

## **Molecular structure and semiexternal molecular motions in 2,4,5-trichlorobenzenesulfonyl chloride, $C_6H_2Cl_4O_2S$**

G. RIGOTTI<sup>1</sup> and P. M. ALZARI<sup>2</sup>  
*Laboratorio de Cristalografía*  
*Departamento de Física*  
*Universidad Nacional de La Plata*  
*C.C. 67, 49, y 115*  
*1900 La Plata, Argentina*

A. NAVAZA  
*Laboratoire de Physique*  
*Centre Pharmaceutique*  
*92290 Chatenay Malabry, France*

A. E. WOLFENSON,<sup>3</sup> D. J. PUSIOL,<sup>4</sup> and A. H. BRUNETTI<sup>4</sup>  
*Facultad de Matemática, Astronomía y Física*  
*Universidad Nacional de Córdoba*  
*Laprida 854*  
*5000 Córdoba, Argentina*

*(Received September 8, 1986)*

### **Abstract**

The molecular structure of 2,4,5-trichlorobenzenesulfonyl chloride has been determined by X-ray diffraction methods. The compound is orthorhombic, *Aba*2, with  $a = 16.253(12)$ ,  $b = 17.016(9)$ ,  $c = 7.146(5)$  Å,  $V = 1976(5)$  Å<sup>3</sup>,  $Z$

<sup>1</sup>Fellow of the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Argentina.

<sup>2</sup>Present address: Immunologie Structurale, Institut Pasteur, rue du Dr. Roux 75724, Paris Cedex 15, France.

<sup>3</sup>Holder of a fellowship of the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

<sup>4</sup>Fellow of the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

= 8,  $D = 1.88 \text{ kg} \cdot \text{mm}^{-3}$ , (Mo  $K\alpha$ ) = 0.7107 Å,  $\mu = 136.8 \text{ cm}^{-1}$ ,  $F(000) = 1104$ . Data were obtained at room temperature; the final  $R$  is 0.029 for 854 independent reflections. The substituted benzene ring is planar within experimental accuracy, the dihedral angle with the C(1)—S(1)—Cl(1) plane being  $66.0(5)^\circ$ . The compound has normal bond lengths and angles; some short intramolecular distances account for the maintenance of the rigid benzene frame. No significantly short intermolecular distances have been found. Confirmation of the oscillatory character of the semiexternal molecular motions operating above 180 K is accounted for.

## Introduction

In previous work it has been found that both the temperature dependence of the  $^{35}\text{Cl}$  NQR frequency,  $\nu_q(T)$ , and the NQR spin-lattice relaxation time,  $T_1(T)$ , in some molecular crystals belonging to the  $X\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl}$  series ( $X = \text{Cl, H, Br, or CH}_3$ ) and to the  $X\text{-C}_6\text{H}_4\text{-CH}_2\text{Cl}$  series ( $X = \text{Cl, H, or CH}_2\text{Cl}$ ), show a peculiar behavior. This effect was ascribed to the triggering of semiexternal molecular motions (SEM).

The SEM are interpreted as molecular vibrations of the two constituent groups of the molecule ( $X\text{-C}_6\text{H}_4$  and either  $\text{SO}_2\text{Cl}$  or  $\text{CH}_2\text{Cl}$ , each considered as rigid bodies), which become external vibrations at temperatures higher than  $T_c$  of about 160–180 °K (Pusiol and Brunetti, 1982, 1983, 1984, 1985a, b; González *et al.*, 1984).

All the NQR measurements performed on the compounds in the series indicate that the SEM are oscillatory motions; semirotations of the  $\text{SO}_2\text{Cl}$  group around the C(1)—S(1) bond are forbidden. In this work we confirm the oscillatory character of the SEM by means of X-ray diffraction measurements.

## Experimental

High-purity 2,4,5-trichlorobenzenesulfonyl chloride samples were obtained from the commercial product (Fluka) by successive recrystallizations and sealed in a TPF container under a nitrogen atmosphere to avoid hydration.

