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Synthesis of a Propella[4_4]prismane with Averaged S_4 Symmetry

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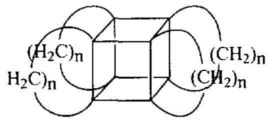
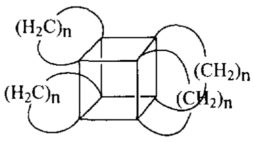
The synthesis of the title compound **7** has been achieved by irradiation of the fourfold bridged tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene **6**; the latter species was prepared by the $AlCl_3$ supported dimerization of cyclododeca-1,7-diyne.

If one connects all adjacent positions of cubane by, say hydrocarbon chains of equal length *n*, one can construct two isomeric propella[n_4]prismanes with D_{4h} or S_4 symmetry.[1]



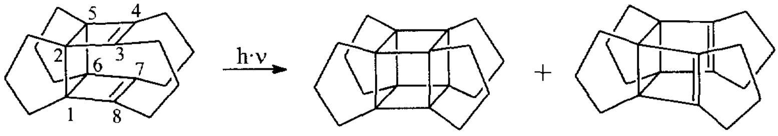
D_{4h}



S_4

One member of the D_{4h} family has been synthesized by irradiation of the fourfold bridged tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene derivative **1**.[2]

Scheme 1

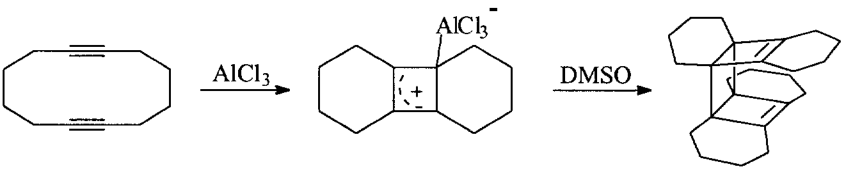


1 **2** **3**

To derive a member of the S_4 family we have followed a related protocol. Starting with cyclododeca-1,7-diyne (**4**) we have used $AlCl_3$ to form the intramolecular cyclobutadiene-σ-complex **5** as intermediate which, when treated with DMSO at -78 °C, dimerizes to *syn*-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-

8b,12b- butanobenzo[3',4']cyclobuta[1',2':3,4]cyclobuta [1,2-e]biphenylene (**6**). This reaction relies on the work by the groups of Schäfer,[3a] Koster[3b] and Hogeveen[3c] and has been used lately to prepare Dewar benzenes.[4]

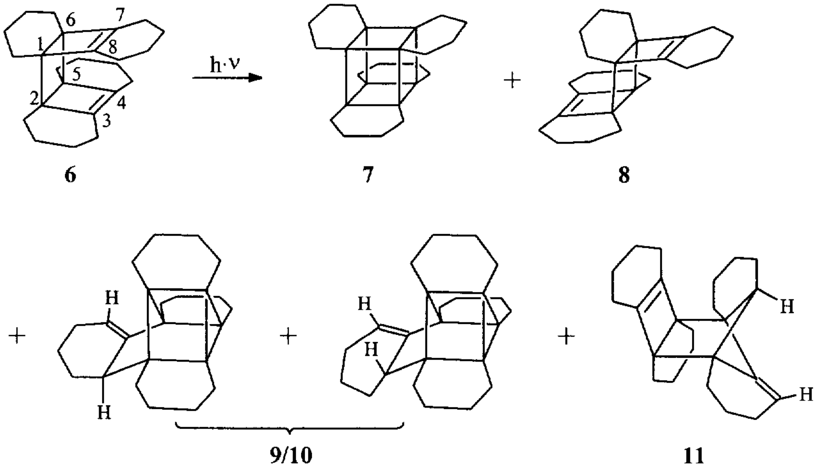
Scheme 2



4 **5** **6**

An alternative path to **6** has been reported by Wittig and Mayer.[5] The structural assignment of **6** is based mainly on its spectroscopic properties. In the ^{13}C NMR spectrum one finds two signals for the quarternary carbons ($\delta = 49.2, 48.0$) and two signals for the sp^2 carbon centers ($\delta = 144.0, 137.7$).[6] We were also able to grow single crystals of **6**. Due to disorder we were unable to elucidate detailed structural parameters. However, the configuration of **6** could be confirmed without any doubt.[7]

Scheme 3



The irradiation of **6** with a mercury high pressure lamp in pentane at 20 °C and subsequent separation by column chromatography (silica gel) affords the propella[4_4]prismane (S_4) (**7**) in 1 - 2 % yield. Furthermore the compounds **8** - **11** could be isolated in 6, 8, 5 and 22 % yield, respectively. The structure of **7** is based on its spectroscopic properties,[6] which are similar to those of **2** and octamethyl cubane[10] and on its supposed mechanism of formation, a [2+2] cycloaddition. The ^{13}C NMR spectrum of **7** shows one signal (δ = 50.0) for the quarternary carbons and two signals (δ = 23.1, 19.8) for the methylene groups. The structures of **8** - **11** are assumed by comparison of their spectroscopic data[6] with those of the products of the analogous irradiation of *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene.[7,10]

