

The Crystal and Molecular Structure of 2-Nitrobenzenesulphonyl Chloride

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Crystals of 2-nitrobenzenesulphonyl chloride are monoclinic, space group $P2_1/a$, with four molecules in a unit cell of dimensions $a=12.47$, $b=8.91$, $c=8.28$ Å, $\beta=108^\circ 0'$. The structure has been determined from a three-dimensional Patterson synthesis using photographically recorded X-ray data and refined by the method of least squares to an R value of 0.12 for 882 observed reflexions. Intramolecular crowding leads to abnormal bond angles at the point linking the aromatic ring with the nitro and sulphonyl groups; the nitrogen and sulphur atoms are displaced from the aromatic plane in opposite directions by 0.05 and 0.17 Å respectively.

Introduction

The interaction of the three mononitrobenzenesulphonyl chlorides and of 2,4-dinitrobenzenesulphonyl chloride with aromatic hydrocarbons under the influence of aluminum chloride has been described by Dart, Holt & Jeffreys (1964). The crystal structures of some of these benzenesulphonyl chlorides are being examined to see if the chemical reactivities can be related to the molecular configurations. The first structure to be determined is that of 2-nitrobenzenesulphonyl chloride, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Cl}$.

Experimental

Crystals of 2-nitrobenzenesulphonyl chloride, supplied by Dr G. Holt, were grown from solution in benzene as fairly large, colourless, monoclinic needles for which the needle axis has been chosen as the c axis. As the

crystals are slightly hygroscopic, specimens cut from the larger crystals were coated with a thin film of diluted shellac in preparation for irradiation by X-rays.

Weissenberg photographs show that the space group is $P2_1/a$ and that the unit-cell dimensions, with estimated limits of error, are $a=12.47 \pm 0.05$, $b=8.91 \pm 0.03$, $c=8.28 \pm 0.08$ Å, $\beta=108.0 \pm 0.4^\circ$.

The density, measured by flotation in an aqueous solution of potassium iodide, is 1.67 ± 0.2 g.cm⁻³. The calculated density is 1.68 g.cm⁻³ with 4 molecules in the unit cell.

Intensity data for the $h0l$, $hk0$, $hk1$, $hk2$, $hk3$, $hk4$ and $hk5$ reflexions were collected by the multiple-film equi-inclination Weissenberg technique using Cu $K\alpha$ radiation. The intensities of the 882 observed reflexions were estimated visually by comparison with an intensity wedge and were corrected for α_1 - α_2 splitting. No correction for absorption was applied; the largest linear dimension in the cross-section perpendicular to the rotation axis was 0.33 mm.

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Table 1. Fractional atomic coordinates with estimated standard deviations (Å) and thermal parameters (Å²)

	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$	B
Cl	0.0546	0.004	0.0686	0.003	0.3343	0.004	*
S	0.0215	0.003	0.2041	0.002	0.1269	0.004	3.2
O(1)	0.1224	0.008	0.2159	0.008	0.0805	0.010	5.1
O(2)	-0.0783	0.008	0.1493	0.008	0.0051	0.010	5.1
O(3)	0.2343	0.009	0.3465	0.009	0.4136	0.011	5.5
O(4)	0.2513	0.010	0.5401	0.010	0.2631	0.013	6.6
N	0.1962	0.010	0.4515	0.009	0.3230	0.013	4.2
C(1)	-0.0079	0.010	0.3760	0.009	0.2104	0.013	2.9
C(2)	0.0761	0.010	0.4827	0.010	0.2809	0.014	3.4
C(3)	0.0471	0.011	0.6210	0.011	0.3312	0.014	3.9
C(4)	-0.0677	0.013	0.6555	0.013	0.2994	0.017	4.9
C(5)	-0.1509	0.013	0.5524	0.012	0.2304	0.017	5.0
C(6)	-0.1223	0.011	0.4140	0.011	0.1781	0.015	3.9
H(1)	0.118		0.693		0.414		8.0
H(2)	-0.092		0.770		0.354		8.0
H(3)	-0.238		0.556		0.183		8.0
H(4)	-0.185		0.324		0.098		8.0

* For the chlorine atom the anisotropic thermal parameters are given by

$$T(hkl) = \exp [-(0.0126h^2 + 0.0103k^2 + 0.0210l^2 + 0.0009hk + 0.0130hl + 0.0050kl)]$$

Determination and refinement of the structure

The positions of the chlorine and sulphur atoms were deduced from a three-dimensional Patterson function which was sharpened by multiplying coefficients by $\exp(2B \sin^2 \theta/\lambda^2)$; an average value for the isotropic temperature factor B was obtained from Wilson (1942) plots.

