Tableau 2. *Principales distances* (Å) *et principaux angles* (°)

S—O(1)	1,496 (3)	C(3)—C(7)	1,537 (4)
S—C(1)	1,816 (2)	C(3)—C(11)	1,539 (4)
S—C(8)	1,792 (4)	C(4)—C(5)	1,541 (4)
O(2)—C(1)	1,434 (3)	C(5)—C(6)	1,535 (3)
O(2)—C(2)	1,457 (3)	C(5)—C(9)	1,538 (4)
C(1)—C(2)	1,479 (3)	C(5)—C(10)	1,533 (4)
C(2)—C(3)	1,512 (3)	C(6)—C(1)	1,501 (3)
C(3)—C(4)	1,539 (4)		

S—C(1)—O(2)	109,5 (1)	C(4)—C(3)—C(7)	108,7 (2)
S—C(1)—C(2)	114,2 (1)	C(4)—C(3)—C(11)	113,9 (2)
S—C(1)—C(6)	117,9 (1)	C(7)—C(3)—C(11)	107,5 (2)
O(1)—S—C(1)	106,8 (1)	C(3)—C(4)—C(5)	117,8 (2)
O(1)—S—C(8)	107,0 (2)	C(4)—C(5)—C(6)	109,5 (2)
C(1)—S—C(8)	97,1 (1)	C(4)—C(5)—C(9)	108,7 (2)
C(1)—O(2)—C(2)	61,6 (2)	C(4)—C(5)—C(10)	113,2 (3)
O(2)—C(2)—C(1)	58,5 (2)	C(6)—C(5)—C(9)	107,7 (2)
C(2)—C(1)—O(2)	60,0 (2)	C(6)—C(5)—C(10)	108,7 (2)
C(1)—C(2)—C(3)	121,1 (2)	C(9)—C(5)—C(10)	108,9 (3)
O(2)·-C(2)—C(3)	116,4 (2)	C(5)—C(6)—C(1)	113,5 (2)
C(2)—C(3)—C(4)	110,9 (2)	C(6)—C(1)—O(2)	117,2 (2)
C(2)—C(3)—C(7)	108,1 (2)	C(6)—C(1)—C(2)	123,6 (1)
C(2)—C(3)—C(11)	107,5 (2)		

valeurs comprises entre 100 et 126°. L'oxygène du groupement sulfoxyde et celui du cycle époxyde sont en *anti* par rapport à la liaison S—C(1). Le groupement méthyle C(8) lié au soufre se trouvent en *cis* de l'époxyde par rapport au plan moyen du cycle cyclohexyle, le doublet libre du S est alors proche de H(1) et l'oxygène de la fonction sulfoxyde, proche de H(4). Une telle géométrie apparaît être le résultat d'un compromis entre la minimisation d'interactions stériques et de réplusions électroniques; elle engendre, en RMN ^{1}H, un système *AB* pour les deux hydrogènes H(5) et H(4) liés au carbone C(6), ainsi qu'un blindage du proton H(1) plus important que dans l'isomère (2).

Cette étude cristallographique confirme les résultats de RMN obtenus à partir des effets induits par les solvants aromatiques sur les déplacements chimiques des protons de soluté. L'identité des résultats obtenus par ces deux méthodes indique que la conformation de la molécule est la même à l'état cristallisé qu'en solution.

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Structure of a Zwitterionic Sulfonic Acid with a Dihydro-*s*-triazine Ring