### *X-Ray measurements*

An irregularly shaped, colorless crystal was mounted on an Enraf-Nonius CAD-4 diffractometer; 936 reflections were measured using graphite-monochromated Mo  $K\alpha$  radiation ( $2\theta_{\text{max}} = 50^\circ$ ; index range, 0 to 18, 0 to 20, and 0 to 8 for  $h$ ,  $k$ , and  $l$ , respectively). Cell constants were obtained from setting

angles of 25 reflections ( $20^\circ < 2\theta < 25^\circ$ ): 854 reflections with  $I > 2\sigma(I)$  were considered observed; the three standard reflections show no significant fluctuations. Lorentz, polarization, and empirical absorption corrections were made. The structure was solved by direct methods with MULTAN 78 (Main *et al.*, 1978) and refined by full-matrix least-squares on  $F^2$ s. Final  $R$  factors were  $R = 0.029$  and  $R_w = 0.034$ ;  $s = 1.358$  for 123 refined parameters.  $(\Delta/\sigma)_{\max} = 0.10$ ;  $w = 1/[\sigma^2(F) + 0.0016 F^2]$ ; maximum height in difference Fourier was  $\Delta\rho = 0.15$  e  $\text{\AA}^{-3}$ . Scattering factors were taken from *International Tables for X-Ray Crystallography* (1974) and computer programs used were those of the Enraf-Nonius (1979) Structure Determination Package. Final positional and equivalent isotropic thermal parameters are given in Table 1, and bond distances and angles in Table 2. Figure 1 shows the molecular geometry in an ORTEP diagram (Johnson, 1965) with the atom labeling.

### NQR measurements

The experimental equipment and method of measurement have been described previously (Pusiol and Brunetti, 1984).

NQR relaxation time ( $T_1$ ) measurements were performed in the 80–220 K temperature range using a conventional pulsed spectrometer as described by (Pusiol and Brunetti, 1984).

The NQR spectrum of this compound at 77 K shows four lines of the following frequencies:  $\nu_1 = 34.283$ ,  $\nu_2 = 37.087$ ,  $\nu_3 = 37.547$ , and  $\nu_4 =$

Table 1. Positional parameters and their estimated standard deviations<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
S(1)	0.95169(5)	0.17575(5)	0.379	4.50(2)
Cl(1)	0.94146(6)	0.10248(6)	0.6014(3)	6.22(3)
O(1)	0.9331(2)	0.1321(2)	0.2197(5)	6.15(8)
O(2)	1.0287(2)	0.2133(2)	0.3980(7)	6.53(8)
C(1)	0.8744(2)	0.2466(2)	0.4251(6)	3.35(6)
C(2)	0.7898(2)	0.2289(2)	0.4185(5)	3.15(7)
Cl(2)	0.75392(6)	0.13582(4)	0.3755(2)	4.65(2)
C(3)	0.7348(2)	0.2888(2)	0.4466(6)	3.77(7)
H(3)	0.672(2)	0.268(2)	0.451(6)	3*
C(4)	0.7612(2)	0.3641(2)	0.4791(6)	3.57(7)
Cl(4)	0.68930(6)	0.43690(6)	0.5105(2)	5.71(2)
C(5)	0.8450(2)	0.3815(2)	0.4855(6)	3.56(7)
Cl(5)	0.87981(8)	0.47511(5)	0.5227(2)	5.40(2)
C(6)	0.9007(2)	0.3218(2)	0.4593(6)	3.57(7)
H(6)	0.957(2)	0.331(2)	0.461(5)	3*

<sup>a</sup>Atoms with a superscript asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(4/3) * [a^2 * B(1, 1) + b^2 * B(2, 2) + c^2 * B(3, 3) + ab(\cos \gamma) * B(1, 2) + ac(\cos \beta) * B(1, 3) + bc(\cos \alpha) * B(2, 3)]$ .

