Acknowledgment. We thank Professor R. M. Carlson for the spectral data of pestalotin. We thank Professor S. Danishefsky for discussions of the stereochemical aspects of the cyclocondensations with his diene. Professor J. J. Sims and S. Castellino have developed a related δ-lactone synthesis.[15] We thank them for helpful discussions. We acknowledge the National Insitutes of Health (GM-24517) for financial support.

Supplementary Material Available: Experimental procedures and NMR data for most compounds (13 pages). Ordering information is given on any current masthead page.

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NMR Isotope Shift as a Probe of Conformation in Carbocations. Determination of Conformation in a Cyclopentyl Cation

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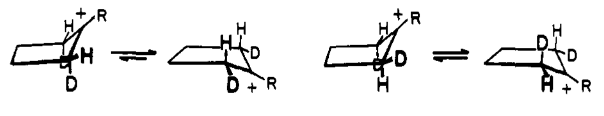
The isotopic perturbation of degenerate equilibria has been developed into a new method to distinguish between static and equilibrating structures, based on the chemical shift difference (the equilibrium isotope shift) between NMR signals for nuclei which are time averaged to equivalence in the absence of the isotopic perturbation.[1] Another type of equilibrium isotope effect occurs when the magnitude of an intrinsic NMR isotope shift is affected by isotopic perturbation of a rapid equilibrium.[2] We now report a demonstration that the additivity characteristics of the intrinsic isotope shift can serve as a probe of conformation.

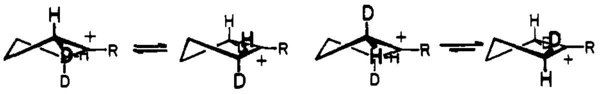
Nonadditivity of isotope shifts is likely to occur if C–H(D) bonds are involved in hyperconjugation or through-space electronic or steric interactions *and* also are conformationally mobile, because of the imposition of an equilibrium isotope effect on the population of conformers which may have different intrinsic NMR isotope shifts. Our example is a cyclopentyl cation, in which the hyperconjugative contributions of the methylene groups adjacent to the cation center can be perturbed by deuterium substitution. Isotopic perturbation of hyperconjugation reduces the electron supply to the cation center, as illustrated by long-range, downfield isotope shifts for nuclei in aryl groups conjugated with the cation center.[2–5]

A cyclopentyl cation could assume a planar, envelope, or twist structure. There would be two equivalent envelope conformations or two equivalent twist conformations. Interconversion between equivalent structures should be a low barrier, rapid process.[6] However, the degeneracy of the proposed equilibria could be removed by appropriate deuterium labeling, which would then lead to nonadditive long-range isotope shifts at any nucleus whose chemical shift depended on charge delocalization from the cation center.

Scheme I



Scheme II



The 1-(*p*-fluorophenyl)cyclopentyl cation, **1**,[7] was prepared as a mixture of deuterated isotopomers by dissolving labeled 1-(*p*-fluorophenyl)cyclopentanol in 1:1 $FSO_3H:SbF_5$ and SO_2ClF at −78 °C. Varied patterns of labeling were achieved by reacting (*p*-fluorophenyl)magnesium bromide with the appropriately labeled cyclopentanones. Cyclopentanone randomly labeled at the C_2 and C_5 positions to ~70% deuteration was prepared by base-catalyzed (K_2CO_3) exchange in D_2O, and a ~98% labeled sample was obtained by further exchanges. In the randomly labeled sample, the dideuterated species should be present in about 1:1:1 proportions of geminal, cis, and trans patterns of labeling. Geminally labeled cyclopentanone-*2,2-d*$_2$ was synthesized by a known method from 2-methoxy-1-cyclopentene-1-carboxylic acid.[8] Predominantly trans labeled cyclopentanone-*2,5-d*$_2$ was prepared by cyclopentanone exchange in D_2O catalyzed by Hine's chiral diamine.[9]

