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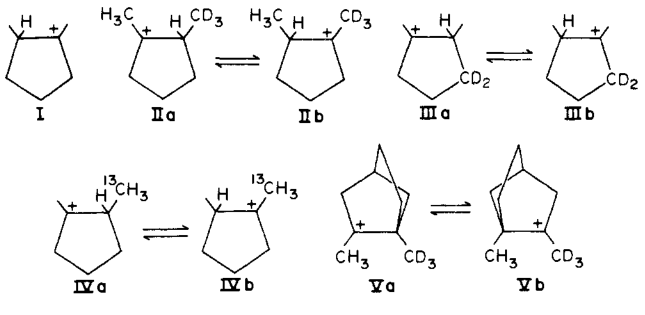
Isotopic Perturbation of Degeneracy. Carbon-13 Nuclear Magnetic Resonance Spectra of Dimethylcyclopentyl and Dimethylnorbornyl Cations

Sir:

We have reported isotope induced splittings and shifts in the ^1H NMR spectra of dimethylisopropyl[1] and dimethyl-*tert*-butyl[2] carbonium ions (undergoing rapid 1,2-hydride and 1,2-methide shifts) where deuterium on the methyl groups perturbs the degenerate equilibria. The observed splitting or shift, δ, depends on the equilibrium isotope effect, *K*, and the difference, Δ, between chemical shifts averaged by the rearrangement. We now report using the large chemical shifts in ^{13}C NMR to greatly increase sensitivity.



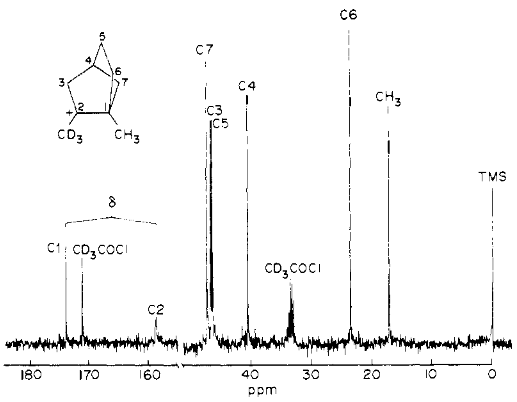


Figure 1. 67.9-MHz ^{13}C NMR spectrum of V at −71 °C.

Labeled dimethylcyclopentyl (I–IV) and dimethylnorbornyl (V) cations were prepared, using standard techniques.[3] Methyl deuteration in II lifts the chemical shift degeneracy of the carbonium and methine carbons, averaged by the rapid 1,2-hydride shift. Two peaks are observed, split symmetrically about the averaged resonance of the protio compound, separated by δ. The chemical shifts are weighted averages of isomer fractions, giving

$$\delta = [(\delta_1 A + \delta_2 B) - (\delta_2 A + \delta_1 B)]/(A + B)$$

where δ_2 and δ_1 are shifts of the carbonium and methine carbons, and *A* and *B* are concentrations of IIa and IIb. Substituting $K = B/A$ and $\Delta = \delta_2 - \delta_1$, yields

$$K = (\Delta + \delta)/(\Delta - \delta)$$

If the reaction is fast, Δ cannot be determined directly. It was estimated for I–IV from the ^{13}C NMR spectrum of a mixture of I and the methylcyclopentyl cation, by doubling the separation between the cationic carbon peak in the static molecule and the averaged carbons in I, that $\Delta = 261 \pm 2$ ppm. An analogous procedure yielded $\Delta = 202$ ppm for V.[4,5] σ-Delocalization[6,7] might reduce this value.

Table I summarizes ^{13}C NMR[8] results for II–V (Figure 1). The *direction* of isotope effects in II and III was determined from proton spectra.[1,4] In V, C–D coupling broadens and hence identifies C_2. The charge prefers to be away from deuterium in these cases.

