

growing indium particles, as suggested previously for indium colloids in polyvinylpyrrolidone (PVP).^[10] The second factor is also in agreement with the need for photochemical decomposition of InCp, which presumably results in rapid production of indium atoms. The organization probably occurs in a similar way to that previously observed for gold–amine complexes.^[13] In contrast to other recently reported processes of nanowire growth, this process does not need a catalyst or even a continuous injection of precursors for growth to proceed. Hence, no seeds are visible at the ends of the wires. However, indium is a low-melting element, and a process involving “molten” indium may be operative. Amorphous, pseudomolten particles, such as those previously observed in PVP,^[10] may condense onto a preferred face of a preformed crystal. Finally, it is noteworthy that small changes in the reaction conditions allow the formation of spherical nanoparticles whose size depends upon the precise conditions, but which are uniform in each case and self-assemble in two and three dimensions.

Received: March 28, 2001 [Z16864]

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[2.2]Paracyclophane/Dehydrobenzoannulene Hybrids: Transannular Delocalization in Open-Circuited Conjugated Macrocycles**

A. J. Boydston, Lidija Bondarenko, Ina Dix, Timothy J. R. Weakley, Henning Hopf,* and Michael M. Haley*

In memoriam Donald J. Cram

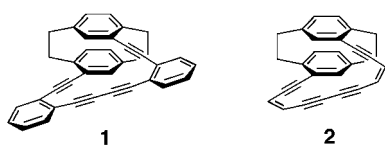
A variety of factors, such as conjugation length, planarity versus nonplanarity, double versus triple bonds, and introduction of donor and/or acceptor groups, can control the physical and chemical properties of an $[n]$ annulene.^[1] We have been involved extensively in developing the chemistry of a particular subset, namely dehydrobenzo $[n]$ annulenes (DBAs),^[2] and have shown the influence of many of the above-listed factors on DBA properties.^[3] Although the transmission of “electronic information” is easily accomplished throughout the macrocycle because of the closed circuit of conjugated π electrons, how would this transmission be affected if a small yet electronically bridgeable “gap” were installed? Inclusion in the DBA skeleton of a moiety capable of transannular interactions would provide such a test case. One particular segment that could provide a possible answer is a cyclophane.^[4] Small-sized cyclophanes are fascinating structures for annelation to a DBA skeleton in order to study transannular interactions in large macrocycles. Since the aromatic rings of a cyclophane can be fixed in a forced proximity and in a desired orientation, [2.2]paracyclophane

[*] Prof. Dr. H. Hopf, Dr. L. Bondarenko, I. Dix
 Institut für Organische Chemie
 Technische Universität Braunschweig
 Hagenring 30
 38106 Braunschweig (Germany)
 Fax: (+49) 531-391-5388
 E-mail: h.hopf@tu-bs.de

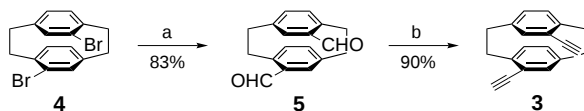
Prof. Dr. M. M. Haley, A. J. Boydston, Dr. T. J. R. Weakley
 Department of Chemistry
 University of Oregon
 Eugene, OR 97403-1253 (USA)
 Fax: (+1) 541-346-0487
 E-mail: haley@oregon.uoregon.edu

[**] This research was supported by the Petroleum Research Fund (administered by the American Chemical Society), the Fonds der Chemischen Industrie, and the Alexander von Humboldt Foundation (fellowship to M.M.H.).

(PC) in particular is characterized by a strong and unique transannular interaction between the two aromatic decks.^[5] Recent research has demonstrated how electronic communication in the PC system can be affected by varying the conjugation length of the appended substituents^[6] and by inclusion of electron-donating and -withdrawing moieties.^[7] These key model studies have provided insights into electronic delocalization between chromophores in the solid state, an important parameter to optimize when designing organic materials for optoelectronic applications.^[8] By incorporating the PC unit as part of an annulene core, we expect to observe enhanced electronic communication between the two fully conjugated decks of the annelated cyclophane. We report herein the synthesis of the novel [2.2]paracyclophane/dehydrobenzoannulene (PC/DBA) hybrids^[9] **1** and **2**, study of the transannular delocalization in these macrocycles using optical properties, and elucidation of solid-state structure of **2** by X-ray crystallography.

