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Communications to the Editor

A Planar and Stable Derivative of 13,14-Didehydrotribenzo[*a*,*c*,*e*]cyclooctene: Synthesis and X-ray Crystal Structure of 5,6-Didehydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene

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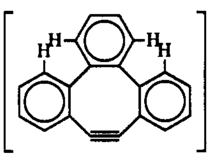
It has long been recognized that annelation of benzene rings would impede oligomerization reactions as well as kinetically stabilize strained cycloalkynes.[2] In support of this argument, a number of relatively stable benzene-annelated cyclooctenynes have been synthesized.[3] However, during Meier's[4a] as well as our[4b] quest for the presumably coplanar tribenzo-annelated cyclooctyne, we were unable to obtain the desired product, namely, 13,14-didehydrotribenzo[*a*,*c*,*e*]cyclooctene (**1**) as a stable compound.



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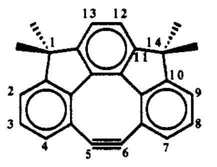

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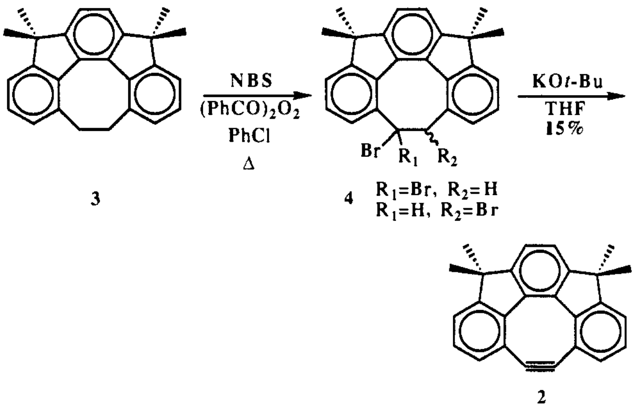
In these endeavors, alkyne **1** was found to have a half-life of ~30 min at -60 °C in CH$_2$Cl$_2$ solution and to exist as a nonplanar molecule.[4a] An important conclusion from these studies is that the peri H-H repulsion of the theoretically coplanar **1** was thought to be responsible for its instability as well as its nonplanar structure. In a continuation of the study of **1**,[5] we reasoned that the structurally related 5,6-didehydrotetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**2**), with the detrimental peri hydrogens removed, might sustain some degree of stability. In this communication, we report the synthesis and characterization of **2** as an exceedingly stable crystalline compound.

Taking advantage of the fact that sizable amounts of **3** had been accumulated either on repeated runs or in modified preparations,[5] we were left with the seemingly easy task to convert **3** to angle-strained **2** via dibromide **4** using the bromination–dehydrobromination procedure. In reality, the introduction of two bromo groups on **3** was not trivial. Indeed, due to the rigidity of **3**, the ethano bridge cannot become coplanar with the benzene rings. Hence the ethano bridge is particularly difficult to functionalize.[6]



