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Structural Features in Germyl Isocyanate from Infrared Spectroscopy

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An infrared spectral study, from 4000 to 33 cm^{-1}, of the product of the reaction between GeH_3Br and silver cyanate has been completed. The product is an isocyanate, GeH_3NCO, but evidence for a small amount of the normal cyanate form is also presented. Germyl isocyanate, unlike SiH_3NCO, has a nonlinear skeleton and an estimate of the deviation from linearity is about 10°. The vibrational spectra of the GeH_3 and GeD_3 derivatives are assigned in terms of a pseudo symmetric-top model of $C_{3v}\simeq C_s$ symmetry. Rotational fine structure in two of the perpendicular-type fundamentals was used to evaluate the nonlinearity in the skeleton.

INTRODUCTION

It had previously been established that the CH_3NCO molecule has a nonlinear skeleton[1–3] but that the similar compounds SiH_3NCO and SiH_3NCS have linear skeletal configurations.[4–7] This is though to arise from the delocalization of electrons in the NCO and NCS units into the vacant 3*d* orbitals of the second-row silicon atom. By contrast, third-row elements, such as germanium, do not seem to be as effective in realizing the use of the more diffuse 4*d* orbitals even though in cases where very electronegative elements are involved, as in GeH_3F, structural consequences of $d_\pi \leftarrow p_\pi$ bonding has been noted.[8] The product of the reaction between germyl bromide and silver cyanate[9] afforded an excellent opportunity to study the bonding situation in a compound containing germanium linked to a group somewhat less electronegative than fluorine. Accordingly, the chemical species formed in such a reaction, be it GeH_3NCO or GeH_3OCN, and the nature of the molecular skeleton is the substance of the present article. The study involves the use of the infrared spectra of the germyl and germyl-d_3 compounds, a preliminary report of which appeared earlier.[10]

SELECTION RULES, STRUCTURES, AND BAND CONTOURS

There are three basic models to be concerned with, two of which represent possibilities for the isocyanate and one for the normal cyanate. These are shown in Fig. 1. The isocyanate may have a linear [Fig. 1(a)] or a nonlinear skeleton [Fig. 1(b)] whereas the normal cyanate [Fig. 1(c)] would most likely have a bent structure. The effective point groups would be C_{3v}, $C_{3v}\simeq C_s$ for small α and C_s, respectively. Table I summarizes the different selection rules for these three models.

Band contours can also play an important role in determining the nature of the skeleton in the compound. If the Ge–N=C=O unit is linear, all of the symmetric a_1 modes should exhibit parallel-type absorption bands with prominent *P* and *R* rotational branches and somewhat weaker *Q* branches. The relative intensities of the *Q* to the *P* and *R* branches is determined by the ratio of the rotational constants, B/A. In this case, the ratio is very small. Vibrational modes in which the dipole-moment changes are perpendicular to the major molecular axis are expected to give rise to some absorption bands showing resolvable fine structure. In some bands, however, the Coriolis coupling coefficients may be large and positive in which case the fine structure would not be resolved or may have over-all contours approaching that of a parallel-type fundamental.

As the linear skeleton is bent, and α assumes positive valves, the point group changes from C_{3v} to C_s which formally splits the degeneracy in the *e* modes into ones belonging to the a' and a'' species. Several problems must be considered. If α in Fig. 1(b) is not too large, the separation of the a' and a'' fundamentals from a frequency point of view may be vanishingly small and the resulting fundamentals would be accidentally degenerate. Furthermore, for small α, the rotational constants *B* and *C* are apt to be so close and the barrier to internal rotation of the GeH_3 group so small that the GeH_3 group may behave as a free rotator (practically no levels in the potential well would be populated at room temperature). Under such circumstances, the fine structure could resemble that of a symmetric C_{3v} molecular species. Accordingly, the observation of rotation–vibration fine structure and the absence of removing the degeneracy in the other *e* fundamentals (under C_{3v}) is not convincing evidence for a linear skeleton. The removal of the degeneracy in an *e*-type fundamental, however, is persuasive evidence for a nonlinear skeleton.

With the introduction of a nonlinear structure,

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[4] M. C. L. Gerry, T. M. Sugden, and J. C. Thomson, Abstr. European Congr. Mol. Spectr. 8th Copenhagen, Denmark, 1965, 259 (1965).

[5] E. A. V. Ebsworth and M. J. Mays, J. Chem. Soc. **1962**, 4844.

