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Reinvestigation of the Molecular Structure of *N,N*-Dimethyl Sulfamoyl Chloride by Electron Diffraction

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An electron diffraction reinvestigation of *N,N*-dimethyl sulfamoyl chloride confirmed the conformation with C_s symmetry in which the N–C bonds stagger the S–Cl bond. The geometric parameters determined include: S–Cl 2.064 ± 0.005 Å, S–O 1.421 ± 0.004 Å, S–N 1.618 ± 0.005 Å C–N 1.481 ± 0.012 Å, C–H 1.096 ± 0.010 Å, N–S–Cl 103.0 ± 0.5°, N–S–O 108.8 ± 1.4°, O–S–O 122.7 ± 2.3°, S–N–C 115.8 ± 0.7°, C–N–C 114.6 ± 2.2°. Some geometrical variations in the molecular structures of simple sulfone molecules are discussed.

In the course of our structural studies on molecules containing S–N bond on one hand and sulfone group on the other, a number of compounds have recently been investigated employing electron diffraction.[1–8] The variations in the geometrical configurations of the sulfur bonds showed interesting trends that were interpreted involving both the VSEPR model and non-bonded interactions [9,7,4] (see also comparisons of simple sulfoxides and sulfones [10,11]).

The molecular geometry of *N,N*-dimethyl sulfamoyl chloride, $(CH_3)_2NSO_2Cl$, has also been investigated earlier [12] by electron diffraction. As the determination of the geometrical parameters suffered from severe approximations, it was decided to perform a reinvestigation.

EXPERIMENTAL

The sample of *N,N*-dimethyl sulfamoyl chloride used in this investigation was prepared by E. Páldi.[13] The purity of the sample was confirmed by mass spectrometry. The electron diffractions patterns were taken with the Budapest apparatus,[14,15] a modified EG-100A unit, with essentially the same technique as in some of the other studies mentioned above.[4,6,7] The temperature of the nozzle of the so-called membrane nozzle system [14] was about 105 °C during the exposures. The wavelength of the electron beam was determined from the diffraction pattern of thallium(I) chloride. The ranges of intensity data used were $1.75 \leqq s \leqq 12.50$ Å^{-1} and $7.25 \leqq s \leqq 31.25$ Å^{-1} with $\Delta s = 0.25$ Å^{-1}. The experimental molecular intensities corresponding to the two camera ranges were obtained as before.[4,6,7] The scaled and averaged molecular intensities, $sM^E(s)$, are shown in Fig. 1.

STRUCTURE ANALYSIS

Most of the calculations were performed for conformer I that was earlier established,[12] however, conformers II and III (see Fig. 2) have also been tested. Forms I and III have C_s symmetry (angle of rotation around the S–N bond, $\tau = 0$ and 180°, respectively), form II has no symmetry ($\tau = 120°$ was tested only). The following independent geometrical parameters were chosen; bond distances r(S–Cl), r(S–O), r(S–N), r(C–N), r(C–H), non-bond distance r(O···O),* and bond angles N–S–Cl, N–S–O, S–N–C, C–N–C, N–C–H.**

Spectroscopic calculations were used to obtain the mean parallel amplitudes of vibration (l values). An approximate force field was constructed by means of results from trimethyl-

* For reasons explained later.

** The CH_3 groups were assumed to have local C_{3v} symmetry. A plane through $H_7C_{10}N$ was assumed to halve the C_{11}–N–S angle and a plane through $H_8C_{11}N$ to halve the C_{10}–N–S angle.

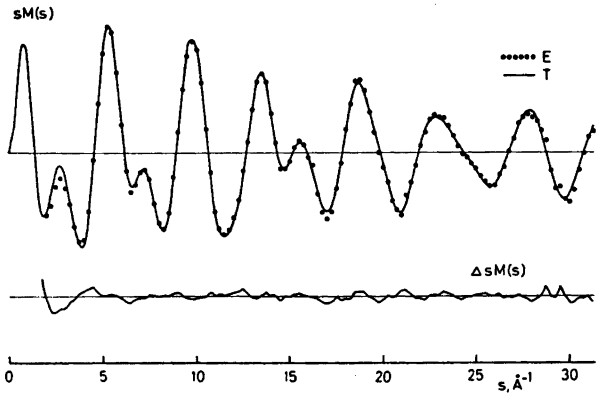

Fig. 1. Molecular intensities. E, experimental; T, theoretical calculated for conformer I with the parameters given in Tables 1 and 2.

