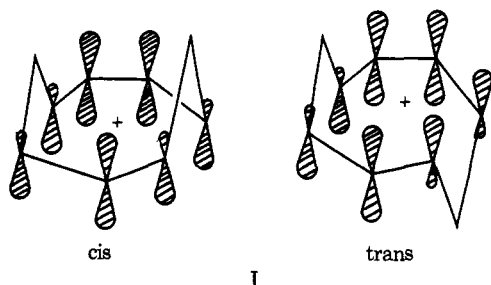


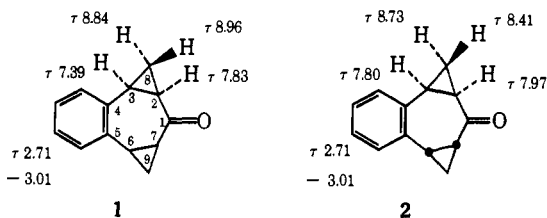
**Stereochemical Requirements for Bishomoaromaticity.**  
**Protonated *cis*- and**  
***trans*-4,5-Benzo-2,3:6,7-bishomotropones<sup>1</sup>**

Sir:

While several bishomoaromatic cations have been reported,<sup>2</sup> or proposed as intermediates,<sup>3</sup> there has been no systematic investigation of the geometric requirements of such delocalization. The two bridging groups of such systems can potentially adopt two distinct geometric arrangements, either *cis* or *trans* with respect to each other.<sup>4</sup> This is illustrated in structure I for the



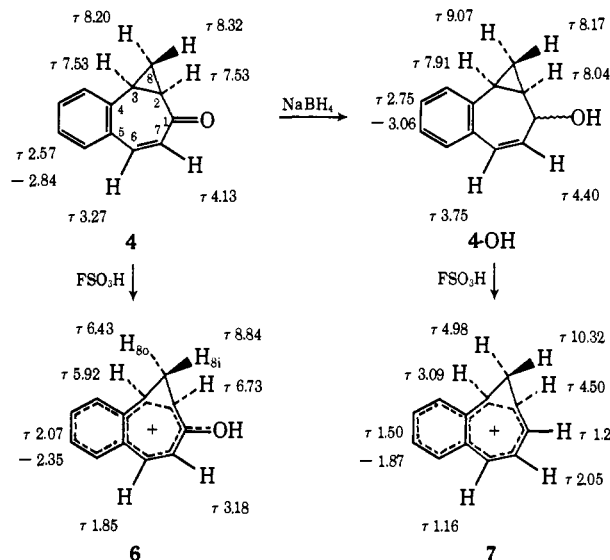
1,4-bishomotropylium cations.<sup>5</sup> To investigate the relative merits of these two geometric forms we have prepared and protonated the two 1,4-bishomobenzo-tropones **1** and **2**.



Ketones **1** and **2** were prepared by cyclopropanation of 4,5-benzotropone **3**.<sup>6</sup> The reaction of dimethyl-oxosulfonium methylide<sup>7</sup> with **3** in dimethyl sulfoxide yielded *cis*-4,5-benzo-2,3:6,7-bishomotropone **1**,<sup>8</sup> mp 63.5–64.5°, and 4,5-benzo-2,3-homotropone **4**.<sup>9a</sup> Ketalization of **3** and reaction of the ketal with C<sub>6</sub>H<sub>5</sub>HgCCl<sub>3</sub> gave predominantly the *trans*-tetrachloro diadduct **5**, mp 133–134°. Removal of the chlorines of **5** with Na–THF–*t*-BuOH followed by acid hydrolysis gave *trans*-4,5-benzo-2,3:6,7-bishomotropone (**2**), mp 90–91°. Reduction of the ketones with NaBH<sub>4</sub> gave the

corresponding alcohols, in each case only one isomer being obtained. The relative stereochemistry of **1** and **2** was established by examination of the nmr spectra of these alcohols. For the *cis* alcohol, **1**-OH, the proton  $\alpha$  to the hydroxy function which is coupled to the two bridgehead protons at C<sub>2</sub> and C<sub>7</sub> was a symmetrical triplet ( $J = 4.0$  Hz), while in **2**-OH the  $\alpha$  hydrogen was a doublet of doublets ( $J = 6.5$  and 1.0 Hz).<sup>10</sup> The signals attributable to the methylene protons in the nmr spectra of **1** and **2** were identified with the appropriately deuterium labeled compounds.