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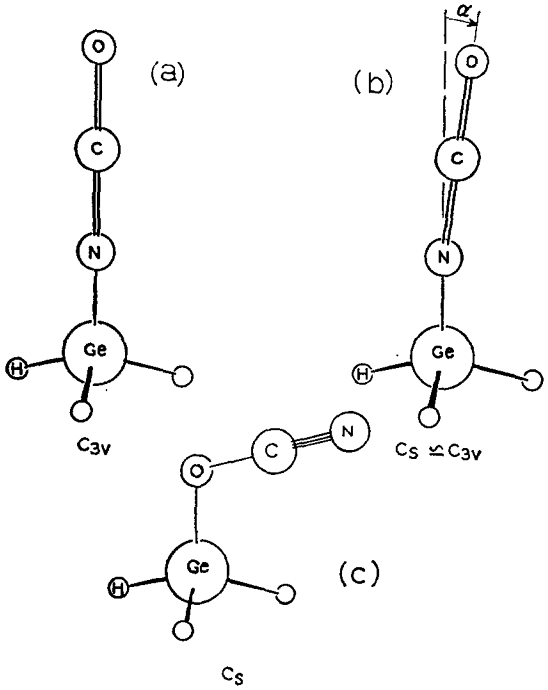

FIG. 1. Structural models for germyl isocyanate and germyl cyanate (a) linear skeleton, (b) nonlinear skeleton, and (c) nonlinear normal cyanate.

changes can also be expected in the band contours of the symmetric a_1 (under C_{3v}) fundamentals. Of prime significance is the fact that in some modes the dipole-moment change may no longer coincide with the figure axis of the molecule and accordingly hybrid contours made up of parallel and perpendicular components may be expected and observed. The relative intensity of each component will vary, of course, depending upon the particular motions involved. The observation of such an effect would also represent credible evidence for a nonlinear skeleton.

EXPERIMENTAL

The compound was prepared by passing the vapors of germyl bromide (or GeD_3Br) over solid silver cyanate[9] in an all-glass mercury-free vacuum system. All stopcocks and ground glass joints were lubricated with a chlorofluorocarbon vacuum grease. The bromides GeH_3Br and GeD_3Br, were made from the reaction of GeH_4 and GeD_4 [11] with bromine.[9] The resulting products had measured vapor densities corresponding to molecular weights of 117.4 and 120.6 (calc. for GeH_3NCO, 117.7 and for GeD_3NCO, 120.7).

Infrared spectra were obtained using Beckman IR-11 and 12 instruments and samples were confined in 10-cm gas cells fitted with CsI, KBr, or high-density polyethylene windows. Far-infrared spectra of liquid samples were recorded with conventional liquid cells using high-density polyethylene windows. The transfer of samples in this case was done in an argon-filled steel glove box. The spectrophotometers were calibrated to ±0.2 cm^{-1} using the narrow lines of CH_4, CO, CO_2, NH_3, HCl, DCl, HBr, DBr, HF, and H_2O.[12–15] Values reported are generally less accurate because natural bandwidths make the determinations of the band centers difficult. For the fine-structure analyses, which depend upon small frequency differences, values are expected to be accurate to ±0.2 cm^{-1} or better.

RESULTS

Survey scan spectra from 2500 to 300 cm^{-1} for the germyl and germyl-d_3 compounds are shown in Fig. 2. Expanded scale spectra for some of the fundamentals appear in Figs. 3–5. The higher-resolution scans of ν_6 and ν_7 are shown in Fig. 4. Data are listed in Tables II–IV. Rotational constants as a function of α and a summary of the fundamental frequencies in terms of a $C_{3v} \simeq C_s$ structure are collected in Tables V and VI, respectively.

ASSIGNMENT OF FUNDAMENTALS

The fundamental modes of vibration can be thought of as arising from the motions within the linear triatomic moiety, N=C=O, from those within the heavy GeH_3 and GeD_3 groups, and from those which involve the molecule as a whole. The frequencies of most of these can be predicted from earlier work with structurally related molecules[16–21] and from frequency shifts encountered in the spectrum of the GeD_3 compound.[20,21] Accordingly, it should be fairly simple to identify the species produced in the reaction, be it GeH_3NCO or GeH_3OCN. The observed spectra are correlated with the isocyanate but small amounts of the normal cyanate

TABLE I. Selection rules for MH_3XYZ molecules.

