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 $\sim$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]

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References and Notes

(1) (a) Spectra were taken on the Bruker HX270 as previously described.[1b] (b) M. Saunders, L. Telkowski, and M. R. Kates, J. Am. Chem. Soc., preceding paper in this issue.

(2) M. Saunders, D. Cox, and W. Olmstead, *J. Am. Chem. Soc.*, **95**, 3018 (1973).

(3) For a review of the literature prior to 1970, see H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson.*, **3**, 63 (1970).

(4) H. K. Ladner, J. J. Led, and D. M. Grant, *J. Magn. Reson.*, **20**, 530 (1975); P. A. J. Gorin, *Can. J. Chem.*, **52**, 458 (1974); H. N. Colli, V. Gold, and J. E. Pearson, *J. Chem. Soc., Chem. Commun.*, 408 (1973); D. Lavor, E. L. Motell, A. D. Traficanti, and G. E. Maciel, *J. Am. Chem. Soc.*, **94**, 5335 (1972); Y. K. Grishin, N. M. Sergeyev, and Y. A. Ustynyuk, *Mol. Phys.*, **22**, 711 (1971); G. L. Lebel, J. D. Laposa, B. G. Sayer, and R. A. Bell, *Anal. Chem.*, **43**, 1500 (1971).

(5) H. Gunther and G. Jikeli, *Chem. Ber.*, **106**, 1863 (1973).

(6) Gunther and Jikeli[5] report a downfield γ-D shift of 0.01 ppm, but this is probably within experimental error limits; unfortunately, their deuterated and undeuterated compounds were observed separately, rather than simultaneously.

(7) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.* **97**, 1539 (1975).

(8) M. Saunders and E. H. Gold, *J. Am. Chem. Soc.*, **88**, 3376 (1966).

(9) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

(10) We have recently obtained a ^{1}H NMR spectrum of deuterated *sec*-butyl cation indicating that the deuterium prefers to be on C_2 rather than C_3 by 150 ± 20 cal/mol. We therefore expect that, if II and IV were equilibrating systems, large isotope effects would be seen in contrast to the small effects actually observed.

(11) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Am. Chem. Soc.*, **93**, 1442 (1971).

(12) R. Haseltine, N. Wong, and T. S. Sorensen, *Can. J. Chem.*, **53**, 1891 (1975).

(13) M. Saunders, M. R. Kates, K. B. Wiberg, and W. E. Pratt, *J. Am. Chem. Soc.*, following paper in this issue.

Martin Saunders,* Mandes R. Kates
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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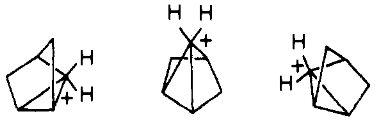
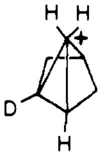
Isotopic Perturbation of Resonance. Carbon-13 Nuclear Magnetic Resonance Spectrum of 2-Deuterio-2-bicyclo[2.1.1]hexyl Cation

Sir:

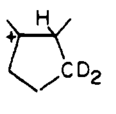
We have observed the ^{13}C NMR spectrum of bicyclo[2.1.1]hexyl cation (I) and its derivatives substituted with deuterium on the methine and methylene positions. The small relative splitting of the methine carbon peak is evidence that we are observing *isotopic perturbation of resonance*,[1] and not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



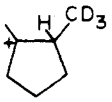
I



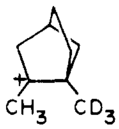
II



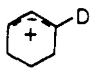
III



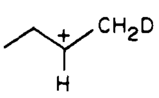
IV



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

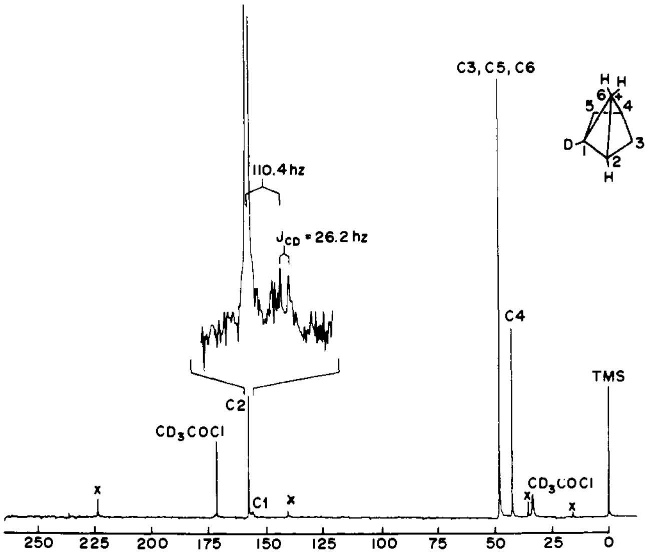


Figure 1. 67.9-MHz ^{13}C NMR spectrum of II at 115 °C. Cyclohexenyl cation peaks are marked x.

Table I. Relative Isotopic Splittings (δ/Δ)

Compd	T, °C	δ per D, ppm	Δ, ppm	δ/Δ per D
III^a	109	46.9	261	0.18
IV^a	110	22.1	261	0.085
VII^b	111	11	261	0.042
V^a	119	6.4	202	0.032
II	115	1.18	200	0.0058
VI^c	110	0.33	94	0.0035

^{a} Reference 2. ^{b} Unpublished results. ^{c} Reference 1.

equilibrium (double minimum energy surface), while small values are characteristic of isotopic perturbation of resonance (single minimum or intrinsically symmetric cases).