Table 2. Bond lengths (Å) and angles (deg), with esd's

Bond lengths											
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S(1)	Cl(1)		2.025(2)	C(1)	C(6)		1.37(2)	C(4)	C(5)		1.394(4)
S(1)	O(1)		1.395(4)	C(2)	Cl(2)		1.715(4)	C(4)	Cl(4)		1.718(4)
S(1)	O(2)		1.412(3)	C(2)	C(3)		1.371(4)	C(5)	Cl(5)		1.71(2)
S(1)	C(1)		1.771(1)	C(3)	H(3)		1.080(3)	C(5)	C(6)		1.37(2)
C(1)	C(2)		1.408(3)	C(3)	C(4)		1.371(12)	C(6)	H(6)		0.92(4)
Bond angles											
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl(1)	S(1)	O(1)	107.2(2)	C(2)	C(1)	C(6)	120.7(3)	C(3)	C(4)	Cl(4)	118.9(3)
Cl(1)	S(1)	O(2)	106.1(2)	Cl(2)	C(2)	C(3)	119.4(3)	C(3)	C(4)	C(5)	120.6(9)
Cl(1)	S(1)	C(1)	102.47(7)	C(1)	C(2)	Cl(2)	122.4(3)	C(4)	C(5)	Cl(5)	121.7(9)
O(1)	S(1)	O(2)	120.7(2)	C(1)	C(2)	C(3)	118.2(2)	C(4)	C(5)	C(6)	119.1(1)
O(1)	S(1)	C(1)	111.1(1)	H(3)	C(3)	C(4)	126.7(3)	Cl(5)	C(5)	C(6)	119.4(7)
O(2)	S(1)	C(1)	107.7(1)	C(2)	C(3)	H(3)	112.0(2)	C(1)	C(5)	C(6)	120.5(5)
S(1)	C(1)	C(2)	122.7(1)	C(2)	C(3)	C(4)	121.1(2)	C(1)	C(6)	H(6)	117.8(7)
S(1)	C(1)	C(6)	116.5(3)	C(5)	C(4)	Cl(4)	120.5(9)	C(5)	C(6)	H(6)	121.5(7)

