Teranthene

DOI: 10.1002/anie.201006705

Towards Polycyclic Aromatic Hydrocarbons with a Singlet Open-Shell Ground State

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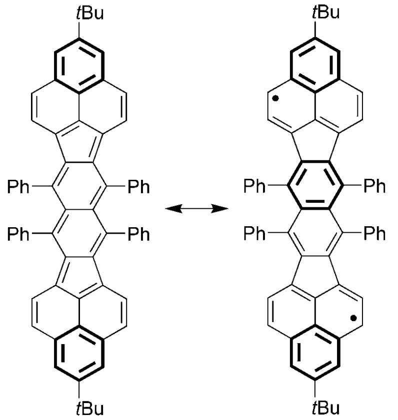
acenes · arenes · hydrocarbons · polycycles · radicals

Polycyclic aromatic hydrocarbons (PAHs) and other organic π systems with an open-shell ground state (singlet or triplet biradical) have been investigated for quite a long time,[1–7] but came again into focus a few years ago when Bendikov et al.[8] published their computational study on oligoacenes. This study supports that the longer acenes possess a nonzero bandgap with a singlet open-shell ground state followed by a triplet state a few kcal mol^{-1} higher in energy. This report and some newer related publications were reviewed by Bettinger,[9] who himself recently published the first syntheses of octacene and nonacene under argon matrix isolation conditions.[10] The reason for the unexpected open-shell character of acenes is the non-disjoint nature of the frontier orbitals, the chemical consequence of which is the high reactivity of the longer oligoacenes. One could easily leave this subject to academic discussion if there were not promising applications associated with many PAHs, which have made them a hot topic in recent years. In the case of, for example, pentacene, its use in organic field effect transistors stimulated the synthesis of many acene derivatives that aim to avoid the high chemical reactivity but retain their high charge carrier mobilities in the solid state.[11] Molecular-sized sections of graphite single layers (graphene) are also expected to play a major role in future molecular electronics.[12]

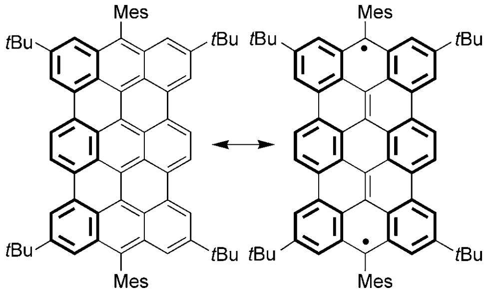
While the singlet open-shell ground-state character of the higher oligoacenes was found accidentally, Kubo et al.[13] and Champagne and co-workers[14] quite recently succeeded in designing and synthesizing two types of relatively stable PAHs that show pronounced singlet open-shell character. One structure is based on bis(phenalenyl) biradical **1**, the other on teranthene biradical **2**. The latter may in fact be considered as a molecular section of graphene, and recent theoretical studies indeed suggest that somewhat larger graphene sections actually possess a singlet biradical structure.[15]

The bis(phenalenyl) biradical **1** can be drawn in a Kekulé valence-bond structure, which emphasizes its singlet character. The biradical character becomes evident if one tries to draw as many (aromatic and thus stabilizing) Clar sextets as possible (given in bold lines in Scheme 1). This is only possible if a double bond is broken and two radical centers are formed.



Scheme 1. Substituted bis(phenalenyl) biradical **1** with a naphthalene spacer.

Teranthene **2** may also be formulated as a closed-shell Kekulé valence-bond structure. Drawing the maximum number of Clar sextets yields a biradical where the radical centers are situated at the zigzag edges. The presence of six Clar sextets in the biradical versus three such sextets in the nonradical form suggest a stronger stabilization of the biradical versus the closed-shell structure and, thus, a strong biradical nature of **2** (Scheme 2). Coming to the facts: both **1**



Scheme 2. Substituted teranthene biradical **2** with Clar sextet. Mes = 2,4,6-trimethylphenyl.

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and **2** are stable at room temperature and even withstand air for a short period. Both compounds were characterized by X-ray crystallography, and show a near-infrared (NIR) absorption at 865 nm (**1**) and 1054 nm (**2**). The NIR absorption indicates a small HOMO–LUMO gap, as demonstrated by the electrochemically determined difference in the redox potential between the first oxidation and the first reduction potential (1.04 V for **1** and 1.05 V for **2**). Although a small band gap is a precondition for a biradical structure, it is by no means sufficient. The NMR spectra of neither compound show any signals corresponding to aromatic protons at room temperature, but the spectra sharpen at around −100 °C. A thermal population of a low-lying triplet state may account for this effect. This was substantiated by SQUID measurements on powdered samples, which show both compounds to have a singlet–triplet energy difference of only 0.16 eV.