Figure 1 shows two of the ^{1}H-decoupled 56.2-MHz ^{19}F spectra obtained from various mixtures of labeled and unlabeled **1**. Several mixtures were necessary to assign the signals with certainty. Figure 1a is a spectrum of the randomly labeled **1** mixed with unlabeled **1**. The spectrum in Figure 1b is from a mixture of the randomly labeled cation enriched with *trans*-**1**-*2,5-d*$_2$. Each deuterated cation gives a different ^{19}F signal with the exception of the precisely overlapping signals for **1**-*2,2-d*$_2$ and *cis*-**1**-*2,5-d*$_2$. The downfield isotope shifts at ^{19}F in **1** are as follows: (cation, shift in ppm ± 0.005) **1**, 0.000; **1**-*2-d*, 0.138; *trans*-**1**-*2,5-d*$_2$, 0.258; *cis*-**1**-*2,5-d*$_2$, 0.299; **1**-*2,2-d*$_2$, 0.299; **1**-*2,2,5-d*$_3$, 0.440; and **1**-*2,2,5,5-d*$_4$, 0.603.

The isotopomers of the 1-(*p*-fluorophenyl)cyclopentyl cation reveal the preferred conformation to be the twist structure. The key observation is the smaller isotope shift (0.258 ppm) for the trans dideuterated cation than for the cis or geminally dideuterated cations (0.299 ppm). Besides this nonadditive isotope shift, the lack of additivity for the mono- and trideuterated cations is also significant; only the geminal and cis deuterated cations give an isotope shift in relation to the tetradeuterated cation that is proportional to the fractional extent of deuteration. The details of this analysis follow.

The nonadditivity of isotope shifts indicates that the cyclopentyl cation is nonplanar. If the planar structure had been preferred, the long-range isotope shifts at fluorine would have been additive for mono- through tetradeuteration at C_2 and C_5, because each C–H(D) bond would have had the same overlap with the p-orbital of the cation center. However, since the cation assumes a nonplanar conformation, the monodeuterated species exhibits an isotope shift that is less than one-quarter the effect of tetradeuteration, i.e., a nonadditive shift, because an isotope effect on the conformational equilibrium preferentially places the C–D bond out of alignment with the p-orbital. Similarly, the trideuterated cation has an isotope shift that is less than three-quarters of the isotope shift for the tetradeuterated cation, again due to an isotope effect on the conformational equilibrium.

More importantly, of the three dideuterated isotopomers, *trans*-**1**-*2,5-d*$_2$ exhibits a reduced isotope shift while the remaining *cis*-*2,5-d*$_2$ isotopomer and the geminally labeled **1**-*2,2-d*$_2$ have

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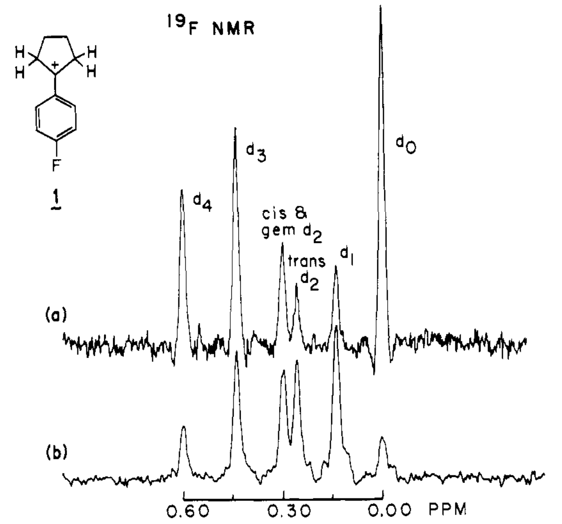

Figure 1. Proton-decoupled 56.2-MHz ^{19}F NMR spectra, at about −75 °C, of the 1-(*p*-fluorophenyl)cyclopentyl cation as mixtures of isotopomers due to deuteration at C_2 and C_5 in the cyclopentyl ring. Spectrum a is of a mixture of the unlabeled ion and a randomly labeled (~70% deuteration) ion sample; spectrum b is of another mixture enriched in the trans-2,5-d_2 isotopomer. Spectra were obtained on a JEOL FX-60Q spectrometer in 30 pulses or fewer, with an 8.3-s pulse repetition rate, and either 500-Hz width with 8192 data points (a), or 1000-Hz width and 16 384 data points (b).

