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Breaking bonds, Forming Nanographene Diradical with Pressure

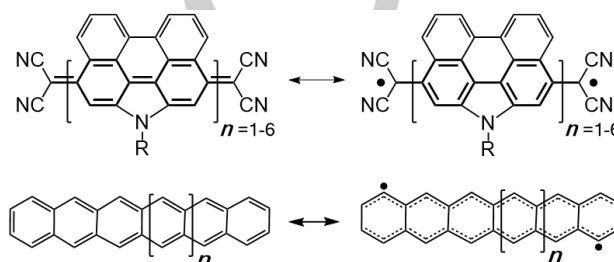
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Abstract: New anthanthrone-based polycyclic scaffolds possessing peripheral crowded quinodimethanes have been prepared. While the compounds adopt a closed-shell butterfly shaped structure in the ground state, a concave-to-convex fluxional dynamic inversion is accessible with a low energy barrier through an open-shell diradicaloid transition-state. Mainly driven by the release of strain attributed to the steric hindrance at the *peri* position of the anthanthrone core, a low-lying open-shell diradical is accessible through planarization of the core, which can be achieved by thermal excitation in solution. Alternatively, planarization can be achieved by application of mild pressure in the solid state, in which case the diradical remains kinetically trapped in an excited open-shell configuration. Cross-information from quantum chemistry, Raman spectroscopy and magnetic experiments allow us to corroborate these hypotheses and determine that the resulting nanographene-like structure possess unpaired electrons mainly localized at the exo-anthanthrone carbons bearing phenyl substituents.

Because of the outstanding spin and electronic properties of graphene (i.e., nanographenes as the molecular versions),¹ the intrinsic beauty of stable molecules with high spin density and the opportunity they provide to investigate fundamental aspects of chemical bonding, the study of diradicals has been the subject of very intense research in the past few years.² Several strategies for attaining such diradicaloid molecules with varying degree of diradical character³ have been developed and some are presented in Scheme 1: i) by the accumulation of pro-aromatic (i.e., quinodimethanes or quinoidal) rings in oligomeric structures, which lead to the formation of a singlet open-shell diradical by the recovery of Hückel aromaticity;^{4,5} ii) by the construction of antiaromatic molecules;^{3a,6} or iii) by the design of nanographenes with appropriate zig-zag edges (i.e., metallic or half-metallic) states such as acenes and fused acenes.^{7,8}

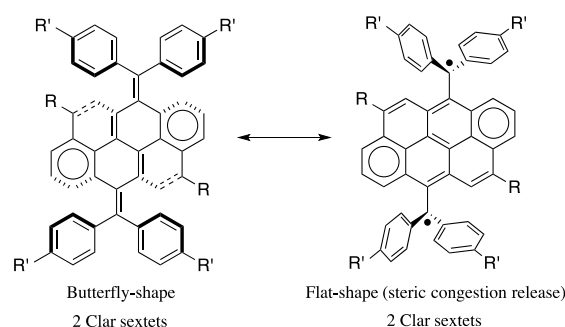
Open-shell diradical molecules are characterized by unique optoelectronic properties^{2c,5a,9} relevant to the field of nonlinear optics,¹⁰ spintronics¹¹ and organic photovoltaics,¹² among others. However, one important aspect to consider in order to enable the exploration of the unique properties of diradical molecules in a practical setting is their chemical stability. In the two cases (i) and (iii) above, the smaller oligomers are closed-shell, highly stable

molecules owing to the full bonding electronic configuration, whereas diradical character is observed in longer oligomers.^{4,5} Yet the preparation of such elongated π systems often requires tedious synthesis and the oligomers suffer from poor stability. Following the pioneering work of Hirai and co-workers on the observation of a fairly stable triplet carbene,¹³ the anthracene substructure has been utilized in the design of open-shell diradicaloid molecules.¹⁴



Scheme 1. Top) formation of a diradical by aromaticity gain from tetracyanoquinoidal rylenes for $n > 1$.^{5c} Bottom) formation of diradical states on the zig-zag edges of acenes for $n > 0$ ⁸ or nanographenes.⁷

In pursuit of a robust polycyclic framework to accommodate stable diradicals, we report the preparation and characterization of a new “nanographene” based on the low-cost commercially available 4,10-dibromoanthanthrone (vat orange 3) building block.¹⁵ While the anthanthrone core can be viewed as a fusion of two anthracene moieties with lateral functionalization, its chemical and physical properties stand in sharp contrast with the parent anthracene subunit,¹⁶ exhibiting remarkable stability because of its extended delocalization. Taking advantage of the readily available molecular complexity provided by this polycyclic aromatic, we aimed to exploit the intrinsic steric congestion and contortion of a disubstituted quinoidal anthanthrone motif to promote diradical formation. We hypothesized that the general target structure shown in Scheme 2 would possess an accessible diradical state, as planarization would result in the release of steric strain along with the formation of two perpendicular π systems and overall gaining of aromatic stability.¹⁷ Interestingly, this system would provide a rare example of a closed-shell to open-shell transition that does not rely on the creation of additional Clar sextets as the major driving force.



