The slower moving epimer (IV) (R_f = 0.55) had m.p. 189–192° dec., $[\alpha]_D$ −3 (pyridine), $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 251 mμ (ε 7350). Calcd. for $C_{19}H_{24}N_2O$: C, 76.99; H, 8.16; N, 9.45. Found: C, 77.13; H, 8.21; N, 9.23. The faster moving epimer (IV) (R_f = 0.71) had m.p. 199–202° dec., $[\alpha]_D$ −60 (pyridine), $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 251 mμ (ε 7000). Found: C, 77.20; H, 8.35; N, 9.31.

The isolation of the chloroyohimbanes[12] and their subsequent conversion to their oxindole analogs by a hydrolytic procedure suggests their role as intermediates in the rearrangement. The details of these and other experiments will be discussed in a forthcoming publication.

[12] Ref. 9 reports the preparation of one chloro derivative of deserpidine by the same method.

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VIBRATIONAL FREQUENCIES OF TRIMETHYLAMINE GALLANE AND TRIMETHYLAMINE GALLANE-d_3[1]

Sir:

Although numerous chemical investigations of the boron hydrides have been reported together with a modest number for aluminum hydride, relatively little work has appeared in the literature dealing with hydrides of the next element in the group, gallium. Spectroscopic studies have reflected chemical interest but to a diminished degree such that in the case of gallium only results for the simple diatomic hydride, GaH, have been reported. Recent work in this laboratory has resulted in the stabilization of gallane, GaH_3, in the form of a Lewis acid–base complex with trimethylamine. In view of the lack of data on gallium–hydrogen compounds, it was felt that a preliminary report listing characteristic frequencies of this compound, and of the Ga–H bond in particular, would be of some interest.

The preparation and properties of the normal and deuterated compound will be described in greater detail elsewhere.[2] Raman spectra of the two compounds were obtained from a few milligrams of the substances which had been sublimed into 4-mm. o.d. Pyrex tubes and sealed off under vacuum. Frequencies were recorded photographically using the Brandmuller technique[3] with multilayer interference filters to reduce the excess amount of exciting radiation. Exposure times varied from ten to thirty hours using heat senzitized Eastman IIa-0 plates. The spectra obtained were of quite satisfactory quality, particularly so considering the rather small amount of substance available in each case. Infrared measurements of the compounds in solution and also as mulls were attempted, but the reactive nature of the compound prevented generally satisfactory results from being obtained. Frequencies associated with the gallium–hydrogen bond were observed, however, and these results were in good agreement with the Raman data.

The observed frequency values and the preliminary assignments are given in the table. Identification of the bands associated with the trimethylamine part of the molecule were made by comparison with the spectra and assignments for trimethylamine borane[4] and free trimethylamine.[5] The gallium–hydrogen stretching frequencies were by far the most intense in the spectrum and occurred at about 1850 cm.$^{-1}$ in the hydrogen compound and 1330 cm.$^{-1}$ in the deuteriated. The symmetric and asymmetric frequencies were almost superimposed, the asymmetric appearing as a shoulder on the low frequency side of the intense symmetric band in the Raman spectrum of the hydrogen compound with the relative positions being reversed in the deuteriated case. Confirmation of the assignments was obtained from the infrared measurements, both bands being observed at the same frequencies as in the Raman spectra but with the intensity of the asymmetric mode appreciably greater than the symmetric. The ratios of hydrogen to deuterium stretching frequencies were 1.40 and 1.35, respectively, for the symmetric and asymmetric modes.

VIBRATIONAL FREQUENCIES AND ASSIGNMENTS FOR $(CH_3)_3NGaH_3$ AND $(CH_3)_3NGaD_3$ (IN CM.$^{-1}$)

δ = est. probable error; s = strong, m = medium, w = weak, br = broad.

$(CH_3)_3NGaH_3$			$(CH_3)_3NGaD_3$			
Infrared	Raman	δ	Raman	δ	*I*	Assignment
	3123	±3	3134	±4	m	C–H stretching
	3044	4	3052	5	m	C–H stretching
	2999	3	3006	5	m	C–H stretching
	2977	2	2985	5	m	C–H stretching
	2934	3	2938	5	m	C–H stretching
	2912	3	2915	4	m	C–H stretching
	2858	2	2863	4	ms	C–H stretching
	2476	3			vw, br	?
	2361	3			vw, br	?
1852	1852	2	1325	1	vs	*sym.* Ga–H stretch
1832	1823	8	1356	5	m	*asym.* Ga–H stretch
	1458	3	1454	3	m	CH_3 deformation
	1407	3	..		w	CH_3 deformation
	1262	5	1270	3	w	CH_3 rock ?
	1229	2	1231	3	w	CH_3 rock ?
	1106	2	..		w	CH_3 rock ?
	1044	1	1037	4	vw	
	1003	2	1002	3	wm	*asym.* C–N stretch
	834	2	829	3	m	*sym.* C–N stretch
745	..		..			*asym.* H–Ga–H deform.
726	730	4	536	3	wm	*sym.* H–Ga–H deform.
	581	?	..		vw, br	?
	521	?	..		vw, br	?
	..		370	2	wm	Ga–N stretch ?

