

Table I. Energies of $B_2H_7^-$ and Related Species^a

species	optimization level			MP4/6-31G**// MP2/6-31G*	zero-point ^c energy	relative energy
	3-21G	6-31G*	MP2/6-31G*			
$B_2H_7^-$						
1 (C_{3v}) ^e	no minimum	-53.39731	-53.59131	-53.69373	43.5 ^d	0
2 (D_{3d})	-53.09545	-53.39661 ^b	-53.58792	-53.69055	43.1 ^d	1.6
3 (D_{3h})	-53.09493	-53.39601 ^b	-53.58710	-53.68968	42.9 ^d	2.0
4 (C_{2v}) ^f	no minimum	-53.39732	-53.59138	-53.69379	43.5	0
$BH_3 + BH_4^-$	-53.05025	-53.35511	-53.53100	-53.63125	39.7	35.4
BH_3 (D_{3h})	-26.23730	-26.39001 ^b	-26.46424	-26.50751	17.4	
BH_4^- (T_d)	-26.81295	-26.96510 ^b	-27.06676	-27.12374	22.3	

^a Absolute energies in hartrees and relative energies in kcal/mol. ^b Reference 5. ^c Calculated at the HF/6-31G* level. ^d The imaginary frequencies were also included in the zero-point energy evaluations to facilitate direct comparisons. ^e The calculated HF/6-31G* (MP2/6-31G*) geometrical parameters not specified in the figure (bond lengths in angstroms, bond angles in degrees) are $H_2-B = 1.209$ (1.206), $H_3-B = 1.216$ (1.217), $H_4-B = 1.219$ (1.221), $H_5-B = 1.212$ (1.210), $H_2-B-H_1 = 110.1$ (114.7), $H_3-B-H_1 = 101.7$ (100.1), $H_4-B-H_1 = 98.8$ (94.7), $H_5-B-H_1 = 107.3$ (109.9), $H_3-B-H_3' = 113.6$ (113.2), $H_5-B-H_3' = 114.6$ (114.8). ^f The calculated HF/6-31G* (MP2/6-31G*) geometrical parameters not specified in the figure (bond lengths in angstroms, bond angles and dihedral angles in degrees) are $H_2-B = 1.218$ (1.220), $H_3-B = 1.214$ (1.213), $H_4-B = 1.210$ (1.208), $H_2-B-H_1 = 99.5$ (95.9), $H_3-B-H_1 = 104.7$ (105.7), $H_4-B-H_1 = 109.3$ (113.2), $H_2-B-H_1-B = 152.4$ (153.6), $H_3-B-H_1-H_2 = 117.6$ (115.9), $H_4-B-H_1-H_2 = -119.4$ (-118.1).

There are two remaining factors that might influence the calculated geometries, viz., the effect of p-type polarization functions on hydrogen and the higher order effects of electron correlation.¹² Both factors were considered to a limited extent. The effect of p functions on hydrogen was probed by performing a complete geometry optimization of **4** with the larger 6-13G** basis¹⁰ at the Hartree-Fock level.¹⁵ All the parameters changed insignificantly from their 6-31G* values with the exception of the B-H₁-B angle, which decreased from 140.8° to 136.7°. The higher order effects of electron correlation were examined by optimizing the angle B-H₁-B at the third-order perturbation MP3/6-31G* level,¹¹ all the other parameters being fixed at their respective MP2/6-31G* values. The B-H₁-B angle changed only slightly, from 126.4° to 126.7°. Considering the flatness of the bending potential energy surface, the changes in the geometry due to both these effects are fairly small.

While we confirm the experimental conclusion that $B_2H_7^-$ prefers a bent structure, many geometrical details are not in good agreement. While the experimental B-H₁-B angle, 136(4)° lies between our values, the B-H₁ distances to the bridging hydrogen, 1.27 (5) and 1.00 (5) Å, are shorter than our calculated values, 1.328-1.303 Å; this is also true of the other B-H distances and the various angles. Even in **1**, where the B-H₁ distances must be nonequivalent, nearly identical values were calculated. The MP2/6-31G* B-B distance (2.33 Å) is larger than the X-ray value (2.11 Å), but in view of the flatness of the potential energy surface and the influence of the counterion and the crystal lattice, this difference is not particularly significant. Especially in such instances, the structure of isolated species may be expected to differ from those in condensed phases. Nevertheless, it is hoped that the planned neutron diffraction study will provide more accurate experimental parameters for comparison.

