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[25] The difference in the ΔSE values for the cyclization of **4** and **3** was calculated to be 2.79 kcal mol^{-1}. Full theoretical calculations will be reported in a forthcoming account of this work.

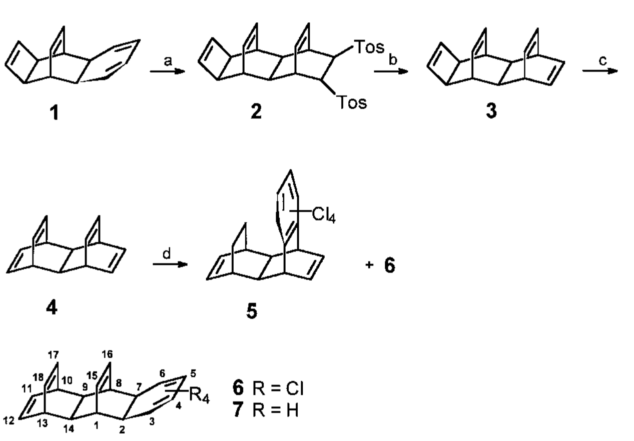
Tetrachloro-*p*-(*o*,*p*)-*o*-tribenzene: A Building Block for Diels – Alder Oligomers of Benzene and for a Laticyclic Conjugated Hexaene**

Wolfram Grimme,* Joachim Gossel, and Johann Lex

Dedicated to Professor Emanuel Vogel
on the occasion of his 70th birthday

Some time ago we reported on *p*-(*o*,*p*)-*o*-tribenzene (**7**), the *endo*,*endo*-Diels – Alder trimer of benzene, and anticipated higher oligomers of this type.[1] However, experiments designed to dimerize the tribenzene by a Diels – Alder reaction failed up to 100 °C and 7.5 kbar, the limits of the compound's stability; dimerization apparently requires an activated tribenzene. We report here on tetrachloro-*p*-(*o*,*p*)-*o*-tribenzene (**6**), which undergoes a Diels – Alder reaction with itself under reverse electron demand.[2]

Cycloaddition of (*E*)-1,2-ditosylethene[3] to the tetracycle **1**[1] yields adduct **2**, which can be detosylated with sodium amalgam to pentacycle **3** (Scheme 1). In the next step the cyclobutene ring is degraded by the Dauben method,[4] which entails cycloaddition of 2,5-dimethyl-3,4-diphenylcyclopentadienone followed by photoextrusion of CO and 1,4-dimethyl-2,3-diphenylbenzene. The resulting sesquibicyclo[2.2.2]octadiene (**4**), synthesized previously by another route,[5] undergoes cycloaddition of tetrachlorothiophene dioxide (TCTD)[6] preferentially at one of the laticyclic conjugated double bonds. Through SO_2 extrusion and a dyotropic hydrogen transfer[7] at room temperature the arene **5** is formed. The desired tetrachlorotribenzene **6** is obtained from addition to one of the terminal double bonds (**6**:**5** = **1**:**3**).



Scheme 1. a) (*E*)-Ditosylethene, EtOAc, reflux, 24 h, 96 %; b) Na(Hg) 2 %, NaH_2PO_4, MeOH, 25 °C, 16 h, 85 %; c) 1. 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer, benzene, 70 °C, 16 h, 95 %; 2. diethyl ether, low-pressure Hg burner, 2 h, 49 %; d) TCTD, benzene, 25 °C, 16 h, 95 %.