Scheme 2. Studied compounds (**1**: $R' = t\text{Bu}$ and **2**: $R' = \text{CN}$) with the closed-shell quinoidal and diradical canonical forms.

The syntheses of **1**, **2** and **3** are depicted in Scheme 3. 4,10-Bis(triisopropylsilylethynyl)-6,12-bis(*gem*-dichlorovinylene)-dihydroanthanthrene were prepared in two straightforward steps from 4,10-dibromoanthanthrone using a previously reported

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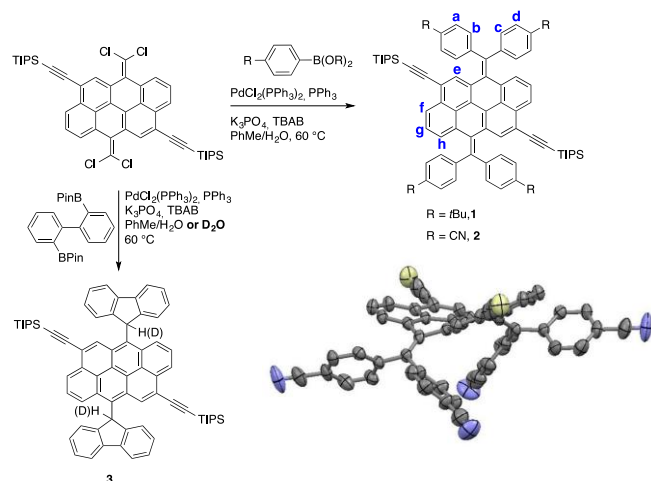
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method (see SI).¹⁵ For **1** and **2**, a fourfold Suzuki-Miyaura coupling using the corresponding *para*-substituted phenylboronic acid or ester was performed using PdCl₂(PPh₃)₂ as the catalyst to provide the desired compounds in 89 and 74% yield, respectively. For **3**, a strategy based on a double fluorene ring-closing reaction by Suzuki-Miyaura coupling using 2,2'-bis(pinacolborane)biphenyl was attempted. Despite numerous efforts, **3** could not be isolated. Instead, the protonated derivative was obtained, suggesting that once formed, **3** rapidly turned into a reactive species that trapped a proton from the solvent. To verify this hypothesis, we performed the reaction using D₂O and deuterated **3** was formed in 17% yield.



Scheme 3. Synthesis of **1**, **2** and **3** and lateral view of the crystal structure of **2** (isopropyl groups and H atoms are omitted for clarity).

Crystals suitable for X-ray diffraction were obtained from slow evaporation of pentane in chloroform at -30 °C. **2** crystallizes in a *Pbcn* orthorhombic space group and adopts a bent, butterfly structure in which the angle of the terminal methylene groups is twisted by 27° (significantly deviated from Thiele's hydrocarbon,¹⁸ 13.9°) and the anthanthrone core is highly contorted along the transversal aromatic axis. Also, the length of the C-C double bond between the core and the germinal carbon that bears the 4-cyanophenyl groups is 1.358 Å, which is 0.018 Å longer than the average double bond in olefins (1.33 to 1.34 Å) and still shorter than Thiele's hydrocarbon analogous C-C bond (1.381 Å).¹⁸ This butterfly conformation can be ascribed to the steric congestion between the protons at the *peri* position of the anthanthrone core and the protons from the peripheral phenyl groups.

