THE MOLECULAR STRUCTURE OF TRIMETHYLSILYLISOCYANATE IN THE GAS PHASE REDETERMINED BY ELECTRON DIFFRACTION

STEPHEN CRADOCK and CHRISTOPHER M. HUNTLEY

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ (Gt. Britain)

J. R. DURIG

Department of Chemistry, University of South Carolina, Columbia, SC 29208 (U.S.A.) (Received 3 September 1984)

ABSTRACT

We have redetermined the molecular structure of trimethylsilylisocyanate in the gas phase by electron diffraction. An r_a structure is defined with bond distances (pm) SiN 174.0(4), SiC 186.4(2), N=C 120.2(16), C=O 117.6(10) and CH 109.9(5), bond angles (degrees) HCSi 109.0(9), CSiC 108.8(25), SiNC 156.9(30) and NCO 165.8(36), with the N=C bond eclipsing one Si—C bond and the Me₃Si group tilted slightly. The methyl groups are twisted 26.9(35)° from the position giving the Me₃Si group C_{3v} symmetry in an (assumed) concerted fashion. The apparent deviations from linearity of the SiNCO skeleton are shown to be compa_ible with a pseudolinear structure similar to that of SiH₃NCO.

INTRODUCTION

The molecular structures of pseudohalide derivatives of carbon, silicon and germanium have been extensively investigated in recent years by a variety of techniques. Isocyanates in particular exhibit a wide range of apparent bond angles at nitrogen depending on the attached atom, the phase and the technique employed, and there are also significant variations in the N=C and C=O bond lengths reported for different compounds. An early electron diffraction study of Me₃SiNCO [1] suggested a skeleton bent at nitrogen, but the large uncertainties of the parameters reported make it difficult to compare the reported structure with those of CH_3NCO [2], C_2H_5NCO [3], SiH₃NCO [4] and GeH₃NCO [5]. The microwave spectrum [6] is not able to define the structure in this case, as the vibrational ground state molecule gives rise to a pattern of lines indistinguishable from that of a symmetric top, giving only one effective rotation constant B_{eff} . We have therefore studied the electron scattering pattern of Me₃SiNCO again using modern data handling methods and refinement techniques as part of a systematic study of alkyl and alkyl-substituted silyl pseudohalides.

0022-2860/85/\$03.30 © 1985 Elsevier Science Publishers B.V.

EXPERIMENTAL

 Me_3SiNCO was prepared [7] by reaction of Me_3SiCl (2 mmol portions) with freshly-prepared and dried AgNCO (excess) in the absence of solvent. After each addition of chloride the reaction mixture was allowed to warm to room temperature and stand for some minutes. The volatile products were removed on a vacuum line and found to be essentially pure Me_3SiNCO by infrared spectroscopy and vapour pressure measurement.

Electron diffraction scattering intensities were recorded photographically using the Cornell/Edinburgh apparatus operating at about 44 kV. Data were converted to digital form using a computer-controlled Joyce-Loebl microdensitometer as described previously [8]. The electron wavelength (5.717(6) pm) was determined by analysis of scattering patterns of gaseous benzene recorded consecutively with those of the compound. Calculations were carried out on ICL 2976 computers using established data-reduction and refinement programs [9]. Complex scattering factors of Schäfer et al. [10] were used in all calculations. Weighting points used in setting up off-diagonal weight matrices, s-ranges and other pertinent data are given in Table 1.

REFINEMENTS

The molecular model used in the refinement assumed C_{3v} local symmetry for each methyl group and C_3 local symmetry for the trimethylsilyl group as a whole. The structure then requires five bonded distances (CH, SiC, NSi, N=C and C=O), four bond angles (HCSi, CSiN, SiN=C and N=C=O) with torsions about SiC, SiN and N=C bonds, and a tilt of the Me₃Si group. There are 60 distinct interatomic distances, each giving a peak in the radial distribution curve; amplitudes were initially set at values suggested by experience and normal coordinate calculations with other molecules, and those for most non-bonded distances involving hydrogen were kept fixed throughout the analysis. Even so, it proved necessary to guard against some of the refining amplitudes adopting physically-unreasonable values in the course of the analysis. The final structure, shown in Table 2, has non-linear SiNC and NCO groups, a twist (fixed at 60° (eclipsed) after refining with a large estimated standard deviation) about the SiN bond and a small tilt of the Me₃Si group

Camera height (mm)	∆s (all n	^S min m ⁻¹)	sw ₁	sw ₂	Smax	Correlation	Scale factor	
285.64 128.36	2 4	20 60	40 50	120	144	0.283	0.797(10)	