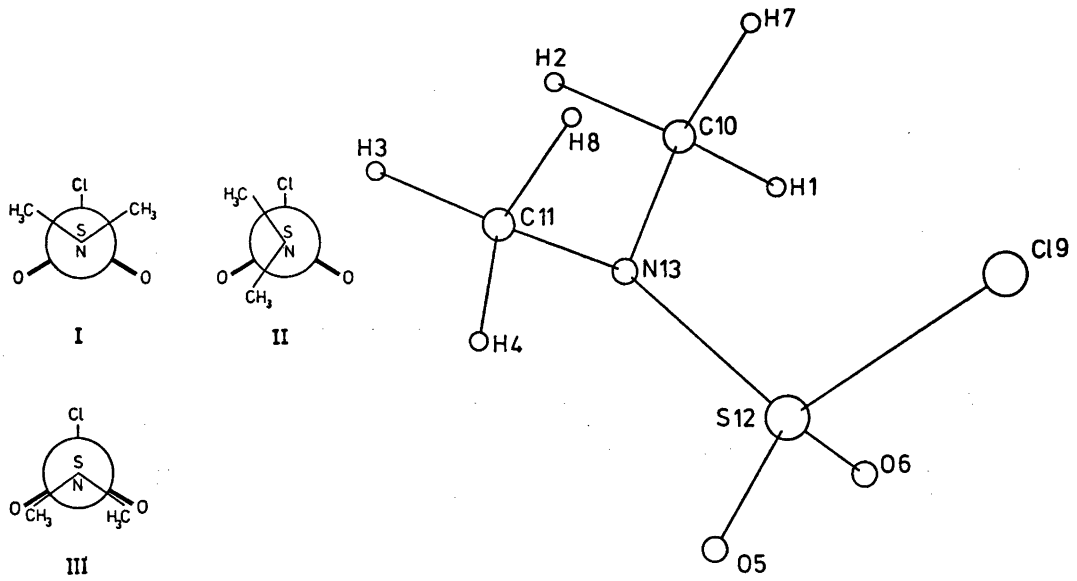

Fig. 2. Newman projections of the molecular models of $(CH_3)_2NSO_2Cl$ representing view along the S–N bond and the numbering of atoms.

amine [16] and the SO_2Cl part of methane sulfonyl chloride.[17] The force field was modified to reproduce the experimental frequencies of Bürger *et al.*[18] Even though the force field was felt to be very tentative, partly because of the low molecular symmetry, the calculated *l* values proved to be very useful. They were first used in the trial structures of the least squares refinements. Most of them, however, were assumed and not varied even in the final stages of analysis because of the strong correlation between the parameters. The *l* values from the spectroscopic calculation that were used in the final structure analysis are given in Tables 1 and 2. Fig. 2 gives the numbering of atoms.

The experimental radial distribution is represented in Fig. 3. The contribution from the S–O, C–N, and S–N bonds appear under the

Table 1. Mean amplitudes of vibration (l) from spectroscopic calculation (for distances that are not listed in Table 2; the labelling of atoms is given in Fig. 2).

Type	Distance (Å)	l (Å)	Type	Distance (Å)	l (Å)
N ···Cl	(2.90)	0.070	C_{11}···H_1	(3.40)	0.103
O ···Cl	(2.81)	0.097	S ···H_1	(2.75)	0.163
O ···N	(2.47)	0.107	H_2···H_3	(2.34)	0.228
C ···C	(2.49)	0.069	O_5 ···H_2	(4.55)	0.138
S ···C	(2.62)	0.093	O_6 ···H_3	(3.86)	0.170
H_1···H_2	(1.81)	0.129	H_3···H_8	(3.07)	0.278
N ···H_1	(2.09)	0.105	Cl ···H_2	(4.35)	0.182
N ···H_2	(2.09)	0.106	C_{11}···H_3	(2.61)	0.158
N ···H_7	(2.09)	0.151	S ···H_3	(3.54)	0.120
H_1···H_3	(3.61)	0.172	O_5 ···H_7	(4.16)	0.254
H_1···H_4	(4.16)	0.139	O_5 ···H_8	(3.27)	0.298
O_5···H_1	(4.04)	0.151	H_7···H_8	(2.63)	0.303
O_6···H_1	(2.44)	0.221	Cl ···H_7	(2.91)	0.303
H_1···H_8	(3.77)	0.223	C_{11}···H_7	(2.79)	0.211
Cl ···H_1	(3.71)	0.268	S ···H_7	(2.92)	0.246

Table 2. *N,N*-Dimethyl sulfamoyl chloride. Results of the least squares refinement. Bond lengths, bond angles and l values that were determined or assumed. The l values for the other distances were taken from spectroscopic calculation and are listed in Table 1. Some dependent parameters are also given.

