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Acenophanes

Anti-[2.2](1,4)pentacenophane: A Covalently Coupled Pentacene Dimer**

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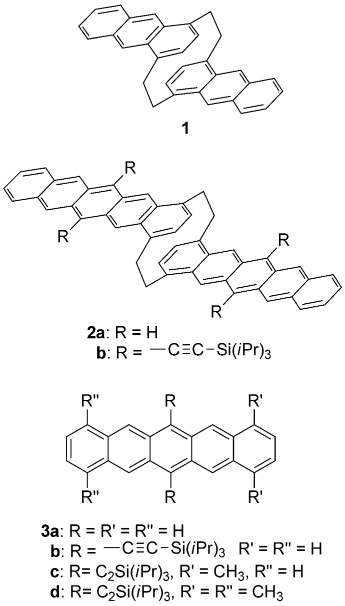
The [2.2]paracyclophane building block has been incorporated into a number of fascinating molecules, including extended orthogonal[1] as well as parallel π systems, which could be increased in length up to anthracene within the latter class. In particular the group of Misumi has contributed significantly to the field by establishing syntheses of a large number of anthracenophanes in the 1970s, such as **1** (Scheme 1).[2]



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2a: R = H
b: R = —C≡C–Si(*i*Pr)$_3$

3a: R = R' = R'' = H
b: R = —C≡C–Si(*i*Pr)$_3$ R' = R'' = H
c: R= C$_2$Si(*i*Pr)$_3$, R' = CH$_3$, R'' = H
d: R= C$_2$Si(*i*Pr)$_3$, R' = R'' = CH$_3$

Scheme 1. *Anti*-[2.2](1,4)anthracenophane (**1**), *anti*-[2.2]-(1,4)pentacenophanes (**2**), and pentacenes (**3**).

The interaction between the anthracene chromophores has received significant attention and was studied by absorption and fluorescence spectroscopy,[3] by ESR or ENDOR spectroscopy in radical anions or cations.[4] Electronic interaction between the two aromatic ring units was also probed by cyclic voltammetry.[4b,c] For the oxidation of the naphthalene[4c] and the reduction[4b] and oxidation[4c] of anthraceno systems, splitting of voltammetric peaks was observed: the presence of a radical ion in one unit renders the electron transfer to or from the second unit more difficult. The effect seems to decrease with increasing size of the units, and is stronger for the *syn* as compared to the *anti* isomer.[4c]

Larger acenes than anthracene have not been used as aromatic units in [2.2]paracyclophanes. We are interested in novel pentacene derivatives, such as **2**, that allow the interconnection of two pentacene (**3**) molecules to achieve an effectively larger conjugated system. Such molecules may have interesting properties and may result in materials with enhanced charge transport characteristics and may also possibly be used as singlet fission materials in organic electronic photovoltaics.[5] One conceivable way of coupling two pentacene molecules is through a [2.2]paracyclophane linkage as in **2**. While a large number of isomers is possible, we assume that too close interaction will result in photochemically very reactive dimers. For example, *anti*-**1** is photostable, while its *syn* isomer was found to undergo wavelength dependent photodimerization.[3a,6] We thus decided that *anti*-[2.2](1,4)pentacenophane would be an attractive model system for studying charge transfer and communication between the pentacene chromophores. Herein we report our synthesis of *anti*-[2.2](1,4)pentacenophane **2b** and the preliminary characterization of its optical and electrochemical properties.