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Abstract. 3-(4-Anilino-1-phenyl-1,6-dihydro-1,3,5-triazin-2-ylthio)-1-propanesulfonic acid, $C_{18}H_{20}N_4O_3S_2$, $M_r = 404.52$, monoclinic, $P2_1/c$, $a = 9.153$ (1), $b = 10.919$ (1), $c = 18.903$ (2) Å, $\beta = 96.35$ (1)°, $V = 1877.6$ (3) Å^3, $Z = 4$, $D_m = 1.428$, $D_x = 1.431$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.297$ mm^{-1}, $F(000) = 848$, room temperature, final $R = 0.058$ and $wR = 0.037$ for 3608 reflections with $I > 0$ and classed as observed [$R = 0.038$ and $wR = 0.036$ for 2811 reflections with $I > 2\sigma(I)$]. The molecule, which has a zwitterionic form, comprises a non-aromatic *s*-triazine system including a C_{sp^3} atom. The geometry around both N atoms bonded to this C atom is trigonal planar; one of the two N atoms carries a phenyl substituent, the other is protonated. The heterocycle shows a severely distorted half-boat conformation. Extensive electron delocalization is observed over four C—N bonds of the ring, and the π system extends over the exocyclic bonds connecting the —S—(CH$_2$)$_3$—SO$_3^-$ and the anilino fragments to the triazine ring. The crystal structure is made up of infinite ribbons extending along the crystallographic **b** axis; molecules within the ribbons are held together by hydrogen bonds involving only two of the O atoms of the sulfonate group.

Introduction. Faranda (1985), while analysing some additives employed in baths for bright copper electroplating, isolated a substance whose elemental composition corresponds to the chemical formula $C_{18}H_{20}N_4O_3S_2$ (found: C, 53.2; H, 5.0; N, 13.7; O, 12.4; S, 15.7%; calc.: C, 53.4; H, 5.0; N, 13.9; O, 11.9; S,

15·8%). A crystal-structure investigation was undertaken to identify the compound. No additional chemical or spectroscopic knowledge was available at the beginning of the analysis, which was part of an introductory course into single-crystal X-ray diffraction.

Experimental. Preliminary checks for crystal quality by Weissenberg photographs, from which the space group was also derived. D_m measured at room temperature by flotation in a benzene–methylene iodide solution; single prismatic crystal 0·27 mm long, with triangular base of approximately equal edges of 0·25 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from 25 reflections in the range $8\cdot4 \le \theta \le 23\cdot1°$. Intensity measurements up to $2\theta \le 55°$, by variable-rate ω-scan technique; 4726 reflections collected $(0 \le h \le 11;\ 0 \le k \le 14;\ -24 \le l \le 24)$ of which 4293 independent; $R_{int} = 0\cdot015$ from merging; 3608 with net intensity above background $(I > 0)$ classed as observed and used for refinement; observational variances $\sigma^2(I)$ based on counting statistics plus the additional term $(0\cdot02I)^2$. Three standard reflections, $13\bar{7}$, $31\bar{5}$ and 226, periodically checked; no deviation from the average intensity greater than $2\cdot5\sigma$; Lorentz and polarization, no absorption correction. Structure solved by direct methods using $350\ E > 1\cdot53$ from a reduced set of data $(2\theta \le 47°)$ for phase determination. The set with the best figure of merit gave an E map which revealed a large portion of the molecule (21 out of 27 non-H atoms). The fragment consisted of two six-membered rings joined by an atom, and an eight-atom branched side chain including the two highest peaks of the map, which were identified as S atoms; the other 19 peaks were provisionally assumed to represent C atoms. A subsequent difference map showed the remaining portion of the molecular skeleton, a third six-membered ring directly bonded to the one carrying the side chain. After a few cycles of isotropic least-squares refinement, the bond distances and angles, as well as the behaviour of the temperature factors, strongly suggested that (i) one of the S atoms was part of a sulfonate group, (ii) the three atoms separating the two S atoms were indeed C atoms, (iii) the atom connecting two of the six-membered rings was an N atom, and (iv) three of the 'C' atoms of the ring bearing the substituents were, in fact, N atoms. With the atoms identified in this way, that is in agreement with the empirical formula of the compound, three least-squares cycles of anisotropic refinement were carried out and a difference map was computed. The latter clearly indicated the positions of all 20 H atoms, and the model was complete. Final full-matrix least-squares refinement based on F; non-H atoms anisotropic, H atoms isotropic; 3608 observations and 325 variables, including a secondary-extinction coefficient [final value $= 2\cdot8\ (1)\ \times 10^{-7}$],

