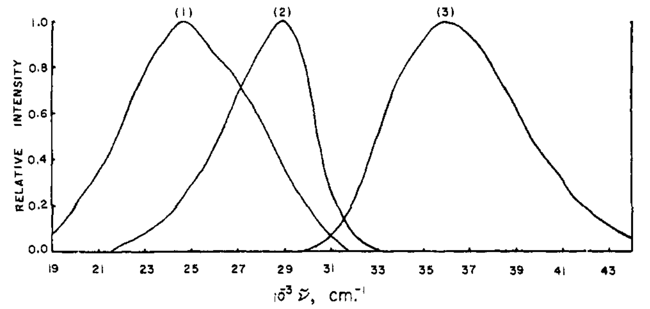

Figure 2. Absorption and emission of acetone in *n*-hexane, normalized to the wavelength maxima, for the excimer fluorescence (1), monomer fluorescence (2), and absorption spectrum (3). Concentrations: (1) 2.2×10^{-2} *M*, (2) 2.7×10^{-4} *M*, and (3) 5.8×10^{-2} *M*.

estimated to be ±25%. Solvents with increasing dielectric constants produce considerable enhancement of monomer fluorescence intensity but have a negligible effect on excimer intensity.[15]

Acetone-d_6 exhibited the same behavior as normal acetone with respect to excimer formation, spectral distribution, and solvent effects. In the deuterated species, however, the fluorescence yield is enhanced for the monomer and excimer. The ratios of the relative intensities of acetone-d_6 to normal acetone were determined to be 2.5 and 1.4 for the monomer and excimer, respectively. Similar results regarding enhancement by deuteration have recently been reported for fluid solutions of deuterated biacetyl.[16]

Kearns and Borkman[2] have reported that energy transfer from acetone to *cis*-pentene-2 is more efficient in neat acetone than in mixed solvent systems. Wagner[17] has shown this effect to be due to dependence of the acetone triplet lifetime on hydrogen abstraction from the solvent. It is also possible that the excimer participates in energy transfer.

The excimer emission of acetone is not unique among aliphatic ketones. We have in fact also observed monomer and excimer emissions from the following aliphatic ketones: diethyl ketone, methyl ethyl ketone, diisopropyl ketone, dicyclohexyl ketone, and di-*t*-butyl ketone. Further studies of ketone excimers are currently in progress.

[15] Unpublished results from this laboratory.

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[17] P. J. Wagner, *ibid.*, 88, 5672 (1966).

M. O'Sullivan, A. C. Testa
Department of Chemistry, St. John's University
Jamaica, New York 11432

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Stereospecific Hydroxyl Proton Spin–Spin Coupling in a Primary Alcohol[1]

Sir:

A number of reports have appeared recently on the use of the hydroxyl proton as a conformational probe,[2] usually including dimethyl sulfoxide as solvent to inhibit proton exchange.[3] In each case, structural conclusions were based on the assumption that angle dependence of the vicinal hydroxyl proton coupling constants, J_{HCOH}, parallels the familiar Karplus relationship for J_{HCCH}.[4] This assumption, though inherently reasonable, has not been demonstrated, a fact which has permitted controversy to develop over conformational equilibria involving the hydroxyl group.[2a] We wish to describe the first case of strongly nonequivalent hydroxyl proton coupling in a primary alcohol,[5] an observation which further supports the proposed angle dependence of J_{HCOH} (see Figure 1).

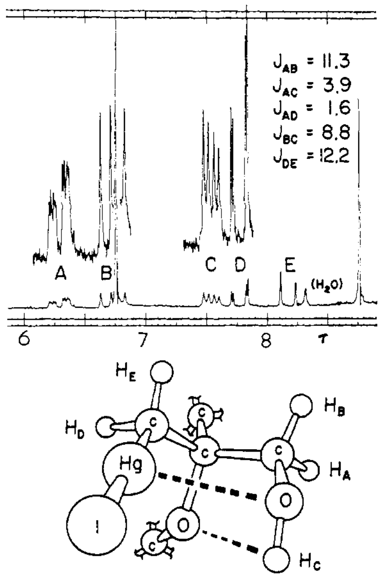

Figure 1. The nmr spectrum (100 MHz, 0.175 *M* in $CDCl_3$) and preferred conformation of 3-iodomercuri-2-methoxy-2-methyl-1-propanol (**1**).

