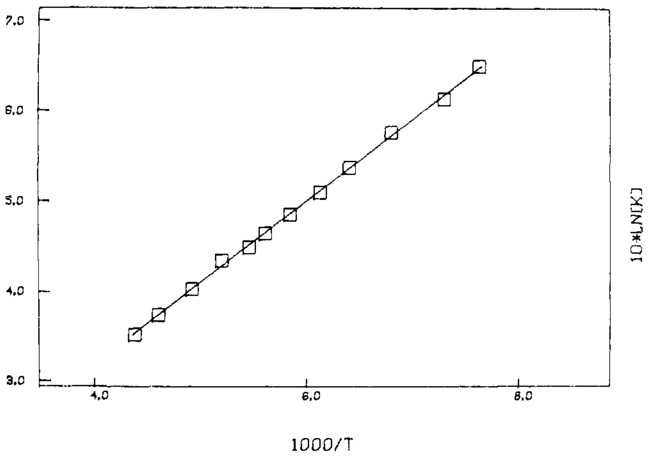

Figure 2. Temperature dependence of the equilibrium isotope effect in II ($10 \times \ln K$ vs. $10^3/T$).

carbon adjacent to the ^{13}C is a 1:1 doublet, (J_{C-C} = 35 Hz) offset downfield from a singlet from the other carbon, indicating that the charge prefers to be next to ^{13}C. This is, to our knowledge, the first reported secondary ^{13}C equilibrium isotope effect.

Each methylene deuterium in III produces an effect 2.3 times that of a methyl deuterium in II. If hyperconjugation is a function of the dihedral angle θ between the C–H bond and the p orbital and the effect depends on $\cos^2\theta$, the ratio should be 1.5. Preference for endocyclic hyperconjugation via a resonance form with a trisubstituted double bond may also contribute.

Acknowledgment. This work was supported by the National Science Foundation. We thank Professor H. C. Brown for a sample of 1-methylnorcamphor. The NMR spectra were obtained using the Southern New England High Field NMR facility supported by the Biotechnology Resources Program of the National Institutes of Health (RR-798).

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Isotopic Perturbation of Resonance. Carbon-13 Nuclear Magnetic Resonance Spectra of Deuterated Cyclohexenyl and Cyclopentenyl Cations

Sir:

We have found that the ^{13}C NMR spectra of 1-deuteriocyclohexenyl (II) and -cyclopentenyl (IV) cations display small isotopically induced splittings of the downfield carbon (C_1 and C_3) resonance due to a novel kind of isotope effect. These observations suggest a way to qualitatively distinguish between systems which are delocalized and symmetrical, and systems which are structurally asymmetrical, but symmetrical on the NMR time scale because of rapid degenerate rearrangement.

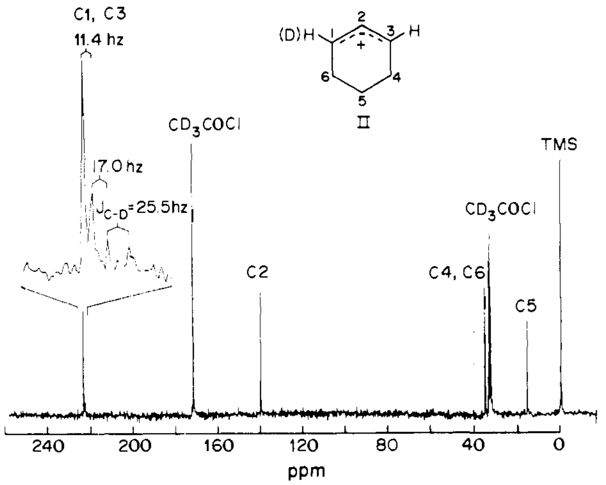
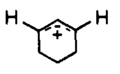


Figure 1. 67.9-MHz ^{13}C NMR spectrum of a 1:4 mixture of I and II at −110 °C.



I

IIa

IIb

III

IV

V

In the ^{13}C NMR[1] at about −110 °C (Figure 1) of a 1:4 mixture of I and II (obtained from the corresponding chloride as described previously[2]), the resonance for C_3 of II appears 11.4 Hz (0.167 ppm) *downfield* from the corresponding resonance of I. Similarly, the C_3 resonance of IV is 11.1 Hz (0.163 ppm) *downfield* from the corresponding resonance of III at about −115 °C. In the literature of isotope induced NMR shifts,[3-5] there is, to our knowledge, no example of a ^{13}C resonance shifted downfield by deuterium substitution.[6] Such substantial *downfield* γ-deuterium shifts are unprecedented.

The carbon bonded to the deuterium (C_1) appears as a 1:1:1 triplet upfield from the corresponding resonance of the parent compound; for II, the shift is 17.0 Hz (0.250 ppm) and J_{C-D} = 25.5 Hz; for IV, the shift is 20.0 Hz (0.290 ppm) and J_{C-D} = 26.6 Hz. The downfield components of the triplets are obscured by the C_3 absorptions. The other carbons experience what we will term *intrinsic isotope shifts* of the same nature as previously reported shifts of deuterium substituted carbon.[3-5] In II, C_2 is shifted 0.26 ppm upfield (a β-deuterium shift); C_5, 0.03 ppm upfield by a γ-deuterium shift; and C_6, 0.16 ppm upfield by a β-deuterium shift. No δ-deuterium shift is observed for C_4. In IV, C_2 and C_5 are shifted upfield by 0.16 and 0.10 ppm, respectively.