Before the results of the protonation of **1** and **2** are discussed it is instructive to examine the attenuating effect of the benzene ring and hydroxy function on these homotropylium cations. Protonation of either **4**



(FSO<sub>3</sub>H)<sup>9b</sup> or the derived alcohol **4**-OH (FSO<sub>3</sub>H–SO<sub>2</sub>ClF) gave the corresponding ions **6** and **7**, respectively, both of which are shown by their nmr spectra to be homoaromatic.<sup>5,11</sup> Thus, for **7**, inside proton H<sub>81</sub> is moved upfield and outside H<sub>80</sub> downfield to give a chemical-shift difference,  $\Delta = 5.34$  ppm. This is comparable to the difference seen with the unsubstituted homotropylium cation ( $\Delta = 5.80$  ppm) and it would seem that the benzene ring is not significantly attenuating the homoaromaticity of **7**.<sup>12</sup> The protonated ketone **6** shows analogous shifts of the inside and outside protons but the magnitude of the difference between these two is now much less,  $\Delta = 2.4$  ppm. The **4**-OH group would seem to be reducing considerably the ring current in **6**.<sup>13</sup>

Extraction of **1** and **2** from CD<sub>2</sub>Cl<sub>2</sub> into FSO<sub>3</sub>H gave cleanly the hydroxy cations **8** and **9**, respectively. The acid solutions of **8** and **9** were stable below –20° and could be quenched in Et<sub>2</sub>O–HCO<sub>3</sub><sup>–</sup> at –78° to give recovered **1** and **2**, respectively, in high yield.

(10) The stereochemical assignment is further confirmed by the nmr spectra of the ketals of the two tetrachloride diadducts obtained. No coupling between this  $\alpha$  proton and the hydroxy proton was observed when CDCl<sub>3</sub> was used as a solvent.

(11) Nmr spectra were obtained on Varian HA-100 and HR-220 spectrometers and referred to internal CH<sub>2</sub>Cl<sub>2</sub> taken as  $\tau$  4.70.

(12) R. F. Childs, M. A. Brown, F. A. L. Anet, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2175 (1972); W. Merk and R. Pettit, *ibid.*, **90**, 814 (1968); G. D. Mateescu, C. D. Nenitzescu, and G. A. Olah, *ibid.*, **90**, 6235 (1968).

(13) O. L. Chapman and R. A. Fugiel, *ibid.*, **91**, 215 (1969); M. Brookhart, M. Ogliaruso, and S. Winstein, *ibid.*, **89**, 1965 (1967); J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

(1) (a) This work was supported by the National Research Council of Canada. (b) First presented at C.I.C. Conference, Quebec, June 1972.

(2) (a) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2146, 4454 (1970); M. Roberts, H. Hamberger, and S. Winstein, *ibid.*, **92**, 6346 (1970); (b) P. Warner and S. Winstein, *ibid.*, **93**, 1284 (1971).

(3) (a) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **94**, 630 (1972); J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **94**, 2904 (1972); J. J. Gajewski and C. N. Shih, *Tetrahedron Lett.*, 2967 (1970); D. Cook, A. Diaz, J. P. Dirlam, D. L. Harris, M. Sakai, and S. Winstein, *ibid.*, 1405 (1971); (b) L. A. Paquette and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **94**, 632 (1972).

(4) The use of the term "double Möbius" to describe the *trans* bishomoaromatic system is misleading,<sup>9b</sup> as both isomers possess a Hückel array of atomic orbitals.

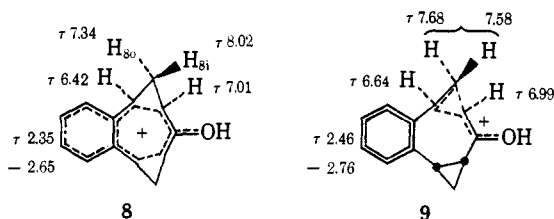
(5) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(6) A. Luttringhaus and H. Merz, *Arch. Pharm.*, **293**, 881 (1960).