Compound **1**, prepared by methoxymercuration of methallyl alcohol as described previously,[1b] shows a quartet for the hydroxyl proton in acetone, chloroform, or carbon tetrachloride at room temperature. Analysis of the five-spin system represented by protons A–E (Figure 1) over the usable temperature range in $CDCl_3$[6] and straightforward statistical treatment of the resulting data[7] gave limiting values of J_{HCOH} = 11.0 and J'_{HCOH}

[1] (a) Nuclear Magnetic Resonance Investigation of Secondary Valence Forces. III. Support by the National Institutes of Health (GM 14533) is gratefully acknowledged. (b) Part II: E. F. Kiefer and W. Gericke, *J. Amer. Chem. Soc.*, **90**, 5131 (1968).

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[3] O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

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[5] F. Hruska, T. Schaefer, and C. A. Reilly, *Can. J. Chem.*, **42**, 697 (1964), have calculated vicinal coupling constants of 5.96 ± 0.03 and 5.80 ± 0.08 Hz from the ABC spectrum of 2-methyl-2-nitro-1,3-propanediol in acetone.

[6] Proton assignments were verified by frequency-swept double resonance. Spectral parameters were obtained for each temperature using the iterative program LAOCOON II (S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3836 (1964)). Solute crystallization and rapid proton exchange precluded measurements below −20° or above 40°, respectively.

[7] G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, **89**, 1135 (1967). A modification of Whitesides' three-parameter calculation was used, in which the rms deviation in the calculated conformational energy difference, ΔE, over the total temperature range was minimized by systematic variation of the limiting parameters J^{OH}_{trans} and J^{OH}_{gauche}.

Table I. Temperature Dependence of Hydroxyl Proton Coupling Constants and Chemical Shift in **1**[a]

Temp, °K	J_{HCOH}, Hz	J'_{HCOH}, Hz	ν_{OH},[b] Hz
311.5	8.72	3.90	224.6
299.0	8.81	3.89	233.9
297.5	8.80	3.91	237.1
283.0	8.92	3.77	252.0
270.5	9.03	3.80	270.0
260.0	9.18	3.74	289.7
253.0	9.30	3.72	302.3
	11.0 ± 0.3[c]	2.8 ± 0.3[c]	

[a] In $CDCl_3$, 0.116 *M*.[6] [b] Downfield from TMS at 100 MHz. [c] Calculated limiting values.[7]

= 2.8 Hz (Table I). It is unlikely that these values represent true *trans* and *gauche* coupling constants, for which values of about 12 and 2 Hz, respectively, appear more reasonable.[2a,b,g] Measurements on Dreiding models, assuming sp^3 oxygen atoms, suggest a deviation of about 20° in HCOH dihedral angle from a perfectly staggered conformation; a deviation of 18° is obtained from a three-parameter Karplus equation[2a] if $J_{180°} = 12.0$ Hz is assumed.

It is clear that, of the two factors responsible for the observed conformational specificity, mercury–oxygen chelation is more important than intramolecular hydrogen bonding. The existence of Hg···OH coordination and absence of significant steric conformational energy differences were established using the nmr criteria developed previously,[1b] including titration with iodide ion, ligand exchange, and solvent basicity and dilution studies. The hydroxyl proton coupling constants appear to be independent of concentration over the range 0.023–0.46 *M*, implying that intermolecular hydrogen bonding has a negligible effect on the average CH_2OH group conformation. The presence of a substantial intermolecular component is indicated, however, by a downfield shift of 0.32 ppm for the hydroxyl signal at 0.116 *M* in $CDCl_3$, relative to the extrapolated value at infinite dilution ($\tau^{OH}{}_0$ 7.99). This amounts to over 50% of the corresponding hydrogen-bond shift observed for isobutyl alcohol ($\tau^{OH}{}_0$ 9.35, $\tau^{OH}{}_{0.116M}$ 8.76). The similar intensities of the free and intramolecular hydrogen-bonded hydroxyl stretching bands of **1** in the infrared (3632 and 3584 cm^{-1}, respectively; 0.0046 *M* in CCl_4) support this interpretation.

