direct methods and refined with full-matrix least squares (SHELX97[12]). CCDC-185351 for [NEt4]3[**4**], CCDC-185352 for [NEt4]2[**5**], and CCDC-185353 for 0.65[NEt4]5[**2**]/0.35[NEt4]4[**3**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Synthesis, X-ray Structure, and Properties of a Tetrabenzannelated 1,2,4,5-Cyclophane**

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Parylene is the most frequently used material in the protective encapsulation of modern electronic components and medical implants.[1] This high-performance polymer is produced by the pyrolytic decomposition of [2.2]paracyclophane.[1c] Another high-performance organic material with even stronger C−C bonds would be produced if another highly strained, all-aromatic cyclophane could be pyrolyzed, thus resulting in a "superparylene". However, contrary to the mode of pyrolytic decomposition of [2.2]paracyclophane, where scission of the $C_{sp^3}-C_{sp^3}$ bond is the important first step leading to a p-xylylene monomer, in the case of a molecule such as **1** (Scheme 2), cleavage of a biaryl bond would produce a very reactive diradical monomer.

Angle and bond strain in organic molecules and their effect on properties also continue to be an active field of research.[2]

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Over the last five decades, a substantial number of chemists have prepared many fascinating, strained saturated and unsaturated molecules.[2,3] The most notable of the strained unsaturated molecules are those of the fullerene C60[4] and the cyclophane families.[5] In the former, the hexagons are essentially cyclohexatrienes[6] and in the latter, the hexagons, while considerably distorted, still retain their benzenoid character. Since the first synthesis of [2.2]paracyclophane diene by Dewhirst and Cram,[7] a variety of [2.2]paracyclophanes with unsaturated or benzannelated bridges have been synthesized.[8] The influence of the bridges on the trans-annular benzene interactions and the geometry of the strained cyclophanes has been widely investigated.[9] To date, only a few unsaturated bridged and benzannelated cyclophanes are known,[9] but no benzannelated [2n]cyclophane with more than two bridges ($n > 2$) has been reported.[10] One would expect that, as the number of o-phenylene bridges increased, the total strain would also increase.

To prepare a superparylene and to test the effect of benzo bridges in place of the alkyl bridges of cyclophanes one needs a rapid, reasonably high-yield synthetic entry. A priori, based on existing cyclophane synthetic methodology, the preparation of a symmetrical tetrabenzannelated [2n]cyclophane tetraene would appear to be rather difficult and lengthy. However, careful consideration of the molecular symmetry of the target revealed that the synthesis could be easily achieved. Herein, we describe the synthesis, X-ray structure, and some of the properties of the symmetrically benzannelated [24]cyclophane tetraene **1**. In future publications we will report on the results of its pyrolytic decomposition.

In Scheme 1 we depict the retrosynthetic analysis with a rather unusual disconnection leading to two dibenzocyclooctadiene-diynes and four methine units. As shown, the latter can originate from a *meso*-ionic precursor.
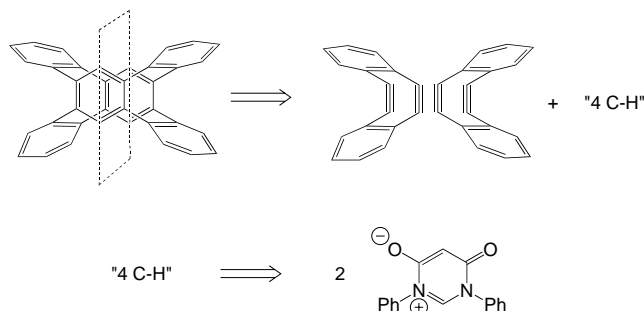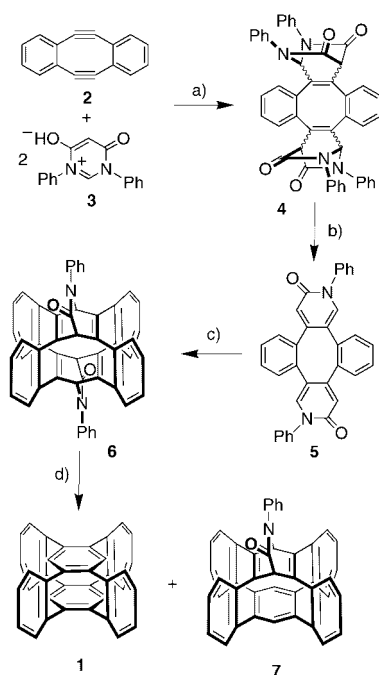

Scheme 1. Retrosynthetic analysis of **1**.