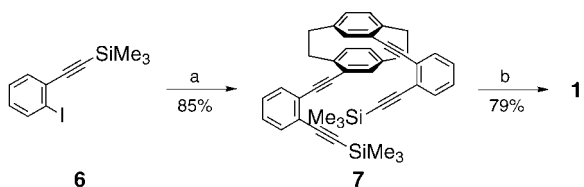


The key to PC/DBA synthesis was preparation of the parent dialkynylcyclophane **3** (Scheme 1). Metallation of dibromide **4**^[10] and treatment with *N*-formylpyrrolidine^[11] gave dialdehyde **5** in 83 % yield. This compound in turn was transformed into **3** (90 %) by using the mild alkylation procedure of Bestmann et al.^[12]



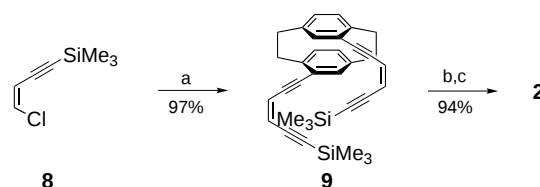
Scheme 1. Reagents: a) 1. BuLi, THF, 2. *N*-formylpyrrolidine; b) dimethyl 1-diazo-2-oxopropylphosphonate, K₂CO₃, MeOH.

PC/DBA **1** was assembled by Pd-catalyzed cross-coupling of iodoarene **6**^[3c] with diynylPC **3**, providing tetrayne **7** (Scheme 2). This material was desilylated and cyclized by using a one-pot procedure^[13] to give **1** in 67 % overall yield from **3**.



Scheme 2. Reagents: a) **3**, [Pd(PPh₃)₄], CuI, Et₃N, THF; b) K₂CO₃, CuCl, Cu(OAc)₂, py, MeOH.

The synthesis of PC/DBA **2** (Scheme 3) required a slight variation of the above route. Cross-coupling chloroalkene **8**^[14] with cyclophane **3** yielded tetrayne **9**. Use of the one-pot deprotection/cyclization method afforded **2** in a disappointing



Scheme 3. Reagents: a) **3**, [Pd(PPh₃)₄], CuI, PrNH₂, THF; b) K₂CO₃, MeOH, THF; c) Cu(OAc)₂, MeCN.

16 % yield. Stepwise deprotection and cyclization with Cu(OAc)₂ in MeCN, however, gave PC/DBA **2** in excellent overall yield (91 %).

Recrystallization from CH₂Cl₂ and pentane gave needles of **2** suitable for X-ray crystallography (Figure 1).^[15] Fusion of the annulene results in a small deviation from the normal

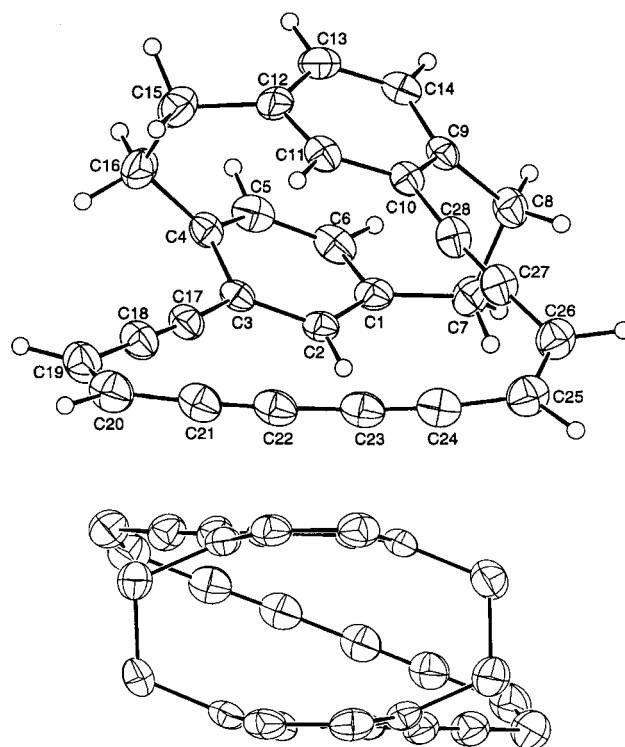
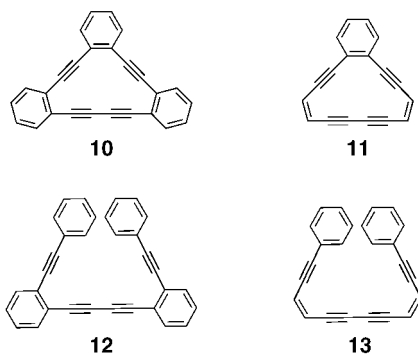


Figure 1. Structure of [2.2]paracyclophane/dehydrobenzoannulene hybrid **2**; ORTEP diagram, ellipsoids shown at the 30 % probability level.