$w = 4F_o^2/\sigma^2(F_o^2)$; final $R = 0\cdot058$, $wR = 0\cdot037$, $S = 1\cdot42$ [$R = 0\cdot038$ and $wR = 0\cdot036$ for 2811 reflections with $I > 2\sigma(I)$]; max. $\Delta/\sigma = 0\cdot05$ for non-H atoms, $0\cdot18$ for H atoms [z of the atom H(N3)]; scattering factors and real and imaginary anomalous-dispersion corrections for neutral S, N, O and C atoms from *International Tables for X-ray Crystallography* (1974), for H atoms from Stewart, Davidson & Simpson (1965); no correlation coefficient greater than 0·46; the five highest residual peaks on the final difference map, all in the range $0\cdot25–0\cdot31\ e\ Å^{-3}$, are located midway along C–N or C–S bonds involving atoms of the triazine ring. Programs: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), *Structure Determination Package* (*SDP-Plus*) (Frenz, 1983); all computations on a PDP11/34 computer.

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, bond distances and angles involving non-H atoms in Table 2.*

As shown in Fig. 1, the compound under study is a sulfonic acid which takes the zwitterionic form. The molecule includes a trisubstituted and partially saturated s-triazine ring, where one of the N atoms, N(1), carries a phenyl substituent, and its neighbouring C atom, C(3), is in the sp^3 hybridization state; in addition, the other N atom, N(3), bonded to C(3) is protonated.

The sum (Σv) of bond angles v around N(1) is $358\cdot2\ (2)°$, that around N(3) is $357\ (1)°$; hence, in both cases the arrangement of the atoms is very close to the ideal, planar trigonal geometry.

The triazine ring is non-planar: four out of the six atoms deviate by more than $0\cdot1\ Å$ from the least-squares plane through the ring, the largest deviation being shown by atom C(3), which is away from the plane by $\sim 0\cdot25\ Å$. Exclusion of the last atom from the least-squares calculation leads to a plane from which the largest deviation [$\sim 0\cdot05\ Å$, now shown by atom C(1)], although greatly reduced, is still indicative of significant non-coplanarity of the five atoms. In fact, the heterocycle shows a severely distorted half-boat conformation with the 'flap' at C(3). Puckering parameters (Cremer & Pople, 1975) $Q = 0\cdot354\ (2)\ Å$, $\varphi = 6\cdot8\ (3)°$ and $\theta = 64\cdot2\ (3)°$ qualify the distortion as occurring in the direction of a boat conformation: indeed, an ideal half-boat requires values of $\varphi = 0°$ and $\theta = 54\cdot7°$, while a pure boat conformation has $\varphi = 0°$ and $\theta = 90°$. Therefore, the ring is folded about the line

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* Lists of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43632 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent iso-tropic thermal parameters with e.s.d.'s in parentheses*

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

	x	y	z	$B_{eq}(\text{Å}^2)$
S(1)	0·11977 (6)	−0·01373 (4)	0·89660 (3)	3·23 (1)
S(2)	0·29987 (6)	−0·35800 (4)	1·04151 (3)	3·05 (1)
O(1)	0·1454 (2)	−0·3550 (2)	1·0477 (1)	5·83 (4)
O(2)	0·3303 (2)	−0·3878 (1)	0·96971 (7)	4·88 (4)
O(3)	0·3815 (2)	−0·4366 (1)	1·09360 (8)	4·78 (4)
N(1)	0·1565 (2)	0·2181 (1)	0·86646 (7)	2·62 (3)
N(2)	0·2155 (2)	0·1627 (1)	0·98648 (8)	2·64 (3)
N(3)	0·2704 (2)	0·3597 (1)	0·94830 (8)	3·29 (3)
N(4)	0·3401 (2)	0·3024 (1)	1·06338 (8)	3·01 (3)
C(1)	0·1699 (2)	0·1365 (2)	0·91955 (9)	2·40 (3)
C(2)	0·2725 (2)	0·2755 (2)	0·99930 (9)	2·55 (4)
C(3)	0·1649 (2)	0·3480 (2)	0·8868 (1)	3·24 (4)
C(11)	0·3704 (2)	0·2252 (2)	1·12375 (9)	2·77 (4)
C(12)	0·2794 (2)	0·1308 (2)	1·1399 (1)	3·80 (5)
C(13)	0·3132 (3)	0·0636 (2)	1·2013 (1)	4·76 (5)
C(14)	0·4358 (3)	0·0911 (2)	1·2474 (1)	5·15 (6)
C(15)	0·5241 (3)	0·1867 (3)	1·2319 (1)	5·22 (6)
C(16)	0·4928 (2)	0·2539 (2)	1·1701 (1)	4·02 (5)
C(21)	0·1005 (2)	0·1882 (2)	0·79451 (9)	2·63 (4)
C(22)	−0·0340 (2)	0·2353 (2)	0·7662 (1)	3·73 (5)
C(23)	−0·0862 (3)	0·2065 (2)	0·6964 (1)	4·82 (5)
C(24)	−0·0068 (3)	0·1324 (2)	0·6566 (1)	4·90 (5)
C(25)	0·1252 (3)	0·0854 (2)	0·6852 (1)	4·47 (5)
C(26)	0·1816 (2)	0·1151 (2)	0·7540 (1)	3·36 (4)
C(31)	0·1674 (2)	−0·0952 (2)	0·9792 (1)	2·77 (4)
C(32)	0·3298 (2)	−0·1199 (2)	0·9957 (1)	3·21 (4)
C(33)	0·3675 (2)	−0·2063 (2)	1·0577 (1)	3·27 (4)