All the above-mentioned observations point towards a singlet biradical ground state, and Champagne and co-workers[14] applied CASSCF(2,2) calculations to quantify the amount of biradical character. According to the occupation number of natural orbitals, a 50 % biradical contribution (occupancy of the LUMO) was calculated for **1** and 42 % for **2**. These values are certainly impressive, but can they be trusted? Kamada, Kudo et al.[16] established an intriguingly simple method that allows the percentage of biradical contribution to be calculated purely by using experimental data. This method is based on a two-site two-electron model. The biradical character y, which ranges from 1 for a full biradical to 0 for fully closed shell, may thus be expressed as Equation (1), where $^1E_{1u}$ is the energy of the first excited

$$y = 1 - \sqrt{1 - \left(\frac{^1E_{1u} - {}^3E_{1u}}{^1E_{2g}}\right)^2} \qquad (1)$$

singlet state of u symmetry, $^1E_{2g}$ is the second excited singlet state with g symmetry, and $^3E_{1u}$ is the lowest energy triplet state, with all the energies relative to the singlet ground state with g symmetry. All these quantities are accessible by experiment, and thus allow comparison of the experimentally evaluated y value with, for example, that from UHF-calculated occupation numbers of natural orbitals. Figure 1 shows such a correlation for a number of PAHs having typical closed-shell ground states as well as for systems with biradical character such as **1** and a pentacene substituted with a triisopropylsilyl (TIPS) group. However, care must be taken! A slope of about 2 indicates systematic errors, whose origin [either in Eq. (1) or the UHF computations] is not known. CI computations with, for example, larger active orbital space are needed to support these data. Nevetheless, Equation (1) gives us a simple tool to estimate the relative biradical character of PAHs, provided that experimental data on the energies of the excited states are available.

This brings me to the final point. What are these singlet biradical PAHs good for? For **1**, Kamada et al.[17] found surprisingly strong two-photon absorption (TPA) cross-sections ($\sigma \approx 2000$ GM at 1610 nm irradiation by the Z-scan open-aperture method). This value is comparable with similarly sized chromophores with the typically employed donor-π-acceptor-π-donor motif. The amazingly high TPA cross-section is clearly due to the biradical nature of **1**, as closed-shell PAHs of similar size show far smaller TPA cross-sections. Theoretical studies suggest that the second-order hyperpolarizability (a quantity related to the two-photon absorption cross-section) is maximal for systems with a singlet biradical contribution of about 36 %.[18] Furthermore, measurement of field effect transistors built with a bis(phenalenyl) singlet biradical derivative indeed showed a nicely balanced ambipolar transport of electrons and holes.[19] The future of these biradical PAHs clearly lies in materials science. Although the PAHs mentioned in this Highlight are much more stable than other biradicals, stability issues have to be overcome before application in (opto)electronic devices can be envisaged seriously.

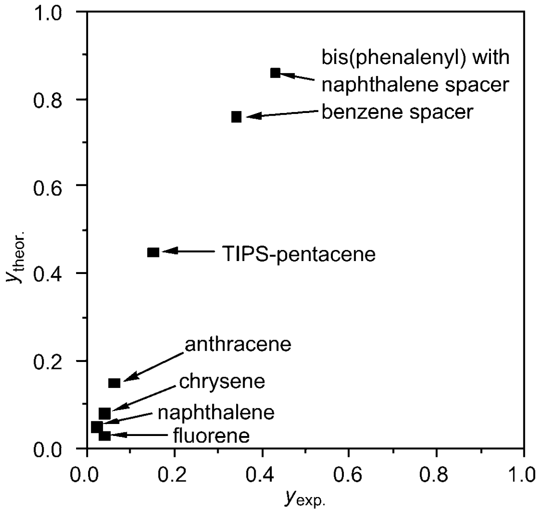

Figure 1. UHF-computed y values versus the experimentally estimated [with Eq. (1)] singlet biradical contribution of several PAHs.

Received: October 26, 2010

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