The minimum binding energy of BH_3 with BH_4^- has been experimentally measured to be -31 ± 8 kcal/mol in the solid phase.¹³ Previous calculations have obtained values of -21 kcal/mol^{2,3} (after applying a 4 kcal/mol correction for the neglected zero-point effects) at the Hartree-Fock level and -24 kcal/mol³ using an approximate CEPA scheme. We have calculated the final energy differences (last column, Table I) at the MP2/6-31G* geometries by including zero-point corrections and higher order electron correlation effects by means of complete fourth-order perturbation MP4 level¹¹ with the 6-31G** basis.

(12) Diffuse functions, although important for anions with lone pairs (Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609), do not improve the description of species like BH_4^- (Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, in press) and $B_2H_7^-$ (present work) significantly.

(13) Evans, W. G.; Holloway, C. E.; Sukumarabandhu, K.; McDaniel, D. H. *Inorg. Chem.* **1968**, *7*, 1746.

(14) **2** and **3** respectively had 2 and 3 negative eigenvalues of the force constant matrix.

(15) A similar 6-31G** optimization of **1** has been recently performed. See: Sapsee, A.-M.; Osorio, L. *Inorg. Chem.*, submitted for publication.

The calculated binding energy (35.4 kcal/mol) is higher than the previous calculated values and is in good agreement with the experimental value.

Acknowledgment. We thank Professor Robert Bau for bringing this problem to our attention and for information prior to publication. We appreciate John Pople's interest and Douglas J. DeFrees' earlier calculations. The work at Erlangen was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

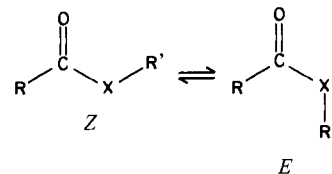
Registry No. $B_2H_7^-$, 27380-11-6.

Dynamic NMR Study of Conjugation in *tert*-Butyl Thioformate¹

Eric A. Noe,* Thomas Sanders, Felicia Badelle, and Liselle Douyon

Department of Chemistry, Jackson State University
Jackson, Mississippi 39217
Received August 18, 1982

The relative importance of conjugation for first row and second row elements such as oxygen and sulfur has long been of interest.² Evidence for the importance of carbon-sulfur π -bonding has been obtained from molecular orbital studies of substituted carbenium ions,³ in which the sulfur of $^+CH_2SH$ was calculated to be a better π -donor than oxygen in $^+CH_2OH$, and from a dynamic NMR study of thioacetic acid (**1**),⁴ which showed the rotational barriers



- 1, R = CH₃; R' = H; X = S
- 2, R = H; R' = H; X = S
- 3, R = H; R' = (CH₃)₃C; X = S
- 4, R = H; R' = (CH₃)₃C; X = O

in this compound to be 7.0 and 7.3 kcal/mol. A DNMR study of thioformic acid (**2**) has been claimed;⁵ however, the reported

(1) (a) Presented at the NIH-MBRS Symposium, Albuquerque, NM, April, 1982. (b) This work was supported by the National Institute of Health (Grant No. SO6RR08047).

(2) Price, C. C.; Oae, S. "Sulfur Bonding"; Ronald Press: New York, 1962.

(3) (a) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Wolfe, S. *Can. J. Chem.* **1975**, *53*, 1144. (b) Bernardi, F.; Csizmadia, I. G.; Epiotis, N. D. *Tetrahedron* **1975**, *31*, 3085.

(4) Noe, E. A. *J. Am. Chem. Soc.* **1977**, *99*, 2803, 7400.