The synthesis of **2b** started from commercially available [2.2]paracyclophane **4**, which was transferred into its tetrabromo derivative **5** as described by de Meijere and co-workers (Scheme 2).[7] De Meijere et al. have shown that **5** may serve as bis(aryne) equivalent that can be used to synthesize the cycloadducts **6** as mixture of stereoisomers (*syn* and *anti*) by Diels–Alder reactions with furan.[7] This mixture was treated with 3,6-di(2-pyridyl)-1,2,4,5-tetrazine in the presence of 1,4-anthraquinone. In this reaction sequence, [2.2]-(4,7)isobenzofuranophane[8] is formed as transient intermediate that undergoes Diels–Alder reactions with 1,4-anthraquinone. In this way, the scaffold **7** of the pentacenophane could be generated. Compound **7** is obtained as a mixture of diastereomers; one isomer could be isolated by column chromatography. It shows 24 signals in the $^{13}C\{^{1}H\}$ NMR spectrum, indicating the presence of only a mirror plane as

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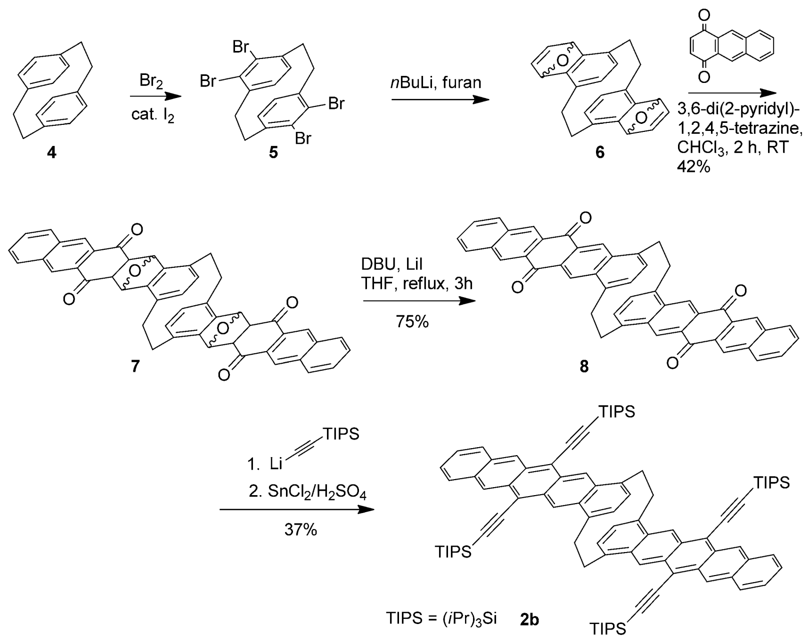

Scheme 2. Synthesis of *anti*-[2.2](1,4)pentacenophane **2b** from commercially available [2.2]paracyclophane **4**. Compounds **5** and **6** have been described previously.[7]

element of symmetry. Based on two-dimensional NMR spectroscopy, computed chemical shifts, and model compounds that were studied by X-ray diffraction, a *syn,syn-endo,exo* stereochemistry of **7** is most likely (see the Supporting Information for details). The attempted dehydration of **7** under a variety of acidic conditions resulted in formation of 1,4-anthraquinone by retro-Diels–Alder reactions. Under basic conditions using 1,8-diazabicyclo-[4.3.0]undecene (DBU), the required pentacenophane-6,13-bisquinone **8** was obtained. This bisquinone **8** is poorly soluble in common organic solvents. In D_2SO_4, the carbonyl oxygen atoms of **8** are protonated and the solubility is sufficient for NMR spectroscopy. Addition of lithium tri(isopropyl)silylacetylide to bisquinone **8** followed by reduction of the intermediate tetraol with tin chloride and sulfuric acid following an established method produces **2b**.[9]

The pentacenophane **2b** is a blue solid that is moderately soluble in common organic solvents. Its NMR spectra are in accord with expectations; in particular in $^{13}C\{^1H\}$ NMR there are eleven signals in the aromatic region in addition to two acetylenic and three aliphatic signals. High-resolution MS using atmospheric-pressure photoionization (APPI) confirms the identity of the sample. Under laser desorption ionization (LDI) conditions, a signal at the half mass is observed rather than that of **2b**. The isotope pattern excludes formation of the doubly charged ion of **2b**. We assume that under LDI conditions **2b** undergoes fragmentation into a *p*-quinodimethane derivative. Such a photoreaction was reported earlier for smaller paracyclophanes in glassy matrices.[10]

