Spectroscopic Data and Bonding in Compounds of Silicon and Germanium with Nitrogen

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From force constants derived from experimentally obtained vibrational frequencies, bond orders for the NSi and NGe bonds of HNSi and HNGe, assumed to be linear triatomic molecules, have been estimated to be 2.7 and 2.3. Inferences regarding the nature of the bonding in these unusual molecules are briefly discussed.

The problem of multiple bonding in which elements beyond the first period are involved continues to be the source of much discussion. The question of the involvement of silicon 3*d*-orbitals in multiple bonding has been a particularly fruitful topic for investigation.¹⁻³ The present contribution arises from a study of intermediates in cryogenic matrices.⁴ The substances produced are unstable under normal laboratory conditions but, because of their structural simplicity, provide a potentially useful source of information on force constants, bond lengths, and, consequently, on bonding of unusual types. In this article we are concerned with covalent bonding of silicon and germanium in small molecules produced in cryogenic experiments.

RESULTS

The directly-measurable spectroscopic quantities are absorption wavenumbers in the infra-red spectrum. Following assignment of the wavenumbers to particular intramolecular modes of vibration, force constants are calculated; in the event of alternative sets of force constants resulting from solutions of quadratic equations, those sets are selected which agree better for isotopic molecules. The vibration wavenumbers of HNSi and HNGe have been obtained from experiments by Cradock and Ogilvie⁴; the wavenumbers of related molecules for comparison have been extracted from published work. The main body of data is collected in table 1. Force constants have been calculated from harmonic frequencies where available. A correction for anharmonicity, which is always least negligible for hydrogen valencestretching vibrations, has been applied to the v_1 frequencies of the triatomic molecules. The correction factor for the frequency is 1.0456 for XH and 1.0331 for XD species in which X is a first-period element.⁵ It has been assumed that the triatomic molecules have a linear equilibrium conformation with the internuclear separations specified. The force constants have been calculated on the basis of a simple valence force field 6 of the form:

$$2V = k_1 (\Delta r_1)^2 + k_2 (\Delta r_2)^2 + k_\delta \delta^2(l^2).$$

For the molecule HXY, Δr_1 is the change in HX internuclear separation from the equilibrium value, Δr_2 is the change of XY bond length, δ is the change of interbond

J. F. OGILVIE AND M. J. NEWLANDS

angle during the vibration, and V is the potential energy. l is a unit length, 10^{-10} m, the same for all molecules, included so that bending force constants have dimensions consistent with other force constants and so that bending force constants of different molecules are directly comparable. Only the first two digits of the force constants have physical significance, but the complete numbers are required in order to reproduce the vibrational frequencies accurately and to permit the prediction of frequencies of isotopically substituted molecules within experimental errors of measurement.

TABLE 1(a).—VIBRATION FREQUENCIES (wavenumbers, cm⁻¹), FORCE CONSTANTS (hN m⁻¹) AND BOND LENGTHS (m×10⁻¹⁰ = Å) FOR SOME TRIATOMIC MOLECULES

IN THE SPECIFIED MEDIU

molecule medium	HCN gas	DCN gas	DCN (calc.)	HNC Ar	DNC Ar	DNC (calc.)	HNSi Ar,N2	DNSi Ar,N2	DNSi (calc.)	HNGe Ar,N2	DNGe (calc.)
٧1	3311.4	2630.4	2599.3	3620	2769	2746.7	3583	2669	2670.0	3521	2620
ν2	712.2	569.1	567.7	477	374	374.6	523	395	399.1	394	300
ν ₃	2096.9	1925.3	1947.8	2029	1940	1949.8	1198	1166	1164.4	969	938
$\bar{k_1}$	6.394			7.831			7.732			7.474	
k_2	17.941			16.390			8.305			6.933	
ks	0.2487	,		0.1036			0.1358			0.0783	
r_1	1.064			(1.000)			(1.000)			(1.005)	
r_2	1.156			(1.19)			(1.54)			(1.69)	
angle	180°			(180°)			(180°)			(180°)	
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Table 1(b).—Vibration frequencies (wavenumbers, cm^{-1}) and force constants (hN m^{-1}) for hydrogen cyanide and hydrogen isocyanide

