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NMR Isotope Shift Evidence for Conformational Structures of Dimethyl-9,10-Dihydroanthracenes and the 1,4,4-Trimethylcyclohexyl Cation*

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NMR isotope shifts provide evidence of rapidly equilibrating nonplanar conformations in solution for 9,9-dimethyl-9,10-dihydroanthracene and trans-9,10-dimethyl-9,10-dihydroanthracene. In each case, labeling with a single deuterium in the 9- or 10-position results in two different methyl signals in ^{13}C NMR spectra. The separation between methyl signals is temperature dependent and characteristic of isotopically perturbed equilibria. For *cis*-9,10-dimethyl-9,10-dihydroanthracene-9-d_1, only intrinsic isotope effects on the chemical shifts are present, indicating a single conformation. Similarly, equilibrium isotope shifts are also seen for the C4 methyls in 1,4,4-trimethylcyclohexyl cation, thereby ruling out the C_2 twist-boat as a viable conformation.

INTRODUCTION

We are pleased to contribute to this issue honoring Dionis Sunko because his review of secondary deuterium isotope effects[1] contributed much to our understanding of the relationship between carbocation structure and isotope effects. Also, two papers with Hehre[2] provided a firm theoretical basis for a hyperconjugative interpretation of the angular dependence of isotope effects that we have frequently invoked to explain NMR isotope shifts.

The NMR isotope shift[3] has proven to be quite useful in examining the structure of long-lived carbocations and other molecules. The distinction between isotope effects on chemical shifts *via* perturbed equilibria and intrinsic isotope effects on chemical shifts was first applied to carbocations by Saunders to provide a means of distinguishing between static, bridged structures and structures undergoing rapid degenerate equilibria.[4] Since then, both intrinsic and equilibrium NMR isotope shifts have been applied to investigate various structural features in carbocations, including bonding type, hyperconjugation, rearrangements, and conformations.[5] Saunders' review of

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.

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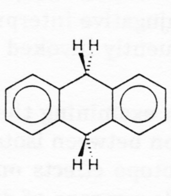
recent studies of carbocations includes very good coverage of the ways in which NMR isotope shift evidence can reveal structural detail.[6]

In this contribution, we describe new observations of equilibrium NMR isotope shifts that provide insight to conformational structure in two systems, the dimethyl-9,10-dihydroanthracenes and the 1,4,4-trimethylcyclohexyl cation. In each case, the type of conformation is at issue, and our observations of an isotopic perturbation of a degenerate equilibrium narrows the conformational possibilities. The perturbed equilibria are detected through the temperature dependent separation of ^{13}C NMR signals for methyl groups which are averaged to chemical shift equivalence in the unlabelled compounds *via* rapid conformational equilibria. This type of signal separation for two methyls has been measured previously in various structures undergoing conformational exchange.[7] All of the previous cases involved chair-chair equilibria; in the present study, other types of conformations are possible.

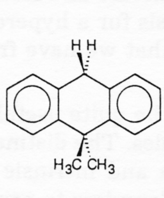
RESULTS AND DISCUSSION

Dimethyl-9,10-dihydroanthracenes

The preferred geometries of 9,10-dihydroanthracene (DHA), its derivatives, and other compounds related to 1,4-cyclohexadienes, have been the subject of considerable debate and experimental investigation.[8] The parent **DHA** was demonstrated to be nonplanar in the solid state by X-ray analysis which showed a folding angle of 145° between the planes containing the benzene rings.[9] Since proton NMR spectra in solution did not resolve separate pseudoaxial (pa) and pseudoequatorial (pe) signals at low temperature, the central ring has been presumed to undergo very rapid boat-to-boat interconversions.[10] Solution NMR studies of several derivatives were interpreted on the basis of boat conformations.[11] Solid state ^{13}C NMR spectra of 9,9-dimethyl-DHA, **1**, and *trans*-9,10-dimethyl-DHA, **2**, indicate nonplanarity by the presence of two methyl signals for each compound, and the close similarity of chemical shifts for liquid and solid states was said to argue strongly for similar structures in the liquid.[12] The liquid and solid state ^{13}C spectra of *cis*-9,10-dimethyl-DHA, **3**, were interpreted as indicating a puckered geometry with the predominant conformation having both methyl groups pseudoaxial.[12,13]



DHA



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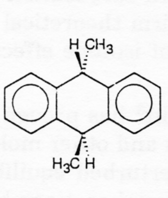

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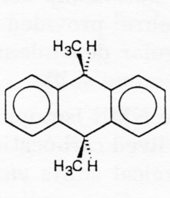