The synthesis of the tetrabenzocyclophane **1** is based on the known Diels–Alder reactivity of diene **3**[11] to afford **4** (as a mixture of *syn* and *anti* isomers),[12] followed by thermal extrusion of phenyl isocyanate, which leads to a new reactive diene **5** (Scheme 2).[13] The twofold addition of **2**[14] to **3** afforded the bisadduct **4** in 70% yield; the monoadduct does not form even with a 1:1 ratio of reagents. Pyrolysis of **4** gave reactive diene **5** quantitatively. Compound **5** has absorption maxima at 252 and 333 nm, and exhibits a weak blue fluorescence at 406 nm (in THF). It reacts with an excess of

Scheme 2. Synthesis of cyclophane **1**. a) *o*-dichlorobenzene (ODCB), 110°C, 1 day; b) neat, 250°C, 1 h; c) **2**, ODCB, 150°C, 3 d; d) neat, 350°C, 4 h.[13]
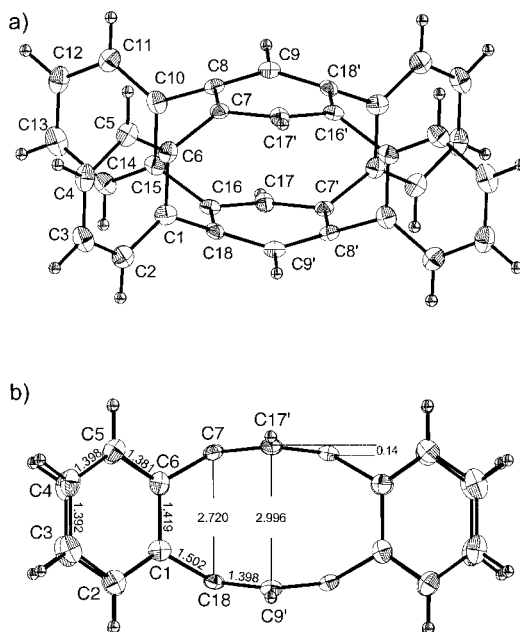

Figure 1. The X-ray structure of **1**. ORTEP view and numbering scheme of the independent molecule located on an inversion center (with 50% probability displacement ellipsoids). Selected bond angles [°]: C10-C15-C16 116.3(3), C17-C16-C18 118.5(4), C17-C16-C15 117.8(3), C18-C16-C15 119.6(3), C18′-C9-C8-C7 12.7(3).

dienophile **2** to give compound **6** in 25% yield, without polymerization but accompanied by decomposition products of diyne **2**. The absence of polymerization is the result of: 1) the high dilution conditions and 2) the preorganization, arising from the boat conformation of the intermediate that results from the intramolecular cycloaddition to form **6**. Pyrolysis of **6** afforded a mixture of **1** (50% isolated) and **7** (30% isolated), which co-sublime at this temperature. In contrast to **4**, cyclophane precursor **6** is less willing to extrude its phenylisocyanate bridges. Thermogravimetric analysis (TGA) of **4** showed that the loss of the isocyanate occurred between 200 and 250°C, whereas with **6** a temperature of 350°C is required (see Supporting Information).

The thermally stable cyclophane **1** was isolated by column chromatography and characterized by ¹H and ¹³C NMR spectroscopy. Slow evaporation of a solution of **1** in CS₂ at 40°C afforded colorless platelike crystals suitable for X-ray structural analysis (Figure 1).[15] To assess the electronic structure of **1** we performed quantum mechanical density functional theory calculations[16] at the B3LYP/6-31G(d) level of theory[17] (used for discussion of structural features) as well as ab initio calculations at the HF/3-21G* level[18] (used for discussion of orbital energies).[19,20]

