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 (τ^{OH}_0 7.99). This amounts to over 50% of the corresponding hydrogen-bond shift observed for isobutyl alcohol (τ^{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]

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(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.

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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.

(2) J. E. Griffiths, *J. Chem. Phys.*, **48**, 278 (1968).

(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.

(6) T. N. Srivastava, J. E. Griffiths, and M. Onyszchuk, *Can. J. Chem.*, **40**, 739 (1962).

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

doublets for the transitions assigned. The combination of centrifugal distortion effects and coupling of internal torsion to over-all rotation will require further analysis and is being delayed until the structure (discussed later) can be determined more accurately from additional isotopic data. Since no b-type transitions were observed, it has been impossible to determine experimentally the a moment of inertia. However, the quantity $(B + C)/2$ has been determined for this nearly symmetric prolate top for $^{74}GeH_3NCO$, $^{72}GeH_3NCO$, and $^{70}GeH_3NCO$ and is tabulated in Table II.

Table II. Rotational Constants $[(B + C)/2]$ of Germyl Isocyanate[a]

Species	$(B + C)/2$, Mc/sec
$^{74}GeH_3NCO$	1839.14
$^{72}GeH_3NCO$	1853.25
$^{70}GeH_3NCO$	1868.11

[a] Since torsion–vibration–rotation analysis has not been performed, a simple averaging of the reported doublets was used and $(B + C)/2$ was calculated in the rigid rotor approximation.

The rotational isotopic shifts contain essentially no information about the Ge–N–C angle because of the large a coordinate (a is the figure axis) and small b coordinate of germanium for any assumed structure. For any structure, an a coordinate of 1.0119 ± 0.0003 Å will fit the isotopic shift in $(B + C)/2$. Accordingly only the absolute value of this quantity contains structural information. In terms of the "average structural parameters" employed by Griffiths[2] (r(Ge–H) = 1.53 Å, r(Ge–N) = 1.81 Å, r(N–C) = 1.21 Å, r(C–O) = 1.17 Å, and the H–Ge–H angle = 111°), the Ge–N–C angle deviates from linearity by 35 to 40°. That is, the angle which best reproduces the quantity $(B + C)/2$ for GeH_3NCO_3 corresponds more closely to the angle found consistent with the microwave data of CH_3NCO[4b] than with the value expected assuming a linear or near-linear skeleton.

Because of the large uncertainties associated with the above assumed parameters, further considerations are required before the range for the Ge–N–C angle can be fixed and the conclusion drawn that there is little $(p \rightarrow d)_\pi$ bonding in GeH_3NCO. The quantity $(B + C)/2$ can be fit by many combinations of structural parameters. In particular, if there is $(p \rightarrow d)_\pi$ bonding, one would expect the Ge–N bond to be shorter than the value employed by Griffiths and the N–C bond length could approximate the corresponding very short value of 1.15 Å found in SiH_3NCO.[3] The effect of such changes would be to open the Ge–N–C angle. To estimate the effect of such changes a calculation was carried out using the parameters listed in Table III (model I), which allows for the maximum back-bonding that might be expected based on that observed for SiH_3NCO. The C–O bond length assumed was that found by electron diffraction for CH_3NCO,[4a] since it is close to the 1.179 Å for the same bond in SiH_3NCO. It is seen that the Ge–N–C angle deviation from linearity must be at least 26° to fit the observed value of $(B + C)/2$. Also listed in Table III is a second set of assumed parameters (model II) based on the electron diffraction data of CH_3NCO.[4a] The Ge–N distance used was that chosen by Griffiths. This set of parameters requires a Ge–N–C angle which deviates from linearity by 37° to fit $(B + C)/2$ for GeH_3NCO. A longer Ge–N bond would close the Ge–N–C angle even more.

Table III. Structural Models

	I	II
Ge–H,[a] Å	1.53	1.53
H–Ge–H, deg[a]	111	111
Ge–N, Å	1.76[b]	1.81[a]
N–C, Å	1.15[c]	1.19[d]
C–O,[d] Å	1.18	1.18
∠Ge–N–C, deg	154	143

[a] Reference 2. [b] Estimated assuming back-bonding similar to that found in SiH_3NCO. [c] Reference 3. [d] Reference 4a.

It seems clear from the above calculations and experimental data that (1) the molecule is indeed bent as reported by Griffiths;[2] (2) the deviation from linearity is probably at least 26° assuming "maximum back-bonding" and the Ge–N–C skeletal bond angle may well approach the value of 40° found for the C–N–C skeletal bond angle in CH_3NCO;[4b] (3) it does not seem likely that $(p \rightarrow d)_\pi$ bonding makes a very significant contribution to the Ge–N bonding in this molecule.

It is to be hoped that an investigation of the ^{15}N and ^{13}C isotopes will enable us to fix the molecular parameters more precisely in the near future. At that time we hope to report also on the barrier to internal rotation, the dipole moment, quadrupole coupling constants, and torsion–vibration interactions for this molecule.

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Thermolysis of *trans*-Chloro(2-allylphenyl)bis(triethylphosphine)nickel(II)

Sir:

Treatment of *trans*-dichlorobis(triethylphosphine)-nickel(II) with 2-allylphenylmagnesium chloride in tetrahydrofuran–ether solution affords high yields of *trans*-chloro(2-allylphenyl)bis(triethylphosphine)nickel(II) (**1**). The yellow compound, mp 63–65°, possesses a *trans*-planar configuration and is monomeric in benzene solution.[1] As in other *ortho*-substituted arylnickel

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[1] Details of the synthesis of **1**, the palladium analog, and the corresponding styryl compounds will be published separately. The experi-