Electron-diffraction Investigation of the Molecular Structure of Sulphonyl Chloride Isocyanate

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The electron-diffraction data for the title compound are consistent with two sets of geometric parameters differing in the relation between the C=O and N=C bond lengths. The other geometric parameters are: S–N 1.656(4), S–Cl 2.019(3), and S=O 1.417(3) Å; S–N–C 123.8(38), N–S=O 108.3(22), N–S–Cl 98.0(30), Cl–S=O 107.8(7), and O=S=O 122.8(24)°. The conformational properties may be characterised in two ways: (*i*) by a mixture of two forms having rotation angles of 109(4) and 70(10)° (0° corresponds to a form in which the S–Cl bond is *anti* to the O=C=N chain) in which the first form predominates [69(7)%]; (*ii*) by one form having a rotation angle of 86(3)° and a large amplitude of rotation around the S–N bond. The observed molecular geometry is consistent with structural variations found in isocyanates and in sulphonyl chlorides.

THE present investigation is an extension of our studies on the molecular structures of simple sulphone molecules (for references to some of the preceding studies see ref. 1). We were interested in how the isocyanate group influences the sulphur-bond configuration. Sulphone molecules with various ligands attached to the SO_2 group display interesting structural variations which can be interpreted as involving both valence-shell electron-pair repulsions and non-bonded interactions. As for isocyanates, no structural data for sulphur derivatives in the vapour phase are available to date,[2] and it is of interest to compare the structure of sulphonyl chloride isocyanate with those of silicon, phosphorus, and chlorine derivatives. Another obvious question was the conformational properties of this compound in the vapour phase.

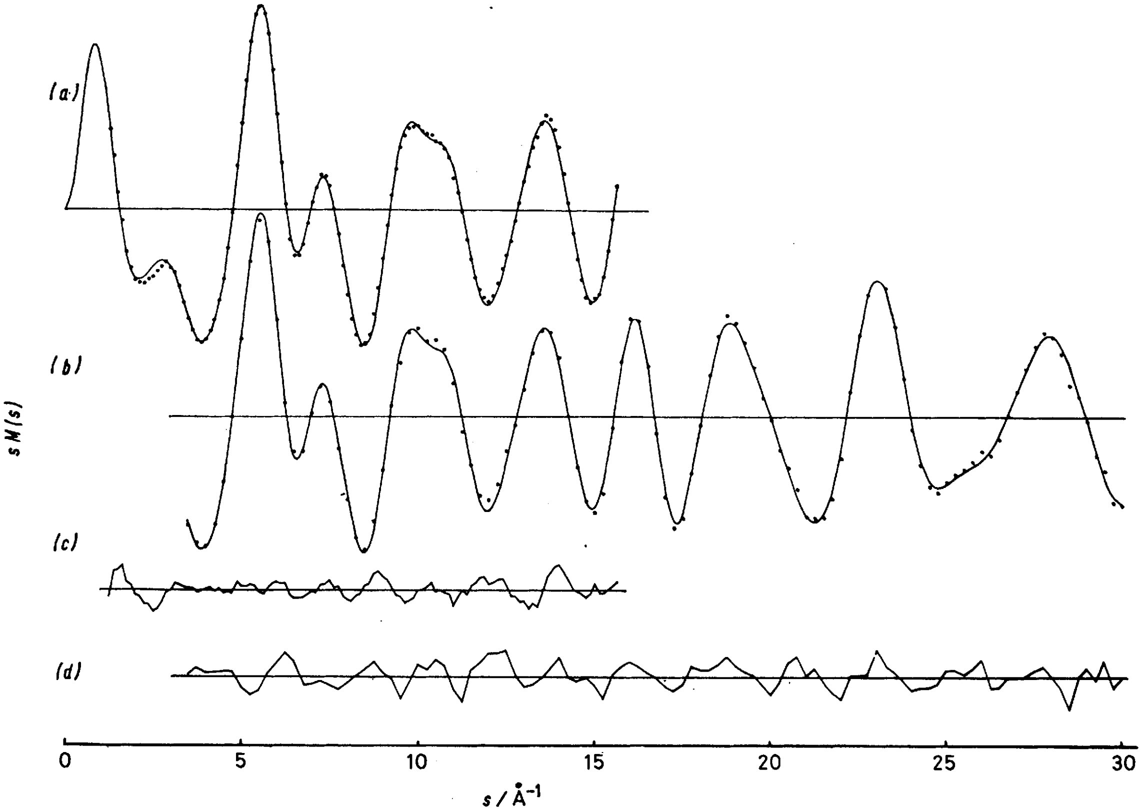

FIGURE 1 Experimental (●) and theoretical (—) molecular intensities for $SO_2Cl(NCO)$ for the two camera ranges 50 (*a*) and 25 cm (*b*) and twice their differences [(*c*) and (*d*)]. The theoretical curves were computed from the parameters of column (*i*) in Table 1