The independent unit in the crystal is located at an inversion center and forms layers. The benzene moiety is significantly bent with deviation from planarity for the carbon skeleton of 0.133–0.139 Å (calcd 0.153 Å) and a C18′-C9-C8-C7 dihedral angle of 12.7–13.7° (calcd 14.6°) between the C—C bonds in the benzene moiety. A very significant strain is reflected in a large angle between the C6—C7 bond and the C7-C8-C17′ plane (19.8–21.4°). The sum of three linear angles around C7 is 355.4–356.0° (calcd 355.8°), which reflects its partial sp³ character. The C-C-C angles (e.g., C1-C6-C7) in the

benzo bridges are distorted to 115.3–116.3° (calcd 116.2°) and the C—C bond in the bridges is elongated to 1.419–1.424 Å (calcd 1.427 Å). The C9—C17 bond between the central carbon atoms of the cyclophane rings is 2.996 Å (calcd 3.060 Å), while the calculated distance between the two strained ring protons is shorter,[21] at 2.912 Å.[22] Consequently, in NMR experiments the C9 carbon atoms of the strained rings resonate at low field (δ: 139.3 ppm)[23] and the adjacent protons resonate at higher field (δ: 6.57 ppm).

The UV/Vis spectrum, with two absorptions at 225 and 285 nm, is comparable to that of previously reported cyclophanes,[24] but with an important exception: the broad "cyclophane band" appears at 330 nm, which is the most red-shifted position of this band recorded to date. Electrochemical experiments show an irreversible oxidation at $E_{p.c.} = +1.49$ V versus the ferrocene/ferrocenium couple[25] and a reversible reduction wave at $E^0 = -2.80$ V for **1**. This observation should be contrasted with the oxidation wave for [2.2]paracyclophane ($E_{p.c} = 1.10$ V, no reduction peak was observed down to −3.0 V) under the same conditions. At first sight, the large negative value observed for **1** is contrary to expectations based on strain arguments in fullerene chemistry, where the electron-accepting property was related to strain (hybridization).[26] However, results of ab initio calculations indicate that although the LUMO (2.45 eV, Figure 2b) is lower lying than that of benzene (4.12 eV), it is higher than that of anthracene (1.81 eV), which reduces at a less negative potential ($E^0 = -2.47$ V). On the other hand, the larger value for the oxidation wave of **1** relative to [2.2]paracyclophane is consistent with increased strain in **1** compared with [2.2]paracyclophane; C₆₀ is also easier to reduce than to oxidize.[27] The HOMO of cyclophane **1** (−8.21 eV Figure 2a) is relatively high, lying between that of benzene (−9.22 eV) and anthra-
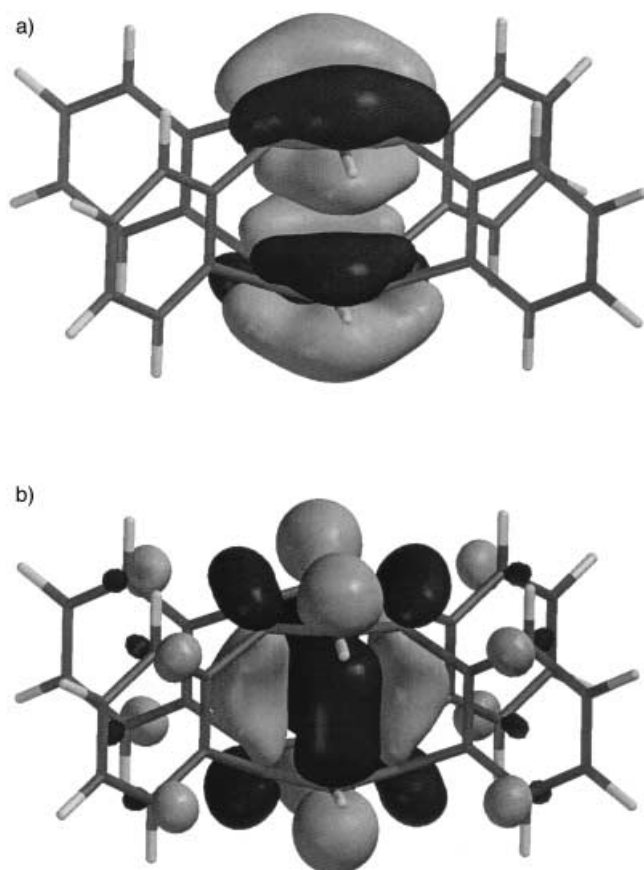
a)

b)

Figure 2. a) The HOMO and b) LUMO of **1** as calculated at HF/3-21G*// HF/3-21G* level, generated with Spartan 5.0.3.

cene (-7.16 eV). These low LUMO and high HOMO energies are further evidence of molecular strain.