While these data suggested a closed-shell ground state singlet in the crystalline form at room temperature, variable-temperature (VT) ¹H NMR experiments were performed to see if a diradical state could be accessed by thermal excitation. First, it should be noted that the broad peaks in the ¹H NMR spectrum of **2** can be attributed to the rigidity of the phenyl groups that cannot freely rotate because of the high steric demand. As a result, their signal cannot be averaged and appear as large doublets. In addition, b and c protons (Scheme 3) appeared as two very large doublets at 0 °C as a result of their different chemical environments. However, the signals merged to a single doublet upon warming to 15 °C and coalesced at 35 °C, suggesting an accessible structural inversion through π-bond breaking resulting in equivalent proton signals. Interestingly, this inversion was likely to occur through the formation of a planar diradicaloid species. This hypothesis was corroborated by the marked decrease in signal intensity at higher temperatures. Moreover, this process was found to be completely reversible and no significant sign of decomposition was observed when the sample was cooled back to room temperature. The loss of signal intensity can be rationalized by the population of an excited triplet state, which would be easily accessible from the planar diradical state found

along the structural inversion by thermal activation. Indeed, small singlet-triplet gaps that result in NMR silent spectra or signal broadening is a common feature of polyaromatic hydrocarbon based organic diradicals.^{5a,14a,19} These results are nicely correlated by quantum mechanical investigations (*vide infra*). It is noteworthy that **1** exhibited the same line broadening in the ¹H NMR spectra with increased temperature, although a significant amount of degradation product was observed after heating. The increased stability of **2** over **1** suggests that the nitrile group is beneficial for radical stabilization, in agreement with previous studies and with its electron-withdrawing character able to stabilize the unpaired electron density.^{5a,20}

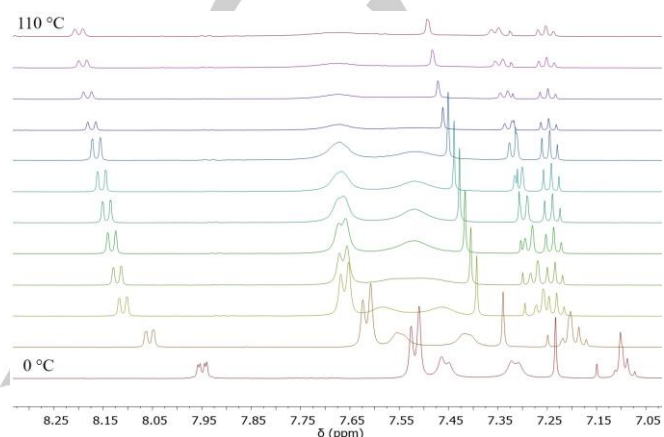


Figure 1. Variable-temperature ¹H NMR spectra of the aromatic region of **2** in tetrachloroethane-*d*₂. The spectra were taken from 0 °C to 110 °C (10 °C increment). The letters refer to the peak assignment found in Scheme 3.

Quantum chemical calculations (SI for further details) for **2** have been carried out to understand the origin of the spectral changes. In its closed-shell structure, the anthanthrone core of **2** adopts a butterfly shape and nicely emulates the structural parameters resolved from the X-ray diffraction study. A relatively small energy barrier of +8.3 kcal/mol for the closed-shell to diradical conversion is found that can be easily overcome at room temperature through fluxional inversion giving rise to a local metastable full planar structure with a net singlet diradical character and a triplet state residing only +0.3 kcal/mol (Figure 2). This diradical state displays most of the unpaired electron density at the exocene carbon atoms. As no new Clar sextet was formed during this transformation (2 sextets in both the closed-shell and open-shell forms), the driving force for this transformation is likely attributed to the release of strain induced by the steric hindrance at the *peri* position of the anthanthrone. To test this hypothesis, phenyl-free4,10-Bis[(triisopropylsilyl)ethynyl]-6,12-bis(dicyanovinylene)dihydroanthanthrone¹⁵ derivative in which no steric hindrance is present at the *peri* position was studied by VT-NMR (Figure S2). As expected, no significant changes in the shape of the ¹H resonances were observed between 0 and 110 °C, meaning that phenyl groups are necessary to force the anthanthrone core out of planarity, eventually leading to the metastable kinetically trapped diradical in which the acene core is planar and the phenyl rings reside perpendicularly, a situation where the steric effects are released at the expenses of the rupture of one double bond and formation of the diradical state. This diradical is also energetically stabilized by the formation in the central core of a chrysene structure that allows π-electron delocalization on it.