Table I. Estimated Values of Parameters Affecting Conjugation in R-XH^a

system	$H_{ij}^{b,c}$	H_{ij}^2	ϵ_i^d	ϵ_j^b	$\delta\epsilon_{ij}$	$(H_{ij}^2)^{(S)}$	$\delta\epsilon^{(O)}$	SE(S)
						$(H_{ij}^2)^{(O)}$	$\delta\epsilon^{(S)}$	SE(O)
*CH ₂ SH	-3.978	15.82	-10.48	-7.66 ^e	2.82	0.633	1.76	1.11
*CH ₂ OH	-4.998	24.98	-12.61	-7.66 ^e	4.95			
C ₆ H ₅ SH	-1.133	1.284	-10.48	+7.27 ^c	17.75	0.526	1.12	0.59
C ₆ H ₅ OH	-1.563	2.443	-12.61	+7.27 ^c	19.88			

^a All energies are in eV. ^b Taken from ref 7a. ^c Computed at the STO-3G level. ^d Estimated from the ionization potentials of H₂O and H₂S (ref 22). ^e Computed at the 4-31G level.

properties are not consistent with the assigned structure.⁶ More recent theoretical calculations⁷ have predicted that the relative importance of oxygen and sulfur π -bonding is dependent upon the π -acceptor, as discussed later. We describe here a dynamic NMR study of *tert*-butyl thioformate (**3**);^{8,9} comparison of the results for **3** with the barriers for *tert*-butyl formate^{10,12} provides information about the relative conjugating abilities of oxygen and sulfur,¹³ with the formyl group as π -acceptor.

The room-temperature NMR spectrum (90.02 MHz) of **3** in acetone-*d*₆ shows a single peak for the formyl proton at δ 10.22. At lower temperatures, the peak broadens and splits into two lines at δ 10.99 and 10.17, with populations of 0.18 and 0.82, respectively, at -105 °C.¹⁶ A free-energy difference at -105 °C of 0.51 kcal/mol was calculated from the relationship $\Delta G^\circ = -RT \ln K$, and populations of 0.20 and 0.80 were estimated at the coalescence temperature (-87 °C), assuming that ΔG° does not change with temperature. Rate constants of 150 and 38 s⁻¹ at -87 °C were obtained by comparison of the experimental spectrum at coalescence with theoretical line shapes¹⁷ generated for different rate constants, and the corresponding barriers were calculated from the Eyring equation (8.9 ± 0.2 and 9.4 ± 0.2 kcal/mol).

The barriers determined for **3** are nearly the same as those reported for *tert*-butyl formate in the same solvent (8.6 and 9.3 kcal/mol).^{12c} The experimental rotational barriers (E) are related to the resonance stabilization (R) of the planar conformations by eq 1,¹⁸ where R_{tw} is the resonance interaction in the conformation

$$E = (R - R_{tw}) - S \quad (1)$$

(5) Kalinowski, H. O.; Hocking, W. H.; Winnewisser, B. P. *J. Chem. Res., Synop.* **1978**, 260.

(6) Noe, E. A.; Sanders, T.; Young, R. Manuscript in Preparation.

(7) (a) Bernardi, F.; Mangini, A.; Epiotis, N. D.; Larson, J. R.; Shaik, S. *J. Am. Chem. Soc.* **1977**, *99*, 7465. (b) Bernardi, F.; Bottoni, A.; Epiotis, N. D. *Ibid.* **1978**, *100*, 7205. (c) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1.

(8) Rotational barriers of acetic acid have not been determined by DNMR spectroscopy for comparison with the values of **1**. The populations of the E isomers of most simple esters are small (e.g., 0.3% for methyl formate at 190 K),¹⁰ and barriers for methyl, ethyl, and isopropyl formate have been obtained only recently using high-field ¹³C NMR spectroscopy.¹⁰

(9) *tert*-Butyl thioformate was synthesized by a modification of the published¹¹ procedure. Potassium carbonate solution was substituted for saturated barium hydroxide solution in the workup of the reaction mixture.

(10) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757.

(11) Bax, P. C.; Holsboer, D. H.; Van Der Veek, A. P. M. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 562.

(12) (a) Oki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2558. (b) Drakenberg, T.; Forsen, S. *J. Phys. Chem.* **1972**, *76*, 3582. (c) Nakanishi, H.; Fujita, H.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 214.