The symmetric deformation frequency of the GaH_3 group is assigned to a band at 730 cm.$^{-1}$ in the Raman spectrum also by comparison with the spectrum of the free base. It shifts to 536 cm.$^{-1}$ upon deuteration, the ratio of the two frequencies being 1.35. No indication of the asymmetric frequency was obtained from the Raman spectrum but

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[2] D. Shriver and R. W. Parry, to be submitted.

[3] Brandmuller, *Z. Angew. Phys.*, **5**, 95 (1953); see also M. C. Tobin, *J. Opt. Soc. Am.*, **49**, 850 (1959).

[4] C. L. Cluff, Thesis, The University of Michigan, 1961; B. Rice, R. J. Galiano and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

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the infrared exhibited a band with a maximum at 745 cm.$^{-1}$ and a shoulder at about 726 cm.$^{-1}$ which presumably encompasses the two bending motions. The N–Ga frequency is estimated to fall in the range 300–450 cm.$^{-1}$. A sharp and moderately intense line at 370 cm.$^{-1}$ in the Raman spectrum of the deuteriated compound may possibly be due to this motion. Unfortunately, halation from the exciting line was too intense to permit satisfactory observation of this region in the spectrum of the hydrogen compound.

It is of interest to note that the Ga–H stretching frequencies observed in the present work clearly fall at higher values than those given in the literature for the Al–H stretching motions in the AlH_3 complex with trimethylamine.[6] The positions of the latter frequencies have not been determined precisely since the bands in the infrared spectra of solutions are rather broad with maxima which appear appreciably solvent sensitive. However, the range reported, from about 1725 to 1800 cm.$^{-1}$, is sufficiently below the Ga–H frequencies that there is no doubt as to their relative position. The significance of this observation and the implied greater strength of the Ga–H bond is not immediately clear. It does appear consistent with the greater sensitivity toward water and the more reactive nature reported for the alane complex and provides another example of the alternation of physical and chemical properties observed in the main groups III through VII.[7]

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STRONG HYDROGEN BONDS TO CARBON IN ISOCYANIDES[1]

Sir:

In continuation of studies on the scope of hydrogen bonding,[2] we have considered the possibility of observing strong hydrogen bonds to carbon. Interaction of proton donors with carbon π-electron systems is now well established,[2,3] but these hydrogen bonds invariably are relatively weak. We wish to report that isocyanides can function as strong proton acceptor groups in hydrogen bonding. The site for such bonding appears most certainly to be to carbon and not to nitrogen.

Table I lists spectral shifts in the 3 μ region of the infrared caused by hydrogen bonding between alcoholic proton donors and isocyanides. Data for similar cyanides taken from a much more extensive study[4] are included for comparison; the spectral shifts are significantly larger for isocyanides than for cyanides. With carbon π-electron systems, the interactions are much weaker. Spectral shifts of phenol in the presence of olefins and acetylenes range up to about 100 cm.$^{-1}$.[3] The Hammett equation[5] is moderately successful in correlating the observed spectral shifts with both the aromatic isocyanides and the aromatic cyanides[4]; the Taft equation[6] correlates the results with the aliphatic compounds.[4,7] The high $\Delta\nu$ for *p*-methoxyphenyl cyanide indicates considerable resonance interaction between the two functional groups, but no such resonance interaction is detectable in *p*-methoxyphenyl isocyanide. Dipole moment studies have given the same conclusion.[8]

TABLE I

HYDROGEN BONDING OF PHENOL AND METHANOL TO ISOCYANIDES AND CYANIDES[a]

Substituent	$\Delta\nu$ Phenol, cm.$^{-1}$[b] Isocyanides	$\Delta\nu$ Phenol, cm.$^{-1}$[b] Cyanides	$\Delta\nu$ Methanol, cm.$^{-1}$[c] Isocyanides	$\Delta\nu$ Methanol, cm.$^{-1}$[c] Cyanides
Cyclohexyl	250	174	...	85
tert-Butyl	245	169	139	85.5
Isopropyl	241	166	136	83
n-Butyl	238	165.5	137	85.5
Benzyl	230	158	128	78
Methyl	228	159	129	78
p-Methoxyphenyl	219	174.5	121	...
Phenyl	203	153.5	...	73
p-Chlorophenyl	191	144	...	67

[a] Solvent, CCl_4; approximate concentrations: isocyanide or cyanide 0.4 *M*, phenol 0.005 *M*, methanol 0.01 to 0.02 *M*; cell thicknesses, 1 cm.; instrument, Perkin–Elmer Model 21 Spectrophotometer with LiF prism. At the concentrations used, proton donor dimer peaks were absent. [b] Spectral shifts measured from the free peak of phenol at 3611 cm.$^{-1}$. [c] Spectral shifts measured from the free peak of methanol at 3643 cm.$^{-1}$. The reproducibility of these measurements is within ±2 cm.$^{-1}$ provided the same concentrations were employed.[4] After standing, the solutions gave identical spectroscopic results, indicating stability under the conditions of measurement.

Abundant physical evidence on the molecular structure of isocyanides is available. Analysis of infrared and Raman spectra,[9] parachor measurements,[10] dipole moment studies,[8,10] microwave[11] and nuclear magnetic resonance[12] spectroscopic results and electron diffraction studies[13] all indicate that isocyanides are best represented by the polar

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(1) Dr. L. L. Ferstandig of the California Research Corporation has discovered this phenomenon independently. We wish to express our appreciation to Dr. Ferstandig for permitting delay in the appearance of his paper to allow simultaneous publication of our observations.

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