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Facile Synthesis, Crystal Structure, and Oxidizability of a Novel Benzene Tris-Annelated with Bicyclo[2.2.2]oct-2-ene[1)]

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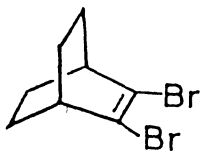
Trimerization of 2,3-dibromobicyclo[2.2.2]oct-2-ene by the use of butyllithium followed by subsequent cyclization gives 1,2:3,4:5,6-tris(bicyclo[2.2.2]oct-2-eno)benzene (**3**), the highly symmetrical structure of which is established by X-ray crystallography. Compound **3** is reversibly oxidized upon cyclic voltammetry at 1.25 V vs Ag/Ag^+ in CH_3CN.

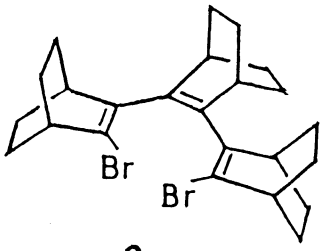
A wide variety of benzene derivatives have been synthesized by transition-metal catalyzed cyclotrimerization of alkynes.[2)] For benzene rings triply annelated with mono- or bicyclic alkenes, however, yields are low because of the severe strain inherent in the corresponding alkynes.[3)] As an alternative method, stepwise C-C bond formation between sp^2 carbons of mono- or bicycloalkenes is conceivable, but no such example has been reported until our recent success in the synthesis of the tris-annelated benzene **3** in a modest yield.[4)] We now report a modified and simple synthetic procedure, which gives an improved yield of **3**, and an X-ray crystal structure establishing its high symmetry.

When treated with one equiv of *n*-BuLi at -78 °C in tetrahydrofuran (THF) for 10 min, 2,3-dibromobicyclo[2.2.2]oct-2-ene (**1**)[5)] underwent very rapid lithiation and coupling, repeatedly, to give the trimeric dibromide **2**[6)] as a main product in 60-70% yield after separation by medium pressure liquid chromatography. The subsequent cyclization of **2** was found to proceed readily without any catalyst when two equiv. of *n*-BuLi was slowly added to **2** at room temperature in THF, giving

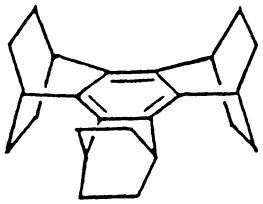
3 as colorless needles[4] in 80% yield after 1 h. The accompanying formation of octane but not 1-bromobutane in the latter reaction indicates that the cyclization of 2 does not involve Li/Br exchange but proceeds directly through intramolecular reductive coupling of the Br-substituted sp^2 carbons.



1



2



3

Reflecting its high molecular symmetry, 3 exhibits a very simple ^{13}C NMR spectrum,[7] but the structural characteristics are best demonstrated by results of X-ray crystallography[8] shown in Fig. 1 and Table 1. Compound 3 has nearly D_{3h} symmetry, and the central ring is only slightly distorted from the normal benzene structure. The torsional angle between the σ-bonds extending from the ring is less than 3.3°. The aromatic bond lengths alternate slightly, averaging 1.408 Å and 1.393 Å in and out of the bicyclic systems respectively, but such slight distorsion should not greatly affect the aromaticity of the molecule.

The steric and electronic effects of the rigid σ-frameworks surrounding the central π-system in 3 are reflected in its ease in one-electron oxidation. As shown in Fig. 2, compound 3 exhibits a well-defined reversible oxidation wave at

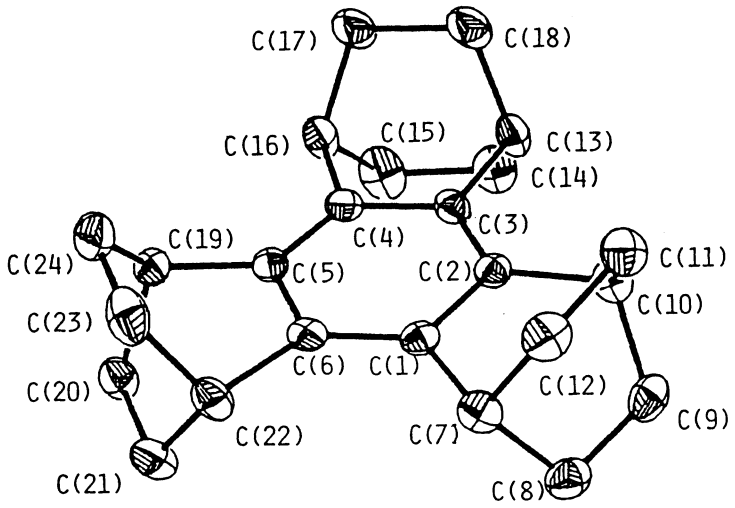


Fig. 1. Crystal structure of 3 with hydrogen atoms omitted.

Table 1. Selected Bond Distances and Angles

Bond distances / Å		Bond angles / degree	
C(1)-C(2)	1.405(4)	C(6)-C(1)-C(2)	120.5(3)
C(2)-C(3)	1.392(4)	C(1)-C(2)-C(3)	120.0(2)
C(3)-C(4)	1.410(4)	C(2)-C(3)-C(4)	119.7(2)
C(4)-C(5)	1.393(4)	C(3)-C(4)-C(5)	120.1(2)
C(5)-C(6)	1.409(4)	C(4)-C(5)-C(6)	120.2(2)
C(6)-C(1)	1.394(4)	C(5)-C(6)-C(1)	119.4(2)
C(1)-C(7)	1.510(4)	C(6)-C(1)-C(7)	127.0(2)
C(7)-C(8)	1.539(4)	C(2)-C(1)-C(7)	112.5(2)
C(8)-C(9)	1.546(4)	C(1)-C(7)-C(8)	108.4(3)
C(9)-C(10)	1.535(5)	C(1)-C(7)-C(12)	107.7(2)
C(10)-C(2)	1.501(4)	C(8)-C(7)-C(12)	108.7(2)