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In contrast to the systems mentioned above, planar or near planar structures were found in the solid state for *trans*-9,10-dipropyl-DHA,[14] 9,9,10,10-tetramethyl-DHA,[12] 9,9,10,10-tetrachloro-DHA,[15] and *trans*-9,10-bis(trimethylsilyl)-DHA.[16] Rabideau *et al.* concluded, on the basis of force field calculations and a re-examination of ^{13}C NMR spectral data, that there is a greater tendency for planarity around the central ring of 9,10-dihydroanthracenes than previously considered.[13] MM2 and MMPI calculations on **DHA** itself show a very shallow energy surface with 1.7 kJ mol^{-1} or less energy difference between planar and boat forms.[17] An *ab initio* calculation suggests an inversion barrier of about 8 kJ mol^{-1} for **DHA**.[18] Molecular mechanics calculations also suggest that the relative stability of boat and planar forms may be controlled by the size of the 9,10-substituents.[8]

From the studies cited above, it seems clear that even if the parent **DHA** prefers the boat form in solution, it is likely that a transition to a planar form would occur with increasing size and/or number of 9,10-substituents. Such a transition would mean a change from rapidly equilibrating conformers to a single planar structure. Thus, this appears to be a good case for application of the tool of isotopic perturbation to detect possible rapid, degenerate, equilibria.

We report here evidence from the isotopic perturbation method that rapidly equilibrating nonplanar forms exist for **1** and **2** in solution. The dimethyl-9,10-dihydroanthracenes **1**, **2**, and **3** were each prepared with a single deuterium in the 9- or 10-position. From ^{13}C NMR spectra of mixtures of the labeled and unlabeled compounds, the temperature dependencies of the chemical shifts of the methyl signals of each labeled compound relative to the reference methyl signal of the corresponding unlabeled compound are plotted in Figure 1.

Labeling with a single deuterium in **1**, *i.e.*, 9,9-dimethyl-DHA-10-d_1, results in separation of the ^{13}C (and ^{1}H) NMR signals for the two methyl groups. The separation

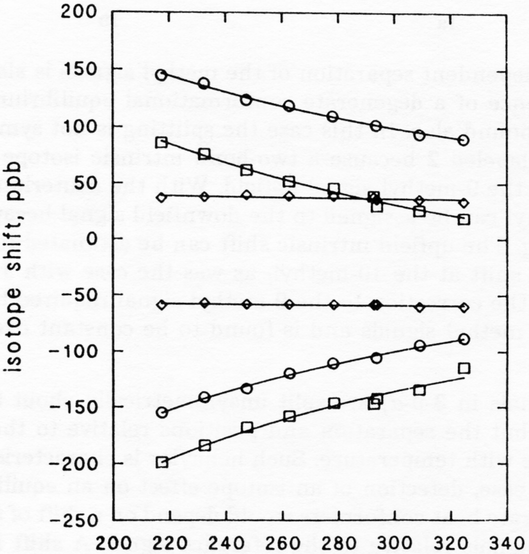
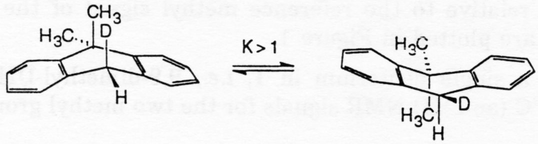


Figure 1. Isotope shifts in ppb (±7 ppb) of the ^{13}C NMR signals of the methyl groups of **1**-10-d_1 (○), **2**-9-d_1 (□), and **3**-9-d_1(◇), relative to the methyl signal of the corresponding unlabeled compound. ^{13}C NMR spectra of mixtures of each pair of labeled and unlabeled compounds in $CDCl_3$ were obtained at 75.43 MHz. Nearly identical isotope shifts were observed for **1**-1-d_1 in acetone-d_6. Positive sign of isotope shift indicates downfield shift from reference methyl signal.

is temperature dependent, becoming larger at lower temperature, and is symmetrical about the signal position of the unlabeled compound. This temperature dependent, symmetrical splitting fits the classic description of an equilibrium isotope shift due to perturbation of a degenerate equilibrium.[4] The observation must be considered as strong evidence for a populated equilibrium between two boat forms of **1**.