Point group	C_{3v}	$C_s \sim C_{3v}$	C_s
No. of fundamentals	15	15	15
ir active	15	15	15
Species	$5a_1$	$10a'-5a_1$	$10a'$
	$5e$	$5a''-5e$	$5a''$

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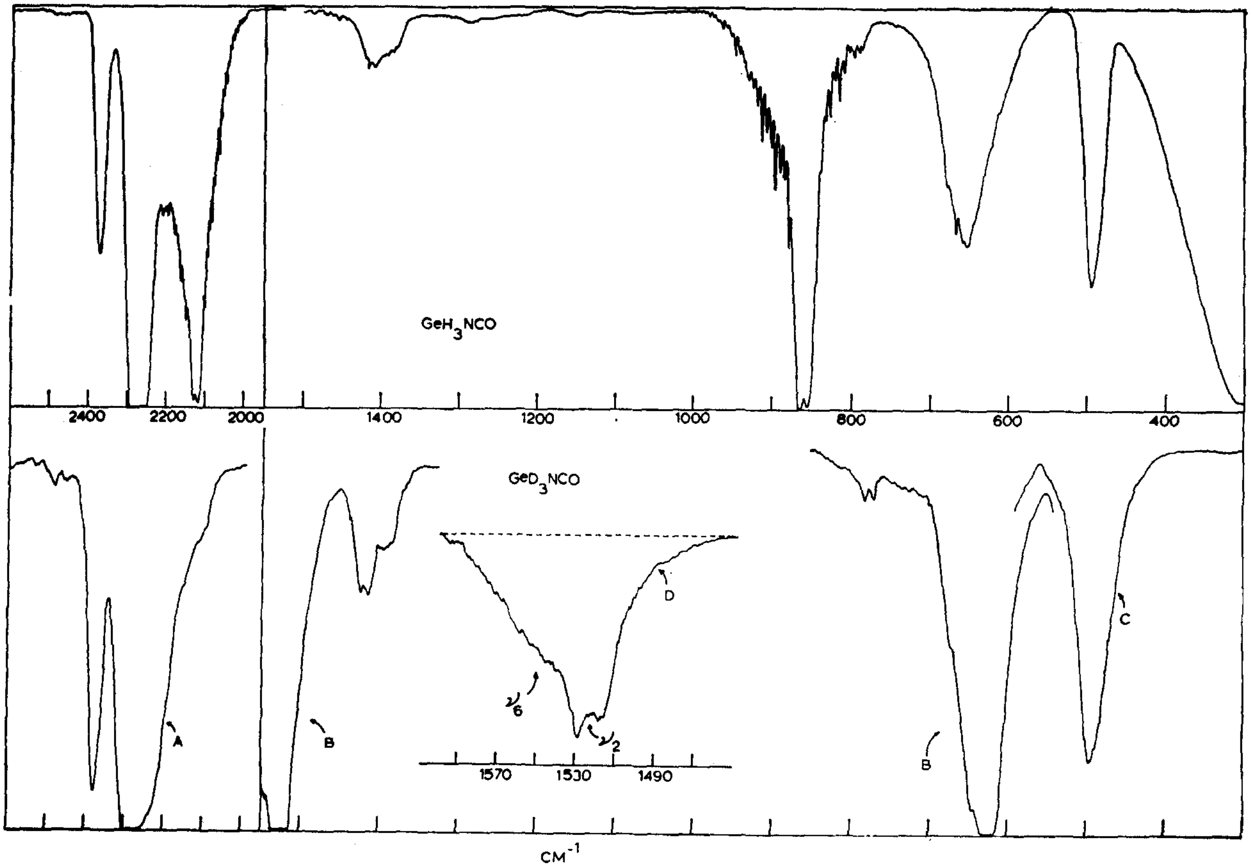

FIG. 2. Infrared survey scan of germyl isocyanate. Top, GeH$_3$NCO, $p=5.6$ mm. Bottom, GeD$_3$NCO, $p=$(A) 72 mm, (B) 35 mm, (C) 10 mm, (D) 7 mm.

also appear to be present. The following discussion is based upon a C_{3v} model [Fig. 1(b)] with refinements in subsequent sections to account for observed anomalies.