isotope shifts almost precisely half that of the tetradeuterated isotopomer. If the cation had assumed the envelope shape, *cis*-**1**-*2,5-d_2* would have preferred the envelope conformation which places both deuterium atoms in quasi-equatorial rather than quasi-axial positions, because a C–H bond is a better hyperconjugative electron donor than a C–D bond[2-5] and an axial position is better aligned for overlap with the p-orbital (Scheme I). The trans labeled cation, *trans*-**1**-*2,5-d_2*, would not have perturbed the equilibrium between envelope conformations, because in either envelope conformation one C–D bond is in and one is out of alignment with the p-orbital. However, since it is the trans labeled cation that exhibits the nonadditive isotope shift, it must be this isotopomer that perturbs the conformational equilibrium to favor the diequatorial placement of the deuterium atoms, which can only occur if the cyclopentyl cation has the twist shape (Scheme II). The cis dideuterated isotopomer leaves the equilibrium between twist conformers unperturbed (Scheme II) and therefore exhibits an additive isotope shift. Geminal dideuteration does not perturb the equilibrium for the twist form and would not for the envelope form either. Only when the equilibrium is perturbed is a reduced, nonadditive, NMR isotope shift observed for ^{19}F in the *p*-fluorophenyl group, because then the C–H(D) bonds are preferentially placed in equatorial positions where they are less strongly involved in hyperconjugation and can have less influence on the charge distribution in the π system.

The cyclopentyl cation examined here adopts the twist conformation, as does cyclopentanone.[6,10] Djerassi et al. have recently demonstrated a conformational isotope effect in cyclopentanone from variable-temperature circular dichroism spectra.[11] They estimate that the deuterium in twist cyclopentanone-*2-d* prefers the quasi-equatorial position by about 10 cal/mol. We anticipate at least an order of magnitude larger energetic effects in cations, based on the greater importance of hyperconjugative interactions. We are now investigating the temperature dependence of the nonadditivity of NMR isotope shifts, as well as further applications of the magnitude and additivity of isotope shifts as probes of conformation in carbocations and carbanions.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8211125).

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Radical Anion of Bis(η^6-benzene)chromium[1]

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The orbitally degenerate benzene radical anion[2] has played a central role in the development of ESR of π-perimeter radicals,[3] and subtle details pertaining to the deviation of the *g* factor from the free-spin value,[4] the line widths in fluid solution,[5] and the related topic of Jahn–Teller instability remain a subject of investigation.[6] In the light of recent interest in the ESR of orbitally degenerate sandwich complexes,[7] the preparation of the unperturbed prototype bis(η^6-benzene)chromium radical anion appeared desirable. We now wish to report the characterization by ESR of a species obtained via reduction of $(\eta^6\text{-}C_6H_6)_2Cr$ (**1**) with potassium in dimethoxyethane (DME) in the presence of dicyclohexyl-18-crown-6, which we believe is the radical anion $\mathbf{1}^{-}\cdot$. During the course of the reduction of **1**, as evident from the appearance of ^{53}Cr satellite spectra, three different organochromium radicals were observed: initially the spectrum of $\mathbf{1}^{+}\cdot$, adventitiously present, prevails; upon contact with the potassium mirror it is replaced by the spectrum of the deprotonated species $(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_5^-)Cr^{+}\cdot$ (**2**), which undergoes intramolecular interannular proton exchange.[8] Further contact with potassium and maintenance at ambient temperature yields $\mathbf{1}^{-}\cdot$. Contrary to binary sandwich complexes of anellated[9] and trimethylsilyl-substituted[10a] arenes, attempts to generate $\mathbf{1}^{-}\cdot$ electrochemically failed down to a potential of −3.3 V (vs. SCE; n-Bu_4NClO_4, DME).[10b] The ESR spectra recorded in fluid and rigid solutions are depicted in Figure 1, the parameters are collected in Table I.

Whereas in the case of $\mathbf{1}^{+}\cdot$ hyperfine splitting caused by 12 equivalent protons reflects a sixfold symmetry axis, the more complicated hyperfine pattern of $\mathbf{1}^{-}\cdot$ signalizes a reduction of symmetry. Analysis of this spectrum in terms of four sets of inequivalent protons led to a simulated trace which is in satisfactory agreement with the experimental spectrum. The line width of 0.7 G (minimum at −55 °C), which most likely contains contributions from the *g* and hyperfine anisotropies, precludes a more stringent dissection of the hyperfine pattern and its behavior under

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