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Synthesis and Characterization of Teranthene: A Singlet Biradical Polycyclic Aromatic Hydrocarbon Having Kekulé Structures

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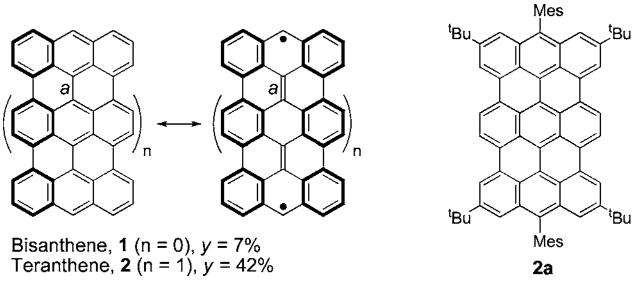
Abstract: A teranthene derivative has been successfully isolated in a crystalline form for the first time. Geometrical considerations and physical property investigations indicate that the molecule possesses prominent biradical character in the ground state.

Singlet open-shell polycyclic aromatic hydrocarbons (PAHs) have been intensively studied[1] because they are closely related to the nanographenes, which display fascinating properties resulting from the spin-polarized state at the zigzag edges.[2] Commonly asked questions about their ground-state electronic structure encompass the relative importance of the biradical (or polyradical) structures and the location of the large spin density. Recent theoretical studies[1e] have presented evidence that the biradical (or polyradical) structures in PAHs with Kekulé structures originate from the aromatic stabilization due to the formation of *Clar sextets*[3] in the quinoidal rings and that the unpaired electrons appear predominantly at the zigzag edges rather than the armchair edges. Questions of particular interest also concern the experimental investigation of the crossover from a closed-shell to an open-shell structure in a homologous series of singlet-ground-state Kekulé PAHs. Because of their simplicity, we paid attention to *peri*-condensed anthracenes, the so-called anthenes,[4] because all anthenes are subject to the loss of only one double bond when the structure is written with a maximum number of Clar sextets (Scheme 1). In these biradical forms, the Clar sextets, the isolated double bonds, and the unpaired electrons have fixed positions, i.e. the influence of migration or delocalization is limited. Therefore, the discussion of the biradical character can concentrate on the energy balance between the formal loss of the double bond and the aromatic stabilization. Herein we report the first synthesis of a teranthene derivative, **2a**, and its characterization in terms of singlet biradical character in comparison with bisanthene **1a**.

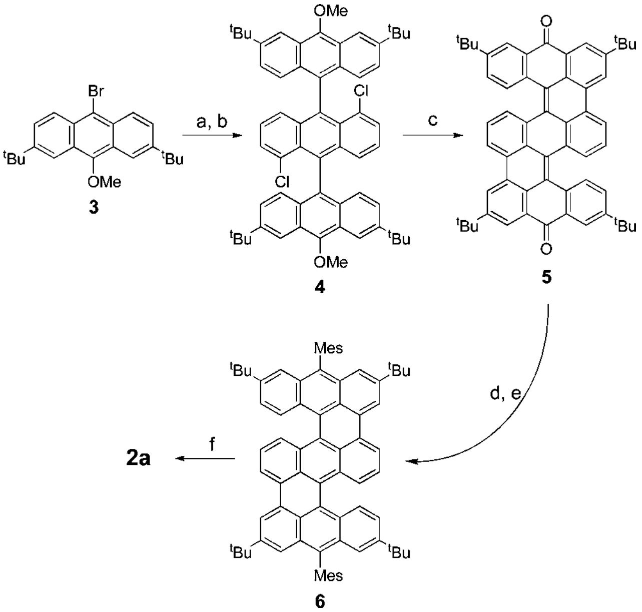
Scheme 1. Resonance Structures of Anthenes and the Synthetic Target Molecule **2a**[a]



[a] The amplitudes of the biradical character (*y*) were calculated at the CASSCF(2,2)/6-31G level. The six-membered rings depicted by bold lines represent the Clar sextets. Mes = mesityl group.