The isotope effect in **1**-10-d_1 shifts the equilibrium towards one of the two conformers so that one methyl occupies the more shielded[12] pe position more frequently, while the other methyl is more often in the pa environment and its ^{13}C signal moves downfield. It is expected that the equilibrium between **1a** and **1b** is shifted in the sense shown below, placing the deuterium preferentially in the pe position, because deuterium prefers the more stiffly bound position in an equilibrium exchange process. The pe position is more sterically crowded and would have a stiffer bending potential for the C–H bond, while force constants for the pa position may be weakened by hyperconjugation. Because the signal separation is symmetrical about the unlabeled position, there is apparently no long range intrinsic isotope effect on either methyl group in **1**-10-d_1.



1a **1b**

A temperature dependent separation of the methyl signals is also found for **2**-9-d_1, indicating the presence of a degenerate conformational equilibrium in the unlabeled *trans* dimethyl compound also. In this case the splitting is not symmetrical about the methyl signal of unlabeled **2** because a two-bond intrinsic isotope shift[1] from the 9-deuterium will shift the 9-methyl signal upfield. With the deuterium preferring the pe position, the 9-methyl can be assigned to the downfield signal because of its more frequent pa positioning. The upfield intrinsic shift can be estimated to be −11 ppb by assuming no intrinsic shift at the 10-methyl, as was the case with **1**-9-d_1 The intrinsic shift is then simply the correction to the 9-methyl signal required to give symmetrical splitting of the two methyl signals and is found to be constant over the temperature range studied.

The methyl signals in **3**-9-d_1 are split unsymmetrically about the position of the methyl signal of **3**, but the separation and positions relative to the reference methyl signal do not change with temperature. Such behavior is characteristic of intrinsic isotope shifts.[1] In this case, detection of an isotope effect on an equilibrium between inherently nondegenerate boat conformers would depend on a shift of the average position of the two methyl signals relative to the reference signal. A shift in the boat-to-boat equilibrium would have the same effect on both methyls, but would also shift their average signal position relative to the signal for **3**. No such shift in average position is seen and thus no perturbation of a conformational equilibrium is detected for **3**. Thus, these data are consistent with the previous conclusion[12,13] that **3** exists as a single boat conformation with both methyl groups pseudoaxial.

Qualitatively, the temperature dependencies of the isotope shifts for **1** and **2** in Figure 1 are similar. The equilibrium constant K_{iso}, for an isotopically perturbed degenerate equilibrium can be calculated by applying Saunders' equation,[4] $K_{iso} = (\Delta + \delta_{eq})/(\Delta - \delta_{eq})$, where δ_{eq} represents the equilibrium isotope shift, here the difference between methyl signals corrected for any intrinsic effect, and Δ is the maximum possible signal separation, determined at the slow exchange limit (Δ and δ_{eq} in same units, ppm or ppb). The Δ values in solution are unknown. If it is assumed that the ^{13}C chemical shifts of the methyl signals of **1** and **2** are the same as found in the solid state,[12] *i.e.*, 25.6 and 33.1 ppm for **1** and 13.4 and 26.6 ppm for **2**, then the Δ values are 7.5 and 13.2 ppm for **1** and **2**, respectively. Use of these values to determine K_{iso} at different temperatures leads to the estimation of $\Delta H_{iso} = -188$ J mol^{-1} and $\Delta S_{iso} = -0.21$ J mol^{-1} K^{-1} for the isotope effect in **1**, and $\Delta H_{iso} = -113$ J mol^{-1} and $\Delta S_{iso} = 0.00$ J mol^{-1} K^{-1} for **2**. On the other hand, if the same Δ value of 13.2 ppm is assumed to apply to both systems, then very similar isotope effects are calculated. When $\Delta = 13.2$ ppm is used for **1**, the resultant $\Delta H_{iso} = -109$ J mol^{-1} and $\Delta S_{iso} = -0.12$ J mol^{-1} K^{-1} are close to those calculated above for the equilibrium isotope effect for **2**. Thus, it is intriguing to consider that the difference between pe and pa methyl environments in **1** and in **2** may be more consistent in solution than in the solid state.

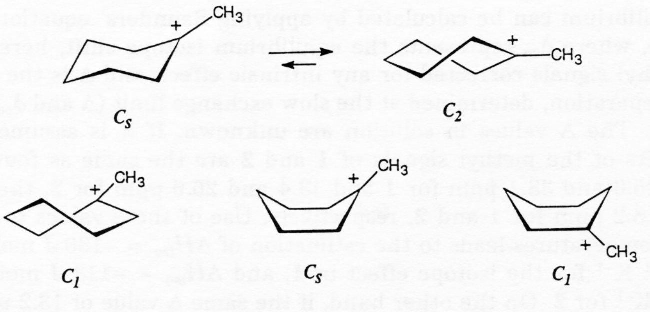
An approximately 110 J mol^{-1} magnitude of the isotope effect is quite reasonable, since it is roughly four times larger than the isotope effect favoring deuterium in the equatorial position in cyclohexanes,[7f,19] but not as large as the effect in cyclohexanones.[7e,h] Cyclohexane does not have equivalent crowding of the equatorial position nor any hyperconjugation for the axial position, while hyperconjugation should be more important in cyclohexanones.