Spectral features characteristic of the GeH$_3$ group are quite evident. The intense band system with prominent *P* and *R* rotational branches at 2128 and 2117 cm^{-1} obviously arises from the symmetric GeH$_3$ stretching mode ν_2 and the rotation–vibration fine structure overlapping this region with its center at 2129 cm^{-1} as assigned as ν_6 representing the antisymmetric GeH$_3$ stretching mode. The corresponding fundamentals in the GeD$_3$ compound are shifted to 1523 and 1550 cm^{-1}, respectively. The GeH$_3$ deformation modes $\nu_4(a_1)$ and $\nu_7(e)$ are observed at 862 and 861 cm^{-1}, respectively. The first shows prominent *P* and *R* rotational branches and the latter has striking rotational–vibrational fine structure. Furthermore, the fine structure in ν_6 and ν_7 has the characteristic s, w, w, s intensity alteration expected for modes of this type. The remaining internal fundamental of the GeH$_3$ group is the rocking mode $\nu_8(e)$. This is identified with the strong band centered near 660 cm^{-1} which is discussed later in relation to the nature of the skeleton. In all cases the fundamental discussed so far shift upon deuteration. The deformation modes in GeD$_3$NCO, ν_4 and ν_7, occur at 622 and 647 cm^{-1}, respectively. The rocking mode ν_8, however, is shifted to 495 cm^{-1}, a region already occupied by a strong pair of bands which are unaffected by deuterium substitution. The latter are discussed below.

The remaining bands are useful in establishing the constitution of the molecule. A very intense band almost completely unaffected by deuteration is due to the parallel-type antisymmetric stretching of the N=C=O unit and, as such, corresponds in a sense with the similar mode in CO$_2$. The frequency of the band (2271 cm^{-1} for the GeH$_3$ compound and 2269 cm^{-1} for the GeD$_3$ derivative) clearly labels the compound as GeH$_3$NCO and not GeH$_3$OCN. The particular conclusion is based upon a comparison of frequencies in similar isocyanates, notably CH$_3$NCO[1] at 2231 cm^{-1}, Ge(NCO)$_4$[22] at 2304 and 2247 cm^{-1} each of which is known to exist in the isocyanate form. Normal cyanates generally absorb at slightly higher frequencies than the isocyanates. The other mode involving the symmetric stretching of the N=C=O unit, corresponding to the infrared forbidden symmetric mode of CO$_2$, occurs as a much weaker band in the spectra of GeH$_3$NCO and GeD$_3$NCO at about

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[22] F. A. Miller and G. L. Carlson, Spectrochim. Acta **17**, 977 (1961).

1420 and 1416 cm^{-1}, respectively. The comparable bands in CH_3NCO and $Ge(NCO)_4$ are observed at 1412 and 1432 cm^{-1}, respectively.[1,22]

The strong 495-cm^{-1} absorption band is identified with the $\nu_5(a_1)$ mode involving the stretching of the Ge–N bond, which as expected, is not significantly shifted upon deuteration. In $Ge(NCO)_4$,[22] the Ge–N stretching fundamental is at 492 cm^{-1}. If the molecule were indeed a normal cyanate, the Ge–O stretching fundamental is expected at a much higher frequency (*vide infra*).

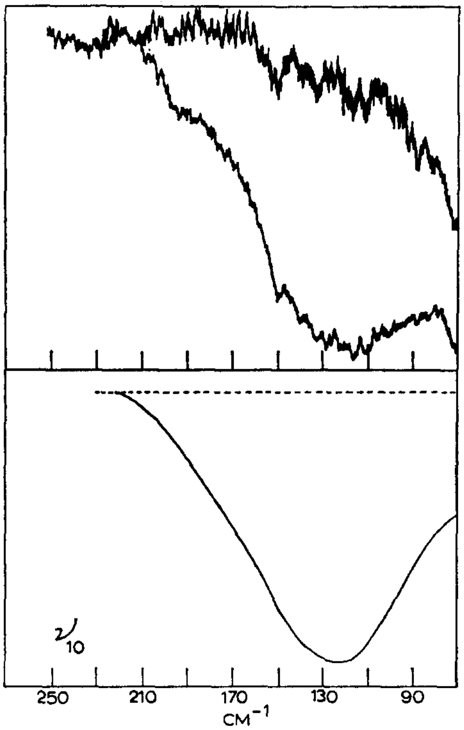

FIG. 3. The ν_{10} fundamental of GeH_3NCO, liquid with $d=0.1$ mm, (top) observed, (bottom) transposed to flat base line.

