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2,4,6-Triisopropylbenzenesulfonamide: Monte Carlo structure solution from X-ray powder diffraction data for a molecular system containing four independent asymmetric rotors

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Abstract

The crystal structure of 2,4,6-triisopropylbenzenesulfonamide, $C_{15}H_{25}NO_2S$, has been solved from X-ray powder diffraction data collected at 120 (1) K using synchrotron radiation and refined by Rietveld methods. The structure was solved by the application of a Monte Carlo method in which trial structures were generated by random movement of the molecule in the unit cell and assessed using a full-profile-fitting technique. Intramolecular flexibility was introduced into the structure solution in the form of four independent asymmetric rotors, allowing the isopropyl and sulfonamide groups to rotate freely within the molecule. The structure is monoclinic $P2_1/c$, a = 16.9600 (6), b = 8.1382 (2), c = 11.7810 (2) Å, β = 104.777 (2)° with Z = 4. The molecules are linked by N—H···O hydrogen bonds, with N···O distances of 2.77 (1) and 2.92 (1) Å, into two-dimensional sheets built from $R_2^2(8)$ and $R_6^6(20)$ rings.

1. Introduction

In organic molecular crystals, hydrogen bonds often constitute the strongest intermolecular synthon (Desiraju, 1995), and hence often dictate the preferred packing arrangement of the molecules. The general principles underlying the formation of hydrogen bonds are reasonably well understood, and the structures of hydrogen-bonded crystals can often be rationalized and codified in terms of preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990; Etter *et al.*, 1990). There are at present few, if any, reliable methods for the prediction of hydrogen-bonding patterns in specific systems, although some progress is being made in the enumeration of the general principles underlying the packing of arbitrarily shaped molecules (Brock & Dunitz, 1994). In general, however, the detailed description of hydrogen-bonding patterns in a given system must be derived from analysis of specific experimental data. Where crystals are available of a size and quality suitable for single-crystal X-ray or neutron diffraction, these techniques remain the method of choice. Where no such material is available, resort must generally be made to X-ray powder diffraction.

While the use of X-ray powder diffraction for *ab initio* structure solution of inorganic materials (Poojary & Clearfield, 1997) and coordination compounds (Masciocchi & Sironi, 1997) is now fairly well established, its use in structure determination of purely organic molecular solids is less common (Harris & Tremayne, 1996). Although traditional approaches to crystal structure solution have met with limited success when applied to these systems, considerable advances have been made in the application of direct space methods of structure solution to molecular crystals (Harris *et al.*, 1994; Tremayne *et al.*, 1997*a*; Andreev *et al.*, 1997; Kariuki *et al.*, 1997; David *et al.*, 1998; Shankland *et al.*, 1998). These methods approach structure solution from powder diffraction data by postulation of trial crystal structures independently of the diffraction data using global optimization techniques, and assessment of these structural models by comparison between the corresponding calculated diffraction pattern and the experimental diffraction data.

In a previous paper we reported the *ab initio* structure determination of three sulfonylamino compounds, using X-ray powder diffraction data collected using a conventional laboratory powder diffractometer (Lightfoot *et al.*, 1993). While the structures of 4-toluenesulfonamide, $CH_3C_6H_4SO_2NH_2$, benzenesulfonylhydrazine, $C_6H_5SO_2NHNH_2$, and 4-toluenesulfonylhydrazine, $CH_3C_6H_4SO_2NHNH_2$, were all readily solved using such data, the corresponding ambient-temperature data for 2,4,6-triisopropylbenzenesulfonamide $(Me_2CH)_3C_6H_2SO_2NH_2$, allowed indexing on the basis of the monoclinic cell a = 17.01, b = 8.26, c = 11.90 Å, β = 104.7°, but attempts at structure solution by traditional methods were unsuccessful. We have now collected a new data set for 2,4,6-triisopropylbenzenesulfonamide (I) (see Fig. 1), using synchrotron X-ray radiation and a sample temperature of 120 K, and we report here the structure solution and refinement.

2. Experimental

2.1. *Crystal data*

$C_{15}H_{25}NO_2S$, M_r = 283.42, monoclinic $P2_1/c$, a = 16.9600 (6), b = 8.1382 (2), c = 11.7810 (2) Å, β =

104.777 (2)°, V = 1572.3 (1) Å^3, Z = 4, D_x = 1.20 g cm^{-3}, λ = 1.3000 Å, $F(000)$ = 616, T = 120 (1) K.

