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Synthesis and Characterization of Trisbicyclo[2.1.1]hexabenzene, a Highly Strained Bicycloannulated Benzene[†]

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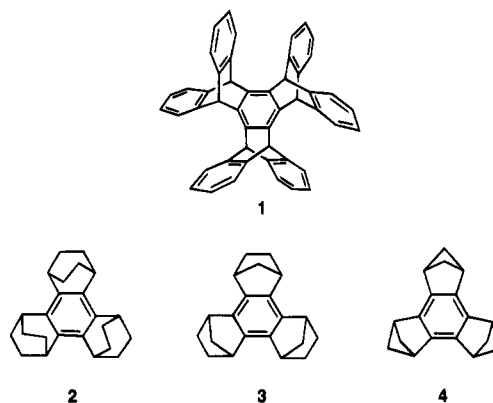
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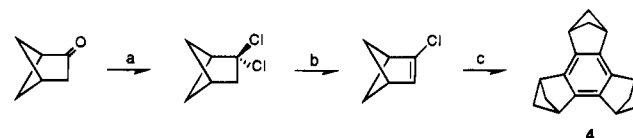
Exploration of the chemistry of highly strained cycloalkynes has led to the isolation of several novel trisannulated benzenes.² Although the cyclotrimerization of unstrained alkynes to form substituted benzenes requires metal catalysis,³ strained trisbicyclobenzenes such as heptitycene (**1**) have been synthesized from alkyne precursors without metal assistance.^{4–6} Consequently, the formation of benzene derivatives from such precursors has been taken as evidence for the generation of cycloalkynes, as in the isolation of trisbicyclo[2.2.1]heptabenzene (**3**).⁵ Even attempts to form bicycloannulated benzenes such as trisbicyclo[2.2.2]octabenzene (**2**)⁶ through reductive coupling of 1,2-dihalobicycloalkenes have been ultimately ascribed to formation of the cycloalkyne. Consideration of the incredible strain induced by alkyne formation in small bicyclic systems motivates one to question the intermediacy of alkynes. We report the synthesis and characterization of the most strained member of this series, trisbicyclo[2.1.1]hexabenzene (**4**), and present *ab initio* computational evidence for excessively high strain in bicyclo[2.1.1]hexyne.

The *D*_{3h} symmetric molecule **4** was prepared by applying the base-catalyzed elimination methodology of Wittig⁷ to 2-chlorobicyclo[2.1.1]hex-2-ene (Scheme 1), synthesized from the well-known bicyclo[2.1.1]hexan-2-one.⁸ Treatment of bicyclo[2.1.1]hexan-2-one with phosphorus pentachloride in phosphorus trichloride for 2 days led to conversion to 2,2-dichlorobicyclo[2.1.1]hexane. Subsequent treatment with potassium *tert*-butoxide in THF at reflux for several days led to complete conversion to 2-chlorobicyclo[2.1.1]hex-2-ene as evidenced by GC/MS. The reaction mixture was then treated with a mixture of *tert*-butyllithium and potassium *tert*-butoxide in a pentane/THF solution at –78 °C, followed by the addition of 10 mol % nickelocene and warming to reflux. Quenching of the reaction with saturated sodium chloride solution and

Chart 1



Scheme 1



^a Key: (a) PCl₅/PCl₃, 25 °C, 2 days; (b) *t*-BuOK/THF, reflux, > 3 days; (c) *t*-BuOK/*t*-BuLi in THF/pentane solution, 10 mol % Ni(Cp)₂, –78 °C to 35 °C.

standard workup in benzene led to a dark red oil. Precipitation with ether, followed by flash chromatography on silica with benzene as eluent, yielded a pale yellow solid. Trituration of the solid with acetone led to a white solid, pure by GC/MS, mp 164–165 (yield <1%).

The molecular weight of **4** was confirmed by high-resolution NH₃-induced CI mass spectrometry (MH⁺, C₁₈H₁₉ *m/z* 235.1492, calcd 235.1487). Proton NMR of the white solid at 360 MHz in C₆D₆ shows three signals (Figure 1): δ 3.22 (t, *J*_{BC} = 2.5 Hz, 6H, H_C, bridgehead), 2.52 (complex multiplet, 6H, H_B, exo bridge), and 2.27 (dd *J*_{AA'} = 2.7 Hz, *J*_{AB} = 1.4 Hz, 6H, H_A, endo bridge). This spectrum displays the characteristic downfield chemical shifts and unusual coupling constants of the bicyclo[2.1.1]hexane framework as seen in bicyclo[2.1.1]hexabenzene and derivatives.⁹ The ¹³C NMR at 500 MHz in C₆D₆ displays three signals: δ 135.89 (aromatic), 58.66 (bridgehead), and 43.96 (methylene). The chemical shifts and symmetry present in the spectra are consistent with a trisannulated benzene containing the bicyclo[2.1.1]hexane system.¹⁰ In the UV absorption spectrum of **4**, the longest wavelength aromatic band displays a broad peak around 265 nm consistent with that found for a range of hexaalkylbenzenes (λ_{max} = 270 ± 5 nm)¹² and trisannulated benzenes (λ_{max} ~ 260–270 nm).¹³

