First Dewar benzene approach to acetylenic oligophenylene macrocycles: synthesis and structure of a molecular rectangle bearing two spindles

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A novel Dewar benzene approach to the construction of oligophenylene macrocycles has been developed by introducing Dewar benzene 1 as a building block and applied to the synthesis of a molecular rectangle 8, whose structure was characterized crystallographically.

During the course of our study on small cyclophanes generated from the corresponding Dewar derivatives,[1] we were interested in exploiting a Dewar benzene for the construction of macrocyclic structures, especially for the synthesis of *p*-phenylene-based rigid, and thus strained, macrocycles. Since the bent shape of Dewar benzene is expected to provide a unique template effect on the cyclization, novel macrocyclic systems which are difficult to access from planar benzene derivatives may well become available based on the Dewar benzene approach. Here we report the rational and efficient synthesis of a novel rectangular macrocycle **8** using acetal-bridged Dewar benzene **1** as a building block, together with its crystallographic characterization. Phenylene acetylene macrocycles have attracted considerable recent attention in supramolecular chemistry and materials science.[2]

Dewar benzene **1** was readily prepared in four steps and on a gram scale from DMAD and 1,2-dichloroethylene.[3] Palladium-catalyzed coupling of **1** with **2**† afforded diethynylation product **3** (55% yield), which was then deprotected to **4** in 80% yield (Scheme 1). Copper-mediated oxidative coupling of **4** with CuCl/Cu(OAc)$_2$[4] in pyridine under pseudo-high-dilution conditions produced cyclic dimer **5**‡ in 70% yield. Acid hydrolysis of **5** followed by the silylation of resulting tetraol **6** afforded **7**§ in 73% yield. Photochemical isomerization of **7** proceeded smoothly and cleanly by irradiation with a high-pressure mercury lamp through Pyrex at 12 °C to afford **8**§ in quantitative yield. The less symmetrical product resulting from the rearrangement of only one of the Dewar benzene units was not detected by ^{1}H NMR monitoring of the reaction.

It is interesting to note that, in the ^{1}H NMR spectra, the benzylic protons of **7** appear as a pair of AB doublets (δ 4.10 and 4.12, J = 11 Hz) while those of **8** appear as a singlet (δ 4.95), indicating that these protons are diastereotopic in **7** and operationally enantiotopic in **8**. These observations would be most reasonably explained by postulating fast interconversion between the rotamers **8a** and **8b**, namely, fast rotation of the *p*-phenylene unit(s) in **8** on the NMR timescale despite the strained nature of the macrocycle.[5]

Crystals of **8** suitable for X-ray structure determination (Fig. 1) were obtained by slow diffusion of EtOH into a solution of **8** in CHCl$_3$ at room temperature.¶ The molecule adopts a nearly planar conformation in the crystal and the dimension of framework is 7.32 × 11.54 Å, as defined by the four inner *m*-phenylene carbon atoms. Interestingly, the framework appears to be distorted to a parallelogram to accommodate two SiMe$_2$OCH$_2$ moieties inside the cavity. The twist angles of the benzene rings from the least-square plane formed by the acetylenic carbon atoms are 3.7 and 0.4° in the *m*-phenylene units and 3.4° in the *p*-phenylene units. The benzene rings are essentially planar (deviation < 0.01 Å) while the acetylene units show small deviation from linearity with the C≡C–C angles of 168.7(3)–179.9(3)°.

In conclusion, we have successfully synthesized and characterized a novel rectangular macrocycle **8** by introducing **1** as a building block. The high efficiency of the macrocyclization of **4** into **5** demonstrates the synthetic utility of a Dewar structure as a ‘masked’ *p*-phenylene unit. Further elaboration and application of the present Dewar benzene strategy are now in progress.

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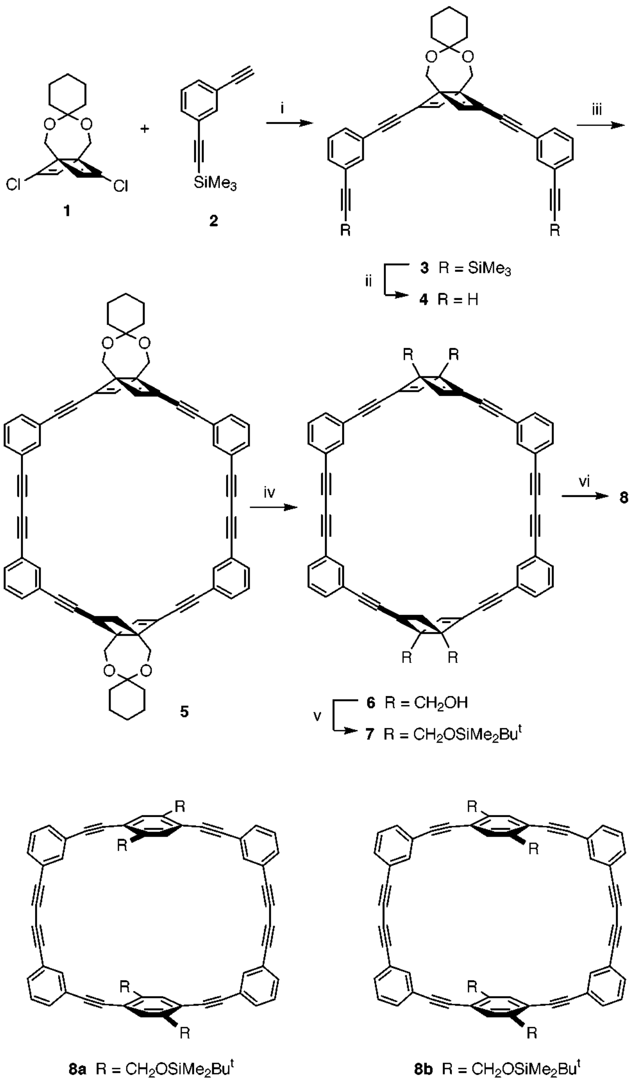