2.2. *Data collection*

The initial data set was collected at room temperature using a Stoe STADI/P powder diffractometer with Ge-monochromated Cu $K\alpha_1$ radiation (λ = 1.5405 Å); this data set allowed the correct identification of the monoclinic unit cell, but insufficient intensity data could be extracted to permit structure solution. Accordingly, a second data set was collected using the high-resolution powder diffractometer at station 2.3 of the Synchrotron Radiation Source, Daresbury Laboratory. The sample was loaded into a 0.5 mm capillary to a depth of approximately 3 cm and the X-ray powder diffraction data were recorded in the range $3 < 2\theta < 50°$ in 0.01° steps and with a count time of 5 s per step. The wavelength of X-rays used was 1.3000 Å and the beam size was 1.0 × 10 mm^2. The data were collected at a temperature of 120 (1) K. It should be noted that a large amount of ice formed on the capillary and contributed some peaks to the diffraction pattern (Bertie *et al.*, 1963).

3. Structure solution and refinement

The powder pattern was indexed using the program *TREOR* (Werner *et al.*, 1985) on the basis of the first 23 observable reflections. This gave the unit cell a = 16.9832, b = 8.1345, c = 11.7905 Å and β = 104.80°. From the systematic absences the space group was assigned unambiguously as $P2_1/c$.

Structure solution was carried out using the Monte Carlo method implemented in the program *OCTOPUS* (Tremayne *et al.*, 1997*b*). The structural model used in the Monte Carlo calculation comprised the complete molecule (I), excluding the methyl H atoms, and was constructed using standard bond lengths and angles. For the purposes of the structure solution calculation, the N atom was entered as an O atom and considered equivalent to the other O atoms in the sulfonamide group as there would be no significant discrimination between these atoms at this point. The benzene ring was maintained as a rigid body and the three isopropyl groups and the sulfonamide group allowed to rotate freely within the molecule, as shown in Fig. 1.

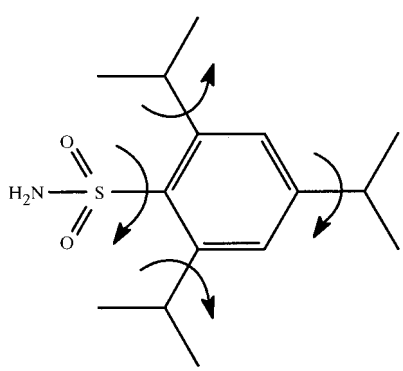

Fig. 1. Schematic representation of (I) showing the structural fragment used in the Monte Carlo calculation together with the internal rotations permitted in the structure solution.

In generating trial structures under the Monte Carlo algorithm, translation and rotation of the structural fragment within the unit cell was carried out simultaneously with the intramolecular rotations. The initial position, orientation and intramolecular geometry of the structural fragment were chosen arbitrarily, and the random movement of the molecule in each Monte Carlo move constrained such that the maximum displacement in any of the (x, y, z) coordinates (in an orthogonal reference frame) was 0.5 Å and the maximum rotation of the molecule about three mutually perpendicular axes was ±45°. The maximum rotation allowed around each bond used as a rotor for intramolecular rotation was also ±45° per move. The scale factor functioning analogous to temperature in conventional Monte Carlo techniques was fixed giving a 40.9% acceptance of trial structures close to the optimum (*ca* 40%; Rao *et al.*, 1979). The calculation was carried out for a total of 200 000 Monte Carlo moves and R_{wp} for the trial structures calculated over the data range $3 < 2\theta < 40°$. The peaks in the diffraction pattern arising from ice formed on the capillary were excluded from both the Monte Carlo calculation and the subsequent Rietveld refinement. The best structure solution (that with the lowest R_{wp}) corresponded to an R_{wp} value of 0.301, whereas the R_{wp} was typically 0.47–0.61 for most random structures sampled in the Monte Carlo calculation.

The best structure solution generated in the Monte Carlo calculation was then taken as the starting model for Rietveld refinement using the *GSAS* program package (Larson & Von Dreele, 1987). The positions of all atoms were refined subject to soft geometrical restraints (weighting factor of 0.01 on bond distances and 0.02 on geminal non-bonded distances) on standard geometry and the methyl H atoms were added to the molecule in positions consistent with standard geometry. Initially, all bonds in the sulfonamide group were treated equally and restrained to be 1.43 Å, but as the refinement progressed one of the bonds tended to become significantly longer than the other two. This longer bond was assigned as S—NH_2 and subsequently restrained according to the new atom-type assignment. For the non-H atoms, isotropic atomic displacement parameters were refined, but constrained according to atom type or environment, *i.e.* S, O or N; aromatic, propyl (*C*HMe_2) or methyl C. For the H atoms, one common isotropic atomic displacement parameter was used for the methyl H atoms and another for the remaining H atoms bonded to C, but neither was refined. The amino H atoms were placed in positions calculated from the coordinates of

