Gas-phase Molecular Structure of *NN'*-Bis(trimethylsilyl)sulphur Di-imide, determined by Electron Diffraction

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The molecular geometry of $Me_3SiNSNSiMe_3$ in the gas phase has been studied by electron diffraction. The molecule has C_2 symmetry with a distorted *syn,syn* conformation. Principal parameters are: r_a(S=N) 153.6(3), r_a(Si–N) 173.8(3), and r_a(Si–C) 186.9(1) pm; NSN 129.5(16), SNSi 132.9(7), and SN twist (relative to *syn,syn* conformation) 42(1)°.

Sulphur di-imides, R_2N_2S, have been known since the discovery of $Bu^t{}_2N_2S$ in 1956[1] and a number of alkyl[2] and aryl[3] derivatives are known. They are isoelectronic with SO_2 and this had led to substantial work on their co-ordination chemistry,[4] including the preparation of the σ-bonded complex *cis*-$[Pt(NSNSiMe_3)_2(PPh_3)_2]$.[5] Structurally, there are three possible conformations: *syn,syn*; *syn,anti*; and *anti,anti*. *X*-Ray crystallographic studies [R = phenyl, (1),[6] or biphenyl, (2)[7]] and an electron diffraction study[8] [R = Me, (3)] indicate that the *syn,anti* structure is often preferred. N.m.r. studies have shown that both *syn,anti* and *anti, anti* exist in solution for both alkyl and aryl di-imides.[9,10] However when R = *p*-ClC_6H_4S, (4),[11] or PhS (5),[12] the *syn,syn* conformation is adopted. Furthermore, we have recently determined the *X*-ray crystal structure of *p*-$O_2NC_6H_4SNSNSiMe_3$, (6),[13] which adopts the *syn,anti* conformation. The *X*-ray crystal structure[14] of an $SnCl_4$ adduct of $(Me_3Si)_2N_2S$, (7), reveals the di-imide to have the *anti,anti* conformation in this case although the proton n.m.r. spectrum of the free di-imide consists of a singlet. Clearly, the RNSNR group has the ability to adopt a wide range of conformations. In view of the extensive use of compound (7) in synthesis[15] we have investigated its structure in the gas phase.

Experimental

The compound $(Me_3Si)_2N_2S$ (7) was prepared by reaction of $Na[N(SiMe_3)_2]$ with $SOCl_2$ as described in the literature.[16]

Electron-diffraction scattering intensities were recorded using the Edinburgh gas diffraction apparatus[17] on Kodak Electron image plates at nozzle-to-plate distances of 95 and 256 mm, with an accelerating voltage of 44.5 kV. The sample and nozzle temperatures were maintained at 338 and 351 K respectively throughout the exposure periods. The intensity data were converted into digital form by scanning the three plates recorded at each camera distance with a computer-controlled Joyce-Loebl MDM6 microdensitometer.[18] Reduction of the data[18] and subsequent least-squares refinement[19] were carried out using established programs, and the scattering factors of Schäfer *et al.*[20] The weighting points used to set up the off-diagonal weight matrix, correlation parameters, and scale factors for the two camera distances are given in Table 1. The electron wavelengths used in the calculations are also included in Table 1; they are determined from the scattering curves of benzene, recorded immediately after those of the sample compound. The benzene data were analysed in exactly the same way as the data for the compound being studied. In this way the systematic errors in wavelengths and camera distances are minimised and they do not contribute significantly to the total errors.

Table 1. Camera distances, weighting functions, and other experimental data

Camera distance (mm)	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor, k	Electron wavelength (pm)
	nm^{-1}							
255.69	2	20	40	128	150	0.089	0.793(9)	5.687
94.52	4	80	100	304	356	0.476	0.710(22)	5.688

Table 2. Molecular parameters (r_a) for $Me_3SiNSNSiMe_3$ (distances in pm, angles in °)

p_1	r(S=N)	153.6(3)	p_7	NSiC	109.1(7)
p_2	r(Si–N)	173.8(3)	p_8	SiCH	109.6(6)
p_3	r(Si–C)	186.9(1)	p_9	Me twist *	22.5(15)
p_4	r(C–H)	114.2(3)	p_{10}	SiN twist *	7.4(21)
p_5	NSN	129.5(16)	p_{11}	SN twist *	138.4(23)
p_6	SNSi	132.9(7)			

* For definition see text.