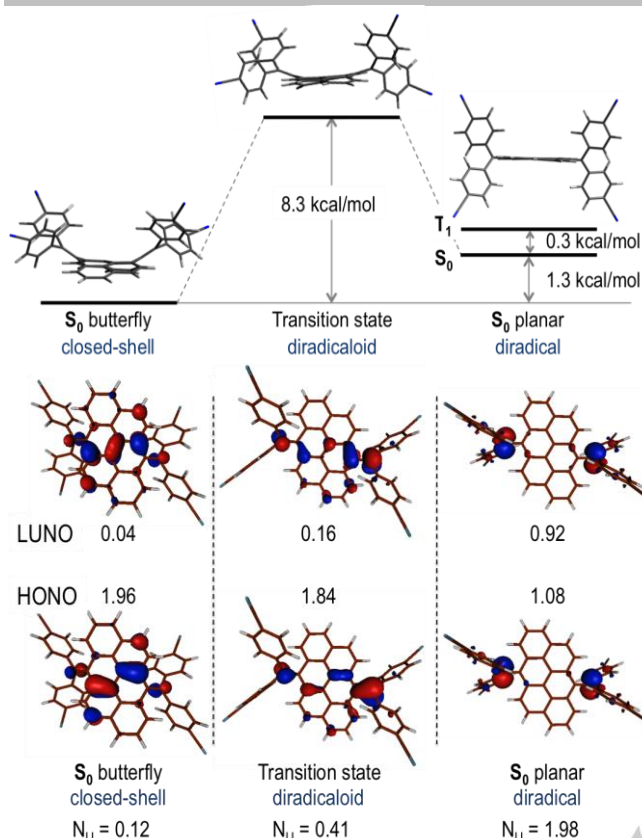


Figure 2. Top) Structures of **2** along the diradical/planar reaction path with relative Gibbs free energies (UB3LYP) and vertical singlet-triplet gaps (RAS-SF) for the planar structure. Bottom) Highest occupied natural orbital (HONO) and lowest unoccupied natural orbital (LUNO), their electron occupancies and the number of unpaired electrons (Nu) for the butterfly, TS and planar structures (obtained at the RAS-SF computational level).

As VT NMR experiments and DFT calculations showed that only a small energy input could induce π -bond breaking, we attempted to access the diradical species through the application of mild pressure. Upon grinding of the orange powder of **2** with a mortar and pestle, the orange sample's color changed to dark brown and reversed back to orange by solvent vapor annealing with dichloromethane (Figure S3). Pressure variable Raman spectroscopy can provide information at the molecular level for this unusual solid transformation (see ESI for experimental details).²¹ Compound **2** changes color from orange to black when compressed in a KBr pellet (≈ 10 Ton/cm²). The Raman spectrum of **2** at room pressure in Figure 3 shows two main bands at 1613 and 1577 cm⁻¹ due to $\nu(\text{C}=\text{C})$ stretching modes of the central naphthoquinoid moiety and of the peripheral benzenoid groups, respectively. In the 10 Ton/cm² pressed KBr black sample of **2**, the Raman spectrum is characterized by a new and more intense band at 1598 cm⁻¹ while the two bands of the non-pressed sample are still present with weak intensity. The variable pressure (VP) Raman experiment in a diamond anvil cell shows that between 0.0 and 0.3 GPa (≈ 3 Ton/cm²), the peaks attributed to the orange sample at 1613/1577 cm⁻¹ completely vanish to make place for a new band at 1598 cm⁻¹ associated with the black powder. Upon release of pressure, a partial recovery of the initial spectrum is observed *i.e.* the open-shell diradical does not fully convert back to the more stable closed-shell species. This can be rationalized by the diradical species being a local minimum on the potential energy surface. Indeed, for the conversion from planar to butterfly structure to occur, a barrier of 7 kcal/mol needs to be overcome, as shown in Figure 2. As for compound **1**, no significant changes in the vibrational Raman spectra were observed after application of pressure.

The theoretical Raman spectrum for this structure (Figure 3) displays two main bands at 1670 and 1590 cm⁻¹ that can be correlated with the experimental bands measured at 1613 and 1577 cm⁻¹, respectively. For the planar diradical state the Raman spectrum has been also calculated (Figure 3), which exhibits a main band at 1615 cm⁻¹ that nicely correlates with the spectrum of **2** under pressure (1597 cm⁻¹). The theoretical band at 1670 cm⁻¹ is present in both the spectra of the closed-shell and of the planar diradical species, indicating that a molecular fragment from the central quinodimethane unit remains unaltered by planarization. Therefore, it is reasonable to assume that under pressure, the anthanthrone core gets increasingly planar and the molecule progressively transforms to a diradical, consistent with the observed changes in the Raman spectra. The UV-visible absorption and emission spectra of orange solids **1** and **2** as a function of the temperature are also fully consistent with this description (see Figure S4 and discussion in ESI file).