EXPERIMENTAL

The electron-diffraction patterns were recorded at the room temperature of the nozzle using an Oslo Balzers KD-G2 apparatus.[3] Five and four (Kodak electron-image) plates from the 50- and 25-cm camera ranges, respectively, were used. The wavelength was determined from TlCl patterns

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[1] I. Hargittai, Gy. Schultz, and M. Kolonits, *J.C.S. Dalton*, 1977, 1299.

[2] I. Hargittai and I. C. Paul, ' The Chemistry of the Cyanates and their Thio Derivatives,' ed. S. Patai, Wiley, London, in the press.

[3] W. Zeil, J. Haase, and L. Wegmann, *Z. Instr.*, 1966, **74**, 84; O. Bastiansen, R. Graber, and L. Wegmann, Balzers High Vacuum Report, 1969, p. 1.

and corrected according to data on benzene. The procedure for data reduction was as previously described.[4] The experimental intensity data are available as Supplementary Publication No. SUP 22182 (3 pp.).* The reduced molecular intensities and radial distributions are shown in Figures 1 and 2, respectively.

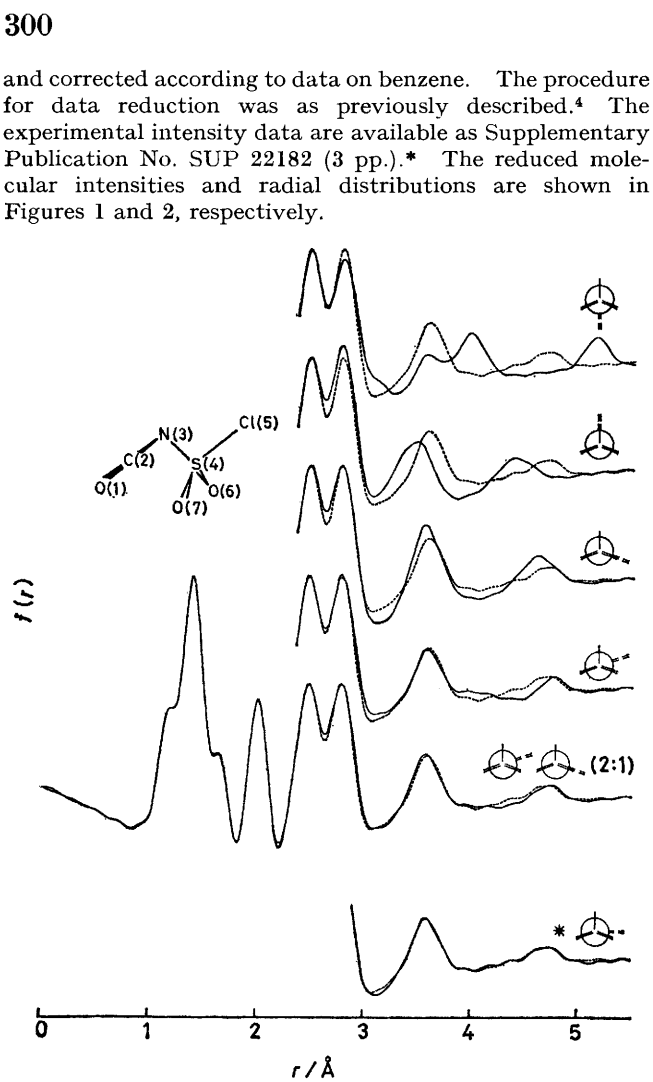

FIGURE 2 Experimental (– – –) and theoretical (——) radial distributions. The first four radial distributions were calculated for individual rotamers whose Newman projections are shown representing the view along the S–N bond. The fifth curve was calculated for a mixture of two forms with rotation angles 109 and 70° (0° corresponds to the form in which the S–Cl bond is *anti* to the O=C=N chain) with a 2 : 1 relative abundance. Spectroscopically calculated l values were used for all the non-bonded distances in computing the top five curves. The bottom curve was calculated for an individual rotamer having larger than calculated l values for the rotation-dependent distances. The numbering of atoms is also shown

STRUCTURE ANALYSIS

The O=C=N chain of $SO_2Cl(NCO)$ was assumed to be linear and the bond lengths and bond angles, which are required to be identical when the Cl–S–N=CO chain is planar (C_s symmetry), were also assumed to be identical in asymmetric models. The angle of rotation around the S–N bond (τ) is 0° when the chlorine atom is *anti* to OCN. When different rotation forms were considered simultaneously, it was assumed that all the geometrical parameters, except the angles of rotation, were the same in all forms. The independent geometrical parameters are listed in Table 1.