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

S(1)—C(1)	1·745 (2)	C(11)—C(12)	1·380 (3)
S(1)—C(31)	1·808 (2)	C(11)—C(16)	1·380 (2)
S(2)—O(1)	1·432 (2)	C(12)—C(13)	1·379 (3)
S(2)—O(2)	1·452 (1)	C(13)—C(14)	1·376 (3)
S(2)—O(3)	1·450 (1)	C(14)—C(15)	1·371 (4)
S(2)—C(33)	1·783 (2)	C(15)—C(16)	1·382 (3)
N(1)—C(1)	1·337 (2)	C(21)—C(22)	1·386 (3)
N(1)—C(3)	1·469 (2)	C(21)—C(26)	1·378 (3)
N(1)—C(21)	1·437 (2)	C(22)—C(23)	1·389 (3)
N(2)—C(1)	1·319 (2)	C(23)—C(24)	1·367 (3)
N(2)—C(2)	1·349 (2)	C(24)—C(25)	1·368 (4)
N(3)—C(2)	1·331 (2)	C(25)—C(26)	1·384 (3)
N(3)—C(3)	1·432 (2)	C(31)—C(32)	1·509 (3)
N(4)—C(2)	1·331 (2)	C(32)—C(33)	1·514 (3)
N(4)—C(11)	1·421 (2)		

C(1)—S(1)—C(31)	102·5 (1)	N(4)—C(11)—C(12)	123·5 (2)
O(1)—S(2)—O(2)	112·0 (1)	N(4)—C(11)—C(16)	116·6 (2)
O(1)—S(2)—O(3)	113·4 (1)	C(12)—C(11)—C(16)	119·8 (2)
O(2)—S(2)—O(3)	111·4 (1)	C(11)—C(12)—C(13)	119·9 (2)
O(1)—S(2)—C(33)	107·0 (1)	C(12)—C(13)—C(14)	120·5 (2)
O(2)—S(2)—C(33)	105·6 (1)	C(13)—C(14)—C(15)	119·3 (2)
O(3)—S(2)—C(33)	106·9 (1)	C(14)—C(15)—C(16)	120·8 (2)
C(1)—N(1)—C(3)	116·7 (1)	C(11)—C(16)—C(15)	119·6 (2)
C(1)—N(1)—C(21)	123·5 (1)	N(1)—C(21)—C(22)	119·3 (2)
C(3)—N(1)—C(21)	118·0 (1)	N(1)—C(21)—C(26)	120·0 (2)
C(1)—N(2)—C(2)	116·4 (2)	C(22)—C(21)—C(26)	120·7 (2)
C(2)—N(3)—C(3)	118·7 (1)	C(21)—C(22)—C(23)	118·7 (2)
C(2)—N(4)—C(11)	129·0 (2)	C(22)—C(23)—C(24)	120·6 (2)
N(1)—C(1)—N(2)	124·6 (2)	C(23)—C(24)—C(25)	120·3 (2)
S(1)—C(1)—N(1)	116·1 (1)	C(24)—C(25)—C(26)	120·3 (2)
S(1)—C(1)—N(2)	119·3 (1)	C(21)—C(26)—C(25)	119·3 (2)
N(2)—C(2)—N(3)	121·8 (2)	S(1)—C(31)—C(32)	113·8 (1)
N(2)—C(2)—N(4)	119·8 (2)	C(31)—C(32)—C(33)	114·0 (2)
N(3)—C(2)—N(4)	118·4 (2)	S(2)—C(33)—C(32)	113·6 (1)
N(1)—C(3)—N(3)	108·0 (2)		

