ion (eq 8). The dehydration of aliphatic alcohols in contact with acidic sites on catalysts, such as γ-aluminum oxide, may proceed through a similar intermediate.[11] Previously it has been suggested that such processes involve two active sites on the catalyst surface.[11] By way of contrast to the present observations, it is of interest to note in unimolecular ion chemistry that 1,2-elimination processes are not prevalent, it being postulated that the distances for abstraction from adjacent carbons are too great.[12] Further mechanistic details of this interesting reaction are under investigation.

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(13) Alfred P. Sloan Fellow, 1968–1970. The author acknowledges the support of this research by the U. S. Atomic Energy Commission under Grant AT(04-3)767-8.

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Nuclear Magnetic Resonance Spectroscopy. Effects of Molecular Asymmetry on Carbon-13 Chemical Shifts[1]

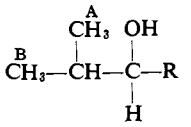
Sir:

A nearby center of molecular asymmetry often induces magnetic nonequivalence of the protons of an isopropyl group (or of a methylene group), and this phenomenon has been the subject of many investigations.[2] We report here the first observance of the effect of molecular asymmetry on the resonances of methyl carbons in isopropyl groups in compounds of the type $(CH_3)_2CH(CH_2)_nCHR_1R_2$.

For substantial nonequivalence of protons, it is usually considered necessary to have a preferred conformation(s) wherein the protons are in quite different magnetic environments. The occurrence or nonoccurrence of nonequivalence thus provides a rather sensitive probe for preferences. In many cases, the chemical-shift differences are small, and the method becomes impractical or even inapplicable.

The very substantial sensitivity of ^{13}C chemical shifts to conformational changes[3] and steric effects[4] and the relatively large magnitudes[3,4] of the resulting chemical-shift effects suggest that there should be considerable utility of ^{13}C nmr in studies of magnetic nonequivalence of the carbons associated with molecular asymmetry.[2] The utility is expected to be enhanced by proton decoupling which would allow easy observance of ^{13}C chemical shifts even where there are very complex proton-spin systems.

The ^{13}C chemical shifts (measured with proton decoupling as previously described)[3b] of the methyl carbons of isopropyl groups in isopropylalkylcarbinols of type **1** appear in Table I. The degree of nonequivalence



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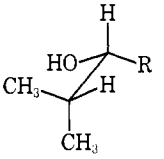
of the methyl groups A and B increases very substantially in the change of R from methyl to ethyl to isopropyl to *t*-butyl in accord with an important nonbonded 1,5 CH_3–CH_3 interaction. When R is methyl, the difference $\nu_A - \nu_B$ is small and probably reflects the difference between a 1,4 CH_3–CH_3 interaction[4] and a 1,4 CH_3–OH interaction.[3] When R is ethyl, or a group more bulky than ethyl, the usual steric arguments[3,4] fail to explain the large shifts encountered, and it appears that a 1,5 CH_3–CH_3 interaction needs to be invoked which produces a *downfield* shift.

Table I. Magnetic Nonequivalence of the Methyl Carbons of Isopropylalkylcarbinols $(CH_3)_2CHCH(OH)R$

R	ν_A[a]	ν_B[a]	$\nu_A - \nu_B$
Methyl	174.5	174.3	0.2
Ethyl	175.1	173.6	1.5
n-Propyl	175.1	173.7	1.4
Isopropyl	175.3	172.6	2.7[b]
t-Butyl	175.7	168.8	6.9

[a] Shifts are in ppm relative to carbon disulfide. The designations A and B are more or less arbitrary (see text). [b] The observation of this shift indicates that the present arguments pertain equally well to disymmetric molecules.

The source of the large shift difference between the methyl carbons (A and B) of the isopropyl group with increasing R seems most reasonably to arise through increases in the population of, and steric effects operating in, conformers of type **2** in which the large alkyl groups are positioned most favorably between CH_3 and H, not between CH_3 and CH_3.[5,5a] That **2** is more favored than **3** with R = $(CH_3)_3C$ is perhaps unexpected in that **2** has two *gauche* CH_3–OH interactions while **3** has only one and a H–OH interaction. However, it will be seen that, if the CH_3–R interaction in **2** is large enough to cause considerable departure from the perfect staggered arrangement, then the interaction between the other CH_3 and the OH group is diminished. With **3**, departure from the staggered arrangement would increase the CH_3–OH interaction. One methyl resonance remains substantially unchanged as R is varied (see Table I), and this fact is in accord with **2** as the favored conformation and suggests that ν_A corresponds to the methyl between hydrogen and hydroxyl in **2**.