No.	Type	Geometric parameter r(Å),∠(°)	l value (Å)	$\sigma_{LS}(r,\angle)$	$\sigma_{LS}(l)$	$\sigma_t(r,\angle)^e$	$\sigma_t(l)^e$
1	S−Cl	2.064	0.061[b]	0.002	0.002	0.005	0.003
2	S−O	1.421	0.038[b]	0.0015	0.003	0.004	0.004
3	S−N	1.618	0.051[b]	0.003	0.004	0.005	0.006
4	C−N	1.481	[0.050][c]	0.008		0.012	
5	C−H	1.096	0.079[b]	0.007	0.007	0.010	0.010
6	O···O	2.494	[0.074][b,d]	0.018		0.026	
7	N−S−Cl	103.0		0.4		0.5	
8	N−S−O	108.8		1.0		1.4	
9	S−N−C	115.8		0.5		0.7	
10	C−N−C	114.6		1.6		2.2	
11	N−C−H	107.4		2.4		3.5	
12	O−S−O	(122.7)[a]		1.6		2.3	
13	O−S−Cl	(105.8)[a]		0.3		0.4	
14	$(O\cdots C)_{short}$	(2.89)[a]	[0.155][c]	0.015		0.02	
15	$(O\cdots C)_{long}$	(3.82)[a]	0.08[b]	0.009	0.03	0.02	0.04
16	C···Cl	(3.37)[a]	0.17[b]	0.018	0.04	0.03	0.06

[a] Dependent parameters. [b] The spectroscopic calculations yielded l(S−Cl) 0.071, l(S−O) 0.037, l(S−N) 0.087, l(C−H) 0.079, l(O···O) 0.112, $l(O\cdots C)_{long}$ 0.101, and l(C···Cl) 0.143 Å. [c] Spectroscopic value assumed. [d] Assumed value. [e] Expressions for estimating the total errors

$\sigma_t(r) = [2\sigma_{LS}^2(r) + (0.002r)^2]^{\frac{1}{2}}$

$\sigma_t(\angle) = \sqrt{2}\sigma_{LS}(\angle)$

$\sigma_t(l) = [2\sigma_{LS}^2(l) + (0.02\ l)^2]^{\frac{1}{2}}$

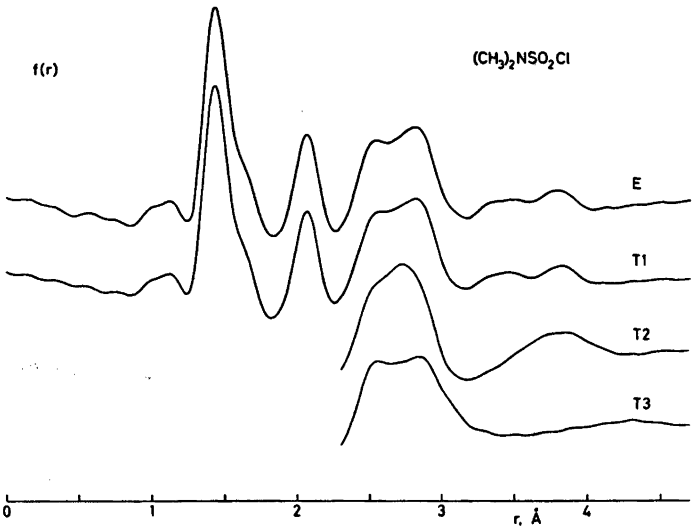

Fig. 3. Radial distributions. E, experimental; T1, T2, and T3, theoretical for conformers I, II, and III, respectively.

same maximum at $r = 1.4$ Å. However, the slight shoulder around $r = 1.6$ Å can readily be assigned to the S–N bond. The maximum at $r = 2.07$ Å originates primarily from the S–Cl bond with a less important contribution from the N···H non-bond distances. All the non-bond distances through one atom in the C_2NSO_2Cl skeleton plus the shortest O···C distances are expected to appear under the double maximum between 2.4 and 3.0 Å. The maxima at about 3.4 and 3.8 Å can be identified primarily with the Cl···C and the longest O···C distances, respectively.