Compound **6** cycloreverts to benzene and tetrachlorobenzene at 110.8 °C with a half life of $t_{1/2} = 52$ min, a reaction rate

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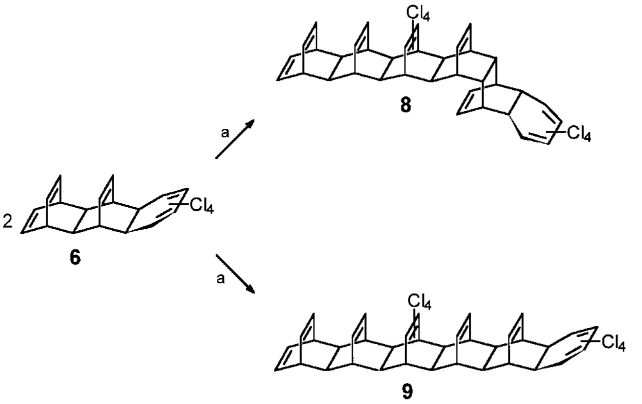
which is similar to that of the parent tribenzene **7** ($t_{1/2}$ = 80 min) and supports our earlier conclusion[1] that the *para*-bonded benzene ring splits off first. Following cycloreversion of **6** in squalane in a differential scanning calorimeter (DSC7, Perkin–Elmer) at a heating rate of 40 K min^{-1}, one observes a heat of reaction of $\Delta H = -23.3$ kcal mol^{-1} in the range of 140–200 °C. Since at this temperature the heat of evaporation of two molar equivalents of benzene must be consumed, the heat of cycloreversion of **6** amounts to $\Delta H_r = -23.3 - 2 \times 7.7 = -38.7$ kcal mol^{-1}. A force-field calculation[8] gives $\Delta H_r = -41.7$ kcal mol^{-1} when one takes into account that the heat of dehydrogenation of 1,2,3,4-tetrachlorocyclohexa-1,3-diene is approximately 4.5 kcal mol^{-1}.[9]

For dimerization, **6** is heated in benzene for 24 h at 70 °C under a pressure of 7.5 kbar (Scheme 2). Subsequent liquid chromatography (silica gel, *n*-hexane) provides recovered **6** (40 %) and, after changing the eluant to CCl_4, a mixture of lower oligomers (40 %). Complete cycloreversion of this fraction to benzene/tetrachlorobenzene (2/1) after 72 h at 110 °C proves that only Diels–Alder oligomers are present. Medium-pressure liquid chromatography (LiChroprep Si 60, 15–25 μm, benzene/cyclohexane 1/10, 5 bar) permits isolation of the angular octachlorohexabenzene **8** (9 %) and the linear all-*endo* isomer **9** (5 %) from this mixture. The former shows two ^{1}H NMR signals above $\delta = 6.2$, which is characteristic of two nonlaticyclic conjugated double bonds, and a singlet at high field ($\delta = 1.59$) for two *endo* protons at the ring junction that interrupts the laticyclic conjugation (Table 1). The extended laticyclic conjugation of **9** gives rise to a broad band at 260–300 nm in the UV spectrum that is partly obscured by the hypsochromic portion of the tetrachlorocyclohexadiene absorption.



Scheme 2. a) Benzene, 70 °C, 24 h, 7.4 kbar.

Cycloreversion of the two hexabenzenes begins at 110 °C with the successive extrusion of two *p*-bonded benzene units and results after 48 h in complete decomposition to benzene and tetrachlorobenzene. In the case of the linear hexabenzene **9**, short reaction times permit isolation of octachloropentabenzene **10** and octachlorotetrabenzene **11** (Scheme 3).

Table 1. Selected spectroscopic data for **5**, **6**, **8**–**15** (^{1}H NMR spectra at 300 MHz and ^{13}C NMR spectra at 75.5 MHz in $CDCl_3$ with TMS as internal standard).

5: M.p. 207 °C (hexane); ^{1}H NMR: $\delta = 6.55$, 6.21, 4.21, 2.35, 1.93, 0.74 (CH_2), 0.52 (CH_2); ^{13}C NMR: $\delta = 142.9$, 137.6, 128.7, 128.4, 42.2, 42.1, 33.7, 19.6; UV/Vis (*n*-hexane): λ_{max} (ε) = 244 (8000, sh), 225 nm (34 500).

