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Estimation using MNDO of Skeletal Bending Frequencies in Linear and Quasi-linear Silyl Compounds

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Electron diffraction studies of a number of silyl pseudohalides, including H_3SiNCO [1], H_3SiNCS [1], F_3SiNCO [2], and $H_3SiNCNSiH_3$ [3] have suggested that these molecules are characterised by very low skeletal bending frequencies δ(SiNC): similar conclusions for these, and related silyl pseudohalides, have been drawn from microwave studies [4–6], and from vibrational spectroscopy [7–10]. The suggestion has been made [1] that most silicon pseudohalides of types R_3SiNCO, R_3SiNCS, and $R_3SiNCNSiR_3$, as well as species such as $Si(NCO)_4$ [11], probably contain SiNCX groups which are either linear at the equilibrium configuration or have only a very small barrier at linearity, and additionally exhibit skeletal bending modes δ(SiNC) which are of low frequency and high amplitude. The substituted oxo compounds $(R_3Si)_2O$ appear to be similar [12, 13].

With few exceptions [1, 2, 6, 9, 10] detailed descriptions of the skeletal motions of these linear or quasi-linear systems [14] have not been achieved, although estimates of the bending frequencies have been made in a number of cases [1, 2, 4, 5, 8, 15]. We recently reported [16] the results of an SCF study, using the MNDO [17] method, of the equilibrium structures of a wide range of substituted methyl and silyl pseudohalides: in the present communication, we report the direct calculation of the skeletal vibrational frequencies for a range of substituted silyl isocyanates, isothiocyanates and carbodiimides.

Calculations were made using the MNDO method [17], as incorporated in the MOPAC program system [18], with the published and atomic parameters [19–21]. No *d* functions were employed: it has been shown [22, 23] that such functions are not necessary for the adequate description of most of the properties of molecular silicon compounds.

The vibrational spectra of H_3SiNCS [9], and of Cl_3SiNCO and Cl_3SiNCS [8] have been studied in great detail, and in Table I we give as examples, a comparison of the calculated fundamental vibrational frequencies and those observed in the vapour phase for H_3SiNCS and Cl_3SiNCS. In Cl_3SiNCS δ(SiNC), ν_{10}, was not observed directly, but its magnitude was inferred from combination bands. With the notable exception of ν_{as}(NCS) which for both molecules is calculated to be too large, the calculated frequencies are in reasonable accord with those observed, and the calculated atomic motions broadly confirm the published assignments [8, 9].

For each of the molecules R_3SiNCO and R_3SiNCS (R = H, F, Cl, CH_3) there is a doubly degenerate skeletal bending mode, described approximately as δ(SiNC), of *e* symmetry in C_{3v}, which is calculated in every case (Table II) to occur at very low frequency.

The second skeletal bend, δ(NCX) is calculated to lie in the range 491–511 cm^{-1} for R_3SiNCO, and in the range 455–474 cm^{-1} for R_3SiNCS. In marked contrast to the very low values calculated for δ(Si-

TABLE I. Comparison of Observed and Calculated Fundamental Frequencies in H_3SiNCS and Cl_3SiNCS

	H_3SiNCS			Cl_3SiNCS		
	Observed frequency (cm^{-1})^a	Calculated frequency (cm^{-1})	Approximate description	Observed frequency (cm^{-1})^b	Calculated frequency (cm^{-1})	Approximate description
a_1 modes	2206	2262	ν(SiH)	2092	2322	ν_{as}(NCS)
	2065	2383	ν_{as}(NCS)	1072	1185	ν_s(NCS)
	1036	1150	ν_s(NCS)	512	623	ν(SiN)
	951	965	δ(SiH_3)	410	409	ν(SiCl)
	492	546	ν(SiN)	210	170	δ($SiCl_3$)
e modes	2207	2269	ν(SiH)	623	639	ν(SiCl)
	950	930	δ(SiH_3)	469	471	δ(NCS)
	707	734	ρ(SiH_3)	264	252	ρ($SiCl_3$)
	478	455	δ(NCS)	170	139	δ($SiCl_3$)
	66	119	δ(SiNC)	Not observed	56	δ(SiNC)

^{a}Ref. 9 ^{b}Ref. 8.

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TABLE II. Calculated Skeletal Bending Frequencies δ(SiNC) in Silyl Pseudohalides

R_3SiNCO				R_3SiNCS			
Compound	ν(calc.) (cm^{-1})	ν(obs.) (cm^{-1})	Reference	Compound	ν(calc.) (cm^{-1})	ν(obs.) (cm^{-1})	Reference
H_3SiNCO	83	20–69[a]	1,5,6,15	H_3SiNCS	119	66[d]	9
F_3SiNCO	72	97[b]	2	F_3SiNCS	80	–	
Cl_3SiNCO	57	29c	8	Cl_3SiNCS	56	24[c]	8
Me_3SiNCO	55	37[d]	10	Me_3SiNCS	73	~45[d]	10

[a] δ(SiNC) has not been directly observed: 20–69 cm^{-1} represents the overall range of estimates derived from various experimental observations. [b] Estimated from electron-diffraction potential function. [c] Estimated from combination bands. [d] Direct observation.