(13) The effect upon amide rotational barriers of oxygen- or sulfur-containing groups attached to the carbonyl group has been studied to obtain information about the π -donating abilities of oxygen and sulfur.¹⁴ DNMR spectroscopy has also been used to obtain barriers to hindered rotation in carbenium ions in which the central carbon is attached to two nitrogens and an oxygen or sulfur.¹⁵

(14) (a) Bernardi, F.; Lunazzi, L.; Zanirato, P.; Cerioni, G. *Tetrahedron* **1977**, *33*, 1337. (b) Hendriksson, S.; Sandstrom, J., Lecture at the 8th International Symposium on Organic Sulfur Chemistry, Portoroz, June, 1978. We thank Professor Sandstrom for a copy of this lecture.

(15) Kalinowski, H. O.; Kessler, H. *Chem. Ber.* **1979**, *112*, 1153.

(16) The relative intensity of the low-field formyl proton signal decreases in CHCl₂/CHCl₂F as solvent, indicating that this peak is associated with the more polar (E) conformation. The low-field formyl peak of *tert*-butyl formate has also been assigned to the E isomer.^{10,12}

(17) Program DNMR, supplied by Nicolet, was used for calculation of the theoretical spectra.

(18) Grindley, T. B.; Katritzky, A. R.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 289.

of maximum energy, and S is the difference in strain energies (including rehybridization) for the conformations of minimum and maximum energy.

The calculated¹⁹ pattern of charge distribution for phenol with an HOCC dihedral angle of 90° shows that conjugation is still important in this twisted conformation, and $(\sigma_R^\circ)_{lw}$ for OCH₃ has been estimated¹⁸ to be -0.23; (σ_R°) for planar anisole = -0.43). In contrast, sulfur is not expected to be an effective π -donor²⁰ in conformations in which the SR group is rotated 90° out of plane. The values of σ_R° for SR in thioanisole (planar; -0.25)^{21a} and *tert*-butyl phenyl sulfide (nonplanar; -0.07)^{21b} are consistent with a greatly reduced π -donating ability for sulfur in the transition state for rotation. Thus, R_{tw} is expected to be large for **4** but substantially smaller for **3**.

The E to Z barriers¹⁰ in *N,N*-dimethylformamide/acetone-*d*₆ solvent for methyl formate (8.0), ethyl formate (8.5), isopropyl formate (8.8), and *tert*-butyl formate (8.3 kcal/mol) suggest that the classical steric strain of the E conformation of *tert*-butyl formate is probably small; at least, it should be largely cancelled in the comparison of **3** and **4** by a similar amount of strain in the thiol ester. The contribution of rehybridization to the strain energy, S , is difficult to evaluate but has been suggested¹⁸ to be significant for rotation in anisole. R_{tw} is likely to be much larger for **4** than for **3**, as discussed above, and it is unlikely that any difference in S for **3** and **4** will offset this factor; the near equality of the barriers for **3** and **4** then indicates that the resonance stabilization, R , is greater for **4**.

The resonance energy of eq 1 will actually be the net result of the various possible orbital interactions involving the lone pair. In esters and thiol esters, the stabilizing interaction of the lone pair orbital on oxygen or sulfur with the vacant π^* of the carbonyl group will be much greater than the destabilizing effect of the $n-\pi$ interaction,^{7b} as shown by the preference for planar conformations in these compounds. As noted earlier, theoretical calculations⁷ predict that the relative conjugating abilities of sulfur and oxygen depend upon the π -acceptor. The energy of interaction, SE , between the LUMO of the π -acceptor and the lone pair orbital on sulfur or oxygen is given by eq 2,⁷ where H_{ij} is the

$$SE = \frac{2H_{ij}^2}{\delta\epsilon_{ij}} \quad (2)$$

(19) Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496.

(20) (a) In thiophenol, the SH group may function as a π -acceptor when the HSCC dihedral angle is 90°; for a discussion of the radical anion, see Bernardi, F.; Mangini, A.; Guerra, M.; Pedulli, G. F. *J. Phys. Chem.* **1979**, *83*, 640. (b) The difference in π -donating abilities for **3** and **4** in the transition states for rotation can be expected because of the difference in hybridization at sulfur or oxygen. The CXC bond angles for dimethyl sulfide (X = S; 98° 52')^{20c} and dimethyl ether (X = O; 111° 43')^{20d} indicate that the bond angle at sulfur in the transition state for rotation in **3** should be smaller than the corresponding angle at oxygen in **4**. A CXC bond angle of 90° in HCOXC-(CH₃)₂ would result in no π donation when the *tert*-butyl group is rotated 90° out of plane. Increasing the CXC bond angle from 90° will result in increased π donation, which should then be more important for **4** than for **3**. (c) Pierce, L.; Hayashi, M. *J. Chem. Phys.* **1961**, *35*, 479. (d) Blukis, U.; Kasai, P. H.; Myers, R. J. *Ibid.* **1963**, *38*, 2753.