Scheme 2 displays the synthetic procedure for **2a**. Lithiation of **3** followed by coupling with 1,5-dichloroanthraquinone and a subsequent treatment of reductive aromatization with NaI/NaH_2PO_2 gave the teranthrylene derivative **4**.[5] Cyclization along with demethylation of **4** was carried out with KOH/quinoline to give the partially ring-closed quinone **5**.[6] Treatment of **5** with mesitylmagnesium bromide in the presence of $CeCl_3$[7] and subsequent reductive aromatization afforded the partially ring-closed hydrocarbon **6**. Cyclization of **6** with DDQ/$Sc(OTf)_3$ followed by a $N_2H_4 \cdot H_2O$ quench[8] gave **2a** as a dark-green solid. Single crystals

Scheme 2. Synthesis of **2a**[a]



[a] Reaction conditions: (a) *n*-BuLi, ether, 0 °C, then 1,5-dichloroanthraquinone, 0 °C to rt; (b) NaI, $NaH_2PO_2 \cdot H_2O$, AcOH, 150 °C, 90% (two steps); (c) KOH, quinoline, 190 °C, 78%; (d) mesitylmagnesium bromide, $CeCl_3$, 4:1 THF/ether, −30 °C; (e) NaI, $NaH_2PO_2 \cdot H_2O$, AcOH, 150 °C, 75% (two steps); (f) DDQ, $Sc(OTf)_3$, toluene, reflux, then $N_2H_4 \cdot H_2O$, toluene, rt, 72%. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

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suitable for X-ray crystallographic analysis were obtained by recrystallization from a CH_2Cl_2/hexane solution under an argon flow. A toluene solution of **2a** showed gradual decomposition with a half-life of 3 days upon exposure to air under room light at room temperature.[9]

The X-ray crystallographic analysis of **2a** revealed an effective D_{2h} symmetry for the teranthene core, with the two mesityl groups nearly perpendicular (dihedral angle = 81°) (Figure 1). The geometry of teranthene reflects the prominent biradical character of **2a**. As shown in Scheme 1, the biradical resonance contribution enforces a shortening of the *a* bonds due to their double-bond character. The length of the *a* bond in **2a** (C8−C18 in Figure 1) is 1.424(4) Å, which is considerably shorter than length of a $C(sp^2)-C(sp^2)$ single bond (1.467 Å),[10] whereas **1a**, the 4-(trifluoromethyl)phenyl derivative[11] of bisanthene (**1**), presents a relatively longer *a* bond having a length of 1.447(4) Å. Additionally, the four corner six-membered rings in **2a** (denoted by *A* in Figure 1) show a considerable decrease in the bond-length alternation, i.e., they bear more benzene character than those in **1a** (Figure 2). The geometry-based aromaticity index HOMA (harmonic oscillator model of aromaticity),[12] which has a larger value for the *A* rings in **2a** (0.854) than for those in **1a** (0.704), fully supports the idea. Moreover, these geometrical findings are in line with the amplitude of the biradical character (y) estimated at the CASSCF(2,2) level, which predicts a large LUMO occupation number of 0.42 for **2** in contrast to only 0.07 for **1**.[13]

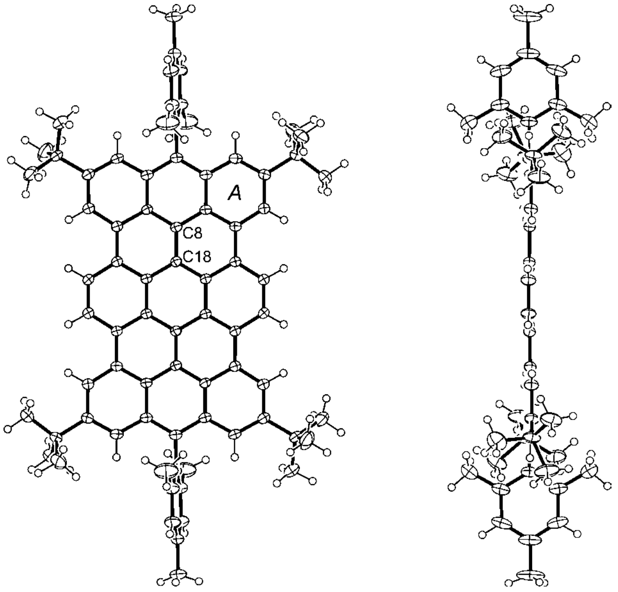

Figure 1. ORTEP drawing of **2a** measured at 200 K: (left) top view; (right) side view.

