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Preparation and Structure Determination of a Stable *cis*-Bis-σ-homobenzene Derivative[‡]

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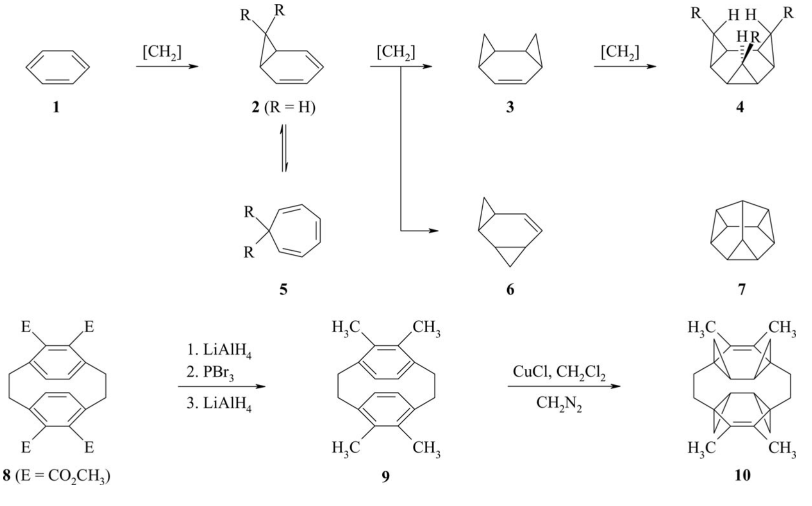
By cyclopropanation of tetramethyl[2.2]paracyclophane **9** the tetramethylene adduct **10** has been prepared. This hydrocarbon is the first stable *cis*-bis-σ-homobenzene for which a structure has been determined by X-ray diffraction.

Introduction

The formal addition of methylene carbene to benzene (**1**) results in the generation of homobenzene (**2**, norcaradiene). It has long been known that this hydrocarbon prefers its valence-isomeric form, 1,3,5-cycloheptatriene (**5**, R = H: tropylidene)[2] into which it is converted by an electrocyclic ring opening process. In fact, the equilibrium between these tautomers can be influenced by various factors, among them the electronic nature of the substituents R at the methylene group of the three-membered ring in **2**. Electron-withdrawing substituents such as the nitrile function favor the “closed” norcaradiene form **2**.[3] If another equivalent of the carbene is added to **2**, bis-σ-homo-benzenes result; since methylenation can take place either at the same or the opposite side of the three-membered ring already present, *cis*- (**3**) and *trans*-bishomobenzene (**6**) can be produced. Finally, if a third methylenation is carried out either *all-cis*- (**4**) or *trans*-tris-σ-homobenzene derivatives result, respectively. In fact the information available on **3** and **4** is rather scarce, especially as far as X-ray structures are concerned. A CCDC[4] search carried out for the tricyclic core framework tricyclo[5.1.0^{2,4}]octane yields 35 hits, none including the X-ray structure of a *cis*-bis-σ-homo-benzene. Most derivatives of this particular polycyclic hydrocarbon are *trans*-configured (**6**),[5] and those prepared in a *cis*-configuration are evidently only generated as reactive and/or thermally labile intermediates. As far as the *all-cis*-tris adducts are concerned, the parent hydrocarbon has escaped all attempts at



Scheme 1. The cyclopropanation of benzene (**1**) and the [2.2]paracyclophane **9**.

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preparation so far. The only stable adducts characterized so far (including X-ray analyses) are the tris-nitrile **4** (R = CN)[6] and the triscyclopropanation product of tris(benzocyclobutadieno)cyclohexatriene.[7] Stability has also been introduced into these systems by removing the "internal" methylene hydrogen substituents by placing a bridging carbon atom into the center of **4** (R = H) as shown by diademane or mitrane (**7**).[8] The price paid here, of course, is that any interaction between these crowded atoms (or substituents) can no longer be studied (Scheme 1).

