Evidence for a Nonclassical Structure of a 1,6-Methano[10]annulene: A Cryogenic ^{13}C CPMAS NMR Study of the 11,11-Dimethyl Derivative

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Received: June 21, 1994[⊗]

High-resolution ^{13}C NMR spectra obtained using cryogenic CPMAS methodology at temperatures as low as 10 K suggest that the structure of 11,11-dimethyl-1,6-methano[10]annulene is nonclassical.

The problem of valence tautomerism of 1,6-methano[10]-annulene (**Ia/IIa**)[1] and its derivatives with two bridge substituents, in particular 11,11-dimethyl-1,6-methano[10]annulene (DIM, **Ib/IIb**),[2] has been of considerable interest for a long time. As shown in Figure 1 these molecules either exist as an interconverting mixture of an aromatic form (**I**) and a bisnorcaradiene form (**II**) separated by an energy barrier (Figure 1d–f) or adopt an intermediate nonclassical structure between the extremes **I** and **II** (Figure 1a–c). Solution ^{13}C NMR studies of a variety of 11,11-disubstituted 1,6-methano[10]annulenes exhibited a surprisingly large range for the chemical shift of the central carbon atoms 1 and 6, 124 ppm > $\delta_{1,6}$ > 40 ppm, where derivatives with a shift at the low-field value were assigned to form **I**.[1a,2,3] Furthermore, for some of these molecules, a temperature dependence of $\delta_{1,6}$ was found and interpreted in terms of a fast tautomerism between the two forms.[2] Similar conclusions were reached in a recent variable-temperature ^{13}C CPMAS NMR study of DIM carried out at temperatures down to 140 K.[3] Theoretical studies also favor interconversion over a barrier.[4] In contrast, room-temperature crystal structures of several 1,6-methano[10]annulenes showed C_1C_6 distances varying between 1.54 and 2.27 Å, indicating nonclassical structures between the two extremes **I** and **II**.[5] In this we report the results of ^{13}C CPMAS NMR experiments on DIM at very low temperatures (100–10 K) which support a nonclassical structure.

A selection of the spectra, obtained at 1.4 T using an apparatus described previously,[6] are shown in Figure 2. The two lines marked A and B at 80 and 74 ppm, respectively, have been assigned[3] to the equivalent carbon atoms C_1 and C_6 of molecules in two nonequivalent sites, A and B, in the asymmetric unit, exhibiting slightly different C_1C_6 distances of 1.836 and 1.780 Å.[7] The position of line A remains remarkably constant over the entire temperature range (10 K to ambient), a phenomenon which at first sight is consistent[3] with a degenerate rearrangement between forms **I** and **II** characterized by an equilibrium constant $K \sim 1$. On the other hand, between room temperature and 140 K, the position of line B shifts slightly to higher fieldas

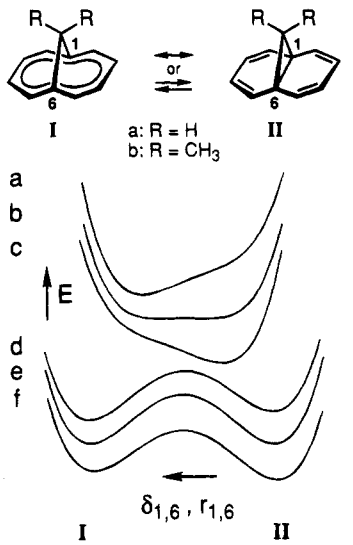

Figure 1. Hypothetical potential surfaces for the valence tautomerism of 1,6-methano[10]annulenes; (a–c) single-minimum potentials, (d–f) double-minimum potentials. $\delta_{1,6}$ is the chemical shift of carbon atoms 1 and 6; $r_{1,6}$ is the distance between carbon atoms 1 and 6.

observed previously.[3] This shift was interpreted in terms of a nondegenerate valence tautomerism (Figure 1f) favoring the bisnorcaradiene form at low temperature. The solid curve in Figure 3 is based on this model and was calculated using published parameters.[3] According to this model, line B should shift to 40 ppm at very low temperatures. The new results we report here, shown in Figures 2 and 3, clearly indicate that the chemical shift of line B remains constant at 60 ppm between 100 and 10 K, the lowest temperature at which spectra were obtained. If this value corresponded to the intrinsic chemical shift of the bisnorcaradiene structure **IIb**, the position of line A would indicate an intrinsic chemical shift of 100 ppm for the annulenic structure **Ib**. In other words, the chemical shift difference between the two forms would be 40 ppm, instead of the 80 ppm found for this class of molecules by solution ^{13}C NMR studies.[1a,2,3] Thus, the new results obtained here are inconsistent with equilibria characterized by the surfaces shown in Figure 1d–f. Moreover, this conclusion is reinforced by

