The radical anion of acepentalene

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In the radical anion (1$^{\bullet-}$) of acepentalene, generated by photooxidation of the corresponding dianion (1^{2-}), the spin population appears to be evenly distributed over the nine-membered perimeter due to a rapid interconversion between two bowl-shaped C_s forms and a relatively low lying planar C_{2v} transition structure (TS).

Although the acepentalene dianion moiety **1**$^{2-}$ in the recently isolated acepentalenediide **1**–Li$_2$[1,2] is non-planar, it must be considered as aromatic undergoing a rapid bowl-to-bowl inversion, according to NMR data. While the parent compound, neutral acepentalene **1**, which thus far was experimentally characterized only by mass spectrometry, is antiaromatic, based on computed data,[3,4] the corresponding radical anion, **1**$^{\bullet-}$, should lie 'in between'. The aromatic nature of open-shell species, in general, is an experimentally unanswered question which was addressed in a computational investigation just recently.[5] In this context, we report on the generation and combined experimental as well as computational characterization of **1**$^{\bullet-}$.

The title species was generated by photooxidation of **1**$^{2-}$ to **1**$^{\bullet-}$.[6,7] Following this procedure, a 10^{-3} M solution of **1**–Li$_2$ in anhydrous THF was sealed under argon in an EPR cell and UV-irradiated *in situ* at 250 K. The resulting spectrum (Fig. 1; g = 2.0022 ± 0.0002) exhibits a septet arising from six equivalent protons spaced by $|a_H|$ = 0.215±0.005 mT. The spectrum did not markedly change in the 200–270 K temperature range. The hyperfine components were very broad, having a peak-to-peak distance of 0.1 mT. The half-life of the observed paramagnetic species was about 10 min at 250 K, as deduced from the decay of the EPR signals.

Undoubtedly, the six-proton septet originates from the radical anion **1**$^{\bullet-}$ formed by loss of an electron from **1**$^{2-}$. The equivalence of the protons and the lack of a marked temperature dependence indicate that any dynamic process must be rapid on the hyperfine time-scale (10^7 s^{-1}). In addition to the bowl-to-bowl inversion, **1**$^{\bullet-}$ should be subject to an interconversion between two Jahn–Teller structures. The large width of the hyperfine components is in line with such an effect,[8,9] although some broadening may also be caused by an unresolved hyperfine splitting from the ^{7}Li nucleus of the Li$^+$ counterions present abundantly in the solution. In contrast to the closed-shell diamagnetic dianion **1**$^{2-}$, the radical anion **1**$^{\bullet-}$ should have a degenerate singly occupied orbital (e or e'') if it pertains C_{3v} or D_{3h} symmetry. Simple Hückel molecular orbital (HMO) models for structures with these symmetries would lead to a description in which the unpaired electron density is distributed evenly over the nine-membered π-perimeter, so that the spin distribution in **1**$^{\bullet-}$ should be similar to that of the hitherto unknown nonatetraenyl radical. Each of the nine peripheral π-centers in **1**$^{\bullet-}$ is thus expected to bear 1/9th of the total spin population which, using the proportionality factor $Q = -2.2$ to -2.6 mT for cyclic radical anions, yields the coupling constant $a_H = -0.24$ to -0.29 mT. The finding that the observed value $|a_H|$ is smaller may be due to the bowl-shaped geometry of **1**$^{\bullet-}$. Deviations of the π-system from planarity are known to decrease the $|a_H|$ value of the proton attached to a π-center because they provide positive contributions to the negative coupling constant of such a proton.[10,11] On the other hand, the symmetry of **1**$^{\bullet-}$ may be lower owing to Jahn–Teller distortion, modifying the coupling constant.

To elucidate this point further, we utilized computational methods to characterize the structure of **1**$^{\bullet-}$ and to determine the barrier for ring inversion. As done before,[3] gradient-corrected density functional theory (Becke–3–Lee–Yang–Parr, B3LYP),[12–14] in conjunction with the 6-31G* basis set[15] as implemented in the GAUSSIAN 94 program suite,[16] was used for geometry optimizations (B3LYP/6-31G*); stationary points were characterized by analytical vibrational frequency computations which were also used to correct for zero-point vibrational energies (ZPVE) and thermal effects. As spin contamination (expressed in the spin operator expectation value of Slater determinants, $<S^2>$) may pose a problem for open-shell species, single-point energies on these geometries were evaluated at two higher levels of theory, namely at B3LYP/6-311+G**[17,18] and MP4SDQ/cc-pVDZ.[19]

Computations in C_{3v} or D_{3h} symmetry result in electronically unstable (symmetry breaking) or higher-order stationary structures, *i.e.* **1**$^{\bullet-}$ undergoes Jahn–Teller distortion to a lower, non-degenerate symmetry (C_s, Fig. 2). The bowl–inversion transi-

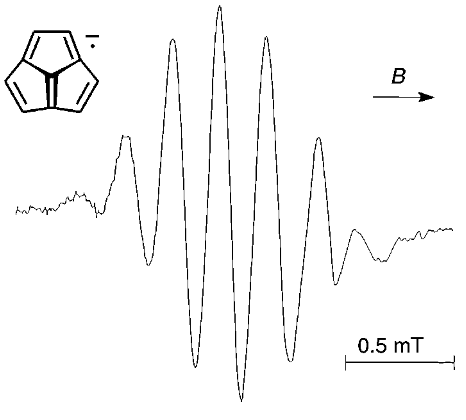

Fig. 1 EPR spectrum of the radical anion **1**$^{\bullet-}$ in THF; counterion Li$^+$, T = 250 K.