Mean amplitudes of vibration (l values) and perpendicular correction terms [$K = <(\Delta x)^2 + (\Delta y)^2> /2r$] were calculated using a standard procedure [5] on the basis of i.r. and Raman spectra reported by Kanesaka and Kawai.[6] The starting force field was an approximate valence force field with only diagonal elements. The force constants were then adjusted to fit the experimental frequencies. The calculated l values are listed in Table 1.

The least-squares method was applied to the molecular intensities.[4] The elastic scattering factors used were obtained by the partial-wave method [7] on the basis of analytical Hartree–Fock potentials.[8] The inelastic scattering factors were taken from Tavard *et al.*[9] The theoretical background (atomic scattering intensities) was used as a modification function.

Trial parameter sets were compiled on the basis of the experimental radial distribution, structural information on other sulphonyl chlorides [1] and isocyanates,[2] and correlations between S=O bond lengths and stretching frequencies.[10] Initially, models containing only one rotation form were tested against the experimental data. Theoretical radial distributions computed for four individual conformers are shown in Figure 2. The experimental data could be approximated to about the same degree with either of the two forms in which τ was 60 (R 0.131) or 102° (R 0.125).† Combinations of these two forms were refined with different starting values for their relative abundance, giving τ_1 108° (65%), τ_2 72° (35%), and R 0.117. Subsequent refinements using improved empirical backgrounds were based on such a model. It is stressed that spectroscopically calculated l values for all the non-bonded distances were used in these calculations.

Because of strong correlation between the parameters, either the bond lengths or the corresponding amplitudes of the O=C=N chain were fixed in the refinements. This procedure was repeated several times. The O···O distance was also fixed (at 2.484 Å) in most of the refinements. Its remarkable constancy at this value has been observed for a relatively large series of simple sulphones.[11] The influence of the assumed constancy on the other parameters was taken into account in the error estimate in a similar manner to that used previously.[1] The results of these refinements are presented in columns (i) of Table 1.

Similar refinements were also performed for the r_α structure using the approximate expression $r_\alpha = r_a + (l^2/r_a) - K$. The results were very much the same as those in column (i) of Table 1, changes in the parameters being well within the stated standard deviations except for S–N=C 123.8(6)° and N–S–Cl 98.0(8)°. The structure refinement was also carried out under the assumption that $r(N=C) < r(C=O)$ since results from some investigations indicate [2] that this possibility cannot be excluded. The

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

† $R = \{\sum_i W_i[M_i^E(s) - M_i^T(s)]^2/\sum_i W_i[M_i^E(s)]^2\}^{\frac{1}{2}}$.

[4] B. Andersen, H. M. Seip, T. G. Strand, and R. Stølevik, *Acta Chem. Scand.*, 1969, **23**, 3224.

[5] S. J. Cyvin, 'Molecular Vibrations and Mean Square Amplitudes,' Universitetsforlaget, Oslo, and Elsevier, Amsterdam, 1968.

[6] I. Kanesaka and K. Kawai, *Bull. Chem. Soc. Japan*, 1970, **43**, 3298.

[7] A. C. Yates, *Comput. Phys. Comm.*, 1971, **2**, 175.

[8] T. G. Strand and R. A. Bonham, *J.Chem. Phys.*, 1964, **40**, 1686.

[9] C. Tavard, D. Nicolas, and M. Rouault, *J. Chim. phys.*, 1967, **64**, 540.

[10] J. Brunvoll and I. Hargittai, *Spectroscopy Letters*, in the press.

experimental data could be equally well approximated [R 0.073 for model (*i*), 0.071 for model (*ii*)] by such a model and the results are presented in columns (*ii*) of Table 1.

The l(N=C) and l(C=O) values were rather uncertain, and another approach was also tested for both models: the difference between the two amplitudes was fixed according to spectroscopic calculations and the bond lengths and amplitudes were then varied. In these cases both r(C=N) and r(C=O) changed by up to 0.01 Å towards each other's values. The amplitudes became l(N=C) 0.043 Å and l(C=O) 0.045 Å.