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

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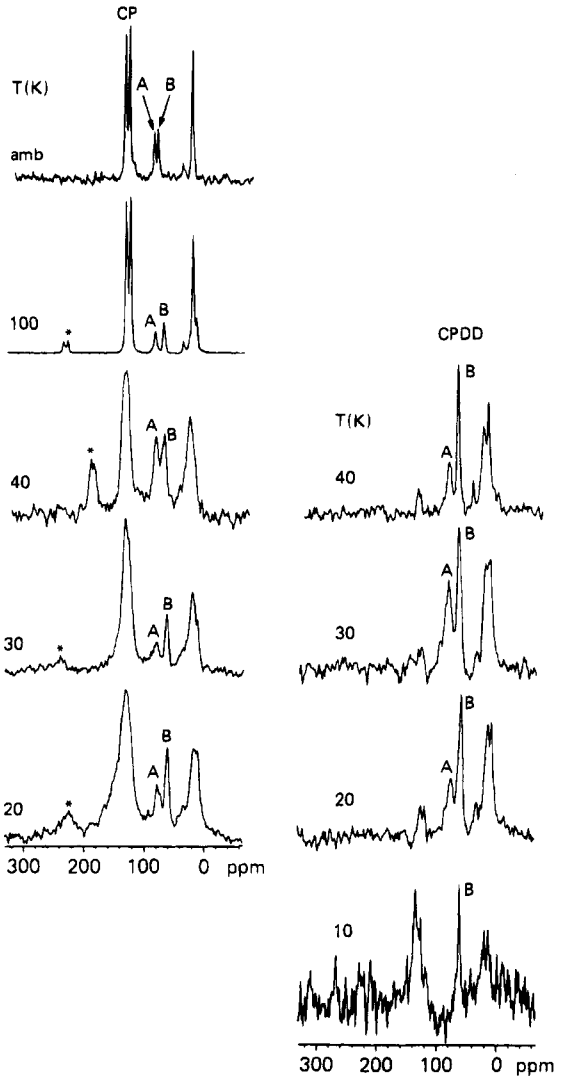

Figure 2. ^{13}C CPMAS NMR spectra of DIM at different temperatures. The spectra on the right, denoted CPDD, were obtained with delayed decoupling (see Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854−5856) in order to minimize the effect of spinning sidebands (marked with an asterisk) from the strong aromatic peaks at 130 ppm. The decoupling was delayed 40 μs before the signal was acquired.

thelack of dynamic line broadening arising from interconversion between forms **Ib** and **IIb** in the spectra of Figure 2.

Therefore, we interpret our very low temperature data in terms of the broad asymmetric potential well shown in Figure 1c. In this model, the chemical shift $\delta_{1,6}$ is a function of the distance between the central carbon atoms 1 and 6 ($r_{1,6}$). The slight temperature dependence of the chemical shift of line B thus reflects a temperature dependence of the C_1C_6 distance. Two possible sources for this distance dependence are (1) as the temperature is increased, higher vibrational levels are populated leading to a change of the average distance between carbon atoms 1 and 6 and/or (2) slight changes in geometry with temperature affect the shape of the potential surface due to neighboring molecules. The width of the line due to molecules

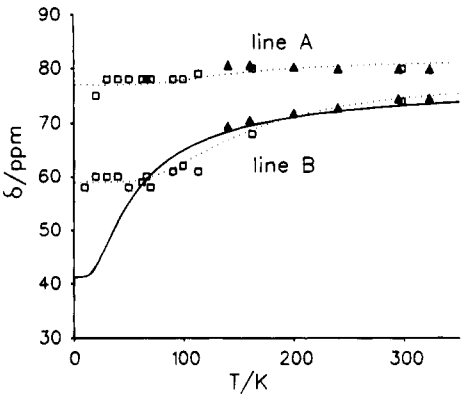

Figure 3. Chemical shift ($\delta_{1,6}$) of carbon atoms 1 and 6 of molecules A and B in DIM as a function of temperature: solid triangles represent data from ref 3, open squares from this study. The solid line was calculated according to the parameters used in ref 3 in terms of a 1,6-methano[10]annulene−bisnorcaradiene equilibrium (Figure 1f). The dotted lines are drawn only to serve as a guide to the eye.

in site A increases very slowly as the temperature is lowered from 323 to 20 K, and the line disappears at 10 K. The origin of this line broadening and intensity loss is currently unknown but would be consistent with a distribution of temperature-dependent C_1C_6 distances in molecules in site A.

In summary, we conclude that the results of cryogenic ^{13}C CPMAS NMR experiments do not support an equilibrium model of valence tautomerism of 11,11-dimethyl-1,6-methano[10]-annulene but do suggest a nonclassical structure in which the bond lengths between carbon atoms 1 and 6 are sensitive to the environment and temperature.

Acknowledgment. Two of us (C.S.Y. and H.H.L.) are grateful for support from a NATO grant and from the Fonds der Chemische Industrie, Frankfurt (H.H.L.). The authors thank R. D. Kendrick for skillful technical assistance.

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