terphenyl bridge. On the other hand, non-bonding distances of those equatorially coordinating O atoms opposite each other are not much influenced by the size of the guest (*ca* 5·4 Å for the Cu^{2+} complex, 5·7 Å for the Pb^{2+} complex, 5·7 Å for the K^+ complex, 5·6 Å for the free ligand). The rather short $O(2)\cdots O(4)$ distance of 4·814 (8) Å in the title structure also seems to be an effect of the terphenyl group.

Intermolecular interactions

The title compound was originally reported to contain two water molecules per formula unit (Rossa & Vögtle, 1981). *A priori*, therefore, an $H-O-H\cdots S-C-N\cdots H-O-H$ linkage similar to those in crystalline complexes of Cs^+ and Rb^+ with the cryptand '2.2.2' (Moras, Metz & Weiss, 1973) seemed possible. The current structure analysis, however, reveals methanol to be the only solvent molecule present, to which the anion is probably hydrogen bonded [$N\cdots O(5) = 2\cdot768\ (9)$ Å]. Since solvents used for crystallization had not been specially dried, replacement of water by the less polar methanol (even if present in large excess) is rather unusual. Normally the uptake of water is preferred with complexes of oligoethers because of the possibilities of forming more extended hydrogen-bond systems (*e.g.* Bush & Truter, 1971; Weber & Saenger, 1980).

There are no other strong intermolecular interactions.

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Structure of 4-Homosulfanilamide Hydrochloride

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Abstract

4-Homosulfanilamide hydrochloride, $C_7H_{10}N_2O_2S\cdot HCl$, $M_r = 222\cdot8$, is a 'sulfa' drug, which crystallizes in the tetragonal space group $I4_1cd$ with $a = b = 23\cdot719$ (8), $c = 7\cdot697$ (14) Å, $Z = 16$, $D_m = 1\cdot44$, $D_c = 1\cdot43$ Mg m^{-3} (flotation in $C_6H_6/CHBr_3$), $V = 4330$ Å^3, $\lambda(Cu\ K\alpha) = 1\cdot5418$ Å, $\mu(Cu\ K\alpha) = 4\cdot9$ mm^{-1}. The structure was solved by direct methods and refined to a final R value of 0·065 for 835 counter reflections. Structural features in the compound are compared with those of other 'sulfa' drugs. The

molecules are stacked roughly parallel to the *ab* plane at average intervals of 3·9 Å and there is a distinct overlap of the benzene rings in the z direction.

Introduction

The crystal and molecular structures of two 'sulfa' drugs have recently been solved by us as part of our general program of structure analysis of drug molecules in our laboratory. A preliminary report of the structure of one, sulfisoxazole, has already been made (Chatterjee, Dattagupta & Saha, 1979) and the structure of 4-homosulfanilamide [*p*-(aminomethyl)-benzenesulfonamide] hydrochloride forms the subject matter of the present paper. The chemical structure of the compound together with its numbering scheme is shown in Fig. 1. This drug is a homolog of sulfanilamide, but in this case the amino group is no longer aromatic. The crystal structure of sulfanilamide has already been studied in its three forms (O'Connor & Maslen, 1965; O'Connell & Maslen, 1967; Allé-aume & Decap, 1965) and it will be interesting to compare its structural parameters with those of 4-homosulfanilamide hydrochloride.

Experimental

The compound was obtained from Sigma Chemical Company. Colorless, needle-shaped crystals were grown from an aqueous solution at room temperature. Rotation and Weissenberg photographs using filtered Cu $K\alpha$ radiation showed that the crystal belongs to the tetragonal space group $I4_1cd$. Accurate cell parameters were obtained from diffractometric measurements.

The crystal used for data collection had dimensions 0·4 × 0·2 × 0·2 mm. Intensities of 845 reflections were collected using Ni-filtered Cu $K\alpha$ radiation, on an automatic Stoe diffractometer in the $\theta/2\theta$ scanning mode. The background was measured by a stationary-crystal stationary-counter technique on each side of the peak. Three standard reflections were monitored after each group of 100 measurements and they did not show any noticeable change in intensity. No correction was applied for absorption.