On the basis of the electron-diffraction data alone, we cannot decide between models (*i*) and (*ii*) of Table 1. However, most of the geometric parameters and the conformational ratio were hardly sensitive to the choice of the relation between the N=C and C=O bond lengths. Although the overall agreement was satisfactory, the radial distributions calculated for the mixture of the two conformers indicated some discrepancy at *ca.* 4.1—4.5 Å. This prompted us to test whether a small amount of the *syn* form could be indicated. The amount of the *syn* form, however, did not exceed the value of its standard deviation. This discrepancy could be easily eliminated, however, by having only one form with an angle of rotation which was the average of τ_1 and τ_2, and allowing the l values of rotation-dependent distances to vary. The rotation-dependent part of the corresponding radial distribution is also shown in Figure 2. The parameters obtained this way are listed in columns (*iii*) of Table 1. These results were independent of the starting relation between r(N=C) and r(C=O).

TABLE 1

Molecular parameters for sulphonyl chloride isocyanate [a] from least-squares refinements

	Geometrical parameters			Amplitudes of vibration			
	(*i*)	(*ii*)	(*iii*)	(*i*)	(*ii*)	(*iii*)	s.c. [b]
(*a*) Independent distances (Å)							
C=O	1.159(11)	1.218(9)	1.233(8)	0.045(14)	0.029(9)	0.025(16) [c]	0.037 9
N=C	1.221(13)	1.152(9)	1.146(8)	0.026(14)	0.044(12)	0.023 [c]	0.035 5
S–N	1.655 5(17)	1.656 7(12)	1.658 4(14)	0.043 7(20)	0.042 9(18)	0.039 9(19)	0.049 8
S–Cl	2.017 5(8)	2.017 8(7)	2.018 5(7)	0.051 6(10)	0.051 8(9)	0.050 9(11)	0.052 2
S=O	1.415 9(6)	1.416 3(6)	1.417 7(5)	0.041 1(13)	0.041 5(9)	0.040 6(15)	0.034 6
O · · · O (O=S=O)	2.484(20)	2.485(12)	[2.484]				0.058 4
(*b*) Independent angles (°)							
S–N=C	122.4(5)	125.8(5)	126.0(5)				
N–S=O	108.5(11)	108.7(6)	108.8(2)				
N–S–Cl	99(2)	98.2(11)	98(2)				
τ_1 (Cl–S–N=CO)	109(3)	103(2)	86(3)				
τ_2(Cl–S–N=CO)	70(6)	63(4)					
(*c*) Dependent distances (Å)							
(*i*) Independent of rotation							
O(1) · · · N	2.379	2.37	2.379				0.042 7
O(1) · · · S	3.553	3.600	3.612				0.093 7
C · · · S	2.530	2.511	2.510				0.070 0
N · · · Cl	2.797	2.787	2.792				0.087 7
N · · · O(6)	2.497	2.502	2.506				0.071 2
Cl · · · O(6)	2.798	2.799	2.800				0.077 3
(*ii*) τ_1 dependent							
O(1) · · · Cl	3.990	4.130	4.409			0.273(28)	0.220
O(1) · · · O(6)	4.759	4.778	4.743			0.108(13)	0.078
O(1) · · · O(7)	3.633	3.677	3.600			0.294(14) [c]	0.192
C · · · Cl	3.250	3.298	3.463			0.254 [c]	0.154
C · · · O(6)	3.639	3.593	3.560			0.134 [c]	0.069
C · · · O(7)	2.897	2.895	2.843			0.254(53)	0.130
(*iii*) τ_2 dependent							
O(1) · · · Cl	4.601	4.723					0.182
O(1) · · · O(6)	4.614	4.592					0.115
O(1) · · · O(7)	3.447	3.551					0.197
C · · · Cl	3.641	3.665					0.132
C · · · O(6)	3·542	3.473					0.089
C · · · O(7)	2.778	2.818					0.133
Amount (%) of form with τ_1	69(4)	67(5)	[100]				

[a] The parameters of models (*i*)—(*iii*) were determined from the electron-diffraction analysis. All the distances are r_a. Standard deviations from the least-squares refinement are given in parentheses. The numbering of the atoms is given in Figure 2. [b] s.c. = Spectroscopic calculations. [c] l Values were refined in groups.

Since most data on isocyanates [2] (see also Discussion section) are consistent with the bond-length combination (*i*), the geometric parameters were chosen from this model. The total estimated errors include a factor of $3^{\frac{1}{2}}$ times the least-squares standard deviations,* 0.1% experimental error. the uncertainties originating from the assumption of r(O · · · O) (*cf.* ref. 1), and also the changes in parameters occurring when refinements were performed under different assumptions concerning the conformational properties.

