sponding t_{2g} orbitals on each metal atom, then, gives three Fe–Fe bonds, one σ and two π.

Concerning the evaluation of the Fe–Fe bond order in this compound, we are in agreement with Cotton[7] that any attempt to find a direct correlation of the metal–metal distance with bond order in this type of structures is meaningless. Therefore, it does not seem unreasonable to affirm that in the $[Fe_2H_3(P_3)_2]^+$ complex cation there are three Fe–Fe interactions, some or all of which are weaker than a full bonding interaction.

Acknowledgments. We wish to thank Professor L. M. Venanzi for measuring the ^{31}P spectrum of the compound.

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Direct Observation of Chair and Boat Conformations for Dibenzocycloocta-1,5-diene by Nuclear Magnetic Resonance

Sir:

Although the conformational properties of 1,5-cyclooctadiene and some of its derivatives have been the subject of several important studies,[1-10] information regarding the nature of the most stable conformation in solution and the modes of interconversion of conformational isomers has been, heretofore, inconclusive or contradictory. Under favorable circumstances, when molecules have relatively high free energy barriers to conformational changes, the "DNMR" method[11] is particularly well suited to this area of investigation. Using this technique, we have studied the behavior of dibenzocycloocta-1,5-diene (**1**), and we wish to report observations which, we feel, make a significant contribution to the understanding of this conformational problem.

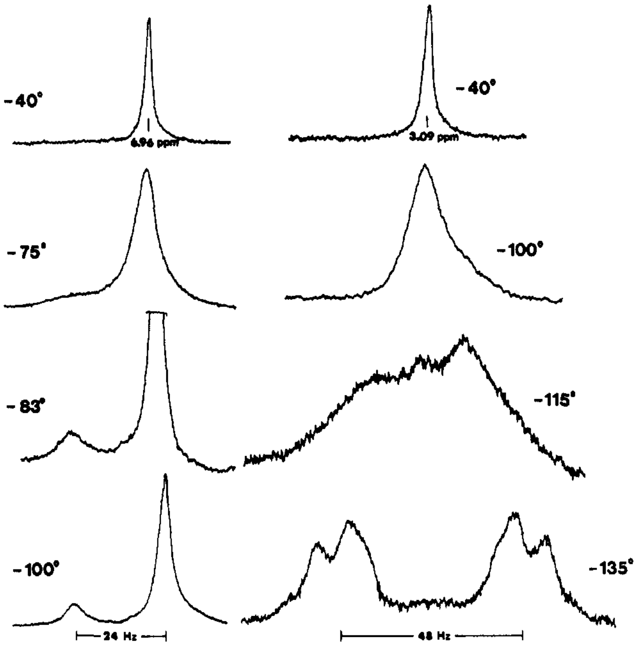

Figure 1. Typical 100-MHz pmr spectra of the aromatic (left) and methylene (right) protons of dibenzocycloocta-1,5-diene at several temperatures.

The 100-MHz pmr spectra of **1**, dissolved in a mixture of methylene-d_2 chloride and propene (2 : 1), are shown in Figure 1 for various temperatures. A spectral change occurs whereby the aromatic signal (δ 6.96 at $-40°$) splits into two peaks below $-72°$ (the coalescence temperature, T_c); the separation between the peaks at $-100°$ is 24 Hz, and their relative areas are in the ratio 87 : 13. On the other hand, the methylene singlet (δ 3.09 at $-40°$) remains essentially unchanged down to about $-90°$. Below this temperature it broadens and at $-115°$ (T_c) changes into an AA′BB′ spectrum whose form closely resembles an AB quartet ($\Delta\nu \approx 48$ Hz) because of the particular magnitudes of the coupling constants.[12]

Solubility problems at low temperatures greatly limit the choice of solvents. Nevertheless it was found that a solution of **1** in a mixture of toluene-d_8 and propene (1 : 1) also revealed similar changes in both the aromatic and methylene regions of the spectrum. Unfortunately, the spectral change in the aromatic region is obscured partly by overlap with peaks from residual protons in the deuterated toluene solvent. Integrations at -40 and $-100°$ can account for these impurities and show that the low field component has increased to about 40% of the total area of the aromatic signal at $-100°$.

Approximate values for $\Delta G^{\ddagger}$ characteristic of the processes underlying the spectral changes can be obtained from standard equations.[13] Estimates of 10.2 ± 1 and 7.5 ± 1 kcal/mol were calculated for the changes at -72 and $-115°$, respectively.

The above results can most readily be interpreted in terms of a mixture of chair and boat (presumably twisted to relieve eclipsing about the CH_2–CH_2 bonds) conformations for dibenzocycloocta-1,5-diene. The spectral change near $-72°$ is then attributed to a chair to boat equilibration (**2** → **3**) while that near $-115°$ is due to an equilibration of equivalent conformations of the boat family (represented by **3** → **4**); the latter process may be called most simply a boat inversion.