C(3)···N(2), and the folding can be described by the dihedral angle, 10·1 (1)°, between the least-squares plane through atoms C(1), N(1), N(2) and S(1) (plane A), and that through atoms C(2), N(2), N(3) and N(4) (plane B). The four atoms defining the first plane are coplanar within 0·006 Å (~3σ), and this maximum displacement occurs for atom C(1); a larger deviation, up to 0·052 (2) Å, is shown by the phenyl ring atom C(21), not included in the least-squares calculation. A less strict coplanarity is observed for the four atoms of plane B: the three N atoms deviate by the same amount, 0·006 (2) Å, on one side of the plane, while atom C(2) is displaced, on the other side, by 0·019 (2) Å; the two H atoms bonded to N(3) and N(4) lie in the plane within 0·03 (2) Å, while atom C(11) is 0·125 (2) Å away. The geometry around the atom N(4) is strictly trigonal planar, $\sum\nu$ being 360 (1)°, and the N atom deviates by 0·064 (1) Å from the plane of the benzene ring to which it is bonded.

The six C atoms of the phenyl ring bonded to N(1) are coplanar within 0·013 Å (~6σ); this plane makes a dihedral angle of 67·4 (1)° with plane A, while the other phenyl ring, where atoms are displaced by no more than 0·009 Å (~3σ) from the corresponding least-squares plane, forms a dihedral angle of 28·0 (1)° with plane B. Concomitantly with the different extent of rotation of the two phenyl groups with respect to the central portion of the three-ring system, we notice that the C(21)—N(1) bond is slightly but significantly longer than the C(11)—N(4) bond: this implies that the double-bond character, although small, of the latter bond is more pronounced than that of the former.

The length of the bond C(3)—N(1), 1·469 (2) Å, is virtually coincident with that, 1·47 Å, commonly assumed for a pure C—N single bond, while the value of the C(3)—N(3) bond distance, 1·432 (2) Å, corresponds to a bond order (Jenkins, 1955) of 1·19. The other four
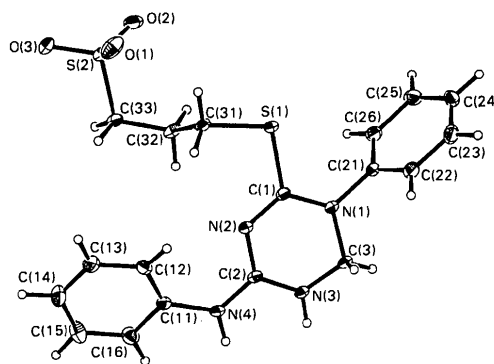

Fig. 1. A view of the molecule along a principal axis of inertia, with the numbering scheme. H atoms, unlabelled, were numbered according to the heavy atom to which they are bonded. Thermal ellipsoids (*ORTEP*; Johnson, 1970) for non-H atoms are drawn at a probability of 0·20; H atoms, treated as isotropic, are on an arbitrary scale.

C—N bonds of the triazine ring have lengths in the range 1·319 (2)–1·349 (2) Å, corresponding to bond orders in the range 1·80–1·62, respectively. This indicates that the π electrons of the ring system are widely delocalized, although the two smallest values among the four bond distances, 1·319 (2) and 1·331 (2) Å, are observed for the bonds that would be drawn as formally double in structural diagrams, i.e. C(1)–N(2) and C(2)–N(3), respectively. The exocylic bond C(2)–N(4), 1·331 (2) Å long, is definitely involved in the delocalization, the corresponding bond order being 1·73. The π system extends also over the other exocyclic bond, C(1)–S(1), where the interatomic distance, 1·745 (2) Å, is to be compared with the values 1·81 and 1·71 Å for a single and a double C—S bond, respectively (Kennard, 1962).