Results and Discussion

To prepare stable homobenzenes we have developed another concept: to force all methylene groups into one orientation, viz. into the *cis*-configuration, we *bridged* one of the hemispheres of the benzene ring, i.e. employed a cyclophane as the substrate to be methylenated. The concept is illustrated in Scheme 1 for the tetramethyl derivative **9**, a hydrocarbon readily obtained by reduction of the four ester substituents of **8**.[9] When **9** was cyclopropanated with diazomethane/CuCl in dichloromethane, two products were formed in 3 and 7% yield, which according to spectroscopic and analytical data were bis and tetra adducts of methylene to **9**.[10] Clearly a fully cyclopropanated derivative of **9** is not produced under these conditions. Both of our products are stable *cis*-bis-σ-homobenzenes that can be kept unchanged at room temperature for years, and for the tetra adduct **10**, crystals suitable for X-ray diffraction could be grown from trichloromethane/methanol.

The structure reveals two closely similar, inversion-symmetric, independent molecules, one of which is shown in Figure 1. The only remaining double bonds in the six-membered rings, C7–C8, are clearly the shortest at 1.349, 1.339 Å (esd's of bond lengths and angles are 0.003 Å and 0.2° respectively; where ranges of values are given, the individual values can be found in the supplementary crystallographic data). All other bond lengths of these rings correspond to shortened single bonds (1.488 Å for the bond joining the cyclopropyl rings, 1.497–1.508 Å for the other bonds). The bond angles within the six-membered rings are all close to sp^2 values, with 122.3–123.2° at the sp^2 atoms C7 and C8, 119.2–120.0° at C4 and C5 (junctions to the cyclopropane rings) and 116.7–117.6° at the bridgehead atoms C3 and C6 (see below). Within the cyclopropane rings, the "outer" bonds C3–C9 and C6–C10 are the longest at 1.518–1.529 Å; the other bond lengths are 1.501–1.511 Å. The cyclopropane rings subtend interplanar angles of 109–110° to the best planes defined by the four atoms including the hinge bond, e.g. C5,4,3,8 for the ring C3,4,9.

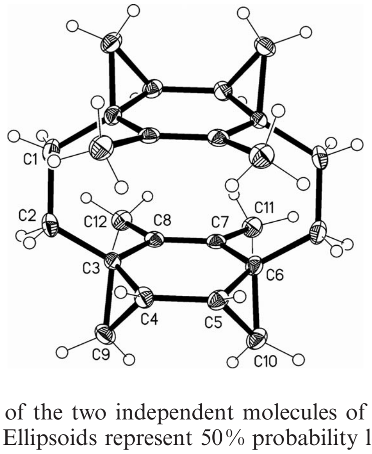

Figure 1. One of the two independent molecules of compound **10** in the crystal. Ellipsoids represent 50% probability levels.

Despite the partial saturation of the six-membered rings, both molecules show some, but not all, of the distortions normally associated with the [2.2]paracyclophane framework. The flattened boat form of the six-membered rings is present, but less pronounced than is usual; the deviations of the bridgehead atoms C3 and C6 from the best plane of the other four atoms amount to 0.097–0.115 Å, whereas the normal amount is ca. 0.15 Å (mean of 326 hits for [2.2]paracyclophanes from the Cambridge Database,[4] not further sorted). Similarly, the distance between bridgehead atoms of opposite rings is 3.11, 3.12 Å (cf. 2.77 Å from the above search) and the bridge single bonds (C1–C2) are not significantly lengthened (1.536, 1.539 Å in **10**, cf. 1.578 Å from the above search). The angles within the six-membered rings at the bridgeheads are 116.7–117.6°, which is normal for paracyclophanes (search result 116.9°). The main strain of the molecules in **10** appears to be taken up in the formally sp^3 C–C–C bridge angles, for which the average search value of 112.8° is greatly increased – to as much as 119.4–120.6° in **10**.

Conclusions

[2.2]Paracyclophanes have been shown to be suitable precursors for *cis*-bis-σ-homobenzenes. To the best of our knowledge the structure reported here for the tetra methylenation product **10** is the first for a representative of this interesting class of hydrocarbons.