6: M.p. 145 °C (decomp); ^{1}H NMR: $\delta = 6.41$(m, 2H, 11,12-H), 5.86 (m, 2H, 17,18-H), 5.82 (m, 2H, 15,16-H), 3.41 (br s, 2H, 10,13-H), 3.10 (br s, 2H, 1,8-H), 3.05 (s, 2H, 2,7-H), 1.95 (s, 2H, 9,14-H); ^{13}C NMR: $\delta = 137.0$ (C-4,12), 132.3 (C-3,6), 131.5 (C-17,18), 123.3 (C-4,5), 50.3 (C-2,7), 41.7 (C-10,13), 41.5 (C-9,14), 39.8 (C-1,8); UV/Vis (*n*-hexane): λ_{max} (ε) = 320 (2500), 305 (4900), 298 (4600), 281 (3100), 268 nm (2500).

8: M.p. > 300 °C (decomp); ^{1}H NMR: $\delta = 6.38$, 6.30, 5.97, 5.76, 5.46, 3.35, 3.18, 3.09, 2.86, 2.85, 2.11, 1.98, 1.89, 1.59; ^{13}C NMR: $\delta = 137.3$, 133.3, 132.1, 131.8, 130.7, 125.9, 123.5, 74.4, 56.7, 50.9, 50.5, 43.5, 42.7, 41.6, 37.5, 35.4; UV/Vis (*n*-hexane): λ_{max} (ε) = 323 (2100), 307 (4000), 295 (3950), 278 (3100), 269 nm (2150); MS (FAB): *m/z* (%) = 742 (8) [$M^{\cdot +}$], 707 (4) [$M^{\cdot +} - Cl$].

9: M.p. > 300 °C (decomp); ^{1}H NMR: $\delta = 6.37$, 5.78, 5.73, 5.52, 5.43, 3.34, 3.12, 3.04, 2.92, 2.84, 2.29, 2.23, 2.02, 1.88; ^{13}C NMR: $\delta = 137.2$, 133.3, 132.3, 131.7, 128.8, 128.2, 124.8, 123.4, 74.0, 56.3, 55.8, 50.1, 43.6, 42.2, 41.5, 38.9, 37.5, 37.2; UV/Vis (*n*-hexane): λ_{max} (ε) = 323 (2200), 307 (4000), 295 (3900), 278 (3700), 369 nm (3250); MS (FAB): *m/z* (%) = 742(6) [$M^{\cdot +}$], 707 (4) [$M^{\cdot +} - Cl$].

10: M.p. > 300 °C (decomp); ^{1}H NMR: $\delta = 6.43$, 6.07, 5.78, 5.50, 3.85, 3.10, 2.95, 2.28, 2.26, 1.99; ^{13}C NMR: $\delta = 137.4$, 132.4, 131.8, 128.9, 124.8, 123.5, 74.6, 56.4, 55.8, 50.1, 42.3, 42.0, 38.9, 37.2; MS (FAB): *m/z* = 663 [$M^{\cdot +}$], 625 [$M^{\cdot +} - HCl$].

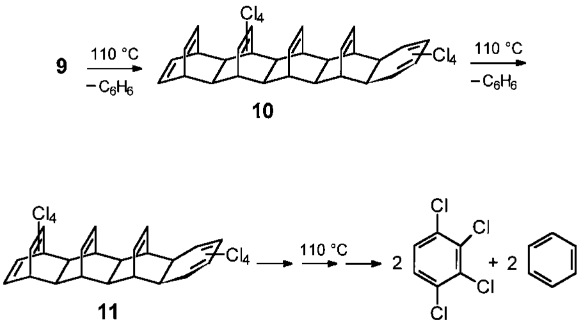
11: M.p. 280 °C (decomp); ^{1}H NMR: $\delta = 6.32$, 5.82, 5.56, 3.15, 3.09, 2.86, 1.98, 1.93; ^{13}C NMR: $\delta = 137.9$, 132.4, 128.6, 128.3, 124.9, 123.8, 74.6, 56.5, 50.1, 42.3, 38.7, 37.1.