Lacking single crystals suitable for X-ray diffraction, we studied the parent compound **2a** using a *meta*-GGA along with empirical dispersion correction and a very large basis set (TPSS-D3/def2-QZVP).[11] Structures of a number of cyclophanes obtained at this level of theory were recently shown to be in excellent agreement with X-ray crystallography.[12] The molecule **2a** is of C_{2h} symmetry. The shortest distance between carbon atoms of different pentacene units is 2.77 Å, while the longer distances are 3.08 Å. The distance between geometrical centers of the upper and lower benzene rings,[12] is 3.08 Å and thus well within the van der Waals radii of carbon. Another important structural parameter is the dihedral angle involving the ethano bridges; this is 18.2° in **2a**.

The electronic absorption spectrum of pentacenophane **2b** shows the typical p band of its pentacene systems with a λ_{max} at 663 nm in dichloromethane (Figure 1). The α band can be detected at 449 nm and the β band at 337 nm. For comparison, 6,13-bis(triisopropylsilylethynyl)pentacene **3b** (synthesized using a different route than used previously;[9] see the Supporting Information for further details) has its λ_{max} of the p band at 643 nm in dichloromethane. The influence of alkyl substitution at the 1,4-positions would be gauged best by comparison with 1,4-dimethyl derivative **3c**, but this compound is not known. The known **3d**[13] hardly shows any shift of the p band compared to **3b**. Therefore, the alkyl groups in **2b** are not expected to appreciably shift the p band. The bathochromic shift (roughly 20 nm) of **2b** compared to **3b** is thus due to coupling of the two pentacene molecules.

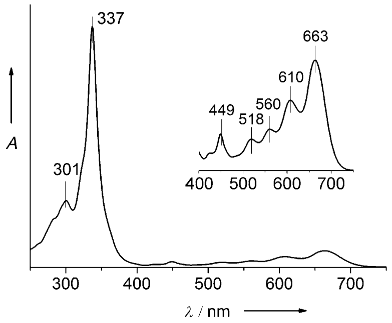

Figure 1. UV/Vis spectrum of **2b** in CH_2Cl_2.

This coupling results in a splitting of the HOMO as well as the LUMO levels in model compound **2a**, as indicated in Figure 2, reminiscent of Davydov splitting in organic crystals. This splitting has consequences for the lowest lying excited state of **2a** (S_1), as revealed by computations at the RICC2/def2-TZVP level of theory. While for pentacene (**3a**) the S_1 state results almost exclusively from a HOMO→LUMO excitation (540 nm at RICC2), the S_1 state in **2a** has a significant contribution from a HOMO-1→LUMO+1 excitation. An additional excited state (S_2) results that is characterized by a large contribution of HOMO-1→LUMO+1 (76.2%) and a minor contribution from a HOMO→LUMO excitation (7.3%). This S_2 state is

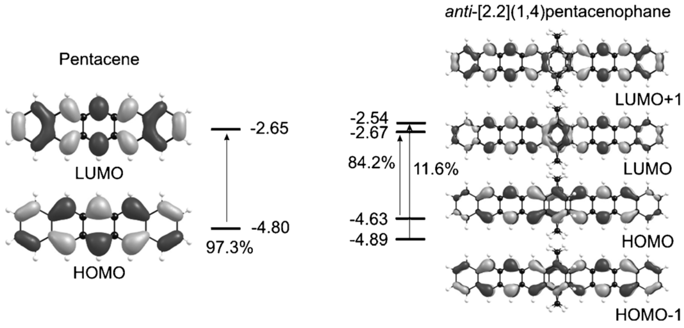

Figure 2. Molecular orbitals and energies [eV] of pentacene and *anti*-[2.2](1,4)pentacenophane **2a** as computed at the B3LYP/def2-TZVP level of theory. The composition of the excited-state wavefunction (S_1) with respect to the Hartree–Fock configuration is given in percent and was computed at the RICC2/def2-TZVP//TPSS-D3/def2-QZVP level of theory.

calculated to lie roughly 5200 cm^{-1} higher in energy than S_1 and is associated with a lower oscillator strength ($f = 0.018$) than S_1 ($f = 0.070$). The incorporation of two pentacene monomers into a dimer **2b** is computed to shift the p band by roughly 1600 cm^{-1}. This shift is larger than the one measured, and it is unclear if this difference is due to the neglect of solvent effects and of the silylethynyl groups in the calculations or due to an overestimation of the interaction at the RICC2 level.