The light induced [2+2] cycloaddition of **6** to **7** was hoped for but was not anticipated in view of several reports in the literature which state that *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene and its octamethyl derivative did neither give the corresponding cubane nor show any photoreaction.[9] Our recent studies on *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene showed however, that a rich photochemistry occurs under certain conditions.[10]

The geometrical parameters of **7** have been calculated by using the ab initio procedure (RHF/3-21 G basis). A structure with averaged S_4 symmetry is predicted. The most stable conformer shows D_2 symmetry with a half chair conformation of the tetramethylene chains.

These experiments reveal a considerable difference in the photochemistry of **1** and **6**. The irradiation of **1** yields only to two products (**2**, **3**), while the irradiation of **6** gives rise to at least five substances. Moreover, the yields of the formal [2+2]cycloaddition products are 10% for **2** but only 1.5% for **7**.

We ascribe these variations to the different ways the double bonds of the tricyclo[4.2.0.0^{2,5}]octa-3,7-diene unit in **1** and **6** are bridged. The bridging of centers 3 - 8 and 4 - 7 in **1** tightens not only the distance between the double bonds (ca. 2.7 Å) and makes the tricyclo[4.2.0.0^{2,5}]octa-3,7-diene skeleton rather rigid, it also changes drastically the electronic structure of the cage. As discussed elsewhere[1,2,11] the sequence of the frontier orbitals in **1** is predicted to be π^- on top of π^+, just the opposite as in tricyclo[4.2.0.0^{2,5}]octa-3,7-diene and its alkyl derivatives.

In **6** the bridging of the 2 - 3, 4 - 5 and 7 - 8 positions neither influences the rigidity of the skeleton considerably nor does it reduce the distance between the double bonds (ca. 3.0 Å). As a result the sequence of the π-orbitals of **6** is predicted to be the same as in the parent system and in the octamethyl congener.

A second point which has to be considered in understanding the difference in reactivity of **1** and **6** is the observation that **6**, like the parent system, rearranges under thermal conditions to the corresponding bicyclo[4.2.0]octa-2,4,7-triene system.[5,7] Such an intermediate could never be found during irradiation of **1**.[2]

These points support the view that the photochemistry of **6** resembles very much that of octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene[8,10] while **1** chooses a different reaction channel.

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Footnotes and References

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[6] *Selected spectroscopic data* for **6 - 11**: **6**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.35-0.95 (m, 32 H); ^{13}C NMR (75 MHz, C_6D_6) δ 144.0, 137.7, 49.2, 48.0, 27.1, 24.7, 24.2, 23.7, 23.6, 23.5, 22.3, 21.6. **7**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75-1.10 (m, 32 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.0, 23.1, 19.8; GC/MS (EI) *m/z* {%} 320 {M^+; 11.3}, 292 {18.2}, 277 {56.6}, 263 {78.8}, 235 {100}. **8**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.40-0.75 (m, 32 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.3, 139.9, 57.6, 52.4, 28.2, 26.7, 26.1, 24.8, 23.48, 23.43, 23.38, 22.0. For **9** or **10**: a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.92 (dd, 1 H, *J* 4.8, 2.3 Hz), 2.25-0.85 (m, 31 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.8, 100.9, 61.3, 50.1, 49.5, 48.5, 43.9, 38.6, 37.7, 26.1, 25.5, 25.2, 24.8, 24.0, 23.9, 23.7, 23.6, 23.2, 22.93, 22.85, 22.4, 22.1, 20.7, 19.9. b) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89 (dd, 1 H, *J* 4.8, 2.6 Hz), 2.05-0.75 (m, 31 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 100.5, 62.4, 54.8, 48.7, 48.0, 40.9, 37.6, 35.0, 25.4, 24.1, 23.9, 23.8, 23.4, 23.2, 23.1, 23.1, 22.9, 22.6, 21.8, 21.7, 21.3, 20.5, 16.5. **11**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.67 (dd, 1 H, *J* 3.9, 3.9 Hz), 2.40-0.90 (m, 31 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.7, 146.43, 146.38, 99.6, 55.1, 54.5, 41.0, 37.6, 25.0, 26.1, 25.3, 23.4, 23.4, 23.3, 23.04, 23.04, 23.0, 22.9, 22.5, 22.34, 22.27, 22.25, 20.3, 20.1.

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