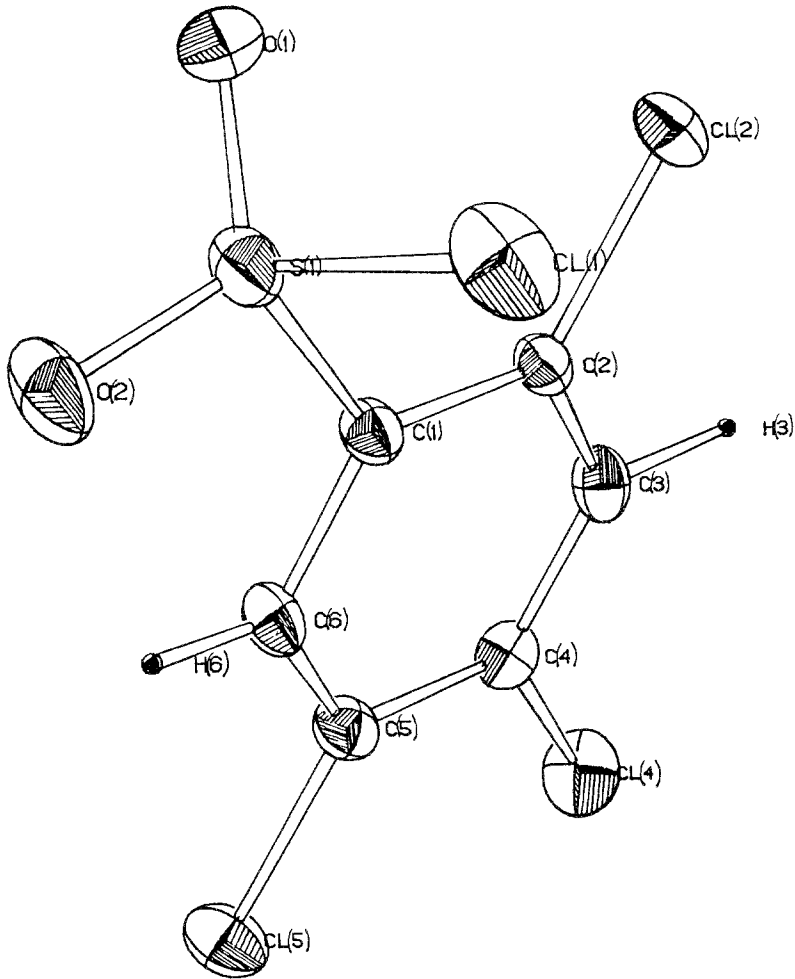


Fig. 1. ORTEP diagram showing the molecular geometry.

38.090 MHz. Comparison between this spectrum and that corresponding to 4-chlorobenzenesulfonyl chloride (Pusiol and Brunetti, 1983) indicates that the lower NQR frequency should be assigned to the  $^{35}\text{Cl}$  nuclei belonging to the  $\text{SO}_2\text{Cl}$  group [Cl(1)], and the other three to the substituted benzene ring [Cl(2), Cl(3), and Cl(4)]. This assignment indicates that the molecules are situated in chemically equivalent sites of the unit cell, in agreement with structural results.

Our measurements of  $\nu_q(T)$  in the  $\nu_1$  line, reveal no structural phase transition in the temperature range of 80 to 220 K.

Figure 2 shows the results of  $T_1(T)$  measurements corresponding to the

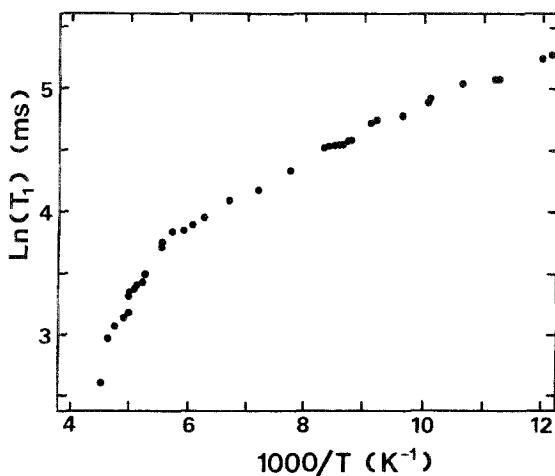


Fig. 2.  $^{35}\text{Cl}$  nuclei spin-lattice relaxation time versus temperature. An abrupt change in the rate of decrease of  $T_1$  with temperature can be observed, indicating the activation of the SEM (see the text).

NQR line assigned to  $^{35}\text{Cl}(1)$ . The observed temperature behavior of  $T_1$  is qualitatively identical to those observed in the other benzenesulfonyl chloride compounds (Pusiol and Brunetti, 1984, 1985a, b). For  $T < 180$  K the  $T_1(T)$  behavior corresponds to that foreseen by the rigid molecule model, and the only relaxation mechanism present is due to the torsional oscillations (Jones *et al.*, 1978). For  $T > 180$  K a new relaxation mechanism appears; it is produced by transitions between semiexternal oscillator energy levels (Pusiol and Brunetti, 1985b), which correspond to the motion of the  $\text{SO}_2\text{Cl}$  group with respect to the benzene ring. This type of mechanism is thermally activated (Pusiol and Brunetti, 1984), and the corresponding activation energy could be calculated using the following equation (Pusiol and Brunetti, 1985b):

$$1/T_1 = AT^\lambda + \frac{BT^{\lambda'}}{(1 + Ce^{E_a/kT})} \quad (1)$$

obtaining  $E_a = 30 \text{ kJ mol}^{-1}$ .