The structure was solved by direct methods using the program *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), employing the 152 E
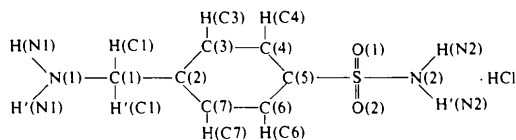

Fig. 1. Chemical structure and atomic numbering of 4-homo-sulfanilamide hydrochloride.

values larger than 1·35. All the non-H atoms could be located from the E map calculated with a phase set having the highest combined figure of merit, and a stereochemically satisfactory model was built. Full-matrix least-squares isotropic refinement and block-diagonal anisotropic refinement converged at $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0\cdot072$ for all 845 measured data. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Two H atoms were found in a difference map and six others were assigned by assuming regular stereochemistry. The H atoms on N(1) could not be placed. In the subsequent refinement, these eight H atoms were included. The H atoms were assigned the isotropic temperature factors of the heavier atoms to which they are attached and their parameters were not varied. The non-H atoms, however, were refined anisotropically. It was noticed at this stage that ten strong reflections were prominently affected by extinction and these were excluded from further calculations. Refinement was carried out until the average parameter shifts were less than their standard deviations and the last cycle gave an R value of 0·065 for 835 reflections. Positional parameters of the atoms with their standard deviations obtained from the correlation matrix are given in Table 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35989 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (×10⁴) *and the isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j (\mathbf{a}_i \cdot \mathbf{a}_j)\beta_{ij}.$$

	x	y	z	B_{eq} (Å²)
Cl	7046 (1)	1392 (1)	2110 (5)	3·6 (1)
S	3957 (1)	733 (1)	2893	2·5 (1)
O(1)	3552 (3)	1085 (3)	1997 (11)	3·9 (3)
O(2)	4177 (3)	240 (3)	2059 (12)	3·9 (3)
N(1)	6313 (3)	2396 (3)	3535 (13)	2·9 (3)
N(2)	3644 (3)	518 (4)	4661 (14)	3·4 (3)
C(1)	5939 (5)	2218 (5)	4958 (15)	3·7 (4)
C(2)	5432 (5)	1862 (4)	4340 (14)	2·8 (4)
C(3)	4885 (5)	2053 (4)	4514 (16)	3·2 (4)
C(4)	4450 (4)	1707 (4)	4087 (15)	2·8 (4)
C(5)	4537 (4)	1166 (4)	3488 (13)	2·4 (4)
C(6)	5077 (4)	971 (4)	3257 (14)	2·4 (3)
C(7)	5532 (4)	1300 (4)	3746 (16)	2·9 (4)
H(C1)	5799	2554	5604	
H'(C1)	6165	1976	5798	
H(C3)	4813	2448	4979	
H(C4)	4054	1860	4177	
H(C6)	5141	589	2729	
H(C7)	5925	1153	3687	
H(N2)	3648	873	5395	
H'(N2)	3904	312	5221	

Discussion

The intramolecular bond distances and angles are listed in Table 2. The equation of the least-squares plane passing through the atoms of the benzene ring and the deviations of atoms from the plane are given in Table 3. The atoms attached to the benzene ring, S and C(1), deviate on either side of the plane, the deviations being 0·019 and −0·111 Å respectively. The sums of the

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Average C–H = 1·01 Å and average N–H = 0·96 Å.

N(1)–C(1)	1·472 (15)	C(6)–C(7)	1·384 (14)
C(1)–C(2)	1·545 (16)	C(7)–C(2)	1·428 (14)
C(2)–C(3)	1·379 (15)	C(5)–S	1·778 (10)
C(3)–C(4)	1·360 (15)	S–O(1)	1·447 (8)
C(4)–C(5)	1·378 (14)	S–O(2)	1·432 (8)
C(5)–C(6)	1·373 (14)	S–N(2)	1·631 (10)
N(1)–C(1)–C(2)	113·4 (9)	C(6)–C(7)–C(2)	119·0 (10)
C(1)–C(2)–C(3)	121·5 (10)	C(7)–C(2)–C(3)	119·6 (10)
C(1)–C(2)–C(7)	118·6 (9)	C(5)–S–O(1)	107·6 (5)
C(2)–C(3)–C(4)	119·4 (10)	C(5)–S–O(2)	107·7 (5)
C(3)–C(4)–C(5)	122·0 (10)	O(1)–S–N(2)	106·1 (5)
C(4)–C(5)–C(6)	119·8 (9)	O(2)–S–N(2)	106·6 (5)
C(4)–C(5)–S	120·5 (8)	O(1)–S–O(2)	120·0 (5)
C(6)–C(5)–S	119·6 (8)	C(5)–S–N(2)	108·5 (5)
C(5)–C(6)–C(7)	120·1 (9)		

Table 3. Equation of the least-squares plane of the benzene ring and deviations of atoms from this plane

Atoms included in the least-squares calculation are denoted by an asterisk. Equation of the plane: $0·0267X + 0·3501Y − 0·9363Z + 1·2452 = 0$ where $X = xa$, $Y = yb$, $Z = zc$.