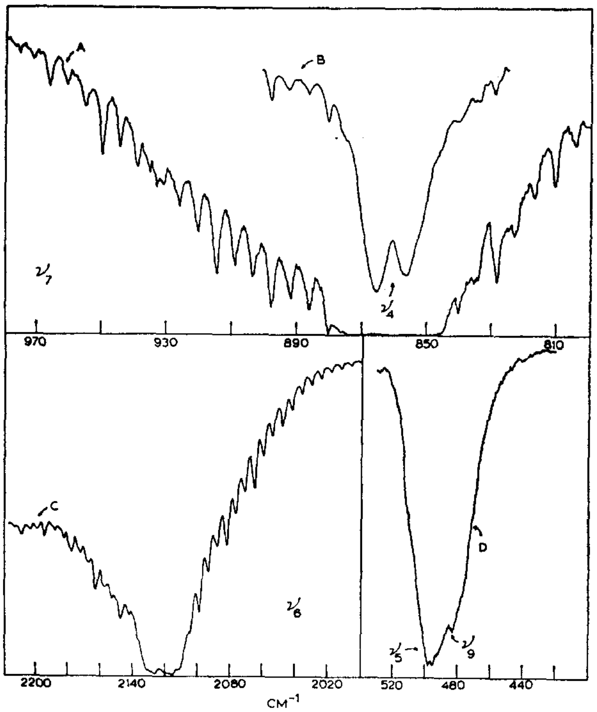

FIG. 4. Expanded scale spectra of fundamentals of GeH_3NCO. Top, ν_4 and ν_7, $p=4.3$ and 2.8 mm. Bottom left, ν_2 and ν_6, $p=5.6$ mm. Bottom right, ν_5 and ν_9, $p=8.0$ mm.

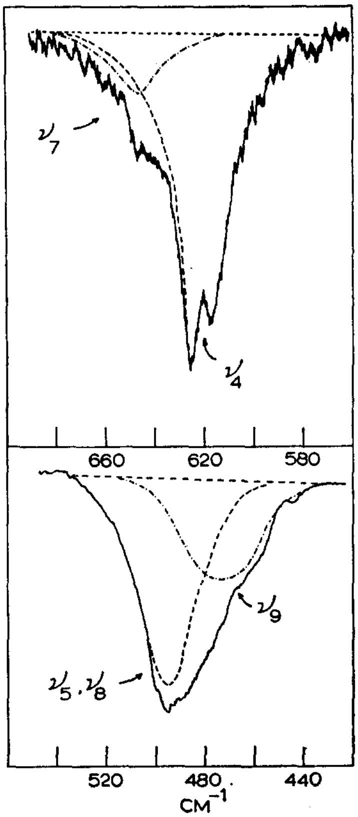

FIG. 5. Expanded scale spectra of fundamentals of GeD_3NCO Top, ν_4 and ν_7, $p=10$ mm. Bottom, ν_5, ν_8, and ν_9, $p=10$ mm.

Only two fundamentals (under C_{3v}) remain to be assigned and only two other major absorption bands were recorded. These represent the two skeletal deformation modes ν_9 and ν_{10} and are identified with the bands at 483 and 115 cm^{-1}, respectively. The first is only marginally shifted in the spectrum of the GeD_3NCO molecule and the latter was not measured for the deuterium compound because of the accidental loss of the sample. Since no definitive information was apt to be gained by measuring this band for GeD_3NCO, the synthesis of a new sample was not considered to be worthwhile. A significant frequency shift was not expected.

In addition to the bands already discussed, two others require specific comments. A weak band at 2374 cm^{-1} can be attributed to a small amount of the normal cyanate largely because it does not seem to be due to

TABLE II. Infrared spectrum of GeH_3NCO.[a]

GeH_3NCO	GeD_3NCO	I[b]	Assignment
3750	···	vw	$\nu_2+\nu_3+2\nu_{10}=3773$
3670	···	w	$\nu_1+\nu_3=3691$
3630	···	vw	$\nu_1+\nu_3'=3659$
3552	···	vw	$\nu_3+\nu_6=3549$
3524	···	vw	$\nu_3'+\nu_6=3517$
3250	···	vw	$\nu_1+\nu_4+\nu_{10}=3248$
2974	···	vw	$2\nu_3+\nu_{10}=2955$
2935	···	w	$\nu_1+\nu_8=2939$
2856	···	w	$2\nu_3=2840$
2764	···	w	$\nu_1+\nu_5=2766$
2374	2372	ms	GeH_3OCN
2272	2270	vs	ν_1
2129	1550	s	ν_6
2128(*R*)	1528		
(2123) (*Q*)	(1523)	vs	ν_2
2117(*P*)	1519		
1424(*R*)	···		
1420.3(*Q*)	1418	mw	ν_3
1412(*P*)	···		
1388	1390	wsh	ν_3'
1284	···		GeH_3OCN
861	647	mssh	ν_7
866.7(*R*)	626.5(*R*)		
(862) (*Q*)	(622) (*Q*)	vs	ν_4
857.4(*P*)	618.4(*P*)		
···	882		
···	875	mw	$GeHD_2NCO$ impurities
···	781		
···	767		
	727	vw	$\nu_5+2\nu_{10}=725$
670.5(*R*)	···		
667.5(*Q*)	495		
662.3(*P*)	···	s	ν_8
659	···		
653	···		
495	495	s	ν_5
483	472	s	ν_9
394	···	vw	GeH_3OCN or ?
115	(115)	w	ν_{10}

[a] Frequencies in cm^{-1}.