		IN	ARGON AN	ND NITROGI	EN MATRICI	ES	
		HCN	DCN	DCN (calc.)	HNC	DNC	DNC (calc.)
ν ₁	N_2	3287.6	2617.8	2585.5	3583	2733	2722.1
	Ar	3303.3	2631.3	2593.5	3620	2769	2746.7
ν2	N_2	736.0	588.4	586.7	535	413	421.0
	Ar	720.2	572.0	574.1	477	374	374.5
ν ₃	N_2	2097.3	1920.6	1944.5	2032	1940	1950.2
	Ar	2093.6	1922.7	1944.3	2029	1940	1949.8
k_1	N_2	6.298			7.669		
	Ar	6.362			7.831		
<i>k</i> 2	N ₂	17.960			16.446		
-	Ar	17.886			16.390		
kδ	N_2	0.2657			0.1329		
	Ar	0.2544			0.1036		

The vibrational frequencies of the diatomic molecules and of HCN and DCN refer to gas-phase measurements,⁷ whereas the corresponding frequencies of the molecules of interest, HNC, HNSi, and their deuterated counterparts, have been derived from matrix experiments. Table 1(*b*) compares the frequencies and the derived force constants for HCN⁸ and HNC⁹ in argon and nitrogen matrices. Frequency shifts occur but are appreciable in relative magnitude for the bending vibration v_2 only. Moreover, the force constants for the stretching vibrations are

2603

only slightly changed; this effect does not alter markedly the significance of these numbers for the purposes of the discussion.

The parameters in parentheses in table 1(*a*) are assumed values for molecules the structures of which have not been accurately determined. The assumed values have been selected by comparison with related molecules: for species containing NH bonds, from spectra-structure correlations¹⁰; for SiN and GeN, by comparison with diatomic radicals for which the vibration frequencies,¹¹ force constants, and bond lengths ¹¹ are as follows: SiN, 1151.7, 6.837 and 1.572; SiO, 1242.0, 9.249 and 1.510; GeO, 985.7, 7.527 and 1.651. Since the GeN radical is not known, it has been assumed that the bond lengths of GeN and GeO are related in the same way as those of SiN and SiO.

The molecular dimensions are required only for the computation of the bending force constant, k_{δ} , but the computed magnitudes of both k_{δ} and the DNX frequencies are insensitive to the selected values of the molecular dimensions. The frequencies calculated for DXY are based on the force constants derived from the corresponding HXY.

DISCUSSION

First we justify the assumption of a collinear nuclear equilibrium conformation for the triatomic molecules. Two factors which can be cited in favour of this hypothesis are (i) the relatively large force constants k_1 of the XH stretching mode in comparison with the force constants of corresponding bonds in known bent or linear molecules, and (ii) the relatively small force constants k_{δ} for the bending mode in comparison with other molecules of the types HXY, H_2X and XY_2 , with linear or bent conformations. (In some of these cases, both σ - and π -bonds link the X and Y atoms.) It might be deemed unwise to extrapolate to molecules containing germanium since most of the models for the comparisons are carbon compounds. However, the small number of force constants available for molecules containing atoms beyond the first period support this extension as a basis for calculation.¹² Moreover, the reasonable agreement between calculated and assigned frequencies for DNSi is reassuring, even though this is not an especially sensitive criterion. As a result of all these considerations, the linearity of the triatomic molecules has been used as a working hypothesis.

It would be interesting to obtain some understanding of the electronic structure of molecules from the force constant data, especially for such examples as HNSi and HNGe for which no other structural data are available. In general, the relationship between force constants and bond parameters (bond order, bond length, bond energy) is uncertain; the dangers inherent in attempts to correlate force constants with such parameters have been frequently stressed, most recently by Ebsworth ¹³ and by Bellamy.¹⁴ Nevertheless, many reasonable attempts have been made to establish such correlations, usually for a small range of related molecules. For example, Goubeau ¹⁵ interpreted the large stretching frequency (1526 cm⁻¹) and large force constant (7 hN m⁻¹) of the BN bond in (H₃C)₂NBCl₂ as indicative of π -bonding from nitrogen to boron. Similarly, Jones ¹⁶ has correlated k_{CO} with bond order in an isoelectronic series of metal carbonyls.

