## Observation of Ring Inversion in a Thiepin Dioxide by Low-Temperature 250-MHz Proton Nuclear Magnetic Resonance Spectroscopy

Sir:

The study of low barriers (*e.g.*, <6 kcal/mole) separating conformations or valency tautomers by high-resolution proton nmr spectroscopy is often not possible because of the broadness of the spectral lines at low temperatures (*e.g.*, < −130°) combined with the rather small proton chemical shifts. The broadness of the lines results from the comparatively small rate of molecular tumbling at low temperatures and is independent of spectrometer frequency.[1] Therefore, operation at a higher spectrometer frequency, which gives larger chemical shift differences (measured in frequency units), is advantageous. Unfortunately, commercially available high-field superconducting-solenoid spectrometers have been limited, until now at least, to sample temperatures of not much lower than −60°. The work described below was carried out on a spectrometer designed for several purposes including very low-temperature operation.[2]

The completely conjugated seven-membered ring system in thiepin 1,1-dioxide[3] (I) is of considerable theoretical interest. Although the ring is nonplanar,[4] there are some unusual features such as large internal C–C–C bond angles, possibly caused by a flattening of the ring induced by conjugation. An investigation of the barrier to ring inversion in this system was therefore undertaken.

I   II
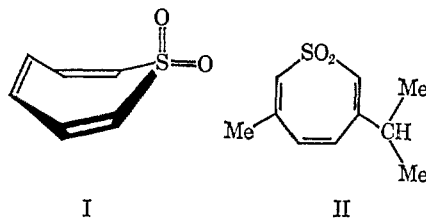
Although the rate of ring inversion in I cannot be determined by proton nmr, such measurements can be made on certain derivatives of I. For example, in 3-isopropyl-6-methylthiepin 1,1-dioxide (II), the methyl groups in the isopropyl chain are diastereotopic[5] because of the nonplanarity of the seven-membered ring and should give rise to separate resonance signals provided that ring inversion is slow on the nmr time scale. The nmr spectrum of II in $CHClF_2$ solution was examined at 60, 100, and 250 MHz from room temperature down to about −150°. At 60 MHz, the band of

(1) For protons the most common relaxation mechanism contributing to $T_2°$ (and equally to T_1) is the direct dipole–dipole interaction modulated by random molecular rotation and translation: J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 9.

(2) Details of the spectrometer, which makes use of a Magnion superconducting solenoid, will be published elsewhere; *cf.* F. A. L. Anet, paper presented at the Tenth Experimental NMR Conference, Pittsburgh, Pa., Feb 1969.

(3) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967).

(4) H. L. Ammon, P. H. Watts, Jr., J. M. Stewart, and W. L. Mock, *ibid.*, **90**, 4501 (1968). The coupling constants have been obtained from a detailed analysis of the nmr spectrum of I, and indicate that the conformation in solution is most probably a flattened boat: M. F. Williamson, W. L. Mock, and S. Castellano, *J. Magnetic Res.*, in press.

(5) K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 38.
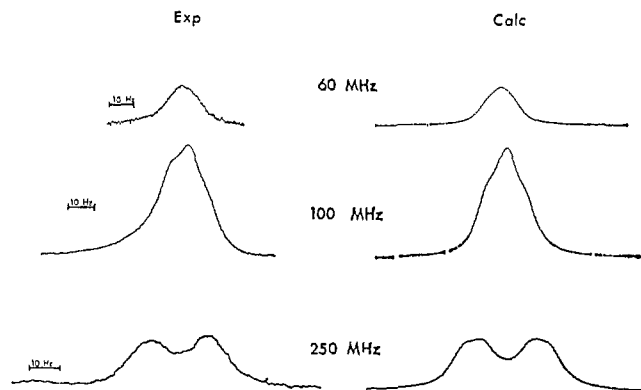
Figure 1. Experimental and calculated methyl bands of the isopropyl group in II at −150° for various spectrometer frequencies.

the isopropyl methyl groups broadened from a sharp doublet (owing to coupling to the adjacent methine proton) at room temperature to a smooth broad band at −150° (Figure 1). At 100 MHz, the band at −150° had a slightly different width from that at 60 MHz and also showed several inflections not visible at the lower frequency (Figure 1). While these facts indicate that ring inversion has indeed become slow at −150°, the 250-MHz spectrum at about −150° showed unambiguously that the isopropyl methyl groups have two different chemical shifts (Figure 1). The spin–spin couplings in this spectrum are not resolved because of viscosity broadening together with some broadening resulting from ring inversion still having an appreciable rate at −150°.