Results

Structural Analysis.—The molecular model used to generate the atomic co-ordinates of $(Me_3Si)_2N_2S$ is described by the molecular parameters in Table 2. It was assumed that the two $S{=}NSiMe_3$ groups were identical with respect to their SNSi, NSiC, and SiCH angles, and their bond lengths. The two groups were allowed to be inequivalent by the inclusion of two torsion angles, around the S=N and Si–N bonds, in each half of the molecule. With all four torsion angles fixed at zero, the molecule possessed C_{2v} symmetry with one Si–C bond in each of the $SiMe_3$ groups eclipsing the neighbouring S=N bond, and the conformation around the two S=N bonds was *anti,anti*. Two further parameters, an $SiMe_3$ group tilt and a methyl group torsion, were also included. These were assumed to be the same for both halves of the molecule. The $SiMe_3$ groups were assumed to have local C_3 symmetry with the individual SiMe groups having local C_{3v} symmetry. The Me group torsion angle was defined to be zero for the staggered conformation. The tilt moved the C_3 axis of the $SiMe_3$ group so that it no longer coincided with the Si–N bond but remained in the local SiNS plane. However, when the tilt was investigated it was found to be very small indeed, and in later refinements it was assumed to be zero.

The radial distribution curve for compound (7) (Figure 1) reveals three peaks below 200 pm corresponding to the C–H, S=N, Si–N, and Si–C bond lengths, the last two giving just one peak. It proved possible to refine all of these parameters, and their associated amplitudes of vibration, as the Si–N and Si–C

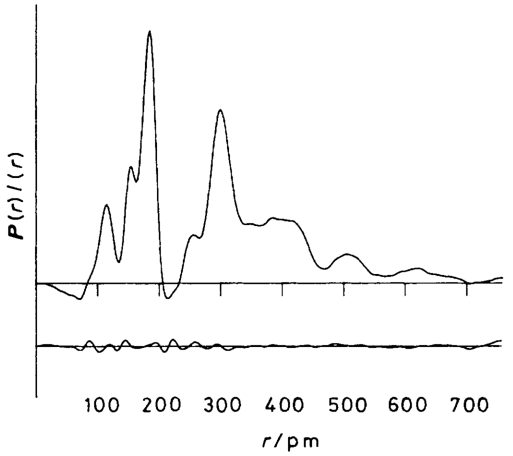

Figure 1. Observed and final weighted-difference radial distribution curves $P(r)/(r)$ for $(Me_3Si)_2N_2S$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.000\,02s^2)/(Z_{Si} - f_{Si})(Z_S - f_S)$

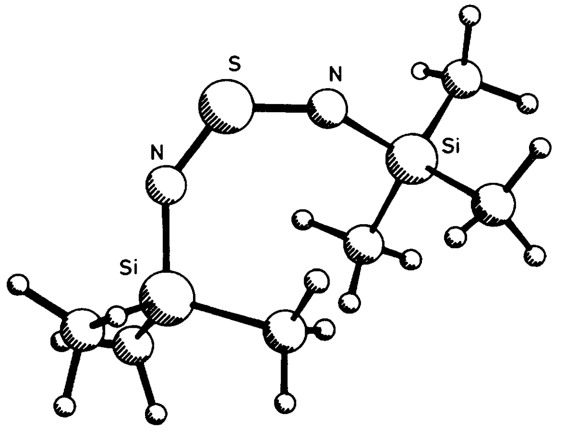

Figure 2. Perspective view of $(Me_3Si)_2N_2S$

Table 3. Least-squares correlation matrix (× 100)*

p_{10}	p_{11}	u_3	u_5	
−84	93			p_5
			77	p_7
	−90			p_{10}
		69		u_2

* Only elements with absolute values ≥60% are included.

