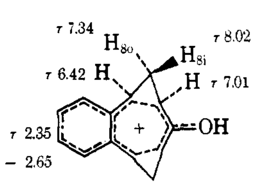
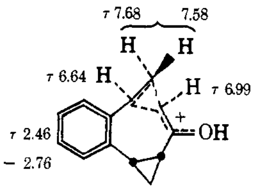


8



9

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.[4]

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_1. 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 π system.[14] 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_1, 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.[2b,15] 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**.[16]

These results stress the importance of the alignment of the methylene bridges and the π system in homoaromatic systems and suggest that care should be exercised in invoking this type of delocalization.[3a]

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[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.

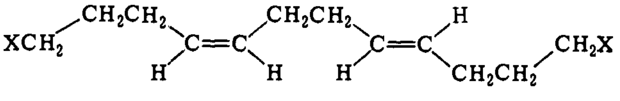
[16] Inside (H_{8i}) and outside (H_{8o}) protons were identified from their coupling constants. The increase in $J_{8i,8o}$ (6.4 $\mp$ 0.2 Hz) for **8** relative to **1** supports these conclusions concerning the homoaromatic nature of **8**. It is interesting that $J_{8i,8o}$ (6.0 $\mp$ 0.3 Hz) for **9** is also increased, which is consistent with C_2C_3 bond lengthening in this unsymmetrical cyclopropylcarbinyl system.[17]

[17] P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2280 (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 α,ϵ-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 ^{13}C Fourier transform (FT) nmr for confirmation of its cis,trans structure.



1, X = H
2, X = OH
3, X = $OSO_2(PhCH_3)$

The synthesis of *cis,trans*-4,8-dodecadiene-1,12-diol (**2**) has been reported.[1] Compound **2** has a diffuse cis HC=CH absorption in the infrared (*ca.* 710 cm^{-1}) and had been characterized as the cis,trans isomer since its 970-cm^{-1} 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[2] to the corresponding ditosylate **3**, followed by treatment of **3** with a fivefold excess of lithium aluminum hydride in ether[3] afforded **1** in 80% yield.[4] Like **2**, the infrared spectrum of compound **1** has a diffuse band in the region 690–725 cm^{-1} which is of limited use for characterizing geometry; the band at 960–970 cm^{-1} of a CS_2 solution of **1** was approximately 50–60% as intense as corresponding bands in solutions of 97% *cis,trans,trans*-cyclododecatriene[5a] or 90% *trans,trans*-3,7-decadiene[5b] at equivalent concentrations.[6] It was thus inferred that **1** was the *cis,trans*-diene.

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[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 ^1H 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 ($M^+ = 166$, base = 83), ^1H nmr (60 MHz, δ ($CDCl_3$) 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 (ν (CS_2) 2960 (m), 1382 (w), 966 (m), 690–725 cm^{-1} (m)) were consistent with its structure. *Anal.* Calcd for $C_{12}H_{22}$: 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 (ν 1400, 725 cm^{-1}) and trans,trans (ν 966 cm^{-1}): C. Pinazzi, D. Reyx, and G. Levesque, *C. R. Acad. Sci., Ser. C*, **270**, 2120 (1970).

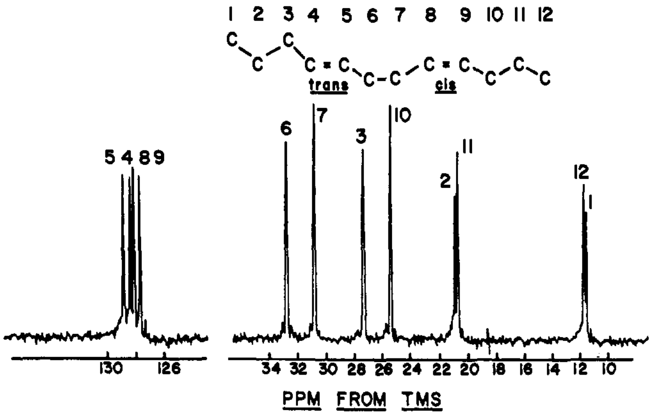

Figure 1. ^{13}C FT nmr spectrum at 25.15 MHz of *cis,trans*-4,8-dodecadiene in dioxane (50% w/v). Reprinted by permission of John Wiley and Sons, Inc.; from ref 7.

