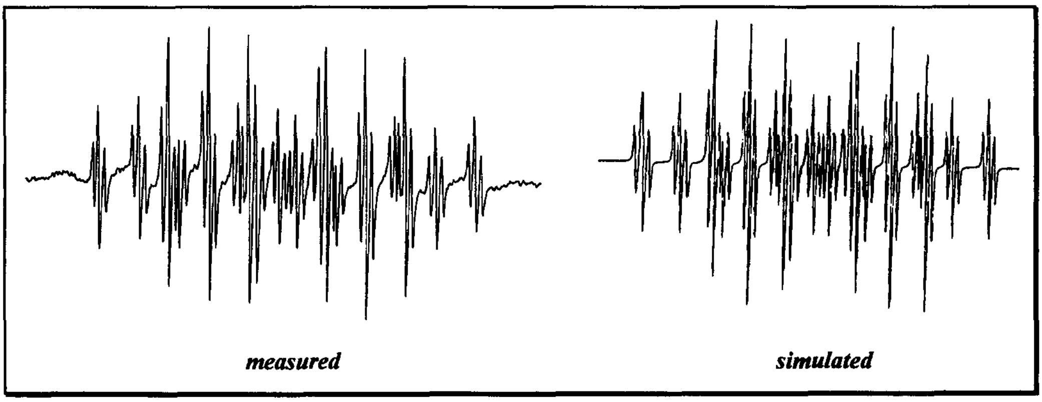


Figure 2: ESR spectrum of radical anion **2** at −50°C in DMF at a platinum grid cathode. The spectrum could be simulated using a_H = 8.10 G (1 H), a_H = 3.59 G (2 H), a_N = 2.06 G (1 N), a_H = 0.33 G (2 H) as hyperfine coupling constants.

Subsequently, we used *ab initio* and DFT calculations to gain a deeper insight into the nature of the radical anion **2**. The substituents of the heterocyclic systems were omitted due to the restrictions imposed by the level of theory and the size of the basis set. At the ROHF/6-31+G* level of theory, two stationary points could be located on the energy hypersurface for this radical anion **2'**, which both correspond to minima. One of them (ROHF/6-31+G*: $E_{tot} = -240.666904$ a. u.) preferentially bears the free electron in the area of the carbenic centre (spin density 0.98 at C1), which is also reflected by the strong elongation of the C1-N1(3) bonds compared with carbene **1'** (parent heterocyclic system of **1**).[3,4] The second structure (ROHF/6-31+G*: $E_{tot} = -240.682826$ a. u.), which proved to be by far the more stable one (henceforth named **2'**), could be considered as an aza-analogous ketyl radical, being formally derived from the imino moiety by transferring one electron into the NBO-LUMO of the C=N double bond (**2'**, figure 3). The calculated spin densities are 0.30 at N2 and 0.67 at C2, respectively. This is also illustrated by the geometrical changes in **2'** compared to carbene **1'**. Whereas the N1-C1-N3 fragment remains virtually unchanged (**1'**: C1-N1 1.331 Å, C1-N3 1.361 Å; **2'**: C1-N1 1.323 Å, C1-N3 1.354 Å), the C2-N2 bond was considerably elongated (**1'**: C2-N2 1.272 Å; **2'**: C2-N2 1.366 Å) and the hydrogen at C2 was twisted out of the heterocyclic plane (sp^3-type character at C2). Similar results were obtained at the VWN/DNP level of DFT theory. The lower stability of the structure bearing the additional electron at the carbene carbon (C1) is comprehensible, since the transfer of an additional electron into the carbenic p_z-orbital would significantly reduce the strongly stabilizing $p(\pi)$-$p(\pi)$ interaction with the adjacent nitrogen atoms.

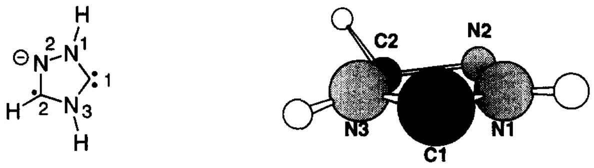


Figure 3: Numbering and geometry of the most stable minimum of the parent heterocycle **2'**.

In order to assess the influence of the adjacent phenyl group on the structure of the radical anion, especially with regard to the delocalization of the single electron, a DFT calculation at the VWN(fc)/DNP level of theory including a phenyl system at C2 was carried out. In contrast to **2'**, the structure turned out to be planar, which could be taken as evidence for the delocalization of the single electron into the phenyl ring system. This was confirmed by a Mulliken population analysis, which illustrated that a major part of the spin density was transferred into the para- and ortho-position of the phenyl ring. The spin density in meta-position was found to be very low, since resonance effects are preferentially operative in ortho- and para-position. The findings are in satisfactory agreement with the coupling constants found in the ESR simulation ($a_H = 8.10$ G, **1 H**, para; $a_H = 3.59$ G, **2 H**, ortho; $a_H = 0.33$ G, **2 H**, meta). These experimental values in combination with the simple McConnell equation indicate a delocalization of more than 50% of the spin density in the phenyl substituent. The spin density found at N2 accounts for the further coupling observed in the ESR spectrum ($a_N = 2.06$ G, **1 N**). However, since our theoretical approach does not explicitly consider π-π-spin polarization effects, merely a qualitative interpretation of these results with regard to the ESR hyperfine structure can be given.

Interestingly, the electron transfer to the carbene **1** in the CV is reversible. Apparently, the dimerization of the radical anion **2** at the surface of the electrode is thermodynamically unfavourable, leading to a prolonged lifetime of the radical anion. This is supported by *ab initio* calculations (ROHF/6-31+G*: $E_{tot(dimer)} = -481.255265$ a. u.), which gave a strongly positive reaction energy for the dimerization of the radical anion **2'** ($\Delta E_{dim} \approx +69$ kcalmol^{-1}). This value, however, is significatly reduced to +42 kcalmol^{-1} if correlation corrections (MP2) and zero point energy are included. The oxidation of the carbene formally leading to the corresponding radical cation is currently being investigated in our laboratories.

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5. At r.t. the generated radical anion reacted fast with acidic impurities (*e. g.* moisture) giving a two electron transfer process. After several sweeps, the surrounding of the working electrode was practically free of these acidic contaminants and a clean, reversible one electron step was observed.

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