12 (Two isomers with respect to the orientation of the ligand tfacac): m.p. 225 °C; ^{1}H NMR: $\delta = 6.30$, 5.61 (tfacac), 4.82, 4.32, 3.05, 2.99, 2.88, 2.12 (CH_3), 2.05 (CH_3), 1.38.

13: M.p. 285 °C; ^{1}H NMR: $\delta = 5.67$(tfacac), 4.45, 3.08, 2.88, 2.16 (CH_3), 1.52.

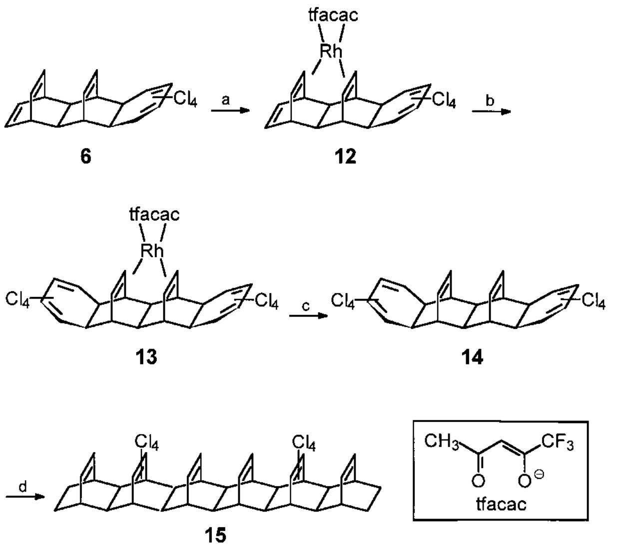
14: M.p. 191 °C (CH_2Cl_2); ^{1}H NMR: $\delta = 5.88$, 3.19, 3.15, 2.12; ^{13}C NMR: $\delta = 131.6$, 131.2, 123.6, 49.8, 40.3, 38.8.

15: M.p. > 300 °C (decomp); ^{1}H NMR: $\delta = 5.92$, 5.44, 2.93, 2.88, 2.28, 2.25, 1.87, 1.43 (CH_2), 1.14 (CH_2); ^{13}C NMR: $\delta = 130.3$, 129.0, 124.6, 74.3, 55.9, 54.2, 44.2, 37.2, 31.4, 25.42; UV/Vis (*n*-hexane): λ_{max} (ε) = 260 nm (1500, sh); MS (FAB): *m/z* = 774 [$M^{\cdot +}$].



Scheme 3. Decomposition of **9** upon heating.

The favored dimerization of tribenzene **6** to the angular hexabenzene **8** demonstrates that, of the two double bonds at the bicyclic terminus of **6**, the one that is laticyclic conjugated adds more rapidly to an electron-poor diene. This is the double bond that also adds nearly exclusively to TCTD, and protection is required to direct the reaction to the other double bond. Dicarbonyltrifluoroacetylacetonatorhodium[10] was chosen for this purpose because in $CHCl_3$ it binds to the two laticyclic conjugated double bonds of **6** to form diolefin complex **12** (Scheme 4). Masked tribenzene **12** adds TCTD at



Scheme 4. a) [Rh(tfacac)(CO)$_2$], CHCl$_3$, 50 °C, 16 h, 62 %; b) TCTD, hexane, 60 °C, 17 h, 59 %; c) CH$_2$Cl$_2$/aqueous NaCN 10 %, 3 min, 72 %; d) 10 equiv of dihydrobarrelene, THF, 75 °C, 96 h, 7.5 kbar, 57 %.