There were two sources for trial structures. A starting set of the geometrical parameters was taken from the results of the earlier investigation.[12] Furthermore, portions of the experimental radial distribution were inverse-Fourier-transformed, and the bond lengths and bond angles refined in separate schemes.

The least-squares method was applied to the molecular intensities.[19] The theoretical background was used as modification function. The coherent and incoherent scattering amplitudes were taken from Cox and Bonham [20] and Tavard *et al.*,[21] respectively.

A diagonal weight matrix was utilized with the following scheme

$W = \exp[-0.1(4.00 - s^2)]$ for $s < 4.00$ Å^{-1}
$W = 1.00$ for $4.00 \leqq s < 30.00$ Å^{-1}
$W = \exp[-0.012 \times (s - 30.00)^2]$ for $s > 30.00$ Å^{-1}

Parameters in selected groups could be refined simultaneously only, because of the strong correlation between the parameters (*cf.* Refs. 8, 22). It was also for this reason that the non-bond distance O···O was treated as independent parameter and kept unvaried in many of the early refinement schemes employing the value of 2.48 Å. A remarkable constancy of this parameter has been observed for a series of simple sulfone molecules.[4,9] This constraint was not used, however, in the final refinements. Likewise, the values 1.47 Å and 109.5° were assumed for r(C–N) and ∠N–C–H in many refinement schemes, but were later allowed to vary. The l values were refined for the bonds S–Cl, S–O, S–N, and C–H and the non-bond distances Cl···C and O···C (longest). The parameters l(C–N) and l(O···O) were adapted from an other study [3] (the calculated values were unrealistically large for them, *cf.* Table 2), and for the rest the spectroscopic values were utilized throughout the entire analysis.

RESULTS

The results of the least-squares refinements are given in Table 2 together with the standard deviations from the least-squares refinement (σ_{LS}) and the total errors (σ_t) which include an estimated 0.2 and 2 % experimental error for the distances and amplitudes, respectively. The σ_{LS} values were obtained in a refinement scheme in which all the independent parameters (geometric and vibrational) were allowed to vary simultaneously with a nearly zero "fudge factor". The correlation coefficients presented in Table 3 are associated with the results given in Table 2. The data of both Tables 2 and 3 should be dealt with caution since they were obtained with many other parameters assumed.

Radial distributions for all three forms are shown in Fig. 3. The experimental distributions could be well approximated with theoretical distributions calculated for conformer I only. Slight deviations from the C_s symmetry of this form (characterized by an angle of rotation around the S – N bond up to about 4°) further improved somewhat the agreement. This was seen not so much in the changes of the generalized R values but in the regions of the radial distributions where the rotation-dependent distances occur. It is stressed also that the other geometrical parameters showed no appreciable changes in the above calculations.

DISCUSSION

The present study confirmed the earlier established form of rotation around the S – N bond in *N,N*-dimethyl sulfamoyl chloride. This form is analogous to those found to be prevailing in the vapours of $(CH_3)_2NSN(CH_3)_2$,[1] $(CH_3)_2NSON(CH_3)_2$,[2] and $(CH_3)_2NSO_2N(CH_3)_2$.[3] In all cases there is at least one symmetry plane and the two N – C bonds plus the lone pair of the nitrogen stagger the sulfur bonds and lone pairs.

The most important differences between the results of the two studies concern the bond lengths. All of them were found shorter than previously. In addition to the possibility of an experimental scale error, was suppose that a $(CH_3)_2NSO_2N(CH_3)_2$ impurity in the first study could account for the differences.

The value found in the present study for r(S – Cl), 2.064 Å, may still be the largest observed for a S – Cl bond. Some results for simple sulfonyl chlorides are (r(S – Cl), r(O···Cl)): $ClSO_2Cl$:[5] 2.011 ± 0.004 Å, 2.781 ± 0.007 Å. CH_3SO_2Cl:[6] 2.046 ± 0.004 Å, 2.816 ± 0.009 Å. $C_6H_5SO_2Cl$:[8] 2.047 ± 0.008 Å, 2.780 ± 0.032 Å. It is of interest to observe that the O···Cl non-bond distances show smaller changes than the S – Cl bonds in the molecules considered. This seems to indicate the importance of the oxygen···chlorine non-bond interactions in the structures of the SO_2Cl fragments.