### Discussion

Benzene ring planes are stacked along [001] [the angle between aromatic rings and (001) is  $10.8^\circ$ ], conforming layers parallel to (010). Within each layer, the nearest ring planes are at a distance of  $3.208(5) \text{ \AA}$  from each other

and make an angle of  $1.9^\circ$ , their centers being shifted by  $2.70(2)$  Å with respect to each other. Benzene rings from adjacent layers make angles of  $21.5^\circ$  to one another; interlayer spaces are filled with opposed chlorosulfonyl groups.

The average values of C—C [ $1.38(1)$  Å] and C—Cl [ $1.71(1)$  Å] bond lengths are in good agreement with commonly accepted values.

The angular disposition of Cl(1), O(1), O(2), and C(1) about S(1) departs significantly from a regular tetrahedral arrangement, the smallest and largest bond angles being, respectively, C(1)—S(1)—Cl(1) [ $102.5(1)^\circ$ ] and O(1)—S(1)—O(2) [ $120.7(2)^\circ$ ]. The Cl—S distance is that of a single bond; the S—O and S—C distances agree closely with the values found in sulfones.

One of the oxygen atoms of the sulfonylchloride group lies approximately in the plane of the aromatic ring [dihedral angles between the benzene plane and the planes C(1)—S(1)—O(1) and C(1)—S(1)—O(2) are, respectively,  $48.3(4)$  and  $3.2(3)^\circ$ ]. The dihedral angle between the aromatic ring and the C(1)—S(1)—Cl(1) plane is  $66.0(5)^\circ$ , differing from other substituted benzene sulfonylchlorides (BSC):  $85.6^\circ$  for 2-nitro-BSC (Gogoi and Hargreaves, 1970) and  $84.3(1)^\circ$  for 4-methyl-BSC (Rigotti *et al.*, 1986). The orientation of the  $SO_2Cl$  group must be strongly conditioned by van der Waals interactions between chlorine and oxygen atoms:  $SO_2Cl$ -chlorine/ring chlorine distances could be increased by rotation of the  $SO_2Cl$  group about the C(1)—S(1) bond in the positive<sup>5</sup> sense until a conformation similar to that of the above BSC is reached (about  $20^\circ$  rotation). However, in this way both  $O(1) - Cl(2)$  and  $O(1) - Cl(3)$  distances decrease continuously and eventually fall  $0.4$  Å below the sum of the van der Waals radii for about a  $30^\circ$  rotation, probably ruling out the possibility of semirotaion beyond this value in the positive sense (see below).

Rotation about the C(1)—S(1) bond in the negative sense brings the chlorine atom in the  $SO_2Cl$  group closer to the aromatic ring plane.  $Cl(1) - Cl(2)$  and  $Cl(1) - Cl(4)$  distances, which are slightly below the sum of their van der Waals radii, fall  $0.6$  Å below the commonly accepted value of  $3.6$  Å, for a rotation of about  $20^\circ$ .

A semiquantitative estimation of the rotation barrier in either sense, determined mainly by the proximity of chlorine and oxygen atoms, was made assuming as a first approximation that the forces operating when chlorine (or oxygen) atoms approach are repulsive. Applying Mie's equation in the form  $\theta_{rep} = A [d_1^{-n} + d_2^{-n}]$  and calculating the  $A$  repulsion constant by assuming that at  $d_0$

<sup>5</sup>To describe this rotation, a right handed orthogonal coordinate system is defined, with  $x$  along the bond C(1)—S(1),  $y$  in the plane defined by C(1), S(1), and Cl(1) and pointing toward Cl(1), and  $z$  perpendicular.