C(1)	−0·111 (12)	*C(5)	−0·013 (10)
*C(2)	0·007 (11)	*C(6)	0·025 (10)
*C(3)	0·006 (12)	*C(7)	−0·025 (12)
*C(4)	−0·001 (11)	S	0·019 (1)

angles around C(2) (359·7°) and C(5) (359·9°), however, indicate planarity. In other 'sulfa' drugs like α-sulfanilamide (O'Connor & Maslen, 1965), β-sulfanilamide (O'Connell & Maslen, 1967), γ-sulfanilamide (Alléaume & Decap, 1965), sulfathiazole II (Kruger & Gafner, 1971), sulfisoxazole (Chatterjee, Dattagupta & Saha, 1981) and sulfaguanidine monohydrate (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976), where the attached atoms are S and N, the deviations of the attached atoms from the least-squares plane are on the same side of the plane. The exocyclic C–C distance in the present compound, C(1)–C(2) 1·545 (16) Å, agrees well with the standard C–C value of 1·542 Å (Pauling, 1960). The C(1)–N(1) distance of 1·472 (15) Å also tallies with the standard C–N bond length 1·47 Å (Pauling, 1960), but is shorter than the C–N$^+$ bond length, 1·505 Å (Hahn, 1957).

Relevant bond lengths and angles in the sulfonamide group of some 'sulfa' drugs have been compared in Table 4. The S–C(5) length of 1·778 (10) Å is seen to be the largest in the present molecule and appears to have less π character in terms of π-bonding molecular orbitals formed by the C with the 3d orbitals of the S (Cruickshank, 1961). However, the lengthening is not significant considering the relatively high standard deviation of the bond. The coordination around the S atom is also seen to be distorted from tetrahedral. The angle O–S–O is greater than the expected tetrahedral value in all the structures, while the other angles around the S atom are smaller.

The conformation of the 4-homosulfanilamide hydrochloride molecule can be described in terms of some torsion angles, listed in Table 5. The torsion angles C(3)–C(2)–C(1)–N(1) and C(6)–C(5)–S –N(2) indicate that the two N atoms in the structure are on the opposite sides of the plane passing through the benzene ring, C(1) and S, and are more or less equally inclined to the plane.

Table 4. Comparison of some bond lengths (Å) and bond angles (°) in the sulfonamide group of 'sulfa' drugs

	S–O(1)	S–O(2)	S–N(2)	C(5)–S	O(1)–S–O(2)	N(2)–S–O(1)	N(2)–S–O(2)	Reference
4-Homosulfanilamide hydrochloride	1·447 (8)	1·432 (8)	1·631 (10)	1·778 (10)	120·0 (5)	106·1 (5)	106·6 (5)	(1)
Sulfisoxazole	1·428 (4)	1·433 (4)	1·653 (3)	1·743 (5)	119·8 (2)	107·8 (2)	103·6 (2)	(2)
α-Sulfanilamide[a]	1·41	1·47	1·61	1·74	119·0	105·7	107·9	(3)
β-Sulfanilamide	1·454 (17)	1·448 (14)	1·620 (16)	1·750 (18)	118·2 (1)	105·5 (1)	107·2 (1)	(4)
γ-Sulfanilamide	1·452 (14)	1·438 (19)	1·666 (15)	1·739 (14)	117·3 (9)	106·4 (8)	107·2 (9)	(5)
Sulfathiazole II	1·444 (2)	1·435 (2)	1·589 (3)	1·759 (3)	116·6 (2)	105·4 (1)	114·1 (1)	(6)
Sulfaguanidine monohydrate[b]	1·456	1·461	1·586	1·752	115·5	114·3	105·1	(7)
Succinylsulfathiazole monohydrate	1·444 (3)	1·442 (3)	1·604 (3)	1·763 (4)	119·0 (2)	104·5 (2)		(8)

(a) The e.s.d.'s vary between 0·01 and 0·02 Å for bond distances and 0·5 and 1·5° for bond angles.
(b) The e.s.d.'s for S–X type bonds are given as $\sigma(S–X) = 0·003$ Å and $\sigma(X–S–Y) = 0·1°$.
References: (1) Present study; (2) Chatterjee, Dattagupta & Saha (1981); (3) O'Connor & Maslen (1965); (4) O'Connell & Maslen (1967); (5) Alléaume & Decap (1965); (6) Kruger & Gafner (1971); (7) Alléaume et al. (1976); (8) Rodier, Chauvet & Masse (1978).