60 °C in hexane at the free double bond, which leads to complex **13** after subsequent loss of SO$_2$. The protecting group of **13** is conveniently cleaved with aqueous NaCN to yield the bifunctional diene **14**. Diels–Alder reaction of **14** with dihydrobarrelene utilizes the same structural elements that are responsible for oligomerization of tribenzene **6**. However, in this case reaction ceases on both sides after the first step. The resulting hexaene **15** consists of six *endo*-fused bicyclo[2.2.2]octene units, and its UV spectrum displays a broad shoulder at 240–290 nm ($\varepsilon = 1500$). An X-ray structural analysis[11] of **15**, recrystallized from CH$_2$Cl$_2$, shows that the basal C atoms are aligned on a circular arc of radius 9.57 Å encompassing an angle of 89° (Figure 1). One molecule of CH$_2$Cl$_2$ is located at the center of gravity of the segment.

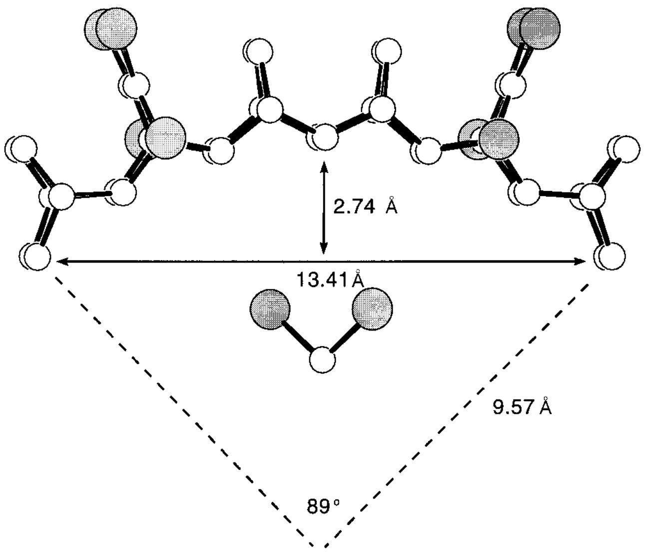


Figure 1. Molecular structure of **15** in the crystalline state. Hydrogen atoms have been omitted for clarity.

The structure of **15** indicates that the strategy used to obtain all-*endo* fusion of the bicyclo[2.2.2]octene units might make the synthesis of a ring of 24 *endo*-fused bicycles from four bifunctional dienes **14** and four Rh-protected dienophiles **4** possible. The closed laticyclic conjugation along its periphery would represent a new and interesting topology for a π-electron system. In principle, the proposed macrocycle could also be obtained by eightfold oligomerization of tribenzene **6**, but, as shown above, the formation of angular products is favored by this route.

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[11] Crystal structure data for **15**: $C_{38}H_{34}Cl_2 + CH_2Cl_2$, $M = 859.18$, crystal dimensions: $0.2 \times 0.1 \times 0.1$ mm, monoclinic, space group *C*2/*c*, $a = 17.994(4)$, $b = 16.901(4)$, $c = 4.006(3)$ Å, $\beta = 118.91(2)°$, $V = 3729(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.531$ g cm^{-3}; $F(000) = 1760$; $\mu_{Mo} = 0.778$ cm^{-1}, $\theta_{max} = 27.04°$; 3159 measured, 3089 independent, and 1297 observed reflections ($F_o > 2\sigma > F_o^2$); $R_1 = 0.0617$, $wR_2 = 0.1722$. Nonius CAD4 diffractometer (room temperature, Mo$_{K\alpha}$ radiation, $\lambda = 0.71069$ Å). The structure was solved by direct methods and refined for all independent reflections against F^2(heavy atoms with anisotropic, H atoms with isotropic temperature factors). Programs used: MolEN (Nonius) for structure calculation and SHELXL-93 (G. M. Sheldrick, Universität Göttingen, Germany) for refinement. The calculations were performed in the Regionales Rechenzentrum der Universität zu Köln. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100595. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).