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* This factor was used to take account of data correlation. However, the effect of data correlation was ignored in estimating the total error in the rotation angles and conformational ratio.

The total errors for the bond lengths S-Cl and S=O were increased to take account of the uncertainty in the vibrational correction terms. Two independent bond angles are also given. Thus the final results for the bond lengths and bond angles are S-N 1.656(4), S-Cl 2.019(3), and S=O 1.417(3) Å; S-N-C 123.8(38), N-S=O 108.3(22), N-S-Cl 98.0(30), Cl-S=O 107.8(7), and O=S=O 122.8(24)°.

DISCUSSION

Of the 14 isocyanates whose molecular geometries have been investigated in the vapour phase,[2] the N=C bond (1.20—1.26 Å) was found to be longer than the C=O bond (1.14—1.18 Å) in eight cases; for one case the two lengths were roughly the same, and the N=C length was assumed in another case. Both trends were reported either as a double solution [$SO_2Cl(NCO)$] or as a result of independent studies [$SiH_3(NCO)$] for two, and in only two cases [MeNCO and $PCl_2(NCO)O$] was r(N=C) < r(C=O) found. The compounds MeNCO and $PCl_2(NCO)O$, as many of the other compounds, have been investigated by electron diffraction, and the parameters characterizing the bonds N=C and C=O are strongly correlated. We suspect that double solutions could have been obtained in more systems if the requisite tests had been made. It is also possible, although we believe unlikely, that the N=C and C=O bonds are so sensitive to substitution that both their lengths may extend over the reported ranges. On the other hand, it is notable that the N=C bond lengths determined for isothiocyanates[2] are similar to those for isocyanates for which r(N=C) > r(C=O). The N=C bond length can be determined more reliably in isothiocyanates than in isocyanates by electron diffraction since there is no other bond of similar length in the thio-derivative.

When the X-N=C bond angles are compared in a series of derivatives in which X = Si, P, S, or Cl a gradual decrease is observed and the present data complement the existing information.[2] There also seems to be a parallel decrease in the double-bond character of the X-N bonds. This is demonstrated by the decrease in the relative shortening of these bonds relative to the estimated single-bond lengths (Table 2). All the available data[2] were considered in estimating the average values for Table 2 (seven, three, one, and one values for the silicon, phosphorus, sulphur, and chlorine derivatives, respectively). The comparison is very crude since there are not enough data for a classification according to the electronegativities of the ligands attached to atom X. The Si-N bond length decreases with increasing electronegativity of the other ligands attached, in agreement with expectation.

TABLE 2

Comparison of observed and calculated X-N bond lengths in isocyanates

	Bond length/Å	
X	obs.[a]	calc.[b]
Si	1.69	1.82
P	1.68	1.76
S	1.66	1.72
Cl	1.70	1.69

[a] For references see ref. 2. [b] Using the Schomaker–Stevenson equation (V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37).

The sulphur-bond configuration in sulphonyl chloride isocyanate is consistent with those determined for other simple sulphones. The Cl • • • O non-bonded distance (2.798 Å) is very similar to those observed for other sulphonyl chlorides.[1] It has been noted[11] that the O • • • Cl non-bonded distances show smaller changes than the S-Cl bonds in the sulphonyl chloride molecules considered. This may indicate the importance of non-bonded interactions in the structures of the SO_2Cl fragments.

Both forms found to be present in the vapour of sulphonyl chloride isocyanate have a planar (within experimental error) five-membered chain.* The coplanarity of some simple isocyanate molecules is an automatic consequence of the linearity of the O=C=N group, for example in NCNCO.[12] The benzene ring and the O=C=N chain are coplanar in phenyl isocyanate.[13] Other isocyanates and their thio-analogues show a great variety of conformational properties.[2]

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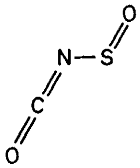

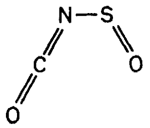

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* This observation refers to the model with the preferred combination of N=C and C=O bond lengths.

[11] I. Hargittai and J. Brunvoll, *Acta Chem. Scand.*, 1976, **A30**, 634.

[12] W. H. Hocking and M. C. L. Gerry, *J. Mol. Spectroscopy*, 1976, **59**, 338.

[13] A. Bouchy and G. Roussy, *Compt. rend.*, 1973, **277**, 143.