Table 5. *Selected torsion angles* (°)

Mean standard deviation is 1·0°. Sign convention as defined by Klyne & Prelog (1960).

C(3)–C(2)–C(1)–N(1)   −115·5   C(6)–C(5)–S–O(1)   −136·6
C(6)–C(5)–S–N(2)   109·1   C(6)–C(5)–S–O(2)   −5·9

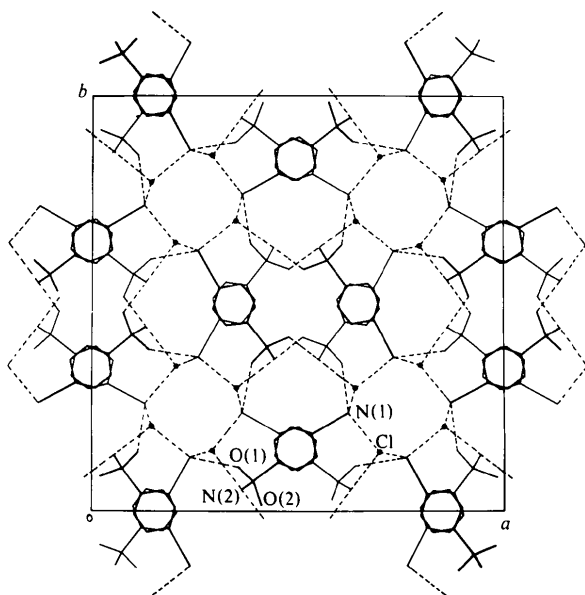Fig. 2. Crystal structure of 4-homosulfanilamide hydrochloride projected down c. H atoms are omitted. Solid circles denote chloride ions.

The projection of the structure down c is shown in Fig. 2. Probable hydrogen bonds are indicated by broken lines. The two H atoms attached to N(2) form two hydrogen bonds, $N(2)-H(N2)\cdots Cl^i$ ($-x,y,z + \frac{1}{2}$) and $N(2)-H'(N2)\cdots O(2^{ii})$ ($x, -y, z + \frac{1}{2}$) with distances 3·246 (10) and 2·869 (12) Å respectively. The angles $S-N(2)-Cl^i$ and $S-N(2)-O(2^{ii})$ are 120·9 (5) and 122·2 (5)° respectively. N(1) is expected to be protonated, with sp^3 configuration, and there are three short intermolecular distances: $N(1)\cdots Cl$ (x,y,z) = 3·147 (9), $N(1)\cdots O(1^{iv})$ ($y - \frac{1}{2}, x, z + \frac{1}{4}$) = 2·891 (11) and $N(1)\cdots Cl^{iii}$ ($y - \frac{1}{2}, -x, z - \frac{1}{4}$) = 3·303 (10) Å. Since the H atoms attached to N(1) could not be located, the angles $C(1)-N(1)\cdots Cl$ = 112·0 (6), $C(1)-N(1)\cdots O(1^{iv})$ = 88·3 (6) and $C(1)-N(1)\cdots Cl^{iii}$ = 146·1 (7)° were calculated with an assumed tetrahedral arrangement around N(1). It is seen that

though the deviation of the first two angles from the tetrahedral value is roughly within expected limits, the deviation of the last angle is rather large. The distance $N(1)-Cl^{iii}$ is also just the sum of the van der Waals radii (Pauling, 1960) for N and chloride ions. So if this short contact is to be taken as a hydrogen bond, it will be a very weak one. Considering the distance and the large deviation of the angle from the tetrahedral value, the interaction between N(1) and Cl^{iii} may also be taken to be simply electrostatic in nature.

The 4-homosulfanilamide hydrochloride molecules are roughly parallel to the *ab* plane and are almost equally tilted towards both the axes. Stacking of the molecules is such (Fig. 2) that there is a distinct overlap of aromatic rings in the z direction with an approximate average distance of 3·9 Å between them; the angle between the molecules is 109°.

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