The length of the S – O bond is intermediate between those in sulfuryl chloride[5] and *N,N'*-tetramethyl sulfamide.[8] It has been noted[4,9] that the changes of r(S – O) and also ∠O – S – O with changing electronegativities of ligands X and Y in simple XSO_2Y sulfones, are consistent with the VSEPR model. Accordingly, as the ligand electronegativity increases, the S – O bond shortens and the O – S – O bond opens

Table 3. Correlation coefficients with absolute values from 0.4 (× 100) associated with the least squares refinement whose results are given in Table 2 (for identification of parameters refer to Table 2, k is the scale factor).

	$r1$	$r2$	$r3$	$r4$	$r6$	∠8	∠9	∠10	∠11	$l1$	$l2$
$r4$		−80									
∠8				−45	−93						
∠9		52		−61							
∠10					−77	73					
∠11	−62			−50		−50		47			
$l2$		68		−82			49				
$l3$		−77		70			−45				−64
$l15$	62			49		−49		−46	−93		
k			49					−44		40	

Table 4. The S – O bond and O···O non-bond distances and O – S – O bond angles in some simple sulfones (vapour phase data).

Compound	Technique[a]	r(S – O), Å	∠O – S – O, °	r(O···O), Å
FSO_2F	MW (i)	1.405 ± 0.003	124.0 ± 0.2	2.481 ± 0.006
FSO_2Cl	MW (ii)	[1.408 ± 0.006]	123.7 ± 1	2.484
$ClSO_2Cl$	ED (iii)	1.404 ± 0.004	123.5 ± 0.8	2.485 ± 0.015
CH_3SO_2F	ED (iv)	1.410 ± 0.003	123.1 ± 1.5	[2.480]
	MW (v)			2.480
$C_6H_5SO_2Cl$	ED (vi)	1.417 ± 0.012	122.5 ± 3.6	2.482 ± 0.039
$(CH_3)_2NSO_2Cl$	ED (vii)	1.421 ± 0.004	122.7 ± 2.3	2.494 ± 0.026
CH_3SO_2Cl	ED (viii)	1.424 ± 0.003	120.8 ± 2.4	2.477 ± 0.013
	MW (ix)	[1.424 ± 0.003]	121.3 ± 0.6	2.483 ± 0.003
$CH_3SO_2CH_3$	ED (x)	1.435 ± 0.003	119.7 ± 1.1	2.482 ± 0.017
	MW (xi)	1.431 ± 0.004	121.0 ± 0.3	
	MW (xii)	[1.425]	122.0	2.493 ± 0.002
	(xiii)	1.433	120.8	2.493 ± 0.002

[a] MW, microwave spectroscopy; ED, electron diffraction. (i) r_o, Ref. 23; (ii) r_o, r(S – O) estimated, Ref. 24; (iii) r_a, Ref. 5; (iv) r_a, r(O···O) assumed from Ref. 25; (v) r_o, Ref. 25; (vi) r_a, Ref. 8; (vii) r_a, present work; (viii) r_a, Ref. 6; (ix) r_o, r(S – O) assumed from Ref. 6; (x) r_a, Ref. 4; (xi) r_o, Ref. 26; (xii) r_o, r(S – O) assumed, Ref. 25; (xiii) r_o, Ref. 25.

somewhat. The relevant data are presented in Table 4. The changes are relatively small, but the trend appears to be real.

Table 4 contains also the r(O···O) distances of the sulfone group. At the same time as the S – O bond lengths and O – S – O angles change as much as up to 0.03 Å and 4°, respectively, the constancy of the O···O distances at 2.48 – 2.49 Å is the more remarkable. This clearly indicates for these structures, that the non-bond oxygen···oxygen interactions may be as much, if not more, important as the electron pair interactions described by the VSEPR model. The geometrical variations may be visualized as the sulfur atom being in the center of a tetrahedron whose two apexes are occupied by the two oxygen atoms of the SO_2 group. As the X and Y substituents are changing, the sulfur atom is moving somewhat up and down in the tetrahedron with the positions of the oxygen atoms unchanged, as determined by their interaction.

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