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Variable-temperature NMR study showed that the energy barrier for free rotation of the ethano bridge of **3** was approximately 20 kcal/mol at 410 K.[5] It was therefore important to perform the bromination at a temperature close to 410 K. After some experimentation, it was eventually discovered that reaction with excess NBS and a catalytic amount of benzoyl peroxide in boiling chlorobenzene (bp 405 K) transformed **3** into a mixture of dibromides and monobromides, whose structures have not been identified. Direct dehydrobromination of this bromide mixture with KO-*t*-Bu in THF provided the desired **2** in merely 15% yield from **3**, after chromatography on a silica gel column impregnated with silver nitrate [eluted with hexanes–ethyl acetate (5:1) and then ethyl acetate]. Compound **2** formed light-yellowish crystals (from EtOH): mp 203–205 °C; accurate mass *m*/*e* (M$^+$) calcd for C$_{26}$H$_{20}$ 332.1565, found 332.1566. Compound **2** was very stable and no apparent decomposition was detected (by proton NMR spectrometry and thin-layer chromatography on silica gel) after standing for several days at room temperature without protection from light or air. The proton NMR spectrum in CDCl$_3$ showed absorptions at δ 1.42 (s, 12 H, CH$_3$), 6.71–6.75 (dd, J = 1.3 Hz, 7.5 Hz, 2 H, H$_{4,7}$), 6.97–7.06 (t, J = 7.5 Hz, 2 H, H$_{3,8}$), 7.12–7.16 (dd, J = 1.3 Hz, 7.5 Hz, 2 H, H$_{2,9}$), and 7.24 (s, 2 H, H$_{12,13}$). The ^{13}C NMR in CDCl$_3$ showed absorptions at δ 27.54 (q), 45.36 (s), 108.38 (s), 119.62 (s), 123.15 (d), 123.75 (d), 124.02 (d), 127.61 (d), 135.41 (s), 148.88 (s), 154.37 (s), and 156.32 ppm (s). It is therefore clear that compound **2** must be planar and belong to the C_{2v} point group because all the methyl protons showed only one signal in the proton NMR spectrum. The appearance of only 12 signals and the fact that all four methyl carbons showed only one absorption signal at δ 27.54 ppm in the ^{13}C NMR spectrum of **2** further confirmed its C_{2v} geometry. Of particular interest is the downfield shift of the acetylenic C$_5$ and C$_6$ absorption (δ 108.38 ppm) as compared with the chemical shifts of other ordinary linear sp-hybridized alkynes.[2] This observation might be attributable to a hybridization change due to angle strain in **2**.[7] The electronic spectrum of **2** was complex and resembled those of related fully conjugated coplanar cycloalkynes,[8] showing absorptions at $\lambda_{\max}$ (*n*-hexane) 233 (log ϵ 4.11), 271 (4.70), 278.5 (4.86), 298 (3.86), 328 (3.74), 339 (3.90), 353 (3.93), 359 (3.86) and 381 (3.14).

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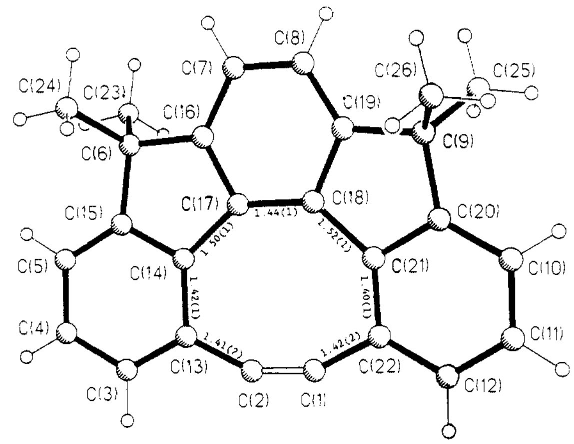

Figure 1. Perspective view of compound **2**. The bond lengths listed are the averages of the corresponding values from three crystallographically independent molecules.

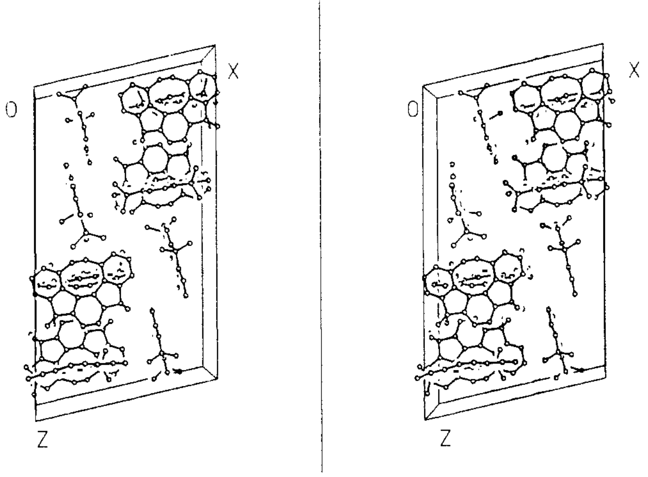

Figure 2. Stereoview of the crystal structure of compound **2**. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right at a slant, *b* toward the reader, and *c* downwards.