(7) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965); cf. Y. Sugimura and N. Soma, *Tetrahedron Lett.*, 1721 (1970).

(8) All new compounds have satisfactory elemental analyses and spectroscopic data.

(9) (a) Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Lett.*, 91 (1971). (b) We find the chemical shifts of **6** to be uniformly shifted downfield by ca. 0.5 ppm to those reported by the authors.



The downfield shift of all the protons of **2** upon protonation is indicative of substantial charge delocalization in the trans cation **9**. While the symmetry displayed by the cyclopropyl resonances is compatible with a planar structure there is virtually no difference in the chemical shifts of the inside and outside methylene protons ( $\Delta = 0.1$  ppm). Using the difference in chemical shift of these protons as a criterion of homoaromaticity it must, therefore, be concluded that **9** is not bishomoaromatic.<sup>4</sup>

Symmetrical cyclic delocalization in **9** can only occur when the seven-membered ring is planar. In such a structure the internal cyclopropane bonds are not in the most favorable orientation for overlap with the electron-deficient center at C<sub>1</sub>. Deviation from a planar structure results in the formation of one of two equivalent boat conformations in which one cyclopropyl adopts the highly preferred bisected conformation and the other is perpendicular to the  $\pi$  system.<sup>14</sup> It would seem that the spectrum of **9** can best be described in terms of a rapid interconversion of these two boat conformations.

The cis cation **8** also exhibits a nmr spectrum that is symmetrical and which is indicative of substantial charge delocalization. It differs from **9** in that there is a difference between the inside and outside methylene protons of 0.7 ppm. In **8**, the bisected conformation of the cyclopropyl with respect to C<sub>1</sub>, the geometry demanded for effective delocalization, is only realized when the seven-membered ring becomes a shallow boat with the cyclopropanes in pseudoaxial positions. Such a geometry can only be attained at the expense of a severe steric interaction between the two inside protons and the gain in cyclic delocalization must be mitigated against this increased steric compression. The close proximity of the two inside protons will result in each being deshielded and for similar systems the magnitude of the van der Waals deshielding has been estimated at ca. 1.5 ppm.<sup>2b,15</sup> Thus, a better estimate of difference between the inside and outside protons would be 0.7 + 1.5 = 2.2 ppm which is comparable to that shown for **6** and would support a bishomoaromatic type delocalization in **8**.<sup>16</sup>

These results stress the importance of the alignment of the methylene bridges and the  $\pi$  system in homo-

(14) G. A. Olah, D. P. Kelly, G. L. Jeuell, and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 2544 (1970); **94**, 146 (1972); B. R. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970).

(15) S. Winstein, F. A. L. Anet, P. Carter, and A. J. R. Bourn *ibid.*, **87**, 5247, 5249 (1965); C. D. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, *ibid.*, **94**, 2291 (1972); L. M. Jackman and S. Sternhill, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, p 71.

(16) Inside (H<sub>81</sub>) and outside (H<sub>80</sub>) protons were identified from their coupling constants. The increase in  $J_{81,80}$  (6.4  $\pm$  0.2 Hz) for **8** relative to **1** supports these conclusions concerning the homoaromatic nature of **8**. It is interesting that  $J_{81,80}$  (6.0  $\pm$  0.3 Hz) for **9** is also increased, which is consistent with C<sub>2</sub>C<sub>3</sub> bond lengthening in this unsymmetrical cyclopropylcarbonyl system.<sup>17</sup>

(17) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2280 (1972).

aromatic systems and suggest that care should be exercised in invoking this type of delocalization.<sup>3a</sup>

H. A. Corver, R. F. Childs\*

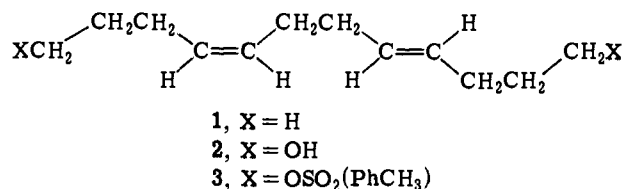
Department of Chemistry, McMaster University  
Hamilton, Ontario, Canada