Theoretical spectra calculated[6] with a rate constant for ring inversion of 10 sec^{-1} together with a natural line width in the absence of exchange of 7.0 Hz (+ 1.5 Hz for the 250-MHz spectrum for extra magnetic field inhomogeneities) are shown in Figure 1 and are in good agreement with experiment at all three spectrometer frequencies. The above inversion rate corresponds to a free-energy barrier of 6.4 kcal/mole. The barrier to inversion in the parent thiepin 1,1-dioxide (I) is probably a little lower than this, since the isopropyl group in II is probably slightly more sterically hindered in the planar form than it is in the nonplanar form. Thus, the barrier to inversion in I appears to be very similar to the 6-kcal/mole barrier in 1,3,5-cycloheptatriene.[7] Long C–S bonds and the small C–S–C bond angle in I would be expected to raise the barrier for ring inversion compared to that in 1,3,5-cycloheptatriene. The compensating effect in I is probably the presence of conjugation. It should be noted, however, that 1,3,5-cycloheptatriene may be stabilized in a nonplanar form by homoconjugation, and this effect also may be present in I. Also, effective conjugation in I may occur in a nonplanar as well as in a planar conformation.[4] More detailed measurements of the rate of ring inversion in II are planned.

(6) The two spin-coupled doublets [δ 0.10 ppm; *J* (to adjacent methine proton) = 6.9 Hz] were treated as a double two-site system. Since the spectra are close to first order, this procedure should not introduce significant errors. The natural line width includes any broadening caused by the finite lifetime of the methine proton spin states. Calculations were carried out with a multisite computer program of Professor M. Saunders on the Health Sciences Computing Facility, UCLA, sponsored by NIH Grant FR-3.

(7) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

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The 3,4:5,6:9,10-Tribenzobicyclo[6.2.0]decapentaenyl Dianion

Sir:

3,4:5,6:9,10-Tribenzobicyclo[6.2.0]decapentaene (1), a (4*n* + 4*n*)-π-electron system, is a nonplanar, nonaromatic molecule.[1] By analogy with cyclooctatetraene,[2] reduction of 1 with alkali metals could give a planar, aromatic dianion. Two factors might be expected to render this reduction less likely: namely, that annelation will increase the compression energy required to flatten the eight-membered ring,[3] and that the cyclobutadienyl character of the four-membered ring will be increased in the delocalized dianion.

We now report that 1 reacts with alkali metals to give eventually, through a series of intermediates, the 3,4:5,6:9,10-tribenzo[6.2.0]decapentaenyl dianion (2),
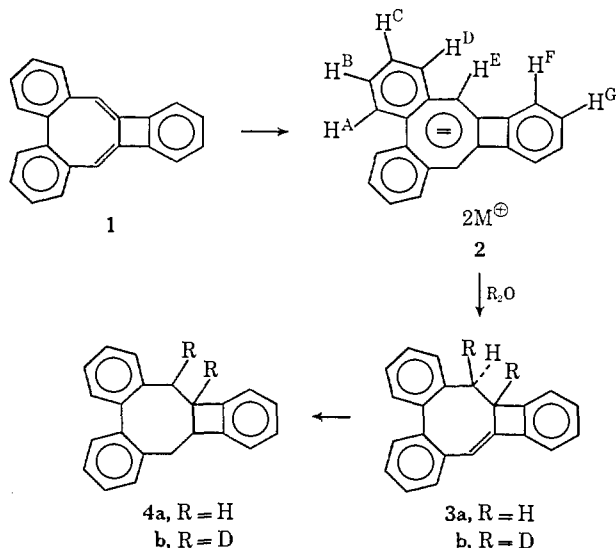
the first analog of a biphenylene in which one of the phenyl rings has been replaced by a ten-π-electron system.[6]

(1) P. J. Garratt and R. H. Mitchell, *Chem. Commun.*, 719 (1968); P. J. Garratt, R. H. Mitchell, and K. P. C. Vollhardt, submitted for publication.