As a result of the high HOMO energy, **1** is expected to be very reactive as a diene in Diels–Alder reactions. Indeed, the unusual electronic properties of the strained rings in **1** are manifested in their high reactivity towards tetracyanoethylene (TCNE).[28] The published cyclophane (closest in structure to **1**), [2$_4$](1,2,4,5)cyclophane,[29] forms a blue charge-transfer (CT) complex which lasts "a few seconds",[30] followed by formation of the Diels–Alder adduct. In addition, a highly strained pyrene belt cyclophane[28] is converted at first into a green CT complex with a lifetime of minutes.[31] In comparison, **1** reacts with TCNE directly, without the detection of a CT band (either visual or spectrophotometric) to produce adduct **8** in almost quantitative yield (Scheme 3). The disappearance of the "cyclophane" band, without the appearance of a CT band, can be followed spectroscopically (see Supporting Information).
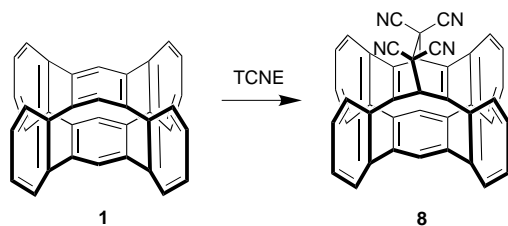
Scheme 3. Addition of TCNE to cyclophane **1**.

In conclusion, we have described a simple, symmetry-driven synthesis of a strained, very thermally stable cyclophane. The distorted aromatic rings are more reactive with TCNE than those in [2.2]paracyclophane. Another consequence of heightened strain is a bathochromic shift of the cyclophane band to 330 nm, the longest wavelength absorption observed for this band to date. By using this methodology other benzo-ring-substituted cyclophanes should now be accessible through functionalized dibenzocyclooctadienediyne.[32]

Experimental Section

All syntheses were performed under argon. See Supporting Information for detailed characterization of **4**–**6** and details of the reaction of **1** with TCNE.

4: A solution of **2** (100 mg, 0.500 mmol) and **3** (315 mg, 1.05 mmol) in *o*-dichlorobenzene (ODCB, 6 mL) was stirred at 110 °C until full conversion of **2** was indicated by thin-layer chromatography (TLC, 1 day). The red reaction mixture was evaporated in vacuo, and purified by column chromatography on silica (eluting with hexane/ethyl acetate, 1:1 v/v) to yield compound **4** (250 mg, 70%), which can be further purified by recrystallization from chloroform, m.p. 250 °C (decomp).

5: Compound **4** (50 mg, 0.069 mmol) was heated to 250 °C for 1 h in vacuo and then purified by column chromatography on silica (eluting with hexanes/ethyl acetate, 1:1 v/v) to give **5** as a light-orange powder (32 mg, 95%), m.p. > 350 °C.

6: A solution of **5** (50 mg, 0.10 mmol) in ODCB was slowly added (16 h, using syringe pump) to a solution of **2** (20 mg, 0.10 mmol) in ODCB (5 mL) at 150 °C. The reaction mixture was stirred at 150 °C until full consumption of **5** (3 days, TLC monitoring), then ODCB was distilled in vacuo and the solid residue was purified by column chromatography on silica (eluting with chloroform) to give **6** as a powder (17 mg, 25%), m.p. 350 °C (decomp).

1: Compound **6** (30 mg, 0.043 mmol) was heated in a sublimation apparatus to 350 °C for 4 h and the sublimed material was purified by column chromatography on silica (eluting with chloroform). The first fraction (R_f ca. 0.8) gave the target product **1** (10 mg, 50%) as a white powder, m.p. > 350 °C (sublim). ¹H NMR (CDCl₃, 400 MHz): δ = 6.57 (s, 4H), 7.21 (q, J = 3.5 Hz, 4H), 7.38 ppm (q, J = 3.5 Hz, 4H); ¹³C NMR (Cl₂(CD)₂Cl₂, 125 MHz): δ = 124.6, 127.0, 139.3, 143.4, 144.3 ppm; UV/Vis (*c*-C₆H₁₂, λ_{max}, (ε)) = 225 (30300), 285 (3020), 330 nm (110); IR (DRIFT): $\tilde{v}$ = 3060, 3024, 2924, 1444, 1234, 916, 750, 516 cm⁻¹; *m/z* (EI): 452 (M^+, 100). HRMS (EI): calcd for [C₃₆H₂₀]: 452.1565; found: 452.1556. The second fraction afforded an intermediate **7** (7.4 mg, 30%), m.p. > 350 °C, which can be converted into **1** under the conditions described for **6**.