Received May 8, 1972

### Synthesis and Carbon-13 Nuclear Magnetic Resonance Spectrum of *cis,trans*-4,8-Dodecadiene

Sir:

We have been interested in the use of model compounds for studying reactions and structures of butadiene polymers. These systems require the presence of  $\alpha,\epsilon$ -diene structures with varying *cis* and *trans* content. We now report the synthesis of one such compound, *cis,trans*-4,8-dodecadiene (**1**) and the use of <sup>13</sup>C Fourier transform (FT) nmr for confirmation of its *cis,trans* structure.



The synthesis of *cis,trans*-4,8-dodecadiene-1,12-diol (**2**) has been reported.<sup>1</sup> Compound **2** has a diffuse *cis* HC=CH absorption in the infrared (ca. 710 cm<sup>-1</sup>) and had been characterized as the *cis,trans* isomer since its 970-cm<sup>-1</sup> absorption (trans HC=CH) was 50% as intense as that of a precursor, *cis,trans,trans*-1,5,9-cyclododecatriene. Conversion of **2** in pyridine<sup>2</sup> to the corresponding ditosylate **3**, followed by treatment of **3** with a fivefold excess of lithium aluminum hydride in ether<sup>3</sup> afforded **1** in 80% yield.<sup>4</sup> Like **2**, the infrared spectrum of compound **1** has a diffuse band in the region 690–725 cm<sup>-1</sup> which is of limited use for characterizing geometry; the band at 960–970 cm<sup>-1</sup> of a CS<sub>2</sub> solution of **1** was approximately 50–60% as intense as corresponding bands in solutions of 97% *cis,trans,trans*-cyclododecatriene<sup>5a</sup> or 90% *trans,trans*-3,7-decadiene<sup>5b</sup> at equivalent concentrations.<sup>6</sup> It was thus inferred that **1** was the *cis,trans*-diene.

(1) H. Takahashi and M. Yamaguchi, *Bull. Chem. Soc. Jap.*, **36**, 1390 (1963). This compound had been named as *cis,trans*-5,9-dodecadiene-1,12-diol.

(2) (a) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, pp 1180–1181, and references therein. (b) Compound **3** was a viscous oil, purified by repeated extraction with petroleum ether. It had characteristic infrared and <sup>1</sup>H nmr spectra.

(3) Reference 2a, pp 587–588, and references therein.

(4) Compound **1** was purified by vacuum distillation, bp 50–51° (0.8 Torr). Mass spectrum (M<sup>+</sup> = 166, base = 83), <sup>1</sup>H nmr (60 MHz,  $\delta$  (CDCl<sub>3</sub>) 5.48 (m, 4 H), 1.96–2.07 (s, 8 H), 1.38 (m, 4 H,  $J = 6.5$  Hz), 0.87 (t, 6 H,  $J = 6.5$  Hz)) and ir ( $\nu$  (CS<sub>2</sub>) 2960 (m), 1382 (w), 966 (m), 690–725 cm<sup>-1</sup> (m)) were consistent with its structure. *Anal.* Calcd for C<sub>12</sub>H<sub>22</sub>: C, 86.6; H, 13.4. Found: C, 86.6; H, 13.2. Vapor phase chromatography revealed a single component using either Carbowax 20M or polyphenylene ether columns.

(5) (a) Obtained from Aldrich Chemical Co., Milwaukee, Wisc. (b) Obtained from Chemical Samples Co., Columbus, Ohio.

(6) The geometric isomers of **1** have been reported, with characteristic infrared absorption bands for *cis,cis* ( $\nu$  1400, 725 cm<sup>-1</sup>) and *trans,trans* ( $\nu$  966 cm<sup>-1</sup>): C. Pinazzi, D. Reyx, and G. Levesque, *C. R. Acad. Sci., Ser. C*, **270**, 2120 (1970).