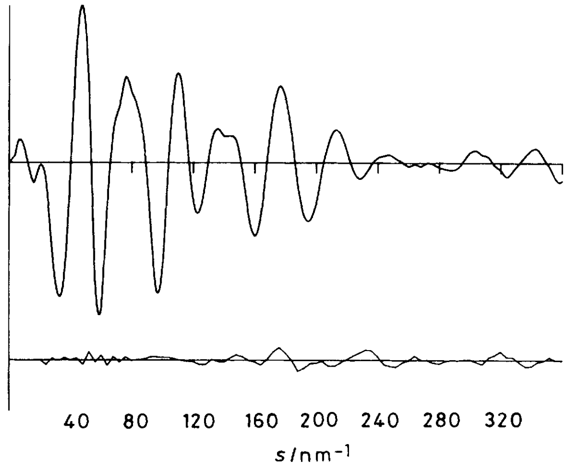

Figure 3. Observed and final weighted-difference combined molecular-scattering intensity curves

distances were not strongly correlated. The two peaks observed at 250 and 300 pm correspond to the major interatomic distances within the $NSiMe_3$ groups. The first of these is solely due to the Si ··· H distance and this allowed the SiCH angle to be determined accurately. The second peak contains contributions from the N(Si)C, Si(N)S, and C(Si)C distances at *ca.* 294, 300, and 306 pm respectively. Despite the proximity of these peaks the SNSi and NSiC angles could be refined independently, although their e.s.d.s were rather high. The angle between the two groups, N=S=N, was effectively determined by the long inter-group distances, since the N ··· N peak contributed little to the molecular scattering. Consequently this parameter was poorly determined. The remaining peaks in the radial distribution curve, beyond 310 pm, determine the overall molecular conformation.

Compounds of the type R–N=S=N–R have been found to adopt various conformations such as *syn,syn* [SN twist 1 = 180, twist 2 = 180°], *syn,anti* [180,0], and *anti,anti* [0,0] and so these conformers were all investigated. It then became clear that the *syn,syn* arrangement was preferred. This conformation was therefore investigated further, varying the SN twist angles over wide ranges from the idealised values of 180°. When the apparent optimum angles had been located, the two SN and two SiN twist angles were all allowed to refine independently. The angles obtained were 10(9) and 7(7)° for SiN, and 139(21) and 136(18)° for SN. The overall symmetry was therefore very close to C_2, and so this was assumed in the final refinement.

Molecular orbital calculations[21] are in agreement with the observed *syn,syn* conformation but predict a planar geometry with a large SNSi angle (164°). We therefore attempted to fit the observed data to a planar model. However, as the SN twist angles are forced from *ca.* 140° up to 180° (*i.e.* planar) the *R* factor rises from 0.06 to more than 0.15 even though the SNSi angle changes by less than 1°. Refinements with an SNSi angle of 164° had an even worse effect on the *R* factor, without affecting the twist angle.

The geometrical parameters obtained in the final refinement, for which the *R* factor (R_G) was 0.06, are listed in Table 2, and the final least-squares correlation matrix is given in Table 3. The major interatomic distances and amplitudes of vibration are given in Table 4. Figure 2 is a perspective view of the molecule, and in Figure 3 the molecular scattering intensity curves are shown.

Discussion

The bond distances and angles for compound (7) and some related molecules are shown in Table 5. The observed structure has the expected bent NSN group with an angle at sulphur [129.5(16)°] which is larger than that observed for *syn,anti* or *anti,anti* di-imides, but closer to the angle in *syn,syn-p*-$ClC_6H_4SNSNSC_6H_4Cl$-*p* [124.0(1)°]. The SN bond distances are appropriate for S=N double bonds. They are not noticeably different from those in any of the compounds in Table 5 and are very similar to those seen for the N=S=N portion of the $[S_2N_2]^{2-}$ ligand in $[Pt(S_2N_2)(PR_3)_2]$ complexes.[22] A particularly interesting feature is the lengthening of the N–Si bond in the tin complex, $SnCl_4[(Me_3Si)_2N_2S]$, [180.5(4) pm] which has an *anti,anti* structure, relative to the equivalent *syn* bonds in