The structure of **4** provides an important test for the possibility of strain-induced bond alternation in benzenoid aromatics.

(9) For bicyclo[2.1.1]hexabenzene, see: (a) Pomerantz, M. *J. Am. Chem. Soc.* **1966**, *88*, 5349–5350. (b) Christl, M.; Reuchlein, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1035–1037. (c) Tanida, H.; Hata, Y. *J. Am. Chem. Soc.* **1966**, *88*, 4289–4290. (d) For the ¹H NMR of bicyclo[2.1.1]hexane derivatives, see: Wiberg, K. B.; Ubersax, R. W. *J. Org. Chem.* **1972**, *37*, 3827–3834.

(10) The chemical shift of the aryl carbons is not significantly shifted compared to hexamethylbenzene (132.2 ppm) and is extremely close to that of the analogous compound **3** (136.2 ppm).⁵ The chemical shifts of the bicyclic skeleton carbons are typical of the model system.^{9b}

(11) Reference deleted in press.

(12) The UV absorptions of hexaisopropyl- and hexamethylbenzene display λ_{max} of 273 and 270 nm, respectively, see: Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729–4731.

(13) The aromatic B band for triscyclopentabenzene and triscyclobutabenzene span the region 261–276 and 254–269 nm, respectively. Heilbronner, E.; Kovač, B.; Nutakul, W.; Taggart, A. D.; Thummel, R. P. *J. Org. Chem.* **1981**, *46*, 5279–5284.

[†] Dedicated to the memory of Paul G. Gassman (1935–1993).

(1) (a) University of California, San Diego. (b) San Diego Supercomputer Center.

(2) (a) Nakayama, J.; Segiri, T.; Ohya, R.; Hoshino, M. *J. Chem. Soc., Chem. Commun.* **1980**, 791–792. (b) Schröder, G.; Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 414–423.

(3) For the cyclotrimerization of alkynes, see: (a) Hoffman, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967; pp 350–355. (b) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1–8. (c) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556. (d) Pericás, M. A.; Riera, A.; Rossell, O.; Serratos, F.; Seco, M. *J. Chem. Soc., Chem. Commun.* **1988**, 942–943 and references cited therein.

(4) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427–4432.

(5) (a) For the preparation of trisbicyclo[2.2.1]heptabenzene, see: Gassman, P. G.; Gennick, I. *J. Am. Chem. Soc.* **1980**, *102*, 6863–6864.

(6) (a) Komatsu, K.; Jinbu, Y.; Gillette, G. R.; West, R. *Chem. Lett.* **1988**, 2029–2032. (b) Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633–634.

(7) (a) Wittig, G.; Weinlich, J.; Wilson, E. R. *Chem. Ber.* **1965**, *98*, 458–470. (b) Montgomery, L. K.; Applegate, L. E. *J. Am. Chem. Soc.* **1967**, *89*, 2952–2960. (c) Fixari, B.; Brunet, J. J.; Caubere, P. *Tetrahedron* **1976**, *32*, 927–934. (d) Bottini, A. T.; Frost, K. A., II; Andersen, B. R.; Dev, V. *Tetrahedron* **1973**, *29*, 1975–1981.

(8) (a) Bond, F. T.; Jones, H. L.; Scerbo, L. *Tetrahedron Lett.* **1965**, 4685–4686. (b) Bond, F. T.; Jones, H. L.; Scerbo, L. *Org. Photochem. Synth.* **1971**, *1*, 33.