A three-dimensional Fourier synthesis, with phase angles deduced from the contributions of the chlorine and sulphur atoms only, revealed the positions of all the remaining atoms in the molecule (other than hydrogen) with reasonable certainty.

Using a B value of 3.8 \AA^2 for all atoms, the residual, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, fell from 0.48 with chlorine and sulphur atoms only to 0.30 with all atoms in positions deduced from the first three-dimensional synthesis. Refinement by the minimum residual method (Bhuiya & Stanley, 1963) and by Fourier synthesis reduced the R value to 0.18 at which stage a difference Fourier map showed clear signs of anisotropic thermal vibration of the chlorine atom.

Further refinement was carried out using a least-squares program (written by G. Shearing in Atlas auto-code) with the facility of calculating and refining anisotropic thermal parameters of the form $T(hkl) = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. The quantity minimized was $\sum w(|F_o| - |gF_c|)^2$, where g is a scaling factor for each reciprocal-lattice layer of reflexions, and the weighting factor w (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) is given by $(a + |F_o| + c|F_o|^2)^{-1}$ where a and c are about $2F_{\min}$ and $2/F_{\max}$ respectively; accidentally absent reflexions were given zero weight. The suitability of the weighting scheme was verified by the approximately equal average values of $w(|F_o| - |gF_c|)^2$ found for zones of $\sin \theta/\lambda$ and of $|F_o|$. Structure factors were calculated with atomic scattering factors given by Hanson, Herman, Lea & Skillman (1964). The refinement covered positional parameters, scale factors g , anisotropic temperature factors for the chlorine atom and isotropic temperature factors for the remaining atoms. Four cycles of refinement, omitting hydrogen atoms, reduced the R value

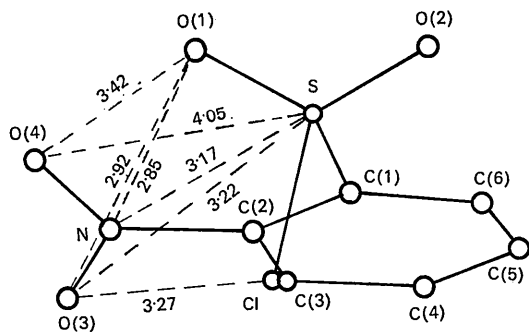


Fig. 1. Non-bonded intramolecular distances (\AA) between atoms in the nitro- and sulphonyl chloride groups. The molecule is viewed along the $[010]$ direction.

to 0.120. Hydrogen atoms were then included in the calculations, using fixed temperature parameters and positional parameters deduced from the geometry of the molecule. The R value fell only slightly, to 0.117, and as the parameters were changing by less than one-third of their standard deviations, refinement was terminated. A list of observed and calculated structure factors may be obtained on request from one of us (AH). The final atomic coordinates, with standard deviations as estimated by the least-squares program, and the thermal parameters are given in Table 1.

Description of the structure

Fig. 1 shows the labelling of the atoms in the molecule and indicates the mutual orientations of the nitro- and sulphonyl chloride groups together with the non-bonded intramolecular distances between atoms in these two groups. Bond lengths and bond angles, with estimated standard deviations, are presented in Tables 2 and 3 respectively. The estimated standard deviations in Tables 2 and 3 were calculated using the formulae of Ahmed & Cruickshank (1953) and of Darlow (1960) respectively.

Table 2. Bond lengths with standard deviations

S—Cl	$2.034 \pm 0.005 \text{ \AA}$
S—O(1)	1.428 ± 0.008
S—O(2)	1.425 ± 0.011
S—C(1)	1.765 ± 0.009
N—O(3)	1.202 ± 0.015
N—O(4)	1.245 ± 0.014
N—C(2)	1.455 ± 0.015
C(1)—C(2)	1.402 ± 0.016
C(2)—C(3)	1.384 ± 0.015
C(3)—C(4)	1.407 ± 0.018
C(4)—C(5)	1.371 ± 0.020
C(5)—C(6)	1.390 ± 0.016
C(6)—C(1)	1.408 ± 0.016