Our evidence that nonplanar forms are populated and in rapid equilibrium for **1** and **2** does not rule out the possibility of populated planar forms. However, it is very unlikely that a planar form is the global minimum in either case. To the extent that the planar form is populated, the apparent free energy change, ΔG_{iso}, for the isotope effect will be reduced below the true value (the extreme case of 100% planar would show no δ_{eq} and thus apparent values of $K_{iso} = 1$ and $\Delta G_{iso} = 0$).[20] High populations of the planar forms would require unreasonably large energies for the isotope effects to produce the chemical shift separations displayed in Figure 1.

All DHA's may not show the same behavior as the dimethyl examples presented here. It will be interesting to see in future studies whether the equilibrium isotope shifts persist as alkyl group size increases, and whether there is a sharp cut-off in such behavior or a gradual diminishment with alkyl group size. A series of 9,10-substituted DHA's may provide the opportunity to observe what happens to isotope shifts in a transition from a double minimum potential surface to a broad, shallow surface with perhaps three minima, to a single minimum.

The 1,4,4-Trimethylcyclohexyl Cation

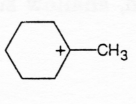
Tertiary cyclohexyl cations pose a surprisingly difficult problem in structure determination. The ^{13}C chemical shifts in superacid solution of the cation centers in the 1-methylcyclohexyl cation (332 ppm),[21] **4**, and the 1-phenylcyclohexyl cation (262 ppm)[22] are quite ordinary and typical of classical tertiary alkyl and benzylic ions, respectively. However, as far as conformational structure is concerned, a simple analogy to the chair structure of cyclohexanones or other typical cyclohexyl structures does not suffice to explain more detailed NMR data. Sorensen found dependence of ^{13}C chemical shifts in **4** on temperature, counterion, and solvent, and concluded that two isomeric structures were present in equilibrium.[21] Initially, Sorensen proposed that a chair structure and twist-boat of C_2 symmetry were in rapid equilibrium, with the latter



Scheme 1

favored. Other possible structures considered (Scheme 1) were a C_1 twist-boat, a C_S boat, and a C_1 boat.

In a later study, Sorensen found additional evidence to support the concept of two different types of cyclohexyl cations, but revised the structures proposed.[23,24] The occurrence of a rapid equilibrium between two isomers was supported by NMR isotope shift measurements. The 1-methylcyclohexyl-2,2,6,6-d_4 cation, **4**-2,2,6,6-d_4, showed chemical shifts for the β-carbons (C3,5) relative to the C3,5 signals in unlabeled **4** that were temperature dependent and very large, on the order of 7 ppm. These large isotope shifts indicated an isotopically perturbed rapid equilibrium between two isomeric structures with quite different C3,5 chemical shifts. Sorensen concluded that one of the cyclohexyl cation types was strongly C–C hyperconjugating and the other was strongly C–H hyperconjugating.[23] Further, a variety of data appeared consistent with both ions having a chair structure. On the basis of the cyclohexyl cation data and related studies of tertiary 2-adamantyl cations,[24] Sorensen proposed that the solvent/counterion interacted primarily with only one face of the carbocation. Thus, the 1-methylcyclohexyl cations were proposed to be the two different chair structures that result from solvation of opposite faces, as in **4a** and **4b**, with significant pyramidal distortion.[24] Pyramidalization allows the electron deficient hybrid orbital to line up well for C–H hyperconjugation in one structure and C–C hyperconjugation in the other.



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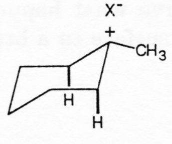
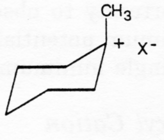
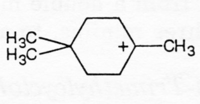


4a



4b



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We present here additional NMR isotope shift evidence regarding the structure of a tertiary cyclohexyl cation. Our work on cyclohexyl cations is still in progress, but the observations reported here do rule out one of the conformational possibilities.