[2.2]paracyclophane geometry. The interatomic distances between C2...C10 and C3...C11 are shortened slightly (3.06 Å) on the side of fusion, whereas the corresponding distances on the opposite side (3.09 Å) are typical for the PC skeleton. The small amount of strain in **2** caused by the 12-atom bridge is contained primarily in the diacetylene linkage, as the triple bonds deviate from linearity on the order of 5.2–9.0°. The remaining bond lengths and angles in **2** are characteristic of their respective subunits. Although Figure 1 depicts the *R* isomer of **2**, both enantiomers are present in the crystal. Given the tremendous interest in planar, chiral molecules,^[16] it should be possible to separate **1** and **2** on a chiral column or synthesize these molecules in optically active form. Such experiments are currently in progress.

To conclude whether or not “global” transannular delocalization was present in the PC/DBAs, the electronic absorption spectra of **1** and **2** were compared with those of **3**, α,ω -polyynes **7** and **9**, and dehydrobenzo[14]annulenes **10**^[17] and **11**.^[18] The most pertinent comparison, however, is with the appropriate “broken” analogues **12** and **13**,^[19] because these systems contain the same chromophores found in **1** and **2**, yet lack the transannular effects enforced by the bridging ethylene units.



For the benzannelated series, the electronic absorption spectrum of PC/DBA **1** exhibits an appreciable bathochromic shift ($\Delta\lambda \approx 25-40$ nm) relative to both the “broken” analogue **12** and tetrayne **7** (Figure 2 a). Interestingly, **1** shows approximately the same shift that is observed for **10**, but with greater absorption intensity. This suggests that the annelated cyclophane has similar electronic delocalization as the [14]annulene, but with increased electronic absorption attributable to the added electron density of the additional benzene ring in the cyclophane unit. In addition to the bathochromic shift, PC/DBA **1** also has an extended absorption cut-off relative to the other compounds in the series. These observations are most likely the result of “global” transannular delocalization occurring throughout the fully conjugated macrocycle by through-space electronic delocalization in the cyclophane.

Comparison of the electronic absorption spectra of PC/DBA **2** with diynyl cyclophane **3**, tetrayne **9**, annulene **11**, and “broken” analogue **13** (Figure 2 b) did not show the expected bathochromic shift that **1** exhibited in the previous series. However, PC/DBA **2** does have an extended cut-off point ($\Delta\lambda \approx 50-75$ nm) in the absorption spectra relative to all other compounds used in this latter series, and shows greater absorption intensity at higher wavelengths than did annulene **11**. These observations are attributable to increased effective conjugation in the hybrid because of incorporation of alkene units in place of benzene rings.

The synthesis and study of [2.2]paracyclophane/dehydrobenzoannulene hybrids has led to strong qualitative evidence of “global” transannular delocalization between the fully conjugated decks of the annelated cyclophanes. The distinct bathochromic shift, increased absorption intensity, and extended absorption cut-off observed in PC/DBAs **1** and **2** when compared to other model systems can only be the result of delocalization through the open circuit of the PC/DBAs. We plan to continue this study through the synthesis of more