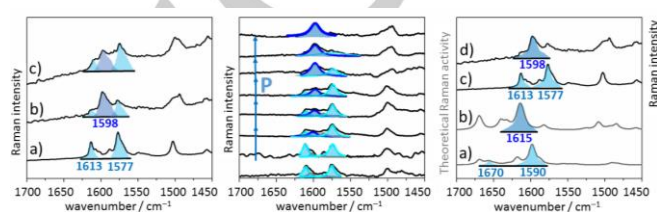


Figure 3. Raman spectra recorded with the 785 nm excitation laser of: left) (a) spectrum of the orange solid at 80 K and at 1 atm; (b) in a KBr pellet at 80 K after the application of ≈ 10 Ton/cm² of pressure and (c) this latter at room temperature. Middle) Variable pressure spectra upon steps of 0.05 GPa up to 0.3 GPa where light blue deconvolutions correspond to the room pressure bands and dark-blue deconvolutions are the emerging band with pressure. Right) (a) B3LYP/6-31G** theoretical Raman spectrum of the butterfly quinoidal singlet closed-shell ground electronic state, (b) UB3LYP/6-31G** theoretical Raman spectrum of the planar open-shell state; (c) 785 nm experimental Raman spectrum of orange solid at 80 K, and (d) 785 nm experimental Raman spectrum of KBr black solid at 80 K.

Direct proof for the formation of a triplet excited state is provided by EPR and SQUID magnetic measurements for compound **2** (Figure 4). For the non-pressed pristine material, no SQUID response was observed in the range of temperature analysed. For **2** after application of a pressure of 10 Ton/cm² a clear increase of the $\chi_m T$ value was observed with increased temperature up to 400 K. This behaviour is typical of singlet diradicals in thermal equilibrium with a triplet biradical. The $\chi_m T$ behavior can be adjusted to the Bleany-Blowers model, also in Figure 4 from which a singlet-triplet energy gap of -0.8 kcal/mol is estimated.²² This is confirmed by EPR spectroscopy that shows a signal at 300 K whose absorbance decreases upon cooling at 200 K in line with the SQUID measurements (Figure 4). These data are also in agreement with quantum chemical calculations, which predict an excited triplet state at $+0.3$ kcal/mol for the planar diradical geometry. For compound **1** the same SQUID and EPR pressure dependent experiments were carried out (Figure S6) without any sign of magnetically active species after pressure application.

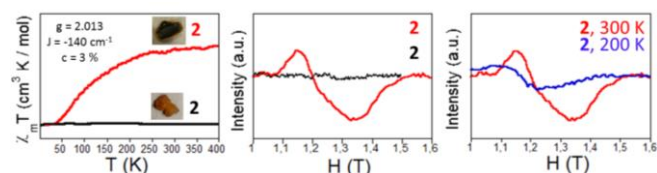


Figure 4. Left) representation of the molar magnetic susceptibility times the temperature versus temperature for the non-pressed orange solid of **2** (black line, orange solid in the insert) and for the pressed sample (red line, black solid in the insert). J is obtained from the Bleany-Bowers fit. Bottom, right) The same for the EPR spectra of **2** and the EPR spectra of the pressed **2** at 300 and 200 K.

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In summary, a chemically robust, highly contorted closed-shell anthanthrone-based quinodimethane has been prepared. In solution, heating promotes the dynamic inversion of the structure through a planar open-shell intermediate in which the triplet state becomes increasingly populated at higher temperatures. Under application of mild mechanical stress (0.3 GPa), the molecule also undergoes planarization, forming a kinetically trapped diradical, which can be characterized in the solid state. The main driving force for the stabilization of the diradical in the quinodimethane units is the release of strain induced by the anthanthrone core, providing a rare example of closed-shell to open-shell transition not driven by the formation of additional Clar sextets. While this rare example of π -bond breaking by mechanochemistry opens the way to the generation of diradicaloid species with accessible high spin states from robust quinoidal structure, current work is focused on stabilizing the diradical state through the design of novel functionalized anthanthrone-based polycyclic aromatics.

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Keywords: quinodimethanes, nanographenes, diradical species, mechanochemistry, quantum chemical calculations, Raman spectroscopy

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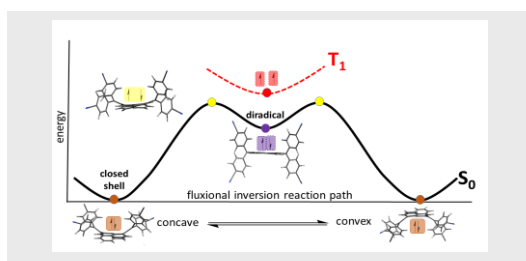
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Breaking a π bond with your bare hands!

Quinodimethane nanographenes with closed-shell structure experience a concave to a convex inversion through a diradical intermediate that is kinetically trapped and has a low energy lying triplet.

**Breaking bonds, Forming Nanographene Diradicals with Pressure,**

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