Scheme 1 *Reagents and conditions*: i, Pd(PPh$_3$)$_4$, CuI, Et$_3$N, 45 °C, 55%; ii, Bu$_4$NF, THF, 0 °C, 80%; iii, CuCl, Cu(OAc)$_2$, Py, syringe-pump addition over 2 h, 60 °C, 70%; iv, aq. HCl, THF, room temp., 98%; v, Bu^{t}Me$_2$SiOTf, Et$_3$N, CH$_2$Cl$_2$, room temp., 75%; vi, $h\nu$, CH$_2$Cl$_2$, 12 °C, 100%.

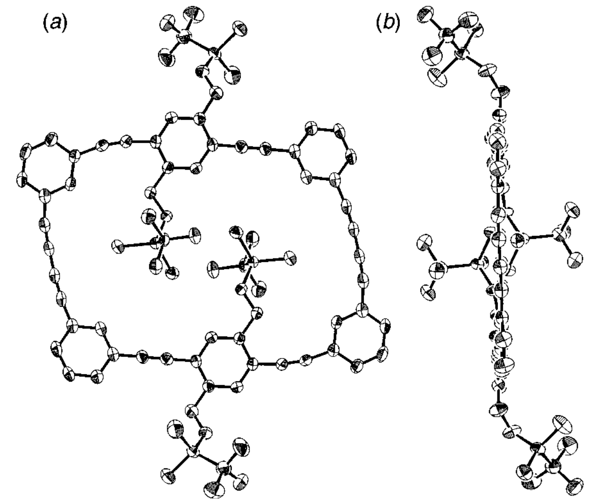

Fig. 1 Molecular structure of **8**: (*a*) top view, (*b*) side view. Hydrogen atoms are omitted for clarity.

Notes and references

† Compound **2** was prepared by partial desilylation of 1,3-bis[(trimethylsilyl)ethynyl]benzene (ref. 6) with aqueous KOH/MeOH in 60% yield.

‡ The isolated **5** was spectroscopically homogeneous although two stereoisomers arising from relative orientation of the Dewar units are possible. Only one of the possible isomers is depicted in Scheme 1. Compounds **6** and **7** were also spectroscopically homogeneous.

§ *Selected data* for **7**: δ_H(400 MHz, CD_2Cl_2) 0.08 (s, 24H), 0.92 (s, 36H), 4.10 (d, *J* 11.0, 4H), 4.12 (d, *J* 11.0, 4H), 6.83 (s, 4H), 7.29 (t, *J* 7.8, 4H), 7.38 (dt, *J* 7.8, 1.5, 4H), 7.52 (dt, *J* 7.8, 1.5, 2H), 7.70 (t, *J* 1.5, 2H); δ_C(100 MHz, CD_2Cl_2) −5.36, −5.23, 18.61, 26.05, 60.93, 66.42, 74.62, 81.31, 85.05, 94.77, 122.42, 124.11, 129.12, 131.75, 131.85, 136.18, 137.14, 146.02. For **8**: δ_H(400 MHz, CD_2Cl_2) 0.15 (s, 24H), 0.96 (s, 36H), 4.95 (s, 8H), 7.36 (t, *J* 7.8, 4H), 7.41 (dt, *J* 7.8, 1.5, 4H), 7.49 (dt, *J* 7.8, 1.5, 2H), 7.66 (s, 4H), 7.88 (t, *J* 1.5, 2H); δ_C(100 MHz, CD_2Cl_2) −5.07, 18.82, 26.24, 63.56, 75.37, 82.73, 89.08, 95.11, 120.79, 122.62, 124.36, 129.32, 130.13, 130.34, 130.92, 139.73, 142.36.

¶ *Crystal data* for **8**: $C_{80}H_{88}O_4Si_4$, $M = 1224.6$, colorless plate (0.60 × 0.30 × 0.05 mm), triclinic, $P\bar{1}$, $a = 12.926(1)$, $b = 17.570(2)$, $c = 8.074(1)$ Å, $\alpha = 93.356(4)$, $\beta = 97.690(3)$, $\gamma = 79.755(4)°$, $V = 1787.1(3)$ Å^3, $D_c = 1.14$ g cm^{-3}, $Z = 1$, Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 203$ K, $\mu = 1.3$ cm^{-1}, $F(000) = 656$. A total of 7513 unique reflections ($2\theta_{max} = 55°$) were collected, of which 5339 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 398 parameters) to give final $R = 0.063$ and $wR = 0.069$. Residual electron density is 0.45 e Å^{-3}. CCDC 182/1496.

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