We have prepared 2-deuterio-2-bicyclo[2.1.1]hexyl cation as previously described.[3,8] In the 67.9-MHz ^{13}C NMR spectrum[9] (Figure 1), C_1 and C_2 appear as a singlet and triplet (J_{C-D} = 26.2 Hz) separated by 110 Hz (1.63 ppm). In the ^{13}C NMR spectrum of a 1:5 mixture of I and II, the triplet of the deuterio carbon is not visible, but the C_1 singlet appears 33 Hz downfield from the averaged absorption of C_1 and C_2 in I. The resonance of I is not exactly between the peaks of the deuterated species, because of intrinsic α- and β-deuterium isotope shifts.[1] β-Deuterium shifts are typically 0.1 ppm upfield;[10] thus the splitting can be corrected by adding 0.1 ppm (7 Hz); so we obtain $\delta = 2(33 + 7) = 80$ Hz, or 1.18 ppm. Δ can be estimated by taking the value estimated for the dimethylnorbornyl cation, 202 ppm;[1] so $\delta/\Delta = 0.0058$.

When I was prepared with a dideuteriomethylene, the undeuterated methylene carbon was shifted 0.94 ppm downfield from the methylene peak of undeuterated I. The methine carbons gave, as expected, a single peak. The observed shift necessarily reflects an equilibrium isotope effect for *either* the classical or the bridged structure, but we cannot tell which structure is consistent with the observed shift, because we are unable to estimate Δ. For the bridged ion, we have no adequate model for chemical shifts; for the classical structure, 2-methylbicyclo[2.1.1]hexyl cation would be an acceptable model but the two types of methylenes are reported to have the same ^{13}C NMR shift.[6] If we *could* estimate Δ, then $K = (\Delta + 3\delta)/(\Delta - 6\delta)$.

In Table I are values of δ/Δ for several systems. The largest value is for III; IV and VII have progressively smaller values because of preferential hyperconjugation with the methylene protons in these two systems;[2] hence the effect of methyl deuteration is reduced relative to methylene deuteration. The still smaller δ/Δ obtained for V is explained similarly, but here delocalization[1,11,12] probably decreases Δ *as well.*

The relative splitting for V, though the smallest value observed for an unequivocal equilibrium isotope effect, is still a factor of 10 larger than that for VI where the splitting reflects perturbation of resonance. That δ/Δ for II is also an order of magnitude smaller than the values for III–V and VII is strong evidence that we are observing, not an equilibrium isotope effect, but isotopic perturbation of resonance in the ^{13}C NMR spectrum of II.[13] In other words, *the relative splitting indicates that the structure of II is extensively σ-delocalized.*

Even if our estimate of Δ is incorrect, the relative splitting for II remains considerably smaller than that of VI, unless one sets Δ to less <50 ppm ($\delta/\Delta = 0.024$). This is equivalent to concluding that I is highly σ-delocalized.

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References and Notes

(1) M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) M. Saunders, M. R. Kates, and L. Telkowski, *J. Am. Chem. Soc.*, accompanying paper in this issue.
(3) G. Seybold, P. Vogel, M. Saunders, and K. B. Wiberg, *J. Am. Chem. Soc.*, **95,** 2045 (1973).
(4) J. Meinwald, A. Lewis, and P. G. Gassman, *J. Am. Chem. Soc.*, **84,** 977 (1962); J. Meinwald, P. G. Gassman, and J. J. Hurst, *ibid.*, **84,** 3722 (1962); J. Meinwald and P. G. Gassman, *ibid.*, **85,** 57 (1963); J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *J. Org. Chem.*, **29,** 3469 (1964).
(5) H. C. Brown, M. Ravindranathan, and C. Gundu Rao, *J. Am. Chem. Soc.*, **99,** 2359 (1977).
(6) G. A. Olah, G. Liang, and S. P. Jindal, *J. Am. Chem. Soc.*, **98,** 2508 (1976).
(7) M. J. S. Dewar, R. C. Haddon, A. Kormornicki, and H. Rzepa, *J. Am. Chem. Soc.*, **99,** 377 (1977).
(8) M. Saunders, D. Cox, and W. Olmstead, *J. Am. Chem. Soc.*, **95,** 3018 (1973).
(9) Spectra were obtained on the Bruker HX-270, as described in note 3, ref 2.
(10) See notes 2 and 3, ref 1.
(11) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Am. Chem. Soc.*, **93,** 1442 (1971).
(12) R. Haseltine, N. Wong, and T. S. Sorensen, *Can. J. Chem.*, **53,** 1891 (1975).
(13) While the deuterium in II cannot participate in hyperconjugation, as can those in III–V and VII, we nevertheless feel that there would be a substantial isotope effect in the ^{13}C NMR of II were it an equilibrating pair of ions. See note 11, ref 1.

Martin Saunders,* Mandes R. Kates
Kenneth B. Wiberg,* William Pratt

Department of Chemistry, Yale University
New Haven, Connecticut 06520

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Biomimetic Syntheses of the Neolignans Guianin, Burchellin, 2-Epi,3a-epiburchellin and Futoenone

Sir:

Neolignans[1] are a group of secondary plant metabolites structurally characterized by the presence of two arylpropanoid units. In contradistinction to the related lignans the β position of one arylpropane moiety is linked to one of three additional positions in the other. Within the class of neolignans substances with bicyclo[1.2.3]octane, hydrobenzofuran and spiro[5.5]-undecane skeleton are encountered. Guianin (**1**)[2] (from *Aniba guianensis* Aubl.), burchellin (**2**)[3] (from *Aniba burchellii* Kosterm.), and futoenone (**4**)[4] (from *Piper futokadzura* Sieb.