[b] s, strong; m, medium; w, weak; sh, shoulder.

the predominating GeH_3NCO species. The band does not shift on deuteration and is fitted by only one possible combination tone and only poorly. The sum band $2271+115=2386\ cm^{-1}$ would require a large anharmonicity, which is not an unreasonable assumption, but the absence of the corresponding difference band at $2271-115=2156\ cm^{-1}$ eliminates such an assignment. For the normal cyanate, the Ge–O and O–C stretching fundamentals would also be expected. The former, unfortunately, is expected to be undetectable because of overlapping by the GeH_3 deformation modes but the O–C stretch should be observable. A very weak band at 1284 cm^{-1}, although at rather a high frequency for this type of mode, would fit our requirements. The conclusion, therefore, is that a small amount of the GeH_3OCN species is present but no information was obtained about its possible stability. It is not known if a $GeH_3NCO \leftrightarrow GeH_3OCN$ equilibrium exists or if the cyanate was merely produced specifically in the preparation.

NATURE OF THE SKELETON

Two band contours in the spectrum of the GeH_3NCO compound lead to the inescapable conclusion that the Ge–N=C=O skeleton is bent. The first of these involves the symmetric N=C=O stretching mode which for a linear skeleton is expected to show a simple band contour with *P* and *R* rotational branches. Experimentally (Fig. 1), the band contour is made up of two components, one with *PQR* rotational structure centered at 1420 cm^{-1} and a weaker shoulder at about 1388 cm^{-1}. The separation of band components in the related nonlinear HNCO molecule[23] for the same type of fundamental is 44 cm^{-1}. The stronger component is considered to be the parallel component because for small α the dipole-moment change perpendicular to the axis is expected to be quite small. The possibility that the second feature in the band at 1388 cm^{-1} arises from an overtone or combination has been rejected. The frequency shift upon deuteration is insignificant and therefore a combination involving the fundamentals of the GeH_3 group is not feasible and none of the combinations of the fundamentals of the NCO group fits from a frequency point of view.

Only one of the *e* modes (under C_{3v}) is obviously split by the lower symmetry of the bent molecule. The fundamental in question in the GeH_3 rocking mode; the absorption band splits into two modes at 667.5(a') and at 656 cm^{-1}. This could not be verified in the spectrum of GeD_3NCO because the band in question shifted to a new position already occupied by bands arising from the Ge–N stretching mode and one of the skeletal deformation fundamentals. Any details of the

TABLE III. Rotational structure of the ν_6 fundamental.[a]

K	^RQ_K (obs)	^RQ_K (calc)	^PQ_K (obs)	^PQ_K (calc)
2	2143.5	2142.1	···	···
3	2147.4	2147.3	···	···
4	2152.6	2152.5	···	···
5	2156.7	2157.5	···	···
6	2162.7	2162.7	2098.7	2099.1
7	2167.0	2167.6	2093.6	2093.6
8	2172.1	2172.7	2088.9	2088.0
9	2177.1	2177.6	2082.0	2082.4
10	2183.0	2182.6	2076.7	2076.8
11	2188.3	2187.5	2071.0	2071.1
12	···	···	2065.0	2065.3
13	···	···	2059.7	2059.6
14	···	···	2053.8	2053.7
15	···	···	2047.8	2047.9
16	···	···	2042.4	2042.0
17	···	···	2036.1	2036.1
18	···	···	2029.9	2030.1
19	···	···	2024.4	2024.0
20	···	···	2018.0	2018.1
21	···	···	2011.8	2011.9
22	···	···	2005.8	2005.8

[a] Frequencies in cm^{-1}.

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[23] G. Herzberg and C. Reid, Discussions Faraday Soc. 9, 92 (1950).

band shapes are masked. Nevertheless, the fact that such features are observed in the spectrum of GeH_3NCO, which leads to the conclusion of a nonlinear skeleton, but are not observed in the spectrum of the linear framework species SiH_3NCS[7] lends confidence to our interpretation.