The values of the internal bond angles of the heterocyclic six-membered ring are significantly different with respect to those usually found in aromatic s-triazines. Apart from the expected narrowing of the bond angle at C(3), we notice that the three bond angles at the N atoms here measured [116·4 (2) at N(2), 116·7 (1) at N(1), and 118·7 (1)° at N(3)] are remarkably larger than those of s-triazine, 113·4 (2)° (Coppens, 1967; Mo data), hexamethylmelamine (HMML), 112·7 (5)° (Bullen, Corney & Stephens, 1972), trihydrazinotriazine (THT), 113 (1)° (mean value) (Brown, Lee & Russell, 1976), and melamine (ML), 115·1 (2)° (Larson & Cromer, 1974) or 114·6 (2)° (Varghese, O'Connell & Maslen, 1977) (mean values). On the other hand, in another substituted s-triazine, where protonation occurs at an N atom as in the present case, namely 2,4-bis(iso-propylamino)-6-methoxy-1,3,5-triazine perchlorate (BIMT) (Kutschabsky, Kretschmer, Kircheiss & Bauwe, 1981), the C—N—C bond angle (v_1) at the protonated N atom has a value, 118·6 (2)°, coincident with that observed for C(3)–N(3)–C(2) within experimental uncertainty. Furthermore, in BIMT one of the two N—C—N bond angles next to v_1 has a value of 121·4 (3)°, again almost coincident with that of N(3)–C(2)–N(2) in our sulfonic acid, and greatly different from the values observed for this class of bond angle in s-triazine [126·8 (4)°], HMML [127·3 (5)°], THT [127 (1)°, mean value], and ML [125·6 (1) and 125·4 (1)°, mean values]. The conclusion can apparently be drawn that not only are the presence of a C_{sp^3} atom in the triazine system and the non-planarity of the ring responsible for the observed changes of the geometry, but also the protonation at an N atom seems to be a relevant factor.

There are some other noteworthy angular deformations in the molecule: (i) the enlargement of the bond angle C(2)–N(4)–C(11) to 129·0 (2)°, a means to relieve too short intramolecular contacts between atom N(2) and the benzene ring of the anilino substituent: the two N(2)···C(11) and N(2)···C(12) distances are

2·897 (2) and 2·915 (2) Å, respectively, and the N(2)···H(12) separation amounts to 2·41 (2) Å; (ii) the less marked deformations of the external ring angles at N(1), where the value of 123·5 (1)° for the bond angle C(1)–N(1)–C(21) is larger, by more than 5°, than that of the bond angle C(3)–N(1)–C(21); again, this geometry helps to relieve overcrowding, atoms S(1) and C(21) being only 2·923 (2) Å apart. This interaction could be weakened also by enlarging the bond angle N(1)–C(1)–S(1), which is, in contrast, narrower than its neighbouring angle S(1)–C(1)–N(2) by more than 3°: clearly, the observed geometry is dictated by the concomitant need of easing two other short intra-molecular contacts, N(2)···C(31), 2·851 (2) Å, and N(2)···H(31)B, 2·56 (2) Å.

The $-S-(CH_2)_3-SO_3^-$ fragment exhibits bond distances and angles which are in good agreement with those found in other substituted propanesulfonic acids [see, for example, Kim, Wakahara, Fujiwara & Tomita (1973a,b, and references therein)]. The bond S(2)–O(1) appears rather short, but the extensive thermal motion of atom O(1) (see Table 1 and Fig. 1), compared with that of the other two O atoms which are engaged in hydrogen bonds, makes the observed difference perhaps only marginally significant.