TABLE 1

Weighting functions, correlation parameters and scale factors

TABLE 2

Parameter	Length	Amplitude				
	109.9(5)	8.6(9)				
rC=0	117.6(10)	4.3(4)	ř(NCO 118.9(4), δr 2.6(17)			
rN=C	120.2(16)	4.3(4)				
rSiN 174.0(4)]		6 6 fired often				
rSiC _m 186.4(2)						
Parameter	Angle	Parameter	Angle			
/ HC_Si	109.0(9)	CH, torsion	26.9(35)			
C_SiC_	108.8(25)	SiN torsion	60 fixed after refining			
∠SiN=C	156.9(30)	Me,Si tilt	5.7(24) away from CO group			
∠N=C=O	165.8(36)	N=C torsion	0 fixed			

(a	 Refined parameters and amplitudes for bonded distance 	s (bond	l lengths an	d amplit	udes
īn	n pm; angle= in degrees)				

(b) Non-bonded distances between non-hydrogen atoms and amplitudes (pm)

Distance ^a	Length	Amplitude	
NO	235.9(13)	7.4(13)	
Si-C	288.4(12)	7.6(10)	
NC	289.9(24)	17.2(16)	
C	303.5(13)	17.3(10)	
CC	384.5(75) 397.2(27)	25.4(42)	
SiO	396.1(13)	10.5(12)	
С _т О	461.1(68) } 505.1(27) }	25 fixed	

 ${}^{a}C_{m}$ denotes the carbon atom of a methyl group. A list of non-bonded distances involving hydrogen atoms and corresponding amplitudes may be obtained from SC (author) on request.

so that its (assumed) C_3 axis does not coincide with the SiN bond. The final R-factor was quite satisfactory (R_G 6.2%, R_D 5.6%) and the final difference radial distribution curve (Fig. 1) showed no significant discrepancies. The final molecular scattering intensities and the corresponding difference curves are shown in Fig. 2, and the correlation between the refining parameters is given in Table 3.

DISCUSSION

The structure given in Table 2 is an r_a structure, with no corrections for the perpendicular amplitude terms K. These are in principle available from a normal coordinate analysis but we have not included them. It is nevertheless interesting to compare the apparent shrinkages of the Si \cdot C and Si \cdot O distances



Fig. 1. Radial distribution curve (P(r)/r) and final difference (observed — calculated) for Me₃SiNCO. Before Fourier inversion the data were multiplied by $s \exp \left[-0.00002s^2/(Z_{\rm Si}-f_{\rm Si})(Z_{\rm N}-f_{\rm N})\right]$. The distance scale is marked in pm.



Fig. 2. Final molecular scattering and difference (observed — calculated) intensity curves for Me₃SiNCO recorded at (a) 285.64 mm and (b) 128.36 mm nozzle-to-plate distances. The scale of s values is marked in nm⁻¹; intensities are scaled arbitrarily.

with those found in electron diffraction studies of SiH₃NCO and some related pseudohalides (Table 4). It is clear that the "shrinkages" found here (defined as $[(r(MX) + r(XY) + r(YZ)) - d(M \cdot Z)]$, by analogy with the linear shrinkage in molecules such as OCS) are comparable with those found for SiH₃NCO, which is known [4] to have a pseudolinear skeleton, rather than with those found for molecules with genuinely-bent skeletons such as CH₃NCO [2] and the azides [2, 11]. It is therefore suggested that the present results are also compatible with a pseudolinear skeleton for Me₃SiNCO. The apparent bends at N and C, the twist about the SiN bond and the tilt of the Me₃Si group are then ascribed to the effects of the high-amplitude, low-frequency bend at

TABLE 3

_	rCH	lδr	∠NSiC	∠HSiC	LSiNC	tCH,	uСН	uSi∙H	k1	k 2
rSiN rNCO δr ∠NCO	-59	68 100			54 66 79	59	85 65	55 53	-52	-60
uCH uN·O uC·C k1	54	65	88	-60	59	-52	100		100	54

Correlation matrix between refining parameters × 100

Only those elements whose absolute magnitude exceeds 50 are shown.

TABLE 4

Shrinkages^a (pm) and apparent angles (degrees) found by electron diffraction studies of some pseudohalides

Molecule R ₃ MXYZ	δ MZ	δΜ…Υ	(L)	Reference
SiH,NCS	4.2	2.8	163	12
Me, SiNCO	15.7(30)	5.8(25)	157	this work
SiH,NCO	12.1	8,6	152	4
CHINCS	22.1	14.6	141	2
CH,NCO	22.1	15.4	140	2
GeH,NCO	24.2	16.3	141	5
GeH,NNN	50.9	33.8	123	11
СН, ЙИИ	54.1	39.4	117	2

^aShrinkage δ defined as (distance between non-bonded atoms) — (sum of bonded distances in linking chain).

nitrogen that is presumably the motion observed in the Raman spectrum of the gas [13] at 37 cm^{-1} .