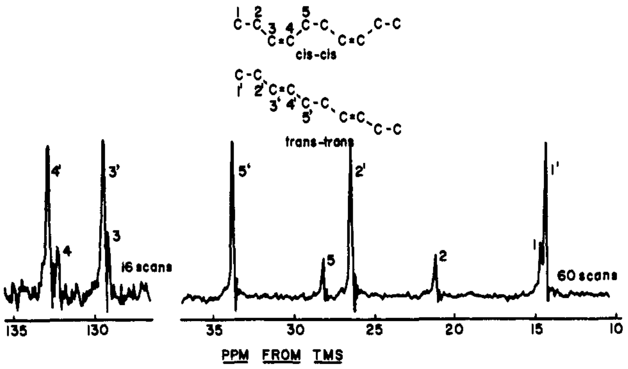

Figure 2. ^{13}C nmr spectrum of an isomeric mixture of 3,7-decadiene in dioxane (50% w/v). Reprinted by permission of John Wiley and Sons, Inc.; from ref 7.

The ^{13}C FT nmr of **1**, given in Figure 1, shows all 12 carbon nuclei clearly.[7] The peaks near 128 ppm show that each of the four olefinic carbons has a slightly different electronic environment. The power of ^{13}C nmr is impressively demonstrated by the fact that the slight difference in methyl carbons (at 12 ppm) is easily discerned. The peaks are separated by 0.14 ppm (or 3.5 Hz). Positive assignment of these peaks to methyl carbons was shown by their quartet structure in an off-resonance decoupling experiment. The peaks of the adjacent methylene carbons (at 21 ppm) show a similar separation (0.15 ppm).

The four remaining peaks are due to methylene carbons 3, 6, 7, and 10. The fact there are four well-separated peaks conclusively shows that: (1) the adjacent carbons and the next-nearest neighbors have a considerable effect on the electronic environment, *e.g.*, carbons 3 and 6 are different from each other as are carbons 7 and 10, and (2) the carbons in a cis–trans linkage (6 and 7) are considerably different from each other. Calculated chemical shifts based upon empirical parameters determined from a series of unsubstituted hydrocarbons[8] do not take into account differences between cis and trans units. Additional terms should be added to the parameters to correct for these sizable effects.

This spectrum clearly confirms that this compound has the geometry of **1**. If it were cis–cis or trans–trans, the olefin region would have only two peaks and the aliphatic region only four. Furthermore, the peak intensities indicate about equal concentrations of cis and trans units, thus supporting cis–trans geometry.

The eight peaks in the aliphatic region are in a pattern of a set of four lower intensity peaks and a set of four higher intensity peaks, as judged by peak heights. Each set probably arises from one structure, cis or trans, reflecting a difference in relaxation times between the two structures. The set with the lower peak heights (1, 2, 3, 6) is assigned to the trans structure and the remaining set to the cis structure. This assignment is supported by ^{13}C nmr spectra of cis and trans 1,4 addition polybutadienes which show the *trans*-methylene carbons are downfield 5.4 ppm from *cis*-methylene carbons.[9]

A further assignment of peaks can be made by referring to Figure 2, which is the ^{13}C nmr spectrum of a mixture of isomers of 3,7-decadiene.[5b] The mixture contains about 90% of the trans–trans isomer (the tall peaks) and about 10% of either the cis–cis or the cis–trans isomer. Since only three small peaks are observed in the aliphatic region, it appears that the cis–cis isomer is the minor component. Again, the trans–trans peaks are downfield from the cis–cis peaks except for the methyl carbons, which are also reversed in the spectrum of **1**. Carbons 2 and 2′ which are "outside" carbons are shifted about 7.5 ppm upfield from the "inside" carbons, 5 and 5′. Therefore, in Figure 1 carbons 3, 10, 12, and 1 are assigned as shown by analogy with Figure 2. The carbons of the cis–trans linkage, 6 and 7, have a separation of 2.4 ppm and are assigned intuitively as shown.

In conclusion, ^{13}C FT nmr supports the previous assignment of the geometry in **2** and confirms the geometry of **1**.

Acknowledgment. We wish to acknowledge the assistance of R. K. Griffith in the synthesis work and the permission of The Firestone Tire & Rubber Co. to publish this communication.

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(7) The spectrum was taken with a JEOL JNM-PS/PFT 100 spectrometer at 25.15 MHz. It was obtained with 512 scans, a pulse repetition time of 2.1 sec, and 16,384 data points. TMS is used as the reference. The most likely assignment of peaks is shown in Figure 1. Reprinted from V. D. Mochel, *J. Polym. Sci., Part A-1*, 10, 1009 (1972).

(8) G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **68**, 1956 (1964).

(9) M. W. Duch and D. M. Grant, *Macromolecules*, 3, 165 (1970).

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Diphenylphosphoryl Azide. A New Convenient Reagent for a Modified Curtius Reaction and for the Peptide Synthesis

Sir:

This communication describes some synthetic utilities of a hitherto unknown reagent, diphenylphosphoryl azide (DPPA). The new reagent is conveniently pre-