The conformation of the skeleton of the chain, defined by the two torsion angles S(1)–C(31)–C(32)–C(33), –170·1 (1)°, and C(31)–C(32)–C(33)–S(2), 65·5 (2)°, is such as to bring the sulfonate group of one molecule into the proximity of the two –NH groups of the adjacent molecule at x, $1 + y$, z. As seen in Fig. 2, infinite ribbons running along **b**, and composed of molecules held together by NH···O hydrogen bonds, are thus formed. The phenyl rings, which constitute the outer portion of the ribbons, all extend along **c**; the polar regions of adjacent ribbons are thus separated, in this direction, by sheets of apolar molecular fragments. There is only one short contact between molecules of
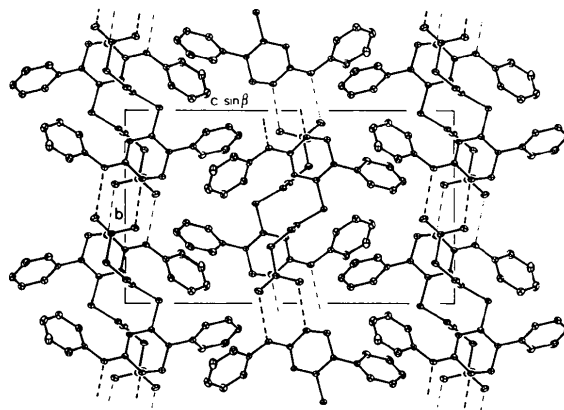

Fig. 2. Packing of the molecules as viewed along **a**.

different ribbons, $O(1)\cdots H(3)A$ (at $-x$, $-y$, $2-z$), $2\cdot27$ (2) Å. The geometry of the hydrogen bonds is as follows: $N(3)\cdots O(2)$, $2\cdot831$ (2), $H(N3)\cdots O(2)$, $2\cdot04$ (2) Å, $N(3)-H(N3)\cdots O(2)$, 164 (2)°; $N(4)\cdots O(3)$, $2\cdot923$ (2), $H(N4)\cdots O(3)$, $2\cdot09$ (2) Å, $N(4)-H(N4)\cdots O(3)$, 161 (2)°.

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Structures of 1,4-Bis(trichloromethyl)benzene (I) and 6-Nitro-2,4-bis(trichloromethyl)-benzo-1,3-dioxin (II)

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Abstract. (I): $C_8H_4Cl_6$, $M_r = 312\cdot8$, triclinic, $P\bar{1}$, $a = 10\cdot402$ (5), $b = 14\cdot790$ (4), $c = 5\cdot944$ (1) Å, $\alpha = 98\cdot72$ (2), $\beta = 82\cdot69$ (2), $\gamma = 102\cdot25$ (2)°, $V = 879\cdot0$ (5) Å^3, $Z = 3$, $D_m = 1\cdot778$ (9), $D_x = 1\cdot773$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot40$ mm^{-1}, $F(000) = 462$, $T = 298$ K, $R = 0\cdot065$ for 3247 observed reflections. (II): $C_{10}H_5Cl_6NO_4$, $M_r = 415\cdot9$, triclinic, $P\bar{1}$, $a = 7\cdot694$ (2), $b = 15\cdot231$ (3), $c = 6\cdot620$ (1) Å, $\alpha = 99\cdot42$ (2), $\beta = 90\cdot50$ (1), $\gamma = 91\cdot58$ (2)°, $V = 765\cdot0$ (3) Å^3, $Z = 2$, $D_m = 1\cdot769$ (8), $D_x = 1\cdot806$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot11$ mm^{-1}, $F(000) = 412$, $T = 298$ K, $R = 0\cdot062$ for 3870 reflections. The Cl–C–Cl and C–C–Cl angles of the CCl_3 groups in (I) deviate significantly from the tetrahedral angle, while those in (II) are close to it. In (I), the intermolecular distance of $3\cdot407$ (3) Å for $Cl(15)\cdots Cl(23)$ is shorter than twice the van der Waals radius. In (II), the $C(11)Cl_3$ and $C(12)Cl_3$ groups are respectively equatorial and axial to the dioxin ring, which has a distorted half-boat conformation.

Introduction. Both title compounds are characterized by their unique polymorphism. The stable phase of (I) (m.p. 383 K) and that of (II) (m.p. 375 K) show nine and six ^{35}Cl NQR signals at 77 K respectively (Hashimoto, 1977; Hashimoto, Adachi & Mano, 1986). These results indicate that the asymmetric unit of crystal (I) contains three crystallographically independent CCl_3 groups and that of (II) two.

Interestingly these signals show the so-called fade-out phenomenon: NQR signals become broader and broader with increasing temperature and above a