

Communications to the Editor

Exceptional Triplet and Quartet States in Highly Charged Hexabenzocoronenes

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Condensed polycyclic aromatic hydrocarbons are important models for π -bonding theory and are a challenge for synthetic and theoretical chemists.¹ We have recently succeeded in making novel giant PAHs and emphasized their role as molecularly defined graphite models.² The characterization of the insoluble disk molecules requires solid-state methods such as X-ray diffractometry³ and scanning tunneling microscopy.⁴ However, suitable alkyl substitutions provide soluble PAHs as well.⁵ Herein we consider soluble hexabenzocoronene (HBC) derivatives **1–3**⁶ (Chart 1) and characterize their charged states from the mono- to the tetraanion in solution by vis–NIR and EPR spectroscopy. The substitution patterns should establish both D_{6h} (**1**, **3**) and D_{2h} symmetry (**2**).

For the dianions and dications of triphenylene (**4**) and 1,3,5-triphenylbenzene (**5**) (D_{3h} symmetry), as well as their substituted derivatives, triplet ground states have been found;⁷ however, coronene (**6**) (D_{6h} symmetry) possesses only thermally excited biradical dianions and dications.⁸ This outcome could be explained on the basis of strong Jahn–Teller distortions leading to D_{2h} symmetry and loss of degeneracy of the frontier orbitals.

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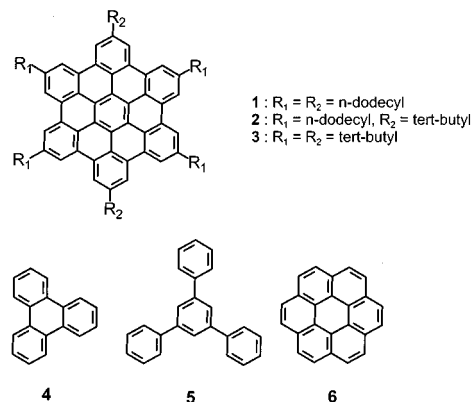
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Chart 1. Molecules **1–6**



Semiempirical AM1-CI calculations for HBC prognosticated degenerate HOMO and LUMO orbitals each (D_{6h}) and an extremely small energy difference to the NHOMO and NLUMO, with the prediction of a quartet–doublet state splitting of only 0.01 eV.⁹ Thus, the trianions seem to be candidates for triradical formation.

The radical anions of HBCs **1–3** were generated by reduction with potassium under high vacuum in THF solution. Different contact times with the metal enable equilibration of higher charged species and the exact adjustment of individual redox states as shown earlier,¹⁰ where vis–NIR control, in addition to EPR measurements, turned out to be essential. Naturally, in the course of the reduction, first monoanions are formed, which are briefly described for unambiguous differentiation from higher charged states (see Table 1). The red solutions of the monoanions give rise to intense absorptions in the visible range at 406 and 556 nm, together with less intense maxima in the NIR range at 775 and 1166 nm, which are regularly split due to additional vibrational couplings. The EPR spectra in solution show 13 signals due to proton hyperfine interaction ($g_{\text{iso}} = 2.0028$). The computer simulations indicate slightly smaller hyperfine coupling (hfc) constants for the hexa-*tert*-butyl derivative $3^{\bullet-}$ ($a_{\text{H}} = 0.097$, 12H) than for $1^{\bullet-}$ ($a_{\text{H}} = 0.103$ mT, 12H), as well as two hfc constants for the less symmetric $2^{\bullet-}$ ($a_{\text{H1}} = 0.103$, 8H; $a_{\text{H2}} = 0.097$, 4H).

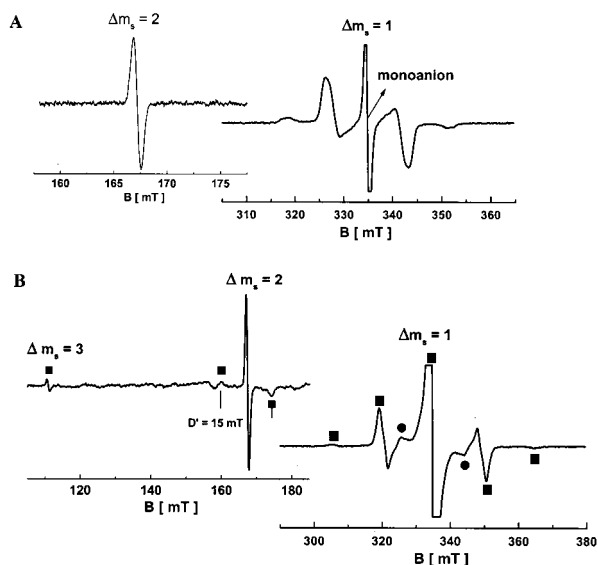
Upon further reduction, the samples turned brown, exhibiting clear changes in their optical spectra, but remained paramagnetic (see Table 1). After freezing the THF solution samples, new zero field splitting components were detectable, with $D'_{\text{di}} = 15.5$ mT, $E' \leq 0.5$ mT, and a half field transition $\Delta m_s = 2$ ($g \sim 4$) identifying their biradical nature (Figure 1A). No characteristic differences in the EPR spectra of the dianions of **1–3** could be found for the three derivatives. In-depth semiempirical calculations of the HBC dianion also favor lowering of symmetry with loss of degeneracy of the former LUMOs. The lowest singlet energy is found for the C_{2h} symmetry ($E_s = 153.3$ kcal/mol, $E_t = 165.5$ kcal/mol), lying roughly 3 kcal/mol below the lowest triplet state found for the D_{6h} symmetry ($E_t = 156.2$ kcal/mol, $E_s = 158.6$ kcal/mol). The calculations, therefore, suggest that the dianions of HBC undergo similar distortions as the coronene mentioned above.

