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SYNTHESIS OF 1,16-DIDEHYDROHEXAHELICENE. A MEMBER OF THE [7]CIRCULENES[1]

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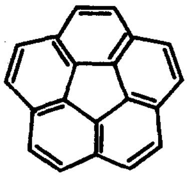
The syntheses of many non-planar aromatic compounds exhibiting a wide variety of structural types have been reported. For example, many cyclophanes containing simple bent aromatic rings[2] have been prepared, the most illustrious being [7]-[3] and [6]paracyclophane;[4] spiral aromatic molecules are exemplified by a range of helicenes,[5,6] and the bowl-shaped [5]circulene, corannulene (**1**)[7] is an example of yet another type of distortion possible in an aromatic carbocyclic compound. Molecular orbital calculations[8] give some theoretical rationalization for both the structure and reactivity of these non-planar compounds. The [7]circulenes[9] provide an opportunity to investigate aromatic compounds having saddle-shaped geometry.[10] We wish to report here the synthesis of 1,16-didehydrohexahelicene which we refer to as hexa[7]circulene[11] (**2**) an analog of [7]circulene (**3**).



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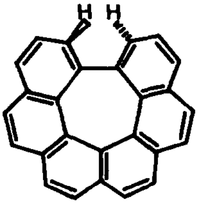

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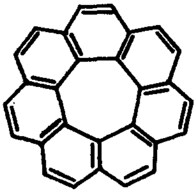

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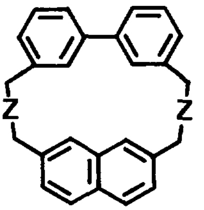
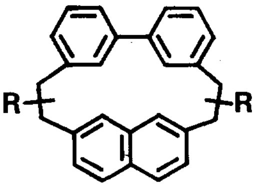
The synthetic route which we used was a modification of a scheme developed by Boekelheide[12] for the synthesis of cyclophane dienes, which has been successfully used in the synthesis of coronene[13] and a thiacoronene.[14]

Reaction between 3,3'-bis(bromomethyl)biphenyl and the dithiolate anion of 2,7-bis(mercaptomethyl)naphthalene in ethanol under high dilution produced the dithiacyclophane[15] **4** in 50% yield as white needles, mp 234-235°.



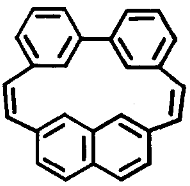
4 Z = S

5 Z = $\overset{+}{S}$-Me BF_4^-



6 R = S-Me

7 R = SO-Me



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Methylation of the dithiamacrocycle 4 with dimethoxycarbonium tetrafluoroborate in dichloromethane produced the corresponding bis(tetrafluoroborate) salt 5 in quantitative yield. Rearrangement of the salt 5 with sodium hydride in tetrahydrofuran formed, in high yield, the bismethylthioether[15] 6 as a mixture of stereo and structural isomers as was evident from its cmr spectrum. Oxidation of the thioether 6 with a 2 molar ratio of m-chloroperbenzoic acid in chloroform gave a quantitative yield of the disulfoxide[15] 7 as pale yellow plates, ir ($CHCl_3$) 1030 cm^{-1} (strong, S=O). The disulfoxide was obtained as a mixture of isomers, again evident from its pmr and cmr spectra. Pyrolysis of the disulfoxide 7 at 300°/5 x 10^{-4} mm produced the biphenylnaphthalenophane diene 8 as pale orange needles, mp 133-134° in 81% yield; mass spectrum, M^+, found 330.14365, calcd 330.14084; pmr ($CDCl_3$) δ, 6.38-8.23 (multiplet); {'H} cmr spectrum ($CDCl_3$/TMS) showed the expected 14 lines, δ, 126.12-141.53.

A solution of the diene 8 (50 mg in cyclohexane; λ_{max} (log ε), 224 (5.2 x 10^4), 250 (sh, 2.1 x 10^4) and 273 nm (sh, 1.2 x 10^4)) was irradiated with a high-pressure mercury-arc lamp in the presence of iodine to produce hexa[7]circulene (2) in 52% yield as pale yellow plates mp 162-163°; mass spectrum, M^+, found 326.10909, calcd 326.10954; pmr ($CDCl_3$/TMS) δ, 7.85-8.65 (multiplet); {'H} cmr showed 7 lines at δ, 126.20-130.74 (tertiary C's) and 7 lines of lower intensity at δ, 130.58-146.45 (quaternary C's); UV (cyclohexane) λ_{max} (log ε), 220 (5.8 x 10^4), 236 (sh, 5.6 x 10^4), 243 (5.5 x 10^4), 268 (5.2 x 10^4), 277 (sh, 4.5 x 10^4), 304 (3.9 x 10^4) and 321 nm (3.0 x 10^4).

Molecular models of hexa[7]circulene (2) indicate that the molecule probably has a saddle-shaped geometry, and consequently, would be dissymmetric and potentially resolvable into enantiomers.

We find that the introduction of the diene system by thermolysis of the disulfoxide[16] *in vacuo* is a highly efficient method, and an alternative to the double Hofmann elimination.[12] We anticipate that the synthetic route described above will be a general method for the preparation of the carbocyclic circulenes, and will complement the previously described route to the heterocirculenes.[9]

Acknowledgement. We gratefully acknowledge financial support from the Australian Research Grants Committee.

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to the size of the central ring, and the prefix refers to the number of aromatic rings about the central ring. Thus, using our nomenclature, [7]circulene (**3**) would be strictly, hepta[7]circulene.

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