Experimental Section

General: *N*-Nitroso-*N*-methylurea (17 g, 0.16 mol) was added in 0.5 g portions over 10 h to an aqueous solution of potassium hydroxide (40%; 250 mL), which had been covered by a layer of decalin (80 mL). The diazomethane generated at the phase boundary was purged by a stream of nitrogen (250 to 300 mL/min) through a drying tower filled with KOH pellets into a solution of 4,5,12,13-tetramethyl[2.2]paracyclophane (**9**; 2.0 g; 7.6 mmol) in anhydrous dichloromethane (60 mL) to which 0.4 g of CuCl had been added. After completion of the cyclopropanation the reaction mixture was passed through a short column filled with silica gel, the solvent was removed, and the oily residue separated by preparative thick layer chromatography (silica gel; *n*-hexane/dichloromethane = 97:3) to yield two fractions. Whereas the first fraction (66 mg, 3%) was the bis adduct, the second fraction (185 mg, 7%) was the tetra adduct **10**; colorless needles ($CHCl_3$/MeOH), m.p. 114–116 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3050 (m), 3020 (s), 2920 (s), 2850 (m), 1445 (m), 1375 (w), 1340 (m), 1067 (s), 1010 (s), 928 (w), 795 (m) cm^{-1}. ^1H NMR (400.1 MHz): $\delta = -0.45$ (m, 4 H, *endo*-cyclopropane-CH_2), 0.27 (m, 4 H, *exo*-cyclopropane-CH_2), 0.93 (m, 4 H, CH_2CH_2), 1.11 (m, 4 H, cyclopropane-CH), 1.73 (s, 12 H, CH_3), 2.22 (m, 4

H, CH_2CH_2) ppm. ^{13}C NMR (100.6 MHz): δ = 16.21 (q, CH_3), 18.44 (d, cyclopropane-CH), 20.09 (s, cyclopropane-C), 21.27 (t, cyclopropane-CH_2), 34.15 (t, CH_2CH_2), 127.56 (s, C=C) ppm. UV (cyclohexane): λ_{max} (lgε) = 212 nm (3.14). MS (EI, 70 eV): m/z (%) = 320 (1.6) [M^+], 305 (1.6), 201 (11), 159 (11), 145 (24), 128 (32), 119 (32), 105 (19), 91 (41), 44 (100), 41 (50). $C_{24}H_{32}$ (320.53): calcd. C 90.00, H 10.00; found C 89.79, H 10.29.

Crystal Structure Determination: *Crystal data* for **10**: Triclinic, space group $P\bar{1}$, a = 7.2772(8), b = 8.7524(10), c = 15.3361(17) Å, α = 95.978(13), β = 90.467(14), γ = 114.338(15)°, Z = 2, crystal 0.5 × 0.25 × 0.1 mm, 29976 intensities to $2\theta_{max}$ 52.7°; refinement to $wR2$ = 0.113, $R1$ = 0.043 for 222 parameters and 3589 unique reflections; max. $\Delta\rho$ = 0.22 e Å^{-3}, S = 1.00.

The data were recorded on an Oxford Diffraction Xcalibur diffractometer at –173 °C using Mo-K_α radiation. The structure was refined anisotropically on F^2.[11] Hydrogen atoms were included using a riding model.

The determination of the correct unit cell and space group was not trivial. The cell as found by the automatic diffractometer routines was *C*-centred monoclinic, but we discarded this cell in favour of the triclinic cell for two reasons. First, the monoclinic α and γ angles deviated from 90° by some tenths of a degree; secondly, the R(int) value for monoclinic symmetry was rather high at 0.16. Structure solution was successful in $P\bar{1}$, but the refinement nonetheless led to unsatisfactorily high R values. We therefore assumed pseudo-merohedral twinning via 180° rotation about the "monoclinic" **b** axis; use of the corresponding twin matrix (1 0 0/–1 –1 0/ 0 0 –1) allowed the refinement to be successfully completed. The BASF parameter (fraction of minor twinning component) refined to 0.318(2). This structure had been investigated in 1980,[12] but the techniques available at the time were probably inadequate for discovering the true cell and twinning law.

CCDC-763450 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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