A single-crystal X-ray diffraction study[9,10] confirmed the planar structure of **2**. The structural determination also revealed that there are three crystallographically independent molecules (designated I-III) in the asymmetric unit. The structures of these three independent molecules are similar to each other and, as an example, Figure 1 shows a perspective view of molecule I. Comparing with the standard triple bond [1.18 (1) Å],[11] the $C\equiv C$ triple bonds [1.19 (2) Å] in molecules I and III are exactly equal to it, but the one in molecule II [1.23 (2) Å] appears to be marginally longer, which correlates with the fact that the planarity of the eight-membered ring and the coplanarity of this ring with the three benzo groups in II are distinctly worse than those in I and III. Also of structural interest is the bent acetylenic angle of **2**. As expected, these angles in molecules I and III are similar to those of other cyclooctynes,[2] showing an average value of 153.3°. Interestingly, the average value of the corresponding angles in molecule II is only 146.5°. The mean deviations of the carbon atoms comprising the eight-membered ring from their respective least-squares plane are 0.02 (2) Å for I, 0.07 (2) Å for II, and 0.01 (2) Å for III; the dihedral angles between the eight-membered ring and the three annelated benzene rings are 3 (1)°, 2 (1)°, and 3 (1)° for I, 6 (1)°, 3 (1)°, and 8 (1)° for II, and 3 (1)°, 1 (1)°, and 3 (1)° for III, respectively. Except for the triple bond, the other corresponding C-C bond lengths of the eight-membered ring in I-III are very close to one another, and the averages for the three molecules are shown in Figure 1. The crystal structure of **2** consists of a packing of discrete molecules with normal van der Waals contacts, and the three independent molecules are almost perpendicular to each other (Figure 2); values of the dihedral angle between pairs of least-squares molecular planes are as follows: I-II 93.0 (9)°, II-III 77.8 (9)°, and I-III 81.4 (9)°.

In conclusion, we have synthesized a stable planar derivative of 13,14-didehydrotribenzo[*a*,*c*,*e*]cyclooctene (**1**), the only elusive member in the family of benzene-annelated cyclooctatrienyne.

Acknowledgment. We thank Yu-Xin Cui for measuring the proton and carbon-13 NMR spectra for all new compounds.

Registry No. 2, 129000-06-2; **3**, 106865-81-0.

Supplementary Material Available: Electronic spectrum, proton NMR spectrum, carbon-13 NMR spectrum, and a listing of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates for **2** (17 pages); tables of observed and calculated structure factors for **2** (26 pages). Ordering information is given on any current masthead page.

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(9) Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.809$ (7), $b = 12.799$ (2), $c = 28.297$ (3) Å; $\beta = 102.99$ (2)°; $V = 5579$ (3) Å^3; $Z = 12$; and $\rho_{\text{calcd}} = 1.187$ g/cm^3. A crystal having approximately dimensions of 0.22 × 0.34 × 0.38 mm was mounted on a Nicolet R3m/V diffractometer. Intensity data of 7285 independent reflections collected with Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature (21 °C) by ω scan mode in the range of $3° \leq 2\theta \leq 45°$ were processed with the profile-fitting procedure and corrected for absorption by using ψ scan data. The structure was solved by direct-phase determination and refined with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were generated geometrically (C-H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of $U = 0.08$ Å^2. The structure was refined to the current residual values of $R = 0.098$ and $R_w = 0.060$ with 704 variables and weighting scheme of $w = [\sigma^2(F_o) = 0.00005|F_o|^2]^{-1}$ for 3327 observed reflections $[|F_o \geq 5\sigma(|F_o|)]$.

(10) Supplementary material.

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Asymmetric Claisen Rearrangement Catalyzed by Chiral Organoaluminum Reagent

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Reported herein is the first successful example of the asymmetric Claisen rearrangement of allyl vinyl ethers catalyzed by a chiral organoaluminum reagent, (*R*)-**1** or (*S*)-**1**.

The Claisen rearrangement of allyl vinyl ethers takes place by a concerted mechanism through a cyclic six-membered chairlike transition state.[1,2] For the asymmetric rearrangement, two possible chairlike transition states, A and B, must be considered, each of which is readily interconvertible and produces enantiomers **3** and **4**, respectively (Scheme I). Our interest is in the ability of chiral organoaluminum reagents of type **1** to discriminate between these two possible chairlike structures.[3]

The reaction of cinnamyl vinyl ether **2** (R = Ph, X = H) with (*R*)-**1** (Ar = Ph)[4] resulted only in C-O bond cleavage without any rearrangement. Introduction of the methyl substituent into substrate **2** (i.e., R = Ph, X = Me) yielded the desired rearranged ketone in 43% yield, but the optical yield was quite low (13% ee).

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