Table 4. Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm)*

		Distance	Amplitude			Distance	Amplitude
r_1	S=N	153.6(3)	4.1(6)	r_{14}	Si···Si	443.9(9)	23.5 (fixed)
r_2	Si–N	173.8(3)	3.5(10)	r_{15}	Si···C	387.6(24)	20.3 (fixed)
r_3	Si–C	186.9(1)	4.2(5)	r_{16}	Si···C	504.2(17)	18.7 (fixed)
r_4	C–H	114.2(3)	8.6(5)	r_{17}	Si···C	615.6(9)	16.4 (fixed)
r_5	S···Si	300.2(5)	12.7(7)	r_{18}	N···C	352.3(20)	15.0 (fixed)
r_6	N···N	277.9(13)	7.5 (fixed)	r_{19}	N···C	493.7(13)	
r_7	Si···H	249.6(5)	9.8(5)	r_{20}	N···C	521.7(20)	
r_8	N···C	293.8(9)	12.7 (tied to u_5)	r_{21}	C···C	377.6(62)	25.0 (fixed)
r_9	C···C	306.0(8)		r_{22}	C···C	378.1(24)	
r_{10}	S···C	345.8(10)	13.9 (fixed)	r_{23}	C···C	572.1(41)	
r_{11}	S···C	417.5(13)	15.2(11)	r_{24}	C···C	573.9(23)	
r_{12}	S···C	428.0(12)		r_{25}	C···C	663.5(15)	
r_{13}	Si···N	379.8(16)	12.1 (fixed)	r_{26}	C···C	785.0(14)	

* Other S···H, Si···H, C···H, N···H, and H···H distances were included in the refinement but are not listed here. Errors, quoted in parentheses, are estimated standard deviations obtained in the least-squares refinements, increased to allow for systematic errors.

Table 5. Structural parameters (distances in pm, angles in °) of some sulphur di-imides

R	R′	Technique	r(NS)	NSN	NX	SNX	Ref.
Me (*syn*)		E.d.[a]	153.2(5)[b]	113.6(8)	146(2)[b]	124.3(6)	8
	Me (anti)					116.5(6)	
p-MeC$_6$H$_4$ (*syn*)		*X*-Ray	153(1)	117.2(4)	146(1)	130.8(6)	6
	p-MeC$_6$H$_4$ (*anti*)		156(1)		141(1)	117.5(6)	
4-Biphenyl (*syn*)		*X*-Ray	151.4(16)	117.5(9)	141(2)	132(2)	7
	4-Biphenyl (*anti*)		157.9(16)		140(2)	117(2)	
Me$_3$Si (*syn*)		*X*-Ray	150.3(5)	114.1(4)	165.3(7)	128.8(4)	13
	p-O$_2$NC$_6$H$_4$S (*anti*)		155.8(7)		174.9(6)	100.5(3)	
(Ph$_3$P)$_2$Pt (*syn*)		*X*-Ray	150.8(10)	121.1(6)	201.5(10)	138.1(5)	5
			149.7(10)	118.5(6)	203.6(10)	123.8(5)	
	Me$_3$Si (*anti*)		150.3(12)		174.9(11)	124.8(8)	
			154.2(10)		172.1(11)	125.4(7)	
p-ClC$_6$H$_4$S (*syn*)			153.9(16)	124.0(1)	126(2)	99.8(1)	11
	p-ClC$_6$H$_4$S (*syn*)		156.1(18)		129(2)	99.7(1)	
Me$_3$Si (*syn*)	Me$_3$Si (*syn*)	E.d.	153.6(3)[c]	129.5(16)	173.8(3)[c]	132.9(7)[c]	This work
(*anti,anti*) SnCl$_4$ complex of (7)		*X*-Ray	153.7(4)[c]	103.7(2)	180.5(4)	125.9(2)[c]	14

[a] E.d. = electron diffraction. [b] *syn* and *anti* values assumed to be equal. [c] *syn* and *anti* values are equal by symmetry.

the free di-imide (7) [173.8(3)]. Inspection of Table 5 reveals that a general feature of these types of structures is that the SNX bond angle is greater for *syn* than *anti* substituents.

As mentioned above there is an appreciable twist of the SiMe$_3$ groups. This probably comes about for steric reasons, although for XNSNX chains, where X is a main group atom such as sulphur (in p-ClC$_6$H$_4$SNSNSC$_6$H$_4$Cl-p, modelled using HSNSNSH), weak S···S interactions are possible. Molecular orbital calculations[21] on H$_3$SiNSNSiH$_3$ indicate that there is a small energy difference between planar *syn,syn* and planar *anti,anti* conformations which favours the former *but* with an exceptionally large SNSi angle. Clearly, although these calculations are useful, they are limited. First, they do not take account of electron correlation and, secondly, they do not take account of the steric problems associated with an SiMe$_3$ group. With respect to this latter point it is interesting that the fit of experimental and observed geometries is good for the ClC$_6$H$_4$S–HS system mentioned above, probably, in part at least, because the phenyl rings have little opportunity to interact.

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