Table 3. Bond angles with standard deviations

Cl—S—O(1)	$107.7 \pm 0.5^\circ$
Cl—S—O(2)	107.4 ± 0.4
Cl—S—C(1)	101.3 ± 0.5
O(1)—S—O(2)	118.9 ± 0.6
O(1)—S—C(1)	110.4 ± 0.5
O(2)—S—C(1)	109.3 ± 0.5
O(3)—N—O(4)	125.5 ± 1.1
O(3)—N—C(2)	118.5 ± 0.9
O(4)—N—C(2)	115.9 ± 1.1
C(1)—C(2)—N	123.4 ± 0.9
C(3)—C(2)—N	116.3 ± 1.1
C(1)—C(2)—C(3)	119.8 ± 1.0
C(2)—C(3)—C(4)	118.9 ± 1.1
C(3)—C(4)—C(5)	121.7 ± 1.1
C(4)—C(5)—C(6)	119.3 ± 1.2
C(5)—C(6)—C(1)	119.7 ± 1.2
C(6)—C(1)—C(2)	119.9 ± 0.9
S—C(1)—C(2)	122.2 ± 0.7
S—C(1)—C(6)	117.0 ± 0.9

The least-squares best plane through the six carbon atoms of the aromatic ring, with deviations of atoms

from this plane, and the best plane through the three atoms of the nitro-group, are given in Table 4. The aro-

Table 4. *Least-squares planes*

(The equations are expressed in orthogonal coordinates X, Y and Z (Å) related to the monoclinic cell by the transformations $X = x \sin \beta$, $Y = y$, $Z = z + x \cos \beta$).

Equation of plane through three atoms of nitro-group
 $0.0374X + 0.1379Y + 0.1868Z = 1$.

Equation of plane through six carbon atoms of aromatic ring
 $0.0389X - 0.2349Y + 0.6126Z = 0.285$.

Deviations of atoms from plane of aromatic ring

C(1)	0.016 Å	C(5)	0.018 Å
C(2)	-0.015	C(6)	-0.027
C(3)	0.009	S	-0.167
C(4)	-0.004	N	0.052

matic ring is planar within the limits of accuracy of the atomic parameters and makes an angle of 57° with the plane of the nitro group. The nitrogen atom is displaced by 0.052 Å to one side of the aromatic ring and the sulphur atom by 0.167 Å to the opposite side, suggesting steric interaction between the nitro- and sulphonyl chloride groups. With one exception the intramolecular contacts between atoms in the two groups (Fig. 1) are at normal van der Waals distances; moreover all these distances could be increased quite easily by rotation of the nitro group about the N-C(2) single bond linkage in a sense which increases the angle between the planes of the nitro-group and the aromatic ring. The one exception is the sulphur-nitrogen distance which cannot be increased by this rotation and which is about 0.2 Å less than the sum of the van der Waals radii for sulphur and nitrogen atoms. It would appear, therefore, that the steric repulsion between the nitro and the sulphonyl chloride groups occurs almost entirely through repulsion between the sulphur and nitrogen atoms. This observation is confirmed in two ways (i) by displacements of the nitrogen and sulphur atoms on opposite sides of the plane of the aromatic ring, described above; (ii) by displacements of the sulphur and nitrogen atoms away from one another in the plane of the aromatic ring so that instead of normal bond angles of 120° we find increases to 122.1 and 123.4° for S-C(1)-C(2) and N-C(2)-C(1) respectively, and decreases to 117.0 and 116.3° for S-C(1)-C(6) and N-C(2)-C(3) respectively. The shortest Cl-O distance (3.27 Å) corresponds to a normal van der Waals separation, suggesting that there is no appreciable electrostatic attraction between the Cl and O atoms; a

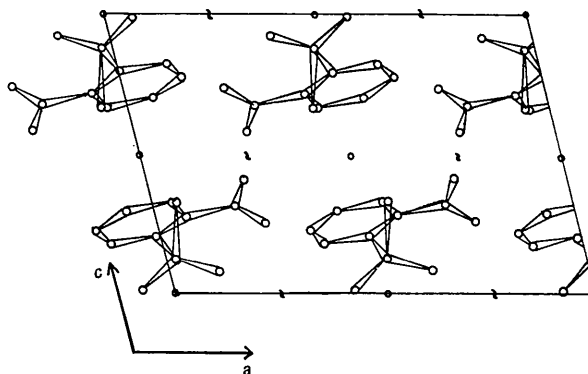


Fig. 2. The arrangement of the molecules viewed along the $[010]$ direction.

closer approach is not inhibited by other intramolecular contacts.

In the sulphonyl chloride group the angular dispositions of Cl, O(1), O(2) and C(1) about S depart significantly from a regular tetrahedral arrangement, with a large O(1)-S-O(2) bond angle (118.9°) and a small Cl-S-C(1) bond angle (101.3°). The S-Cl distance is that of a single bond whilst the S-O and S-C distances agree closely with the values found in sulphones.

The dimensions of the nitro group, the aromatic ring and the C-N bond length are normal.

The packing of the molecules is shown in Fig. 2.

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