The low-frequency bending modes ν_{10} have been estimated to occur at about 30 and 60 cm^{-1} in the spectra of SiH_3NCO[4] and SiH_3NCS,[6] respectively. As α in Fig. 1(b) increases, one might reasonably expect the frequency of ν_{10} to increase as well. The value of 115 cm^{-1} for ν_{10} in the spectrum of GeH_3NCO is qualitatively in agreement with this argument but an attempt to evaluate α from this frequency and other measurements already discussed is not feasible. An estimate of α is tractable from an analysis of the rotational fine structure and is given in the next section. For such calculations it is necessary to have estimates of the rotational constants as a function of α. An assumed structure based upon structural parameters of related molecules was used. The values 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 an H–Ge–H angle of 111° are average values obtained for a number of GeH_3 and NCO compounds.[16–20,24] The calculated rotational constants are listed in Table V. The quantity $B-C$ is virtually insensitive to α but as the angle increases large contributions to the small moment of inertia by the heavy off axis atoms reduces the large rotational constant quite rapidly.

TABLE V. Moments of inertia of GeH_3NCO.[a]

α	A	B	C	$\frac{1}{2}(B+C)$
0°	2.662	0.0557	0.0557	0.0557
5°	2.624	0.0558	0.0558	0.0558
10°	2.515	0.0561	0.0560	0.0561
15°	2.353	0.0566	0.0564	0.0565
20°	2.160	0.0574	0.0571	0.0572
25°	1.956	0.0584	0.0579	0.0581
30°	1.755	0.0596	0.0589	0.0592
35°	1.568	0.0611	0.0601	0.0606
40°	1.399	0.0629	0.0616	0.0622

[a] Rotational constants are in cm^{-1} and are based upon 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°.

ROTATIONAL STRUCTURE OF PERPENDICULAR BANDS

Even though the GeH_3NCO molecule is not a true symmetric top, two of the perpendicular bands (under C_{3v}) have rotational structure characteristic of a highly symmetric rotor. It would appear that the asymmetry is small and perhaps the barrier to internal rotation of the GeH_3 group, whose major axis is not along the axis of the linear NCO group, is also so small that the rotational characteristics of the spectrum, as they appear superimposed upon the vibrational spectral bands, are preserved. Subsequent discussion of the rotational fine structure will assume, for the time being, a pseudo symmetric-top structure.

TABLE IV. Rotational structure of the ν_7 fundamental.[a]

K	^RQ_K (obs)	^RQ_K (calc)	^PQ_K (obs)	^RQ_K (calc)
3	881.0	881.1	···	···
4	887.1	886.9	841.1	840.8
5	892.7	892.6	835.2	835.1
6	898.4	898.4	829.2	829.3
7	904.2	904.1	823.4	823.6
8	909.8	909.9	817.9	817.9
9	915.3	915.7	811.2	812.4
10	921.2	921.4	805.2	805.7
11	926.9	927.1	···	···
12	···	···	···	···
13	939.9	939.6	···	···
14	945.2	944.5	···	···
15	950.6	950.3	···	···
16	955.9	956.0	···	···
17	961.5	961.8	···	···

[a] Frequencies in cm^{-1}.

A degenerate vibration of a symmetric-top molecule containing an MH_3 group is expected to show an absorption band upon which appear a number of sharp Q branches. Because of the spin properties of the H atoms, these closely spaced Q branches occur with an s, w, w, s intensity alteration and the frequencies of the transitions can be fitted to an equation of the form

$$\nu_{ik}=\nu_0+[A_i'(1-2\zeta_i)-B_i']\pm 2[A_i'(1-\zeta_i)-B_i']K +[(A_i'-A_i'')-(B_i'-B_i'')]K^2, \quad (1)$$

where ν_0 represents the fundamental frequency of the ith mode, A and B are the large and small rotational constants, and ζ_i is the Coriolis coupling coefficient. The single and double primes refer to the excited and ground vibrational states, respectively, and A (or B) = $\hbar/2I_A$ (or $\hbar/2I_B$). Since $\Delta K=\pm 1$ and $\Delta J=0$, ± 1 the plus and minus signs in the K term of Eq. (1) refer to the ^RQ_K and ^PQ_K subbands. In the absence of perturbations, the $^RQ_0$ subband is the strongest in the band.