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Table 1. Vis-NIR and EPR Data of Charged States of HBC **1** in THF/K

	monoanion	dianion	trianion	tetraanion
vis-NIR/nm	406, 556, 775, 1166	452, 525, 770, 1021, 1315	460, 680, broad NIR bands	362, 577, broad NIR bands
isobestic points/nm	neutral/mono: 397	mono-/dianion: 417, 546, 571	di-/trianion: 536, 991	tri-/tetraanion: 486, 928
EPR/mT	$g = 2.0028$, $a_{\text{H}} = 0.103$	$g = 2.0027$, $D' = 15.5$, $E' \approx 0.5$	$g = 2.0015$, $D' = 15.0$, $E' \leq 0.3$	$g = 2.0025$, $D' = 16.0$, $E' \leq 0.6$

**Figure 1.** EPR frozen solution spectra at $T = 130$ K (THF/K) and zero field splitting components (A) for the dianion $1^{2-}/2K^+$ and (B) for the trianion $1^{3-}/3K^+$ (●, biradical; ■, triradical).

Temperature-dependent measurements of the EPR signal intensity of a frozen solution of 1^{2-} reveal a gradual deviation from linear Curie-like behavior at $T < 20$ K for the plotted signal intensity versus $1/T$. A fit of the plot for thermally excited triplet states indicates very small activation energies of only $\Delta E_{\text{ST}} \approx -15$ cal/mol.

Further reduction of the dianionic samples leads to green solutions of the trianions, and broad unresolved EPR spectra are found at room temperature ($g = 2.0015$). The greatest surprise occurred upon freezing the samples ($T = 135$ K), where instead of doublet-state characteristics, even larger zero field splitting over a range of 60 mT indicated a novel quartet state (total splitting $4D'$, $D'_{\text{tri}} = 15.0$ mT, $E' \leq 0.3$ mT). Further evidence for the triradical is the detection of the $\Delta m_s = 2$ and $\Delta m_s = 3$ transitions (Figure 1B). Especially the $\Delta m_s = 3$ signal and the $D' = 15$ mT splitting in the $\Delta m_s = 2$ region are unique for this spin state and serve as unambiguous proofs for the quartet state, which has been found for the first time in fully condensed PAHs. Even [60]-fullerene, with three degenerate LUMOs, undergoes strong Jahn-Teller-distortion upon charging, with formation of a biradical as

highest spin state.^{10c} The appearance of this spin state can only be explained on the basis of the extremely low lying unoccupied NLUMO orbital, which is exceptional for such large π -systems. The temperature-dependent measurements of 1^{3-} revealed thermal excitation of the quartet state, whose population still increases with increasing temperature from 110 to 160 K.

Novel tetraanions (+4e) of the HBCs **1–3** are formed upon further reduction, which exist as biradicals and not as diamagnetic π -molecules. The EPR spectra in frozen solutions are very similar to those of the dianions ($D'_{\text{tetra}} = 16.0$ mT, $E' \leq 0.6$ mT). The temperature dependence of EPR signal intensities of 1^{4-} again demonstrates a deviation from Curie-like behavior, with a very small triplet activation energy of roughly $\Delta E_{\text{ST}} \approx -20$ cal/mol. Further reduction leads to loss of zero field splitting components in frozen solution EPR samples, indicating a $S = 1/2$ pentaanion. Therefore, it has to be assumed that HBC (planar C_{42}) can take up six electrons, reaching a diamagnetic stage again.

Although solid neutral HBC with n -alkyl substituents tends to form liquid crystalline phases at high temperatures,⁶ the higher spin states presented here for the charged **1–3** derivatives do not indicate intermolecular interactions, as sometimes presented by Rabinovitz et al.¹¹ Furthermore, the well-defined isobestic points in the optical spectra (see Table 1) document a clean and exact adjustment of the redox states.

In summary, we have shown that HBC forms biradicals upon doubly charging, where the triplet states are significantly stabilized as compared to those of coronene. Upon further charging, we have succeeded to identify tri- and biradicals for the tri- and tetraanions, respectively. Finally, it should be noted that planar HBC can take up six electrons, as many as the curved [60]-fullerene.

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Supporting Information Available: Details of the spectral characteristics of charged states and the temperature-dependent measurements of EPR signal intensities of the zero field splitting components (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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