(21) (a) Brownlee, R. T. C.; Hutchinson, R. E. J.; Katritzky, A. R.; Tidwell, T. T.; Topsom, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 1757. (b) Katritzky, A. R.; Pinzelli, R. F.; Topsom, R. D. *Tetrahedron* **1972**, *28*, 3441.

(22) "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions". *Natl. Bur. of Stand. (U.S.) Circ.* **1969**, No. 26 (quoted in ref 7a).

interaction matrix element and $\delta\epsilon_{ij}$ is the energy difference between orbitals. The relative importance of sulfur and oxygen π -bonding is then given by eq 3. Some estimates^{2a} of the various parameters

$$\frac{SE(S)}{SE(O)} = \frac{(H_{ij}^2)^{(S)} \delta\epsilon_{ij}^{(O)}}{(H_{ij}^2)^{(O)} \delta\epsilon_{ij}^{(S)}} \quad (3)$$

for $^+CH_2$ and phenyl as π -acceptors are given in Table I. With a good π -acceptor such as $^+CH_2$, sulfur is predicted to be the better π -donor, due to control of eq 3 by the energy gap ratio, $\delta\epsilon_{ij}^{(O)}/\delta\epsilon_{ij}^{(S)}$. This ratio will be close to unity for a poor π -acceptor such as phenyl, and oxygen will be the better π -donor due to domination of eq 3 by the term involving the interaction matrix elements.²³ If the energy of π^* for the formyl group is taken as 4.35 eV,^{24,25} then $\delta\epsilon_{ij}^{(O)}/\delta\epsilon_{ij}^{(S)}$ for **3** and **4** can be estimated as 1.14. This ratio is only slightly larger than the value for phenyl as π -acceptor, and a ratio of $(H_{ij}^2)^{(S)}/(H_{ij}^2)^{(O)}$ close to the values in Table I would lead to the prediction that conjugation should be more important for **4** than for **3**, as observed experimentally in this work.

Registry No. **3**, 32779-88-7; $^+CH_2SH$, 54043-03-7; $^+CH_2OH$, 18682-95-6; C_6H_5SH , 108-98-5; C_6H_5OH , 108-95-2.

(23) The ratio of the σ_R° values for thioanisole (-0.25) and anisole (-0.43) is 0.58, in agreement with the conclusion from the theoretical studies that oxygen is the better π -donor in these systems.

(24) Reference 7c, p 11.

(25) The uncertainties in this energy and those of Table I are probably large. The LUMO energy of ethylene,²⁴ calculated by the same method as for formaldehyde (CNDO/2), is 5.43 eV. The electron affinity of ethylene is given²⁴ as -2.8 eV.

Isotopic Perturbation of Resonance in Benzylic Cations

David A. Forsyth* and Matthew M. MacConnell

Department of Chemistry, Northeastern University
Boston, Massachusetts 02115

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Deuterium substitution in the methyl groups of the phenyldimethylcarbenium ion (**1**) induces downfield shifts of the ^{13}C NMR signals of the ortho and para carbons.^{1,2} These long-range isotope shifts apparently arise from isotopic perturbation of hyperconjugation, with the CH_3 group behaving as a better electron donor than the CD_3 group.¹⁻⁴ Other recent studies indicate a hyperconjugative contribution to isotope shifts in neutral, allylically or benzylically deuterated compounds.⁵⁻⁷

In this paper, we investigate the possibility that isotope shifts in arylcarbenium ions could serve as a probe of π charge distribution and also provide evidence for the origin of long-range isotope shifts. The premises are that isotopic perturbation of hyperconjugation will reduce slightly the supply of electrons to the carbenium center and that this additional electron deficiency will be distributed among the aryl positions in a pattern reflecting the existing charge distribution. The isotope shift at each position would then indicate the amount of charge, assuming a direct relationship between the change in chemical shifts and change