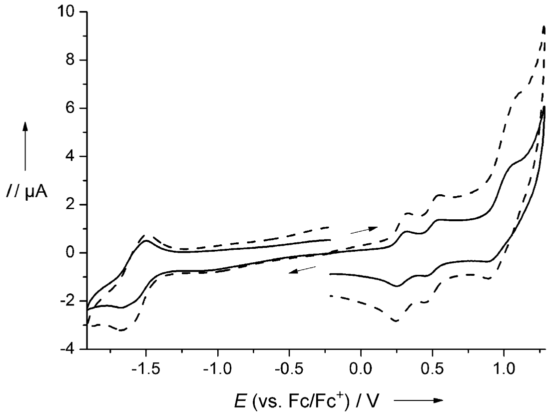

Figure 3. Voltammograms of **2b** ($c = 0.11$ mM) in CH_2Cl_2/0.1 M NBu_4PF_6 at Pt at scan rates $\nu = 0.2\ Vs^{-1}$ (——) and $\nu = 0.5\ Vs^{-1}$ (-----); start potential −0.215 V for the anodic and the cathodic cycle; voltammograms are not corrected for background current.

Cyclic voltammograms (Figure 3) of **2b** in CH_2Cl_2/0.1 M NBu_4PF_6 at a Pt electrode show signals in both the oxidation and reduction potential range. Two reversible peak couples with mid-point potentials at $\bar{E} = +0.285$ and $+0.515$ V (all potentials vs. the Fc/Fc$^+$, Fc = ferrocene) are followed by a more intense third oxidation peak close to the anodic potential limit with only a minor reverse peak that increases in relative intensity with faster scan rates (chemical follow-up reaction). We attribute the first two redox processes to the stepwise two-electron oxidation of **2b** to the radical cation and dication. The current of the first oxidation peak is proportional to the square root of the scan rate, indicating a diffusion-controlled electron transfer. The potential splitting ($\Delta\bar{E} = 0.23$ V) is larger than observed for the tetramethoxy derivative of the [2.2](1,4)anthracenophane and almost as large as in the corresponding naphthalenophane.[4c] A direct comparison with these compounds bearing electron-donating substituents, however, is hampered by possible substituent effects.

The reduction signal at about −1.6 V indicates again chemical reversibility. It is composed of two closely spaced peak couples and corresponds to the two-step reduction to the radical anion and dianion. Compared to **1** with $\Delta\bar{E} = 0.275$ V,[4b] the potentials of the two redox steps are separated by only about 0.1 V, indicating attenuation of the interaction between the two redox sites with increasing extension of the ring systems. The experimental differences in the $\Delta\bar{E}$ for the two oxidation and the two reduction steps, respectively, are in good agreement with density functional computations (M06-2X/6-311 + G**)[11] that arrive at approximate values of 0.3 V (oxidations) and 0.1 V (reductions). From the peak maxima of the first oxidation and the first reduction (shoulder), the HOMO–LUMO gap of **2b** is estimated as 1.9 eV, while λ_{max} implies an optical value of 1.87 eV (Figure 1) and theory at the B3LYP level gives 1.96 eV for model compound **2a** (see Figure 2).

In summary, we have described herein a synthetic access to a novel pentacene dimer covalently coupled by a [2.2]paracyclophane bridge. A combination of experimental analytical techniques and computational chemistry models provides insight into the electronic structure of this dimer. Further investigations with respect to the solid-state structure of **2b** and the interaction between the two coupled redox sites by spectroelectrochemistry and photophysical techniques are ongoing.

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