Table 1. *Fractional atomic coordinates and isotropic displacement parameters (Å²) for the refined crystal structure of (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.0849 (5)	0.3869 (9)	0.6677 (6)	0.072 (4)
C1	0.186 (1)	0.481 (3)	0.709 (2)	0.039 (4)
C2	0.199 (1)	0.627 (3)	0.647 (2)	0.039 (4)
C3	0.274 (1)	0.705 (2)	0.686 (2)	0.039 (4)
C4	0.337 (1)	0.634 (2)	0.773 (2)	0.039 (4)
C5	0.323 (1)	0.497 (3)	0.834 (1)	0.039 (4)
C6	0.247 (1)	0.414 (3)	0.798 (2)	0.039 (4)
C7	0.1306 (7)	0.715 (1)	0.551 (1)	0.064 (6)
C8	0.4210 (9)	0.723 (1)	0.811 (1)	0.064 (6)
C9	0.2456 (6)	0.241 (2)	0.857 (1)	0.064 (6)
O1	0.0724 (8)	0.349 (2)	0.550 (1)	0.046 (5)
O2	0.0771 (8)	0.265 (2)	0.741 (1)	0.046 (5)
N1	0.0199 (9)	0.540 (2)	0.681 (1)	0.017 (7)
C71	0.1659 (9)	0.715 (2)	0.447 (1)	0.063 (4)
C72	0.1057 (8)	0.876 (2)	0.593 (1)	0.063 (4)
C81	0.4853 (9)	0.625 (2)	0.775 (1)	0.063 (4)
C82	0.4501 (9)	0.759 (2)	0.940 (1)	0.063 (4)
C91	0.2575 (9)	0.265 (2)	0.985 (1)	0.063 (4)
C92	0.3061 (9)	0.123 (2)	0.830 (1)	0.063 (4)
H3	0.285 (4)	0.824 (9)	0.647 (9)	0.05
H5	0.364 (4)	0.465 (9)	0.920 (6)	0.05
H7	0.079 (1)	0.630 (2)	0.535 (2)	0.05
H8	0.412 (1)	0.840 (2)	0.762 (2)	0.05
H9	0.183 (1)	0.195 (3)	0.818 (2)	0.05
H711	0.166 (7)	0.589 (3)	0.414 (7)	0.07
H712	0.128 (5)	0.794 (9)	0.378 (5)	0.07
H713	0.228 (3)	0.763 (9)	0.472 (4)	0.07
H721	0.159 (3)	0.960 (6)	0.613 (9)	0.07
H722	0.056 (6)	0.930 (8)	0.524 (5)	0.07
H723	0.084 (7)	0.856 (4)	0.672 (6)	0.07
H811	0.467 (4)	0.495 (3)	0.768 (9)	0.07
H812	0.492 (6)	0.670 (9)	0.690 (6)	0.07
H813	0.543 (2)	0.638 (9)	0.842 (6)	0.07
H821	0.477 (6)	0.648 (4)	0.987 (2)	0.07
H822	0.496 (4)	0.858 (8)	0.954 (2)	0.07
H823	0.398 (2)	0.799 (9)	0.974 (3)	0.07
H911	0.198 (1)	0.277 (9)	1.006 (2)	0.07
H912	0.290 (6)	0.159 (7)	1.033 (2)	0.07
H913	0.293 (6)	0.377 (8)	1.014 (3)	0.07
H921	0.294 (6)	−0.001 (3)	0.859 (9)	0.07
H922	0.301 (6)	0.123 (9)	0.735 (2)	0.07
H923	0.368 (1)	0.160 (9)	0.877 (9)	0.07
H1	0.018	0.579	0.761	†
H2	−0.008	0.605	0.610	†

† The coordinates of H1 and H2 were calculated from those of N1 and the neighbouring oxygen atoms O1^{i} and O2^{ii}. Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$ (see text).

the hydrogen-bond donor and acceptors, but these H atoms had no effect whatsoever on the refinement.