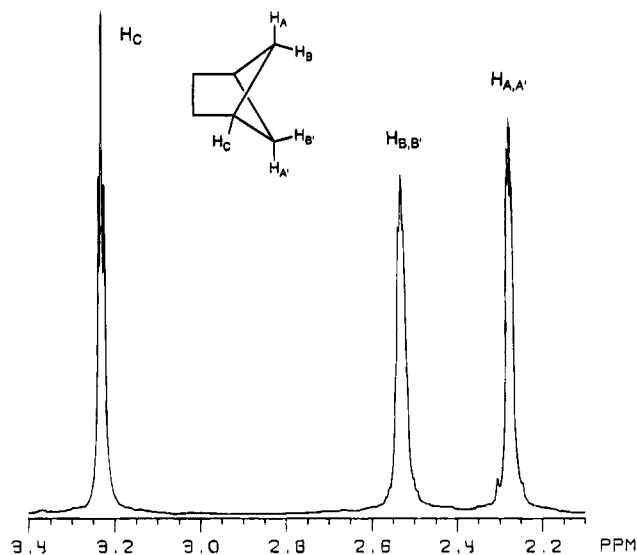


Figure 1. ^1H NMR of trisbicyclo[2.1.1]hexabenzene in C_6D_6 at 360 MHz.

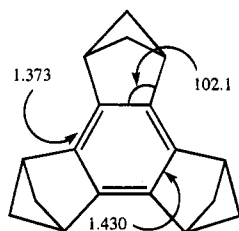


Figure 2. Bond alternation in **4** as gauged by MP2/6-31G(D) *ab initio* calculations; bond lengths in angstroms, bond angles in degrees.

Unfortunately, to date only disordered crystals of **4** have been grown, and the diffraction pattern has only been resolved well enough to confirm the chemical connectivity but not the molecular geometry. *Ab initio* MP2/6-31G(D) computations¹⁴ corroborate our earlier predictions, based on local density functional theory, that **4** should show ca. 7 pm difference between the endo and exo bond lengths (Figure 2).¹⁵

The strongly basic conditions used to prepare **4** are typical of those employed in the conversion of cyclohaloalkenes to cycloalkynes.¹⁶ Trapping experiments support the formation of strained alkynes such as bicyclo[2.2.2]octyne and dibenzo-

(14) Computational methods: Møller-Plesset order 2 (MP2) optimizations were performed using GAUSSIAN92 (Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. G.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92; Gaussian, Inc.: Pittsburgh, PA, 1992). The 6-31G(D) split level basis set which includes a set of six d polarization functions on all heavy atoms was employed, see: (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **1973**, *28*, 213–222. All structures were confirmed to be minima by normal mode analysis.

(15) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583–9587.

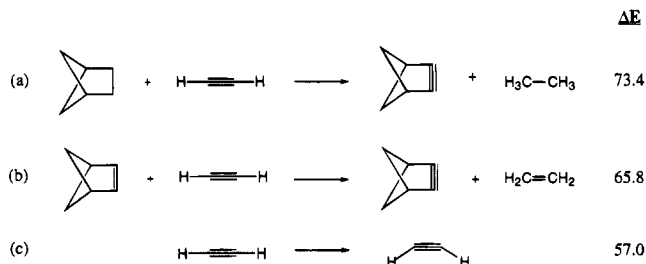


Figure 3. (a–b) Homodesmotic bond separation reactions to assess the strain in bicyclohexyne (full optimization at MP2/6-31G(D)). (c) Structural deformation energy of ethyne to assess the strain in bicyclohexyne; a single point calculation at MP2/6-31G(D) of ethyne with internal CCH angle of 104.5° .

bicyclo[2.2.2]octyne under similar conditions.^{4,18} It has been claimed that **3** is formed via norbornyne, though labeling experiments point to a manifold of reactive intermediates, only one of which might be norbornyne.¹⁷

The bicyclohexyl frame is far more strained than the norbornyl or bicyclooctyl; thus, it would be cavalier to assume that the formation of **4** proves the intermediacy of bicyclo[2.1.1]hexyne. To evaluate the rough strain energy of bicyclohexyne, *ab initio* MP2/6-31G(D) computations were done for the homodesmotic reactions a and b and for the simple distortion of acetylene from a linear to a bent geometry comparable to that computed for bicyclohexyne (Figure 3). All of these models indicated that the bicyclohexyne is ca. 60–70 kcal/mol higher in energy than the reference structures. Such extreme energy demands weaken the case for the formation of bicyclohexyne; however, complete labeling and stereochemical studies are underway to pin down the mechanism for the formation of **4**.¹⁸

Note Added in Proof: Through collaboration with Hans-Beat Bürgi, the disorder in **4** has just been resolved. The molecular structure in this solution validates the *ab initio* predictions. Details of the structure elucidation will be presented elsewhere.

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