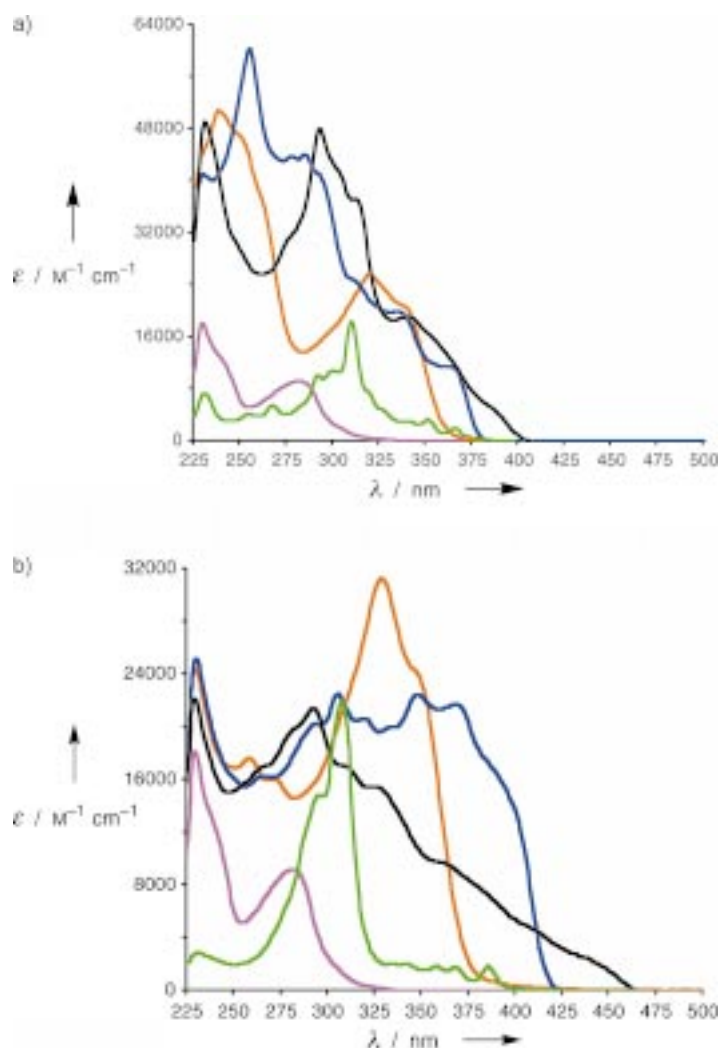


Figure 2. a) Electronic absorption spectra of PC/DBA **1** (black), diyne **3** (violet), tetrayne **7** (red), annulene **10** (green), and “broken” analogue **12** (blue). b) Electronic absorption spectra of PC/DBA **2** (black), diyne **3** (violet), tetrayne **9** (red), annulene **11** (green), and “broken” analogue **13** (blue).

complex PC/DBAs involving higher degrees of delocalization and possible “transannular aromaticity”. In addition, we are also exploring the use of these and other [2.2]paracyclophanes with polyunsaturated bridges as precursors to fullerenes and fullerene fragments, as beautifully demonstrated by the groups of Tobe^[9d] and Rubin.^[9e]

Received: April 6, 2001
Revised: June 5, 2001 [Z16913]

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The Remarkable Stable Emerald Green $C_{60}F_{15}[\text{CBr}(\text{CO}_2\text{Et})_2]_3$: The First [60]Fullerene That Is also the First [18]Trannulene**

Xian-Wen Wei, Adam D. Darwish, Olga V. Boltalina, Peter B. Hitchcock, Joan M. Street, and Roger Taylor*

The fluorofullerene $C_{60}F_{18}$ is notable for having a fully delocalized and planar hexagonal ring and a normal curved “fullerene” region; it is also a hexa-substituted benzene.^[1] Derivatives that have been made include oxides, which are produced by oxygen insertion into long FC–CF bonds (the first examples of oxahomofullerenes),^[2] trifluoroalkyl derivatives produced by insertion of CF_2 groups into C–F bonds,^[3] and a triphenyl derivative produced by nucleophilic substitution of three fluorine substituents by phenyl groups.^[4]

Annulenes have long been of interest because of the question of whether the combination of $[4n+2]$ π -electrons and approximate planarity leads to aromaticity. A number of examples are now known in which this latter condition is indicated, notably by small differences in bond lengths (which usually range from 1.38–1.40 Å) in a cyclic chain comprising either sp^2 or sp/sp^2 carbon atoms.^[5] The [18]annulenes have been of particular interest because of their presence in porphyrins, phthalocyanines, chlorophyll etc., and some have been prepared notably by Sondheimer et al., for example light brown plates of tridehydro[18]annulene.^[6] In these compounds, the C–C bonds α to the double bonds are in either an *all-cis* or a *cis,trans* relationship. Very recently, the feasibility of annulenes having *all-trans* relationships (“trannulenes”, which must have a hoop or barrel-like structure) has been

* Dr. R. Taylor, Dr. X.-W. Wei, Dr. A. D. Darwish, Dr. P. B. Hitchcock
School of Chemistry, Physics & Environmental Sciences
Sussex University, Brighton BN1 9QJ (UK)
Fax: (+44) 1273-677-196
E-mail: R.Taylor@sussex.ac.uk
Dr. O. V. Boltalina
Chemistry Department, Moscow State University
Moscow 119899 (Russia)
J. M. Street
Chemistry Department, University of Southampton
Southampton, SO17 1BJ (UK)

** This work was supported by the Royal Society (Joint Project Grant and a Sino-British Trust Award), NATO, INTAS (grant no. 97-30027), and the Russian Programme “Fullerenes and Atomic Clusters”.