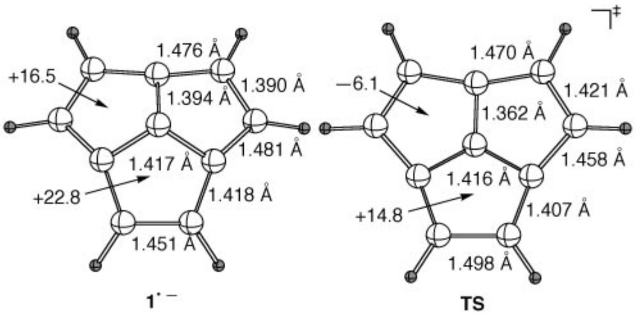

Fig. 2 B3LYP/6-31G* optimized structures of **1**$^{\bullet-}$ (C_s) and the **TS** (C_{2v}) for the bowl-to-bowl inversion. Ring centers: NICS values (see text).

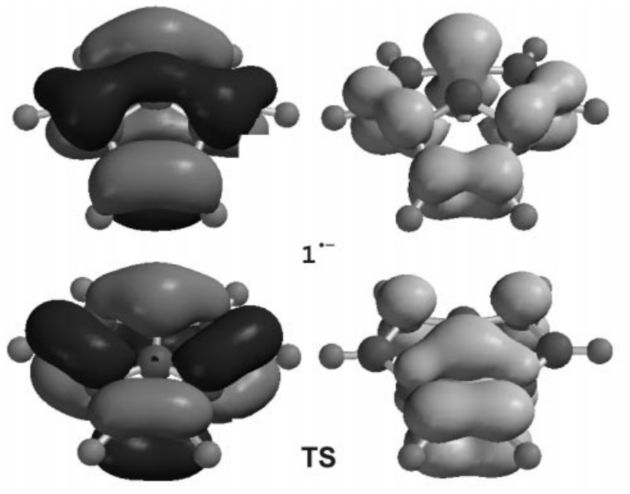

Fig. 3 SOMO (left) and spin populations (right) of the acepentalene radical anion (top) and its transition structure for bowl-to-bowl inversion (bottom).

tion structure, **TS**, is, as expected, planar (C_{2v}) and is associated with a relatively low barrier: $\Delta G^{\ddagger}_{298} = 6.9$ and 6.1 kcal mol^{-1} at B3LYP/6-311+G** ($\langle S^2 \rangle = 0.76$) and MP4SDQ/cc-pVDZ ($\langle S^2 \rangle = 1.13$), respectively. This is in accord with a rapid exchange of the two bowl-shaped $\mathbf{1}^{\bullet-}$ minima on the EPR time scale so that the corresponding spectrum shows only a time-averaged structure. Hence, the hyperfine coupling constants reflect the electron spin distribution of $\mathbf{1}^{\bullet-}$ *and* the **TS**, which are complementary due to symmetry (Fig. 3, right). By analogy, the highest singly occupied molecular orbitals (SOMOs) for these two structures are similarly shaped (Fig. 3, left), so that the overall spin and electron distribution averaged over both structures indeed appears to be rather symmetrical, in agreement with the observed EPR spectrum.

The inversion barrier for $\mathbf{1}^{\bullet-}$ is low and comparable to that of **1** and $\mathbf{1}^{2-}$: $\Delta H^{\ddagger} = 5.4$ and 7.1 kcal mol^{-1} at B3LYP/6-311+G*//B3LYP/6-31G* + ZPVE, respectively.[3] The inherent strain energy in the **TS** apparently is overcome by a significant aromatic character of the five-membered rings in the **TS** as assessed by computing the nucleus-independent chemical shifts (NICS computed in the geometric ring centers; NICS is a probe for aromaticity: negative values correspond to aromatic, positive to antiaromatic character) [20] which are much smaller in the **TS** than in $\mathbf{1}^{\bullet-}$ (Fig. 2). While $\mathbf{1}^{\bullet-}$ clearly has antiaromatic cyclopentadienyl moieties, the **TS** consists of two aromatic and one antiaromatic ring. The same arguments hold true for **1** which is, at least in its bowl-shaped singlet state, highly antiaromatic (the ground state is a triplet).

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