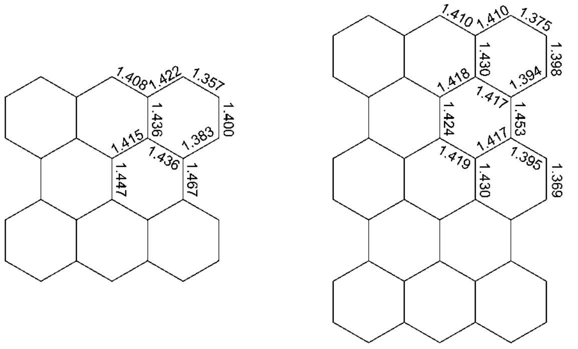

Figure 2. Bond lengths (mean values) in the main core rings of (left) **1a**[11] and (right) **2a**.

Another aspect to consider is the biradical character of these molecules in terms of the energy balance between the formal loss of the double bond and the aromatic stabilization. The aromatic stabilization energy of benzene based on the homodesmic stabilization energy is ∼90 kJ/mol,[14] three times which is comparable to the C−C π-bond energy of ∼270 kJ/mol.[15] Upon transformation to the biradical form, **1** contains only two additional sextets; therefore, the destabilization energy due to the π-bond cleavage cannot be fully compensated, so electron pairing is favored in **1**. In contrast, **2** includes three additional sextets in its biradical form, so both the Kekulé and biradical forms contribute similarly to the ground state.

Physical property investigations for **2a** thoroughly support its intermediate biradical character. A CD_2Cl_2 solution of **2a** showed no ^1H NMR signals from the teranthene core at room temperature, while progressive line sharpening was observed upon cooling (Figure 3). This behavior was also seen in the phenalenyl-based singlet biradicals we investigated previously[16] and is caused by a thermally excited triplet species. The small singlet−triplet energy gap (ΔE_{S-T}) of **2a** was estimated by SQUID measurements on a powdered sample (Figure S1 in the Supporting Information). The measurement showed an increasing susceptibility above 220 K. From careful fitting of the observed increase, the value of ΔE_{S-T} was determined to be 1920 K (16.0 kJ/mol).[17] Thus, the two unpaired electrons in **2a** are coupled very weakly in comparison with most Kekulé compounds ($\Delta E_{S-T} > 10^4$ K). It is further noted that the sharp ^1H NMR signals observed for **1a** indicate that the influence of the triplet species is negligible as a result of a larger $\Delta E_{S-T.}$[18]

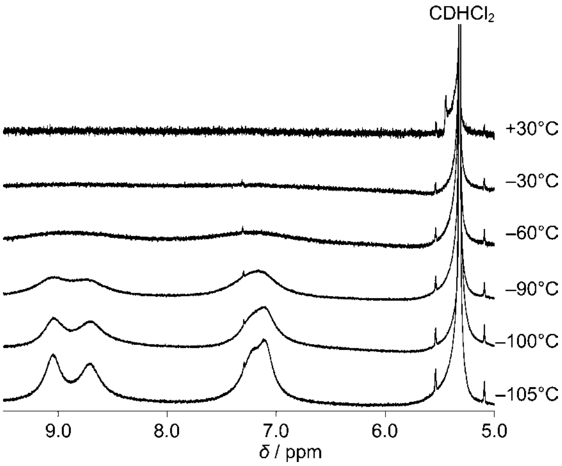

Figure 3. Variable-temperature ^1H NMR spectra of **2a** in CD_2Cl_2 in the aromatic region.