The 1,4,4-trimethylcyclohexyl cation, **5**, apparently exists as a single isomer of the C–H hyperconjugating type.[23] Although two isomeric types are not present, nonetheless, a rapid conformational equilibrium is occurring. Only a single signal is seen for

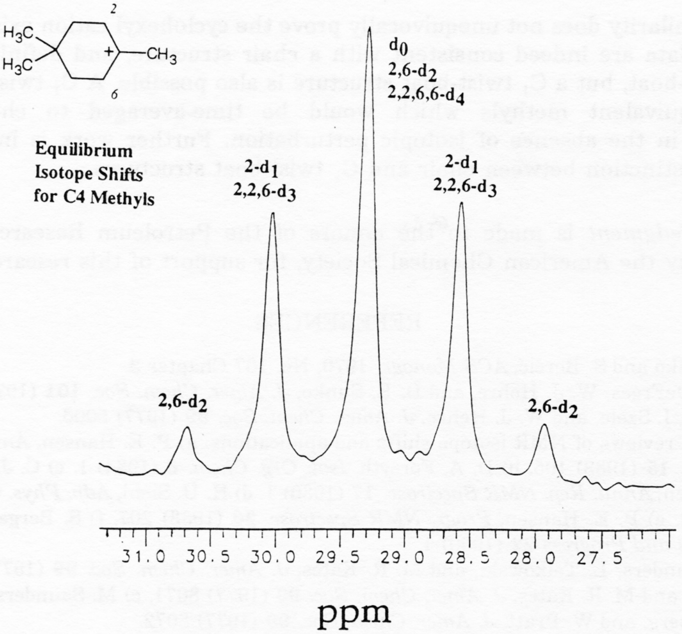

Figure 2. The C4 methyl region of a 75.43 MHz ^{13}C NMR spectrum at −110 °C of the 1,4,4-trimethylcyclohexyl cation as a mixture of isotopomers labeled with deuterium at C2,6.

the two methyls in the ^{13}C NMR spectrum (at 29 ppm) of either unlabeled **5** or **5**-2,2,6,6-d_4.[23] However, we find that some partially deuterated isotopomers show separation of methyl signals about the central position, as shown in Figure 2. This behavior is typical of isotopic perturbation of a degenerate equilibrium wherein nuclei exchange between nonequivalent sites but are averaged to chemical shift equivalence.[4] Upon isotopic perturbation, the equilibrium is shifted so that the methyls are no longer time-averaged to chemical shift equivalence. This observation clearly demonstrates that any proposed structure must have nonequivalent methyl environments at C4. Thus, the original suggestion of Sorensen[21] that the C–H hyperconjugating form has the C_2 twist-boat structure is absolutely ruled out, because the C_2 symmetric structure includes equivalent methyls at C4.

The ^{13}C spectrum in Figure 2 is of a mixture containing all of the different isotopomers due to deuteriation at C2 and C6 in **5**. Most of the methyl signals have been assigned by varying the proportions of isotopomers present. However, while it is known that the outer pair of signals arises from either the **5**-*trans*-2,6-d_2 and **5**-*cis*-2,6-d_2 isotopomer, it is not known which of the two gives those signals. The inner pair of signals displays the separation of methyl signals due to the effect of a single deuterium, in both the 2-d_1 and 2,2,6-d_3 isotopomers. (In the 2,2,6-d_3 isotopomer, the effects of the two deuteriums at C2 cancel). A very similar pattern is observed for 4,4-dimethylcyclohexanone[25] in which the *cis*-2,6-d_2 isotopomer accounts for the outer pair of signals, because *cis* labeling perturbs the chair-chair equilibrium with two deuteriums exchanging between nonequivalent diaxial and diequatorial alignments. However, the similarity does not unequivocally prove the cyclohexyl cation exists in a chair form. The data are indeed consistent with a chair structure, and definitely rule out the C_2 twist-boat, but a C_1 twist-boat structure is also possible. A C_1 twist-boat would have nonequivalent methyls which would be time-averaged to chemical shift equivalence in the absence of isotopic perturbation. Further work is in progress to make the distinction between chair and C_1 twist-boat structures.

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SAŽETAK

NMR izotopni pomaci pri proučavanju konformacije izomernih dimetil-9,10-dihidroantracena i *tert*-cikloheksil kationa

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Na osnovi izmjerenih ravnotežnih i intrinzičnih NMR izotopnih pomaka izvedeni su zaključci o konformaciji dimetil-9.10-dihidroantracena i *tert*-cikloheksil-kationa. Za 9,9-dimetil-9,10-dihidroantracen i *trans*-9,10-dimetil-9,10-dihidroantracen rezultati upućuju na prisutnost više neplanarnih konformera u ravnoteži, dok je za *cis*-9,10-dimetil-9,10-dihidroantracen-9-d_1 utvrđena prisutnost samo jednog konformera.