Twist boat forms are presumably more stable than boat forms. However, interconversion (or rocking) between two twist boats such as **5** and **6** is expected to have a very low energy barrier such that it should be rapid on the nmr time scale at $-135°$ and should result

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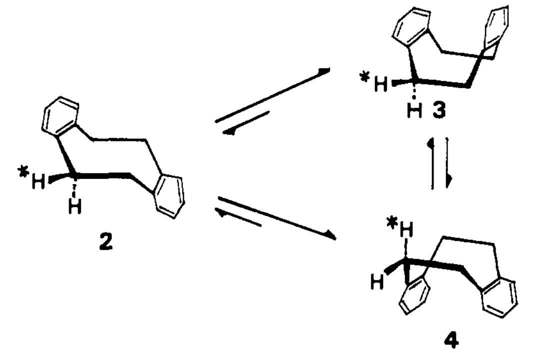
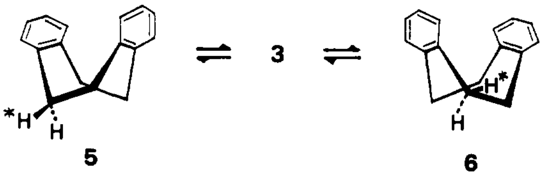


in an averaged symmetry equivalent to that of the boat **3**. Thus **3** and **4** represent rapidly equilibrating twist boat conformations and, being easier to visualize, are used to represent the effect of boat inversion and chair to boat interconversion.



The aromatic protons in conformations **5** and **6** are located in the shielding zone[14] of the aromatic ring across the boat. This effect, being more important for the boats than the chair, then suggests that the more intense high field component of the aromatic signal at −100° is due to protons of the boat forms whereas the less intense low field component belongs to the protons of the chair. Thus, when the equilibrium **2** → **3** becomes rapid both types of aromatic protons become averaged together and one peak results.

The change from **3** to **4** causes an "outside" proton in **3** (starred proton) to become an "inside" proton in **4**. Thus, when boat inversion is slow on the nmr time scale, a complex pattern is expected for the methylene protons, and when it becomes rapid, all methylene protons of the boat family become equivalent, resulting in a singlet as observed. It should be noted that, because of the relatively small amount of chair form at −100°, the multiplet for the methylene protons of molecules in this conformation is barely visible compared to the larger signal for protons from molecules in the boat conformations. On the other hand, these protons appear responsible for part of the deformation (asymmetry) of the spectra at −100 and −115°.

Thus compound **1** has been found to exist as a mixture of conformations in solution. The interpretation of the spectral data suggests that a member of the boat family, most likely the twist boat, is present in a larger proportion than the chair form. This conclusion is particularly revealing since this compound has been reported to exist in a centrosymmetrical form (presumably the chair) in the crystalline state.[1] On the other hand, our nmr results agree partially with those from dipole moment studies[3] on the same molecule but differ in the nature of the predominant conformation. In view of the observed solvent dependence of the relative proportions of chair and boat conformations and the inherent difficulties of the dipole moment method, this difference does not appear too surprising.

Pmr studies[4] of 1,5-cyclooctadiene (**7**) were inconclusive since they failed to reveal a spectral change down to −150°. On the other hand, electron diffraction work[15] on this compound indicates that a mixture of chair and boat conformations exists with the latter predominating, whereas recent X-ray work on crystals of *syn*-3,7-dibromo-*cis,cis*-cycloocta-1,5-diene has shown that it possesses a twist-boat conformation.[10] Interestingly, theoretical predictions of the most stable conformation of **7** appear to disagree with each other; one calculation[7] favors a twist-boat conformation whereas the other[8] argues for a chair. It therefore appears that **1** and **7** might have similar conformational properties, the main differences between them being lower free energy values for the various equilibrations in **7**.

Future work on this subject will include a complete solvent study as well as the synthesis of deuterated derivatives to simplify the spectral changes thereby providing more precise information on the properties of the stable conformations and more accurate thermodynamic and kinetic parameters.

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(15) Personal communication from K. Hedberg to J. D. Dunitz, as quoted in footnote 26 of ref 9.

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Concerning the Mechanism of Action of Coenzyme B_{12} in Dioldehydrase and Related Enzymes. Synthesis and Reactions of Postulated Organocorrin Intermediates

Sir:

Recently, new mechanisms of action of coenzyme B_{12} in dioldehydrase[1] and in related enzymes were postulated,[2-4] which differ substantially from the mechanism we proposed[5,6] on the basis of model experiments. A typical version of the potentially alternative mechanisms is shown in Scheme I, which since has been modified to apply to the mechanism of ethanolamine ammonia-lyase.[7] The new mechanisms suggest an initial homolysis of the Co–C bond of the coenzyme and several hypothetical reactions of postulated organocorrin intermediates or of free radicals derived from the substrate and

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(1) Abbreviations used are: dioldehydrase, DL-1,2-propanediol hydrolase (EC 4.2.1.28); coenzyme B_{12}, α-(5,6-dimethylbenzimidazolyl)-*Co*-5′-deoxyadenosylcobamide; cobaloximes are derivatives of bis(dimethylglyoximato)cobalt.

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