At sufficiently low temperatures, ln *K* should vary linearly with $1/T$,[9] and analysis yields enthalpy and entropy differences. Data from II (Figure 2) are typical. We obtain for II, $\Delta H = 60 \pm 1$ cal/mol and $\Delta S = 0.012 + 0.001$ cal/deg per D; for III, $\Delta H = 137 \pm 4$ cal/mol and $\Delta S = 0.05 \pm 0.01$ cal/deg per D; for IV, $\Delta H = 1.2 \pm 0.7$ cal/mol and $\Delta S = 0.002 \pm 0.002$ cal/deg; for V, $\Delta H = 20 \pm 1$ cal/mol and $\Delta S = 0.002 \pm 0.002$ cal/deg per D. Positive ΔS means that the isotope effect extrapolated to $1/T = 0$ is *opposite* from that at low temperature. Reported error limits are standard deviations.

Case IV demonstrates the sensitivity of this method. The

Table I. Isotope Splittings

Compd	*T*, °C	δ^a	Compd	*T*, °C	δ^a	Compd	*T*, °C	δ^a
II^b	−142	81.8	II	−56	48.2	IV	−65	0.10
	−136	77.5		−45	45.4	V^c	−127	20.5
	−126	73.0	III^b	−130	105.3		−121	20.2
	−117	68.4		−126	102.4		−119	19.1
	−110	65.0		−122	98.4		−108	18.8
	−102	62.0		−109	91.0		−89	16.4
	−95	59.4		−101	86.6		−71	14.9
	−90	57.5		−91	81.6		−60	13.8
	−81	55.7	IV^b	−125	0.25		−40	12.6
	−70	51.8		−90	0.15		−21	11.9

[a] In parts per million. [b] $\Delta = 261 \pm 2$ ppm. [c] $\Delta = 202$ ppm.

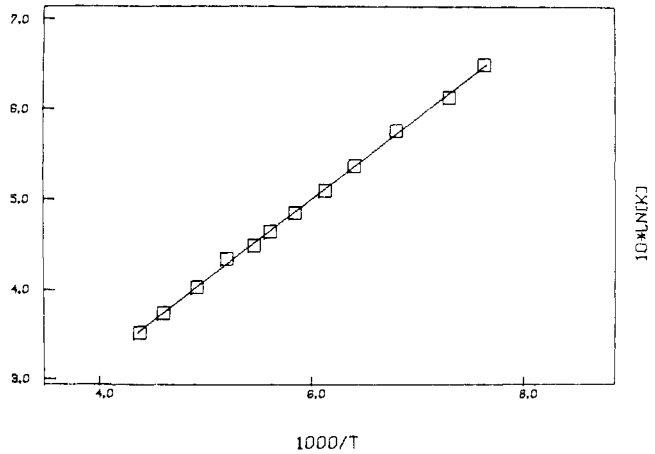


Figure 2. Temperature dependence of the equilibrium isotope effect in II ($10 \times \ln K$ vs. $10^3/T$).

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.

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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.

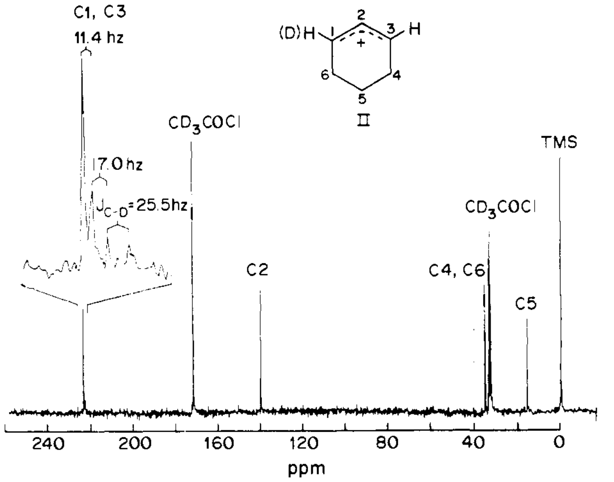

Figure 1. 67.9-MHz ^{13}C NMR spectrum of a 1:4 mixture of I and II at −110 °C.

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