The two fundamentals, whose fine structure was resolved, are ν_6 and ν_7, representing the antisymmetric stretching and deformation of the GeH_3 group. The fine structure shown in Fig. 4 was fitted, with the aid of a computer multiple regression analysis, to the following equations:

$$\nu_6=2131.6\pm 5.290K-0.019K^2, \quad (2)$$

$$\nu_7=863.8+5.753K+0.006K^2. \quad (3)$$

For ν_6 and ν_7, the standard deviations for the coefficients of the K term are ±0.18 and ±0.13, respectively, and for the coefficients of the K^2 terms are ±0.18 and ±0.12,

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[24] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., New York, 1955).

TABLE VI. Fundamental frequencies of GeH_3NCO and GeD_3NCO.[a]

No.	Assignment	Species	GeH_3NCO	GeD_3NCO
1	N–C–O stretch	a_1	2271	2269
2	GeH_3 stretch		2123	1523
3	N–C–O stretch		1420	1418
4	GeH_3 deformation		862	622
5	Ge–N stretch		495	495
6	GeH_3 stretch	e	2129	1550
7	GeH_3 deformation		861	647
8	GeH_3 rocking		668	495
9	Skeletal deformation		483	472
10	Skeletal deformation		115[b]	(115)

[a] Frequencies in cm^{-1}. [b] Liquid-state value.

respectively. The mean square of the error for the frequency fits for ν_6 and ν_7 are 0.35 and 0.13 cm^{-1}, respectively. In infrared studies of this kind the difference $B'-B''$ is trivial and can be neglected without compromising the results. Further, the small values of the coefficients of K^2 in Eqs. (2) and (3) allows us to ignore the small difference $A'-A''$ as well. Since B is very much smaller than A and is also absolutely small ($\sim$0.05 cm^{-1}), a value for A_i can be calculated if ζ_i is known or ζ_i can be calculated if the parameters used to calculate B are also used for A_i. It is desirable to get an estimate of the angle α shown in Fig. 1(b) and, since A is quite sensitive to this angle and B is not, values for ζ_i are known for a number of related molecules and, at least for the ζ associated with ν_6, vary only slightly (-0.03 to -0.07) in GeH_3X compounds where $X=F$,[16,25] Cl,[25] Br,[16,25] I,[25] CN,[17] CH_3,[18] and GeH_3.[19] An average of these is -0.04. For ζ_7, the average value would be -0.16 but in this case the variation from molecule to molecule is somewhat larger (-0.10 to -0.31). Nevertheless, using these average ζ values and the B value (0.056 cm^{-1}) calculated from the assumed structure in the previous section, A_6' and A_7' are calculated from the coefficients of the K terms in (2) and (3) to be 2.597 and 2.519 cm^{-1}, respectively. Although the accuracy of such calculations is poor, it appears significant that the variation in calculated A values corresponds to a variation in α of only three degrees ($\alpha=7°$ to $10°$). The fundamental frequencies calculated from the first terms in Eqs. (2) and (3) using the A and ζ values discussed above are 2128.9 and 860.5 cm^{-1} for ν_6 and ν_7, respectively. Each of these are probably accurate to ±1 cm^{-1}, the large uncertainty resting primarily on the assumptions inherent in the present treatment.

DISCUSSION AND SUMMARY

The results reported in this work clearly point to a nonlinear skeleton in germyl isocyanate. The deviation from linearity is estimated at 10° but because this value is not very precise a final decision must await the results of a more accurate pure rotational microwave study. Nevertheless, the qualitative features deduced here indicate that d_π–p_π bonding is responsible for the near-linear skeleton and that such bonding is somewhat weaker than in comparable silicon compounds. These conclusions support our earlier contention that d_π–p_π bonding in germanium compounds is not entirely negligible but depending upon the atoms or groups bonded to the central atom can produce substantial stereochemical consequences.[8,9]

The vibrational analysis was satisfactory in terms of a pseudo C_{3v} static point group and the fundamental frequencies for both GeH_3NCO and GeD_3NCO are summarized in terms of this approximate model in Table VI. Using the structural parameters mentioned earlier, the Teller–Redlich product rule ratios, with calculated values in parenthesis, were found to be a_1 species$=0.51(0.51)$ and e species$=0.39(0.39)$. The vibrational analysis also indicated the presence of a small amount of the normal cyanate, GeH_3OCN and GeD_3OCN, but no information about its formation, equilibrium with the isocyanate, or its relative stability was determined.

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[25] K. H. Rhee and M. K. Wilson, J. Chem. Phys. **43**, 333 (1965).