In the present article we have attempted to use a correlation between force constants and bond order as the basis for some tentative ideas on the bonding in the molecules HNSi and HNGe. An examination of the listed force constants (table 2) indicates that constants for single, double and triple bonds are in the approximate ratio 1:2:3 (in fact, the relation seems to be a curve rather than a straight line, cf. ref. 18). The three examples of heteroatomic triple bonds (both atoms from the first

2605

J. F. OGILVIE AND M. J. NEWLANDS

period) have similar force constants to the CC triple bond. Unfortunately, there are no unambiguous examples of SiN and GeN single bonds. It was therefore decided to use k_{XH} as the single-bond parameter. On this basis the SiN bonds in trisilylamine, $(H_3Si)_3N$, have a bond order of 1.36 (cf. Kriegsmann's suggestion of 1.26;¹⁹ the difference is not significant) and that in HNSi has a bond order of 2.7. On a similar basis the GeN bond in HNGe has an order of 2.3.

TABLE 2.—Force constants (hN m^{-1}) for selected bonds in diatomic or triatomic molecules ^a

H—C	4.5-6.0	H—N	6.5-8.0	H—Si	3.08 ^b
СС	4.5-5.6	N—N	3.6-5.5	H—Ge	2.86 ^b
C=C	9.5-9.9	N=N	13.0-13.5	NSi	4.1 ^c
C==C	15.6-17.0	$N \equiv N$	22.9		
C≡O	19.2				

^a from ref. (12), unless otherwise cited.

 b calculated from frequencies cited in ref. (1) after correction for anharmonicity.

^c from ref. (13).

The assignments made above are tentative and involve many assumptions. Nevertheless, there is interest in qualitative speculation about the bonding in HNSi and HNGe. If the NSi bond in HNSi is indeed of order 2.7, or some similar magnitude, two bonding situations can be visualized. In the first, the $3p_z$ - and $3p_x$ -orbitals of silicon are used to form σ - and π -molecular orbitals, respectively, with the appropriate nitrogen orbitals, while a second π -bond arises from interaction of the unshared pair of electrons on nitrogen ($2p_v$ -orbital) and the empty $3p_v$ -orbital of silicon. In the second, pairs of 3p- and 3d-orbitals of silicon hybridize to form one orbital directed towards nitrogen plus another oppositely directed (combinations of $3p_x$ and $3d_{xz}$ and of $3p_y$ and $3d_{yz}$). In this case, improved overlap with the nitrogen orbitals would be obtained at the expense of hybridization energy; furthermore, only one of each pair of hybrid orbitals can be used in bonding. Also, there are insufficient electrons to fill all the low-energy orbitals. Consequently the coefficient of the 3dorbitals is likely to be small (<0.1), and the second bonding situation can be regarded as perturbation of the first. Similar arguments can be advanced to account for the bonding in HNGe.

We have reasoned above on the basis of a comparison of k_{SIN} and k_{SIH} . One might also argue that we should have compared k_{SIN} with force constants for other bonds to nitrogen. For instance, $k_{HN} = 7.8$, $k_{CN} = 17.9$, but k_{SIN} is only 8.3, and $k_{GeN} = 6.9$. An apparent paradox then arises that the SiN and GeN bonds are of order one based on nitrogen force constants, but of order between two and three based on force constants of the heavier atoms. However the same difficulty is implicit in the result of Kriegsmann,¹⁹ referred to above. Therefore, on the basis of a comparison of the ratio of force constants for SiN bonds in $(H_3Si)_3N$ and HNSi, the bond order in the latter can be deduced to have increased by a factor of two or more. Although force constants of elements beyond the first period are generally markedly smaller than for their counterparts lithium to fluorine,¹⁴ our conclusions founded on the ratio of force constants are independently significant.

The notable point is that in both HNSi and HNGe bonds of order greater than two can be described without invoking interaction with the 3*d*-orbitals of silicon and germanium. Such a description is not possible for disiloxane and trisilylamine.

SPECTROSCOPIC DATA AND BONDING

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