The final Rietveld refinement using the profile over the range $3 < 2\theta < 50^\circ$ gave agreement factors R_{wp} = 0.0705, R_p = 0.0497 and R_{F^2} = 0.0997 for 517 reflections, 143 refined parameters, 120 geometrical restraints and the refined unit cell a = 16.9600 (6), b = 8.1382 (2), c = 11.7810 (2) Å, β = 104.777 (2)°. The final Rietveld plot for (I) is shown in Fig. 2 and the final refined structure is shown in Fig. 3. Positional and displacement parameters are given in Table 1, and selected bond distances and angles including important intermolecular distances listed in Table 2.†

In Fig. 4 the structure solution obtained from the Monte Carlo calculation is compared with the final refined crystal structure of (I). The mean distance between corresponding atoms in the two structures ranges from 0.19 Å for the S atom to 0.97 Å for one of the isopropyl H atoms. It is clear that the Monte Carlo approach has located a molecular position close to the true position in the crystal structure and that the orientations of the isopropyl groups relative to the ring (defined using the intramolecular rotors in the Monte Carlo calculation) have also been resolved in the structure solution.

The initial room-temperature data set collected using a laboratory X-ray source could be indexed, but the structure could not be determined using these data. The synchrotron data were collected at 120 (1) K and this raises the possibility that the attempted structure solution at room temperature may have been hampered by the occurrence of intramolecular rotations at room temperature. While rotation of the sulfonamido group about the C—S bond is unlikely because of the hydrogen bonding, rotation of the isopropyl groups about the C(aryl)—$CHMe_2$ bonds seemed plausible. However, solid-state CP-MAS NMR investigations have shown that while intramolecular rotation of —CMe_3 groups, and of the isosteric —NMe_3^+, are very common, the analogous rotations of —$CHMe_2$ and —NMe_2^+ groups are not observed (Riddell & Rogerson, 1996, 1997). Hence we rule out any possibility of any intramolecular motion in (I), even at room temperature, and conclude that it is a combination of the superior resolution of the synchrotron data and the application of improved structure solution software which has now permitted structure determination.

4. Description of the structure

4.1. *Molecular dimensions and conformation*

The structure of (I) is built from discrete molecules (Fig. 3) linked together by N—H···O hydrogen bonds. It is instructive to compare the refined bond lengths with those obtained for molecules of similar type in refinements using powder X-ray diffraction data (Lightfoot *et al.*, 1993) or single-crystal X-ray diffraction (Ferguson & Glidewell, 1988; Ferguson *et al.*, 1989), as well as those obtained from analysis (Allen *et al.*, 1987) of information in the Cambridge Structural Database (CSD; Allen & Kennard, 1993). The refinements from powder data, whether collected using a conventional laboratory X-ray source or using synchrotron radiation, generally lead to

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG0009). Services for accessing these data are described at the back of the journal.

Table 2. *Selected bond distances (Å), including intermolecular distances, and angles (°) involving the non-H atoms in the refined crystal structure of (I)*

S1—O1	1.38 (1)	C7—C71	1.494 (7)
S1—O2	1.34 (1)	C7—C72	1.499 (7)
S1—N1	1.70 (1)	C8—C81	1.497 (7)
S1—C1	1.83 (1)	C8—C82	1.502 (7)
C2—C7	1.57 (1)	C9—C91	1.484 (7)
C4—C8	1.56 (1)	C9—C92	1.497 (7)
C6—C9	1.57 (2)		
O1—S1—O2	117 (1)	C3—C4—C8	119 (1)
O1—S1—N1	109 (1)	C5—C4—C8	119 (1)
O1—S1—C1	105 (1)	C2—C7—C71	102 (1)
O2—S1—N1	108 (1)	C2—C7—C72	112 (1)
O2—S1—C1	112 (1)	C71—C7—C72	118 (1)
N1—S1—C1	105 (1)	C4—C8—C81	110 (1)
S1—C1—C2	118 (1)	C4—C8—C82	115 (1)
S1—C1—C6	120 (1)	C81—C8—C82	108 (1)
C1—C2—C7	124 (1)	C6—C9—C91	109 (1)
C3—C2—C7	118 (1)	C6—C9—C92	113 (1)
C1—C6—C9	126 (1)	C91—C9—C92	112 (1)
C5—C6—C9	114 (1)		
C1—C2—C7—C71	−123 (1)	C1—C2—C7—C72	109 (1)
C3—C4—C8—C81	−113 (1)	C3—C4—C8—C82	124 (1)
C1—C6—C9—C91	−122 (1)	C1—C6—C9—C92	113 (1)
C2—C1—S1—O1	59 (1)	C2—C1—S1—O2	−172 (1)
C2—C1—S1—N1	−55 (1)		
N1···O1^{i}	2.92 (1)	N1···O2^{ii}	2.77 (1)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$.