(2) T. J. Katz, *J. Amer. Chem. Soc.*, 82, 3784, 3785 (1960).

(3) The barrier to ring flattening is overcome in both *sym*-dibenzocyclooctatetraene[4,5] and tetraphenylene,[5] which are reduced by alkali metals.

(4) T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, 87, 4516 (1965).

(5) A. Carrington, H. C. Longuet-Higgins, and P. F. Todd, *Mol. Phys.*, 8, 45 (1964).

(6) Recently the biphenylene analog has been reported in which a phenyl ring has been replaced by the six-π-electron cyclopentadienyl anion: M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, 91, 2378 (1969).
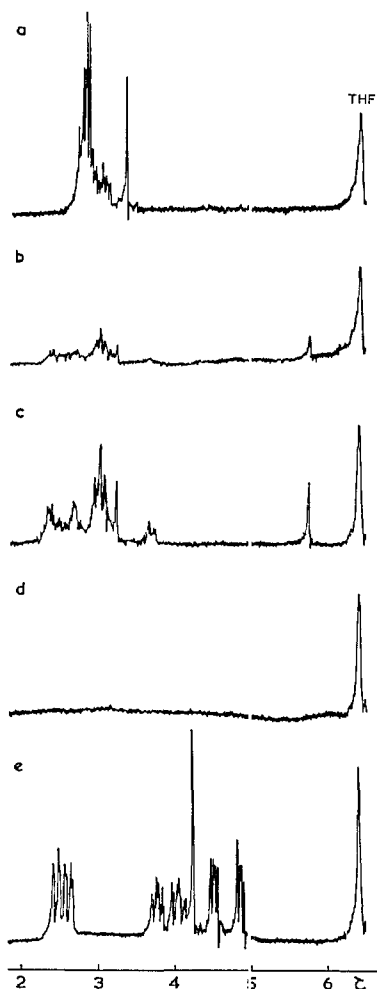
Figure 1. Nmr spectra (100 MHz, 35°) of a 0.2 *M* solution of 1 in THF-*d*₈ taken at different time intervals after contact with a potassium mirror.

A 0.2 *M* solution of 1 in dry THF reacts *in vacuo* with distilled potassium to give a dark green solution.[7] The assignment of 2 to the dianion in solution is based on its spectral and chemical properties. The nmr spectrum (THF-*d*₈, 35°, see Figure 1e) shows multiplets at τ 2.52 (4.0 H, H^A, H^D) and 3.90 (4.2 H, H^B, H^C), a singlet at τ 4.23 (1.8 H, H^E), and multiplets at τ 4.51 (1.9 H, H^G) and 4.87 (2.1 H, H^F). The low-field multiplet (4 H) consists of two doublets (J = 8 Hz), as expected for aromatic protons coupled to only one *ortho* proton (H^A, H^D). The multiplet at τ 3.9 is composed of two bands centered at τ 3.76 (2 H) and 4.06 (2 H), both consisting of an overlapping double doublet (J = J' = 8 Hz), with further small couplings, as expected for aromatic protons coupled to two *ortho* protons (H^C, H^B). The two high-field multiplets appear as overlapping double doublets (J = 4, J = 3 Hz), consistent with the H^F, H^G protons having a small *ortho* and a relatively large *meta* coupling. The attribution of the τ 4.51 band to H^G and that at τ 4.87 to H^E is based on the expected effect of charge localization on these positions, and the relative chemical shift of the equivalent protons in biphenylene (see below and footnotes 9, 10). The

(7) Solutions of 1 also react with lithium, but the course of this reaction has been less well studied.