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[12] Compound **4** should be formed as a mixture of *syn* and *anti* isomers; the relative ratio of *syn:anti* cannot be determined on the basis of NMR spectroscopy (see Supporting Information). We speculate the *anti* isomer for compound **4** to be preferentially formed as a result of 1) steric repulsion between two phenyl substituents (located on opposite sides of the saddle-shaped dibenzocyclooctatetraenene ring and 2) minimization of dipole–dipole interactions of the lactam carbonyls.

[13] Although a single isomer is shown for compounds **5** and **6**, one cannot say with certainty if it is the *anti* isomer (as shown). Chromatographic isolation of **5** and **6** produces a single isomer, as evidenced by NMR spectroscopy. However, final structural determination will have to rest with X-ray crystallography. It is possible that recrystallization of **4**, prior to pyrolysis, allowed selection of only one isomer, which could then only produce a single isomer of **5** (and hence **6**).

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[15] Crystal data for **1**: Single crystals were obtained by slow evaporation from CS_2. Compound **1** ($C_{36}H_{20}$, $M_r = 452.52$) crystallizes in the triclinic space group $P\bar{1}$, $a = 8.541(6)$, $b = 8.651(6)$, $c = 9.114(6)$ Å, $\alpha = 83.671(12)$, $\beta = 68.044(12)$, $\gamma = 62.543(10)°$, $V = 552.6(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.360$ g cm^{-3}, $F(000) = 236$, $T = 100(2)$ K. Data collection: Bruker AXS CCD with graphite-monochromatic Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystal dimensions: $0.10 \times 0.15 \times 0.20$ mm; $4.8 \leq 2\theta \leq 56.04°$; 3102 measured reflections, of which 2136 [$R_{int} = 0.047$] were independent and were used for the structure refinement of 163 parameters. An empirical absorption correction (SADABS) was applied. The structure was solved by direct methods using SHELXS-97 and refined by the full-matrix least-squares method on F^2 using SHELXL-97 (G. M. Sheldrick, SHELXS-98, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**) with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions (riding model) with C_{sp^2}–H bond lengths of 0.95 Å. At convergence, $R1 = 0.0888$ ($I > 2\sigma(I)$) and w$R2 = 0.2345$; min/max residual electron density: $-0.371/ + 0.490$ e Å^2. CCDC-184166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+ 44)1223-336-033; or deposit @ccdc.cam.ac.uk).

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[20] All molecules were fully optimized and frequency calculations were performed at the same level for all stationary points to check that all frequencies are real and, consequently, all the calculated structures are minima on the potential energy surface. **1** has molecular D_{2h} symmetry.

[21] The perspective in Figure 1b, which shows a wider distance between the protons at C9′ and C17′ than the carbon atoms to which they are bonded, is misleading since the actual positions were not determined from the data and are an artifact resulting from hydrogen atom placement by the program.

[22] The known X-ray structure of [2$_4$](1,2,4,5)cyclophane (A. W. Hanson, *Acta Crystallogr. Sect. B* **1977**, *33*, 2003) is very similar to **1**: the separation of the central carbon atoms of the two rings is 2.950 Å, and that between the two strained ring protons is 2.919 Å (calcd value). The dihedral angle between the C–C bonds in the benzene moiety is 12.2°.

[23] GIAO-B3LYP/6-311 + G(d,p)//B3LYP/6-31(d) calculations corrected for the chemical shift of benzene ($\delta = 134.8$ calcd, 128.0 ppm exptl) predict chemical shifts of $\delta = 141.4$, 147.8, 148.3, 125.0, and 126.6 ppm for C9, C8, C6, C5, and C4, respectively, which allows an assignment of the experimentally observed resonance at $\delta = 139.3$ ppm to the C9 carbon atom.

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