<sup>6</sup>(i)  $x; y; z$

(ii)  $\frac{1}{2} - x; -\frac{1}{2} + y; z$

(iii)  $x; -\frac{1}{2} + y; -\frac{1}{2} + z$

equal to the sum of the van der Waals radii,  $A d_0^{-n} = kT$ , with  $n = 12$  (Moelwyn-Hughes, 1964), the following conclusions are obtained: (i) the contribution to the strain energy in the crystal due to the proximity of chlorine and oxygen atoms [ $\text{Cl}(\text{i})$  to  $\text{Cl}(\text{ii})$  and to  $\text{Cl}(\text{iv})$ , and  $\text{O}(\text{i})$  to  $\text{Cl}(\text{ii})$  and  $\text{Cl}(\text{v})$ ] is of the order of  $20 \text{ kJ mol}^{-1}$ ; and (ii) rotations of  $-21$  or  $+30^\circ$  about the  $\text{C}(1)-\text{S}(1)$  bond are required to increase the energy  $30 \text{ kJ mol}^{-1}$  (experimental activation energy). This implies that the relaxation mechanism operating through such rotations (above 180 K) is extremely effective in view of the small fraction of molecules with energy above  $30 \text{ kJ mol}^{-1}$  ( $11.8 kT$  at room temperature).

The findings are in good agreement with the proposed quadrupolar relaxation mechanism operating for  $T > 180^\circ\text{K}$  since energy requirements are reached for  $\mp 15^\circ$  oscillations of each rigid body with respect to the crystallographic position.

The intramolecular distances  $\text{S}(1)-\text{Cl}(2)$  [ $3.286(4) \text{ \AA}$ ] and  $\text{Cl}(4)-\text{Cl}(5)$  [ $3.166(5) \text{ \AA}$ ] are shorter than the corresponding sums of the van der Waals radii, indicating a steric interaction, which is confirmed by displacements of these atoms from one another and out of the plane of the aromatic ring, so that the bond angles depart from the normal values of  $120^\circ$  (Table 2). These close contacts, although implying a contribution to the strain energy of about  $21 \text{ kJ mol}^{-1}$ , are energetically more favorable than larger distortions of the rigid molecular frame.

## Conclusions

(i) NQR experimental data support the assumption of the appearance of semiexternal molecular motions in the 2,4,5-trichlorobenzenesulfonyl chloride, showing the same qualitative behavior as the other compounds in the series.

(ii) X-Ray structural determination for the compound confirms the oscillatory character of SEM.

(iii) The probability of relaxation increases drastically with rotation about the  $\text{S}(1)-\text{C}(1)$  bond.

## Acknowledgments

We thank the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) and the Consejo de Investigaciones de la Provincia de Córdoba (CONICOR) for financial support.



## References

- Enraf-Nonius (1979) *SDP, Structure Determination Package* (Delft, Holland).
- Gogoi, B. N., and Hargreaves, A. (1970) *Acta Crystallogr.* **B26**, 2132.
- González, C. E., Pusiol, D. J., and Brunetti, A. H. (1984) *J. Mol. Struct.* **116**, 221.
- International Tables for X-Ray Crystallography, Vol. IV* (1974) (Kynoch Press, Birmingham, England).
- Johnson, C. K. (1965) *ORTEP Report ORNL-3974* (Oak Ridge National Laboratory, Oak Ridge, TN).
- Jones, L. V., Sabir, M., and Smith, J. A. S. (1978) *J. Phys.* **C11**, 4077.
- Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P., and Woolfson, M. M. (1978) *MULTAN* (York, UK).
- Moelwyn-Hughes, E. A. (1964) *Physical Chemistry*, 2nd ed. (Pergamon Press, New York).
- Pusiol, D. J., and Brunetti, A. H. (1982) *J. Mol. Struct.* **81**, 131.
- Pusiol, D. J., and Brunetti, A. H. (1983) *J. Mol. Struct.* **96**, 293.
- Pusiol, D. J., and Brunetti, A. H. (1984) *J. Phys.* **C17**, 4487.
- Pusiol, D. J., and Brunetti, A. H. (1985a) *J. Phys.* **C18**, 413.
- Pusiol, D. J., and Brunetti, A. H. (1985b) *J. Phys.* **C18**, 3819.
- Rigotti, G., Rivero, B. E., and Filgueira, R. (1986) *Z. Naturforsch.* **41B**, 1107.
- Structure factor data and least-squares planes have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 67019 (11 pages).