The microwave spectrum of Me₃SiNCO is very complex [6], but a symmetric-top pattern has been assigned as due to molecules in the vibrational ground state. The measured B_{eff} is 1203.8 MHz, and D_{JK} is large (117.5 kHz) but not as strikingly large as those found for SiH₃NCO [4] (642 kHz), CH₃NCS [14] (6 MHz) or CH₃NCO [15] (9 MHz). Our r_a structure and the r_0 structure relating to the ground state rotation constants are not of course expected to be strictly comparable, as vibrational corrections are needed to convert each to a common basis, the $r_{\alpha}^0 = r_z$ structure. The r_a structure of Table 2 may even so be used to calculate "rotation constants", and the mean of B and C from this calculation is 1200.5 MHz, very close to the observed B_{eff} , and with an estimated uncertainty of about 3 MHz. There is thus no conflict between the microwave rotation constant and the electron diffraction structure. A pseudolinear skeleton is also compatible with the rest of the microwave spectrum, ascribed to molecules in vibrationally-excited states, as for molecules such as CH_3NCS [14] and CH_3NCO [15] with lighter three-fold rotors. The vibrational spectrum [13], as it appears to follow the selection rules for a linear skeleton, is also compatible with a pseudolinear model.

The remaining structural parameters are much as expected; r(SIN) is not perhaps as long as suggested by Bauer [1] (176(2) pm) but is definitely not as short as deduced by Kroto [6] (169 pm). r(SiC) is definitely shorter than the 189(1) pm found by Bauer, and Kroto's assumed r(N=C) of 115 pm is too small. (The combined effects of these two short bonds made it necessary for the skeleton to be linear to fit the microwave B value [6].) The bond angles at Si and the methyl carbon atoms are very close to tetrahedral. The SiN bond is somewhat longer than that found in SiH₃NCO [4] (170.3 pm), and this may be ascribed to the electron-donating effects of three methyl substituents. The N=C and C=O bond lengths are very similar to those found in SiH₃NCC [4] (r_a 120.0(5), 118.0 assumed; r_0^* 119.9(12), 117.4(6) pm) and in GeH₃NCO [5] (r_a 119.0(7), 118.2(7) pm).

ACKNOWLEDGEMENTS

We thank Dr. H. E. Robertson for assistance with the electron diffraction measurements and Dr. D. W. H. Rankin for the use of his equipment and programs and for invaluable discussions. This work was carried out in part as part of a collaborative program made possible by a grant from NATO.

REFERENCES

- 1 K. Kimura, K. Katada and S. H. Bauer, J. Am. Chem. Soc., 88 (1966) 416.
- 2 D. W. W. Anderson, D. W. H. Rankin and A. Robertson, J. Mol. Struct., 14 (1972) 385.
- 3 S. Cradock and J. R. Durig, in preparation.
- 4 J. A. Duckett, A. G. Robiette and M. C. L. Gerry, J. Mol. Spectrosc., 90 (1981) 374.
- 5 J. D. Murdock, D. W. H. Rankin and B. Beagley, J. Mol. Struct., 31 (1976) 291.
- 6 A. J. Careless, M. C. Green and H. W. Kroto, Chem. Phys. Lett., 16 (1972) 414.
- 7 G. S. Forbes and H. H. Anderson, J. Am. Chem. Soc., 70 (1948) 1222.
- 8 S. Cradock, J. Koprowski and D. W. H. Rankin, J. Mol. Struct., 77 (1981) 113.
- 9 A. S. F. Boyd, G. S. Laurenson and D. W. H. Rankin, J. Mol. Struct., 71 (1981) 217.
- 10 L. Schäfer, A. C. Yates and R. A. Bonham, J. Chem. Phys., 55 (1971) 3055.
- 11 J. D. Murdoch, Ph.D. Thesis, Edinburgh (1972).
- 12 S. J. Cyvin, J. Brunvoll and A. G. Robiette, Chem. Phys. Lett., 11 (1971) 263.
- 13 J. R. Durig, J. F. Sullivan, A. W. Cox, Jr. and B. J. Streusand, Spectrochim. Acta, Part A, 34 (1978) 719.
- 14 S. Cradock, J. Mol. Spectrosc., 92 (1982) 170.
- 15 S. Cradock and J. R. Durig, unpublished observations.