Table I. ^{13}C Chemical Shifts, Deuterium Isotope Effects, and π Charge Densities for Aryldimethylcarbenium Ions

compd	carbon	δ_c^a	$\Delta\delta_c^b$	q_π^c
1	C-2,6	142.4	0.170	0.147
1	C-3,5	133.3	0.031	0.042
1	C-4	155.9	0.222	0.200
2	C-2	150.6	0.191	0.184
2	C-4	159.2	0.241	0.225
2	C-4a	135.0	-0.036	-0.017
2	C-5	134.4	0.070	0.084
2	C-7	136.8	0.084	0.107
2	C-8	127.5	0.042	0.010
3	C-1	153.2	0.205	0.210
3	C-3	128.4	0.064	0.050
3	C-4a	145.5	0.093	0.074
3	C-6	142.8	0.111	0.116
3	C-8	137.8	0.061	0.067
4	C-2,6	142.4	0.03, 0.11	
4	C-4	155.9	0.11	

^a ^{13}C chemical shifts in ppm for the unlabeled ions, measured relative to external (capillary) Me_4Si (from ref 8 and new measurements at 15.0 and 125.8 MHz). ^b Deuterium-induced isotope shift at aryl carbons in ppm; positive sign indicates downfield shift in the deuterated compound. Measured at 125.8 MHz on mixtures of deuterated and unlabeled ions. Error estimate ± 0.012 ppm, digital resolution better than 0.007 ppm. ^c SCF- π MO charge in $ArCH_2^+$ (ref 8).

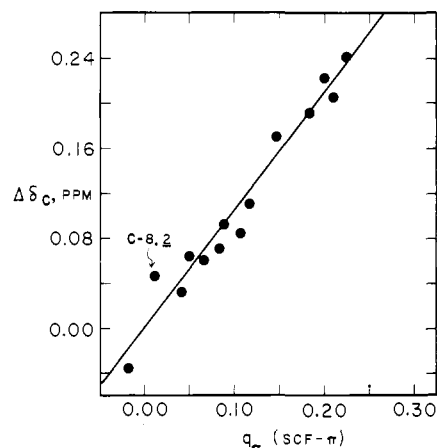
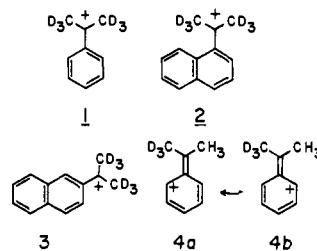


Figure 1. Plot of isotope shifts vs. π -charge densities.

in charge density. We expected that the isotope shifts would be a better probe of charge than shifts induced by other substituents,⁸ because of the very minor structural perturbation involved. However, this expectation is only partially borne out in the results described below.

Isotope shifts observed at aryl carbons of ions **1-4** are listed



in Table I, along with the ^{13}C chemical shifts for the unlabeled ions. Not all carbons displayed measurable isotope shifts. The smallest resolved peak separation was 0.031 ppm; smaller isotope shifts may be unresolved due to the broadened resonances typical of cations (3-5-Hz line widths). Also listed in Table I are values of q_π , the π charge at each position, from SCF- π MO calculations

(1) Servis, K. L.; Shue, F.-F. *J. Am. Chem. Soc.* **1980**, *102*, 7233-7240.

(2) Forsyth, D. A.; Lucas, P.; Burk, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 240-245.

(3) Timberlake, J. W.; Thompson, J. A.; Taft, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 274-276.

(4) For a review of isotope effects on ^{13}C spectra, see: Forsyth, D. A. In "Isotopes in Organic Chemistry"; Lee, C. C., Buncl, E., Eds.; Elsevier: Amsterdam; Vol. 6, in press.

(5) Ernst, L.; Eltamany, S.; Hopf, H. *J. Am. Chem. Soc.* **1982**, *104*, 299-300.

(6) Hansen, P. E.; Led, J. J. *Org. Magn. Reson.* **1981**, *15*, 288-293.

(7) Wisener, J. R.; Günther, H. *Tetrahedron Lett.* **1982**, *223*, 2845-2848.

(8) (a) Forsyth, D. A.; Spear, R. J.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2512-2518. (b) New values for chemical shifts of **2** are reported here, but the assignments remain the same as in the above paper.