The conformational rigidity of **1** is only slightly decreased when hydrogen bonding is eliminated by replacing the hydroxyl group with methoxyl; the remainder of the spectrum is qualitatively similar to that of Figure 1, including long-range H_A–H_D coupling.[1b] Elimination of the mercury atom by iododemercuration,[8] however, effectively restores free rotation. The iodomethylene protons appear as a sharp singlet and the oxymethylene and hydroxyl protons as somewhat broadened singlets in $CDCl_3$, with the hydroxyl signal shifted 0.57 ppm to higher field relative to **1**.[9]

(8) W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967).

(9) Without careful sample purification, the hydroxyl singlet is quite sharp, and the CH_2O protons appear as a tight AB quartet, $\Delta\nu_{AB} = 5.3$ Hz.

(10) National Science Foundation Undergraduate Research Participant, 1968.

Edgar F. Kiefer, Wolfgang Gericke, Sherwin T. Amimoto[10]
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

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The Microwave Spectrum of Germyl Isocyanate[1]

Sir:

A recent study of the infrared spectrum of germyl isocyanate by Griffiths[2] has led that author to the conclusion that the molecular skeleton is not linear, but that there is an approximate deviation of 10° from linearity about the Ge–N–C bond. Since this approximates the strict skeletal linearity of SiH_3NCO[3] rather than the bent structure of CH_3NCO (angle C–N–C = 125°,[4a] 140°[4b]), the author concludes that $(p \rightarrow d)_\pi$ bonding plays a significant role in the germanium to nitrogen bonding for this molecule.[2] We have recently begun a microwave investigation of this molecule to ascertain if the molecule is indeed bent and to determine more precisely, if possible, the Ge–N–C angle.

The spectra were taken with a traditional Hughes–Wilson type spectrometer[5a] employing 100-kc/sec Stark modulation and oscilloscope display. A Micro-Now Frequency Multiplier Chain, Model 101, standardized against WWVB,[5b] was used as our frequency standard.

Germyl isocyanate was prepared by a slight modification of the method of Srivastava, Griffiths, and Onyszchuk.[6] Germyl iodide was first prepared, following Griffiths and Beach,[7] and this was allowed to react with solid silver cyanate. The product was identified by its infrared spectrum.[2]

The general features of the microwave spectrum, namely the density of absorptions and the presence of internal rotation doublets, indicate that the molecule is bent and that the barrier to internal rotation is low. Indeed the general characteristics of the spectrum closely resemble those observed in methyl isocyanate[4b] where the density of the spectrum was interpreted in terms of the population of many internal rotation quantum states.

To date we have observed only a-type absorptions and have been able to assign definitely only $K_{-1} = 0$, $v = 0$ (torsional quantum number) transitions. We report in Table I the center of the internal rotation

Table I. Assigned Frequencies of Germyl Isocyanate[a]

Species	Transition	Frequency, Mc/sec
$H_3{}^{74}GeNCO$	$2_{02} \rightarrow 3_{03}$	11034.84
	$3_{03} \rightarrow 4_{04}$	14713.30
	$4_{04} \rightarrow 5_{05}$	18391.08
$H_3{}^{72}GeNCO$	$2_{02} \rightarrow 3_{03}$	11119.54
	$3_{03} \rightarrow 4_{04}$	14825.80
	$4_{04} \rightarrow 5_{05}$	18532.50
$H_3{}^{70}GeNCO$	$2_{02} \rightarrow 3_{03}$	11208.74
	$3_{03} \rightarrow 4_{04}$	14944.68
	$4_{04} \rightarrow 5_{05}$	18681.14

[a] Estimated uncertainty, ±0.2 Mc/sec.

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(1) This report is based on portions of a thesis to be submitted by K. R. Ramaprasad to the Graduate School of New York University in partial fulfillment of the requirements for the Ph.D. degree.

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(3) M. C. L. Gerry, J. C. Thompson, and T. M. Sugden, *Nature*, **211**, 846 (1966).

(4) (a) E. H. Eyster, R. H. Gillette, and L. O. Brockway, *J. Am. Chem. Soc.*, **62**, 3236 (1940); (b) R. F. Curl, Jr., V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, *J. Chem. Phys.*, **39**, 3335 (1963).

(5) (a) R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.*, 71, 562 (1947); (b) the 10-Mc/sec signal of the National Bureau of Standards at Boulder, Colo.

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(7) J. E. Griffiths and A. L. Beach, *ibid.*, **44**, 1227 (1966).