The splitting between C_1 and C_3 represents a novel isotope effect which we call *isotopic perturbation of resonance.* This is related to the common substituent effects on resonance. An example is the 1,1-dimethylallyl cation (V), in which C_2 and C_4 have different ^{13}C NMR shifts[7] because the tertiary canonical form contributes far more to the structure. In extreme cases, one form may predominate to the extent that resonance is no longer important.[8] One might consider this new isotope effect in a similar way, concluding that deuterium substitution increases the effective importance of one canonical form over the other. Since the proton substituted carbon is shifted downfield, and the deuterium substituted carbon upfield, IIb contributes more than IIa; i.e., the positive charge prefers to be on the carbon bearing the proton.

However, the Born-Oppenheimer approximation implies that energy surfaces are unchanged by isotopic substitution and isotopes have the *same* electronegativity. Nevertheless, zero-point motion on this surface *is* affected by the isotopic mass. Since NMR chemical shifts are *averages* over zero-point motion they *can* be effectively perturbed by isotopic substitution.

One can compare experimental phenomena of isotopic perturbation of resonance with analogous equilibrium isotope effects.[1b] In both cases, in the isotopic compound, pairs of ordinarily equivalent nuclei give doublets split approximately symmetrically (not exactly symmetrically, because of intrinsic isotope shifts) about their ordinary chemical shift. The difference is that, in the equilibrium case, we have an energy surface with two minima separated by a low barrier and observe the isotopic influence on their relative stability.[9] In the present case, there is only *one* minimum and we observe the change in the single structure, averaged over vibration, upon isotopic substitution.

We expected, and we have found, that the splitting in the ^{13}C NMR is *considerably* smaller for isotopic perturbation of resonance than for equilibrium isotope effects. Indeed, the splittings in cyclohexenyl and cyclopentenyl ions are about two orders of magnitude smaller than those in equilibrium cases such as the 1,2-dimethylcyclopentyl cations.[1b,10] We suggest that the relative splitting, δ/Δ (where δ is the isotope splitting and Δ the chemical shift difference estimated for the "frozen" equilibrium), is an indicator of the extent of delocalization. The chemical shifts of C_1 and C_3 in IIa are provided by V: so Δ is estimated to be ~98 ppm.[7] δ is twice 0.167 ppm, or 0.33 ppm. $\delta/\Delta = 0.0035$, considerably smaller than the value obtained for methylene deuterated dimethylcyclopentyl cation, 0.18.[1b]

Dimethylnorbornyl cation, which is thought to be an equilibrating pair of partially σ-delocalized ions,[11-13] gives an intermediate value $\delta/\Delta = 0.032$. (This value probably should be greater since Δ is very likely to be reduced by the partial delocalization.)

The very large difference between the δ/Δ values obtained in these cases where there is little doubt about the structures and general form of the energy surfaces encourages us to predict that this parameter will be of value in providing reliable information about systems where the structures are in doubt.[13]

Acknowledgment. This research was supported by the National Science Foundation. We thank Professor M. Wolfsberg for his helpful discussion of this work. The NMR spectra were obtained using the Southern New England High Field NMR facility supported by a grant from the Biotechnology Resources program of the National Institutes of Health (RR-798).

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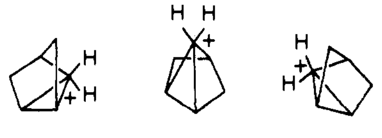
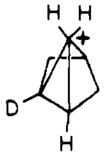
Isotopic Perturbation of Resonance. Carbon-13 Nuclear Magnetic Resonance Spectrum of 2-Deuterio-2-bicyclo[2.1.1]hexyl Cation

Sir:

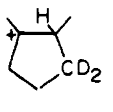
We have observed the ^{13}C NMR spectrum of bicyclo[2.1.1]hexyl cation (I) and its derivatives substituted with deuterium on the methine and methylene positions. The small relative splitting of the methine carbon peak is evidence that we are observing *isotopic perturbation of resonance,*[1] and not an equilibrium isotope effect.[2] This, in turn, is evidence that the structure of I is σ-delocalized and probably symmetrically bridged.



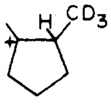
I



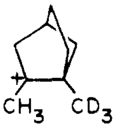
II



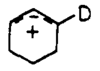
III



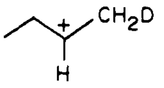
IV



V



VI



VII

I was first observed by Seybold, Vogel, Saunders and Wiberg,[3] who suggested that it is the group of interconverting bridged ions (I). Meinwald and Gassman had drawn a similar conclusion from a solvolysis study.[4]

More recently, the view that I is the group of equilibrating *classical* ions has been favored by Brown[5] on the basis of solvolysis data on 2-bicyclo[2.1.1]hexyl *p*-nitrobenzoates, and Olah has stated that, for I, "bridged carbonium ions . . . may not contribute significantly to the observed NMR parameters".[6] However, the position of the peak for C_1 and C_2 in I (δ 157 ppm[6]) is not what is expected for the average shift of a secondary carbonium ion and an adjacent sp^3 carbon. In a recent study of delocalized cations, I was the *only* ion in which Dewar[7] concluded that the nonclassical species was the most stable.

In the preceding paper,[1] we presented a criterion, based on the relative isotopic splitting, δ/Δ, for distinguishing between symmetrical, delocalized systems and rapidly equilibrating systems. Large values of δ/Δ indicate isotopic perturbation of