$E_{1/2}$ 1.25 V (E_{pa} 1.29 V) vs Ag/Ag^+ upon cyclic voltammetry in CH_3CN. In contrast, hexamethylbenzene (**4**) is only irreversibly oxidized at E_{pa} 1.38 V under the same conditions. This higher oxidizability of **3** with excellent reversibility is interpreted in terms of σ-π conjugative interaction of the bicyclic frameworks with the aromatic system, stabilizing the cation radical.[9] On the other hand, **3** (3×10^{-3} mol dm^{-3}) does not exhibit any charge-transfer (CT) absorption with tetracyanoethylene (3×10^{-3} mol dm^{-3}) in CH_2Cl_2, even though **4** gives a clear CT absorption at 540 nm under the same conditions. The lack of CT complex formation by **3** can be attributed to steric shielding by the bulky bicyclic substituents, which would also be responsible for the unusual stabilization of the cation radical as has been mentioned above.

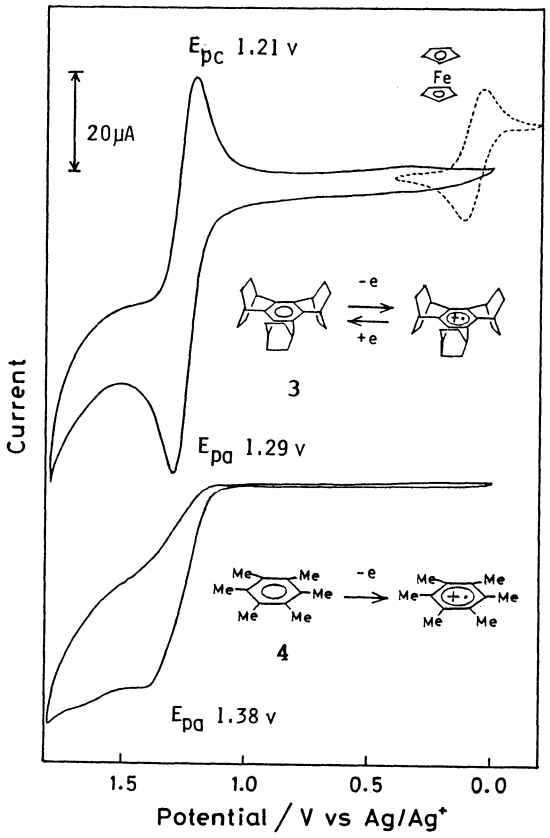


Fig. 2. Cyclic voltammograms of **3** and **4** in CH_3CN with Bu_4NClO_4 as a supporting electrolyte; scan rate 0.1 V s^{-1}.

References

1) σ-π Conjugated Molecules. Part 2. For Part 1 see Ref. 4.

2) H. Heaney in "Comprehensive Organic Chemistry," ed by J. F. Stoddart, Pergamon Press, Oxford (1979), Vol. 1, p. 250.

3) For example see P. G. Gassman and I. Gennick, J. Am. Chem. Soc., 102, 6863 (1980), and the references cited therein.

4) K. Komatsu, H. Akamatsu, Y. Jinbu, and K. Okamoto, J. Am. Chem. Soc., 110, 633 (1988).

5) The dibromoolefin **1** was synthesized in 93% yield by dehydrobromination of 2,2,3-tribromobicyclo[2.2.2]octane using t-BuOK in t-BuOH: **1**, mp 51.5-53.3 °C; ^{1}H NMR ($CDCl_3$) δ=2.94 (br s, 2H), 1.56 (br s, 8H); ^{13}C NMR ($CDCl_3$) δ=122.5 (s), 43.8 (d), 26.2 (t). Anal. ($C_8H_{10}Br_2$) C,H. The tribromide was prepared in 88% yield by treatment of 2-bromobicyclo[2.2.2]oct-2-ene (N. A. LeBel, J. E. Huber, and L. H. Zalkow, J. Am. Chem. Soc., 84, 2226 (1962)) with bromine in refluxing CCl_4.

6) For the spectral data see Ref. 4. The corresponding dimeric and tetrameric dibromides as well as monobutylated derivatives were also formed but only in small amounts.

7) Only three signals are observed at δ 134.2 (s), 28.7 (d), 26.5 (t): Ref. 4.

8) Crystal data for **3**: $C_{24}H_{30}$ (0.17x0.20x0.75 mm^3), M=318.5, monoclinic, space group $P2_1/N$, a=11.510(7) Å, b=10.223(5) Å, c=15.550(7) Å, β=100.77(3)°; V=1797.5 $Å^3$, Z=4 (at 173 K; based on 25 reflections centered at both plus and minus 2θ), d_{calcd} = 1.18 g cm^{-3}. Data were collected on a Nicolet $P1$ diffractometer with graphite monochromated MoK_α radiation (λ=0.71073 Å) using θ-2θ scans (2724 unique measured reflections). The structure was solved by direct methods and refined by blocked cascade least square refinement based on F using 1868 data with $Fo > 3\sigma(Fo)$. Final discrepancy indices are R1=0.057, R2=0.061, GOOF=1.17.

9) A preliminary ESR experiment indicated generation of the cation radical **3**$^{+\cdot}$ upon electrolytic oxidation of **3** in CH_3NO_2 at 1.5 V vs Ag/Ag^+, as evidenced by a 13-line signal due to coupling with 12 equal methylene protons at the anti position (a_H = 0.140 mT, g = 2.00261).

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