Thermal excitation to the triplet state requires a small HOMO−LUMO energy gap. The cyclic voltammogram of **2a** shows four reversible redox waves: $E_2^{ox} = +0.09$, $E_1^{ox} = -0.35$, $E_1^{red} = -1.40$, and $E_2^{red} = -1.76$ (all values in V vs Fc/Fc$^+$; Figure 4). On the basis of the difference between the first oxidation and reduction potentials, the electrochemical HOMO−LUMO gap amounts to 1.05 eV, which is 0.58 eV smaller than that of **1a**.[11] The electronic absorption spectrum of **2a** in CH_2Cl_2 (Figure 5) exhibited a low-energy band at 1054 nm ($\varepsilon = 8000$ M^{-1} cm^{-1}), from which the optical HOMO−LUMO gap was determined to be 1.18 eV. This value is 0.64 eV smaller than that of **1a**. The smaller HOMO−LUMO gap of **2a** is consistent with its larger biradical character, because

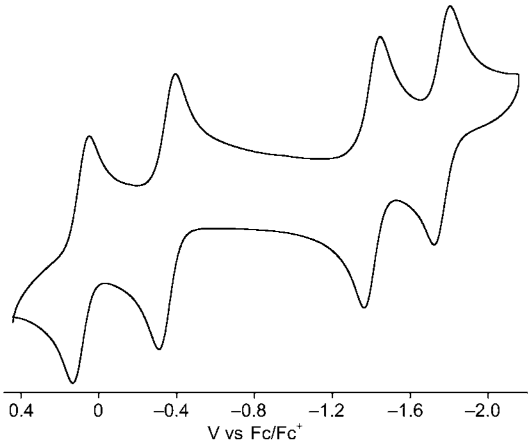

Figure 4. Cyclic voltammogram of **2a** (V vs Fc/Fc$^+$, in 0.1 M $^nBu_4NClO_4$/CH_2Cl_2, scan rate 100 mV/s, room temperature).

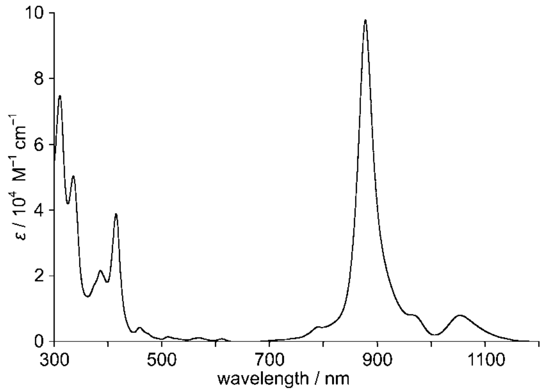

Figure 5. Electronic absorption spectrum of **2a** in CH_2Cl_2 at room temperature. λ_{max}/nm (ε/10^4 M^{-1} cm^{-1}): 1054 (0.80), 878 (9.78), 415 (3.89), 336 (5.03), 311 (7.48).

the smaller the gap, the easier it is to promote electrons from the HOMO to the LUMO. Admixing the doubly excited configuration $^1\Phi_{H,H\rightarrow L,L}$ into the ground state leads to a strong static correlation between two unpaired electrons and consequently to a pronounced singlet biradical character.

In conclusion, we have demonstrated the uncoupling of the electron pair in a Kekulé PAH, the extent of which is governed by the energy balance between the formal loss of the double bond and the formation of aromatic sextets. Our study further shows that the singlet biradical character in PAHs can be investigated experimentally in an unexpectedly small molecule. This finding would encourage a bottom-up approach for establishing spintronics and nonlinear optics, both based on molecular-sized nanographene compounds.[19]

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Supporting Information Available: Experimental procedures for all new compounds, crystal data, a magnetic susceptibility plot, a crystal packing diagram, details of the theoretical calculations, and a CIF file for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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