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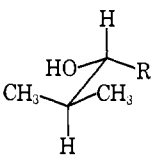

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(1) Supported in part by the Public Health Service, Research Grant 11072-05-06 from the Division of General Medical Sciences, and the National Science Foundation. We are pleased to acknowledge the help and suggestions of Dr. Frank J. Weigert in the course of this work.
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(5a) NOTE ADDED IN PROOF. Substantial proportions of conformations having *gauche* interactions involving *t*-butyl groups have been observed in other systems: D. C. Best, G. Underwood, and C. A. Kingsbury, *Chem. Commun.*, 627 (1969).

The averages of ν_A and ν_B for the compounds in Table I show a downfield shift trend as R becomes larger, in qualitative agreement with the series of hydrocarbons in which OH is replaced by H.[6,7] That the 1,5 interaction results in a downfield shift is especially interesting in view of the usual upfield shifts associated with steric effects.[3,4]

The degree of proximity of the isopropyl group to the asymmetric center on the magnitude of the shift difference $\nu_A - \nu_B$ has been examined for compounds of the type $(CH_3)_2CH(CH_2)_nCH(CH_3)C_2H_5$, and the results appear in Table II. The monotonic decline of

Table II. Dependence of Isopropyl Group Nonequivalence on Proximity to the Asymmetric Carbon (Marked with an Asterisk)

Compound	ν_A[a]	ν_B[a]	$\nu_A - \nu_B$
$(CH_3)_2CH^*CH(CH_3)CH_2CH_3$	174.7	172.5	2.2
$(CH_3)_2CHCH_2{}^*CH(CH_3)CH_2CH_3$	170.3	169.3	1.0
$(CH_3)_2CHCH_2CH_2{}^*CH(CH_3)CH_2CH_3$	170.1	169.9	0.2
$(CH_3)_2CHCH_2CH_2CH_2{}^*CH(CH_3)CH_2CH_3$	170.0	169.9	0.1

[a] Shifts are in ppm relative to carbon disulfide. The assignments A and B are arbitrary.

$\nu_A - \nu_B$ with n presumably reflects attenuation of the steric effect with increasing distance. The largest isopropyl methyl group nonequivalence we have so far observed is 7.2 ppm for $(CH_3)_2CHCH(CH_3)C(CH_3)_3$.

The use of ^{13}C nmr should provide a powerful additional tool for the elucidation of structure and the determination of optical purity of diastereomers. The latter technique has been shown to be complicated when observing protons[8] by small shift differences, a difficulty which the present work shows should be significantly alleviated by use of ^{13}C spectra.

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The Direct Measurement of the Magnetic Susceptibility Tensor Elements in 1,3-Cyclohexadiene and Comparison with Benzene and Other Small-Ring Compounds

Sir:

We have observed the molecular rotational Zeeman effect in 1,3-cyclohexadiene at magnetic fields near 21,000 G which gives the molecular g values and magnetic susceptibility anisotropies. Our observations show that (1) the electric quadrupole moments of benzene and 1,3-cyclohexadiene are nearly equal; (2) the magnetic susceptibility anisotropies in benzene (and other aromatic compounds) are much larger than the values reported here for 1,3-cyclohexadiene; (3) the large anisotropy in benzene relative to 1,3-cyclohexadiene is strong evidence for a nonlocal contribution in benzene (ring currents). The previous estimates of local contributions to the magnetic susceptibility anisotropies in aromatic rings may be too large.

Ring currents[1,2] in molecules and their relation to observed molecular magnetic susceptibility anisotropies have been interesting subjects for speculation for some time. Ring currents were first postulated to explain the large directly measured[3] anisotropy in the magnetic susceptibility of the benzene molecule. A current induced in the benzene ring would lead to a larger diamagnetic susceptibility along the axis perpendicular to the ring than the equal in-plane susceptibilities. Later modifications[4] of the original classical ring-current theories have apparently indicated that the ring currents can only contribute about one-half of the observed magnetic susceptibility anisotropy in the benzene ring.[4-7] The remaining anisotropy is apparently due to local contributions.[5,8,9] Indeed, Musher[10] claims that the magnetic susceptibility anisotropies in benzene and other conjugated rings can be explained completely on the basis of local effects.[11]

One major problem in the above analyses is the lack of experimental magnetic susceptibility anisotropies in a system of small-ring compounds. The susceptibility anisotropies are either obtained for very large molecules by measurements[12] on single crystals or for small compounds from chemical shift effects which lead indirectly[9,13] to numbers which may or may not be correct.

Recently, we have developed theoretical[14] and experimental[15,16] methods of using gas-phase microwave spectroscopy to measure the magnetic susceptibility anisotropies in any molecule which has a microwave spectrum. Recently we have presented these methods and resultant magnetic susceptibilities for several small-ring compounds including fluorobenzene,[17] ethylene oxide,[18] ethylene sulfide,[19] thiophene,[20] furan,[20] and other compounds including formaldehyde[15] and formic acid.[21]

In this paper we report the measurements of the molecular g values, magnetic susceptibility tensor elements,

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