NC) in R_3SiNCO and R_3SiNCS, in the fulminates H_3SiCNO and H_3SiCNS, the values calculated for δ(SiCN) are much higher, 202 cm^{-1} and 160 cm^{-1} respectively, with δ(CNO), 421 cm^{-1} and δ(CNS), 418 cm^{-1}.

A carbodiimide $R_3MNCNMR_3$ having a linear MNCNM skeleton will exhibit two δ(MNC) modes, of e_g and e_u symmetry in D_{3d}, or e' and e'' in D_{3h}: the mode δ(NCN) has e_u symmetry in D_{3d} or e' symmetry in D_{3d}. In $SiF_3NCNSiF_3$ and $SiCl_3NCNSiCl_3$, the e_u δ(SiNC) modes occur at 30 cm^{-1} and 25 cm^{-1} respectively, and the e_g modes at 69 cm^{-1} and 53 cm^{-1} respectively. The skeletal bend δ(NCN) is calculated to occur at 496 cm^{-1} in $SiF_3NCNSiF_3$ and at 495 cm^{-1} in $SiCl_3NCNSiCl_3$.

Finally, we have calculated the skeletal bending frequency, δ(SiOSi), in three ethers $(R_3Si)_2O$ for R = H, F, and Cl. The frequencies calculated are 72 cm^{-1}, 70 cm^{-1}, and 37 cm^{-1}, respectively. The observed band maximum in $(SiH_3)_2O$ occurs at around 70 cm^{-1} [12, 24, 25], and in $(SiF_3)_2O$ and $(SiCl_3)_2O$ the bending frequencies have been measured as 85 cm^{-1} [26] and 63 cm^{-1} [27] respectively. Again the MNDO calculations within an (*s,p*) basis set reveal extremely low skeletal bending frequencies.

In every example, the occurrence of a very low frequency skeletal bending mode, perhaps the most characteristic common feature of these molecules, is reproduced by the calculations.

References

1 C. Glidewell, A. G. Robiette and G. M. Sheldrick, *Chem. Phys. Lett., 16,* 526 (1972).
2 W. C. Airey, C. Glidewell, A. G. Robiette and G. M. Sheldrick, *J. Mol. Struct., 8,* 435 (1971).
3 C. Glidewell and A. G. Robiette, *Chem. Phys. Lett., 28,* 290 (1974).
4 D. R. Jenkins, R. Kewley and T. M. Sugden, *Trans. Faraday Soc., 58,* 1284 (1962).
5 M. C. L. Gerry, J. C. Thompson and T. M. Sugden, *Nature (London), 211,* 846 (1966).
6 J. A. Duckett, A. G. Robiette and I. M. Mills, *J. Mol. Spectrosc., 62,* 34 (1976).
7 E. A. V. Ebsworth, R. Mould, R. Taylor, G. R. Wilkinson and L. A. Woodward, *Trans. Faraday Soc., 58,* 1069 (1962).
8 D. F. Koster, *Spectrochim. Acta, Part A:, 24,* 395 (1968).
9 J. R. Durig, K. S. Kalasinsky and V. F. Kalasinsky, *J. Phys. Chem., 82,* 438 (1978).
10 J. R. Durig, J. F. Sullivan, A. W. Cox, Jr. and B. J. Streusand, *Spectrochim. Acta, Part A:, 34,* 719 (1978).
11 K. E. Hjortaas, *Acta Chem. Scand., 21,* 1381 (1967).
12 J. R. Durig, M. J. Flanagan and V. F. Kalasinsky, *J. Chem. Phys., 66,* 2775 (1977).
13 C. Glidewell and D. C. Liles, *J. Organomet. Chem., 212,* 291 (1981).
14 W. R. Thorson and I. Nakagawa, *J. Chem. Phys., 33,* 994 (1960).
15 S. J. Cyvin, J. Brunvoll and A. G. Robiette, *Chem. Phys. Lett., 11,* 263 (1971).
16 C. Glidewell and H. D. Holden, *J. Mol. Struct., 89,* 325 (1982).
17 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99,* 4899 (1977).
18 J. J. P. Stewart, *QCPE Bull., 3,* 43 (1983).
19 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99,* 4907 (1977).
20 M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc., 100,* 58 (1978).
21 M. J. S. Dewar, H. S. Rzepa and M. L. McKee, *J. Am. Chem. Soc., 100,* 3607 (1978).
22 C. Glidewell and C. Thomson, *J. Comput. Chem., 3,* 495 (1982).
23 C. Glidewell and C. Thomson, *J. Comput. Chem., 4,* 9 (1983).
24 J. R. Aronson, R. C. Lord and D. W. Robinson, *J. Chem. Phys., 33,* 1004 (1960).
25 D. W. Robinson, W. J. Lafferty, J. R. Aronson, J. R. Durig and R. C. Lord, *J. Chem. Phys., 35,* 2245 (1961).
26 J. R. Durig, V. F. Kalasinsky and M. J. Flanagan, *Inorg. Chem., 14,* 2839 (1975).
27 J. R. Durig, M. J. Flanagan and V. F. Kalasinsky, *J. Mol. Struct., 27,* 241 (1975).