S—N and S—C distances significantly longer than those obtained from refinements with data collected using single crystals. The values of these distances found for (I) (Table 2) are very similar to those found for $PhSO_2NHNH_2$ from powder data (Lightfoot *et al.*, 1993), but should be compared with S—C distances of 1.760 (3) and 1.770 (3) Å found from single-crystal data for toluenesulfonamide and benzenesulfonamide in adducts with Ph_3PO and Ph_3AsO, respectively (Ferguson & Glidewell, 1988; Ferguson *et al.*, 1989), and with S—N distances of 1.597 (2) and 1.598 (3) Å, respectively, in the same two adducts. On the other hand, the S—O distances in (I) are somewhat shorter than those found in these adducts [range 1.426 (2)–1.433 (2) Å; mean 1.428 Å]. However, the bond angles around sulfur in (I) show no unusual features and, in particular, the O—S—O angle is significantly greater than tetrahedral, as typically found in RSO_2R' systems.

The exocyclic bond angles at C2 and C6, although not at C4, show slight deviations from 120°; the large angles at C2 and C6 *cisoid* to the sulfonamido substituent are probably connected to the overall molecular conformation. At the same time, the conformation of all the isopropyl groups is such that the C—H bonds at C7, C8 and C9 all lie approximately parallel to the plane of the aryl ring, with the methyl substituents at C7 and C9 remote from the sulfonamido group (Table 2). These features together are indicative of repulsive interactions between the isopropyl groups at C2 and C6 and the sulfonamido group. This conformation of the three independent isopropyl groups appears to be the norm for 2,4,6-triisopropyl species $(Me_2CH)_3C_6H_2X$, regardless of the identity of the α-atoms in the substituent X (Sigel & Power, 1987; Bartlett *et al.*, 1990; Du Mont *et al.*, 1990; Driess *et al.*, 1991; Archibald *et al.*, 1992; Du Mont *et al.*, 1992; Archibald *et al.*, 1993; Petrie *et al.*, 1993; Wehmschulte *et al.*, 1994; Mishra *et al.*, 1995; Tokitoh *et al.*, 1995; Fu *et al.*, 1997; Fukushima *et al.*, 1998). In nearly all these examples the 2,4,6-triisopropylphenyl group was employed simply as a sterically bulky blocking group to protect some other part of the molecule, and none of these structure reports comment

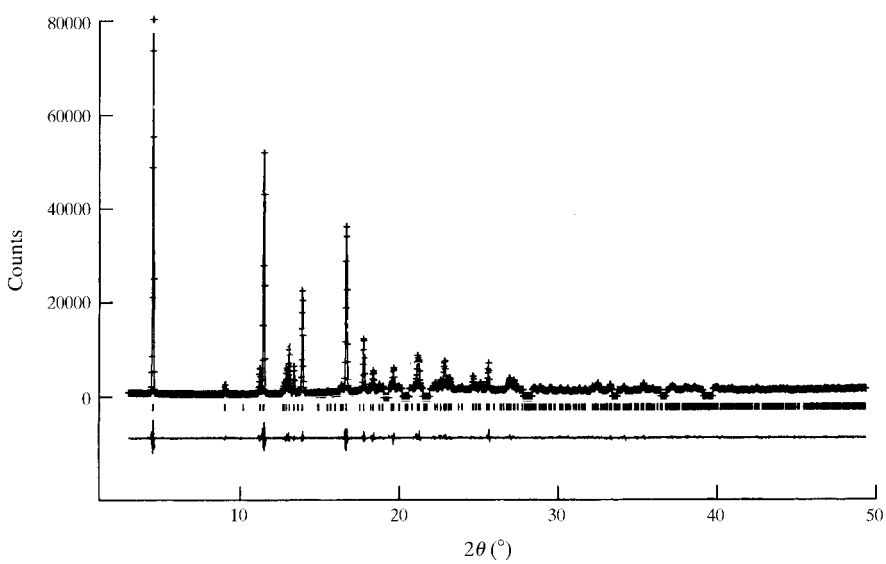

Fig. 2. Final observed (+ marks), calculated (solid line) and difference (below) X-ray powder diffraction profile for the final Rietveld refinement of (I). Reflection positions are also marked.

on its conformation. However, our analysis shows that the conformation of the isopropyl groups is essentially the same in all cases.

4.2. *Hydrogen bonding and molecular packing*

The NH_2 group in (I) acts as a double donor of hydrogen bonds, with a sulfone oxygen in each of two different molecules acting as the acceptors. N1 in the molecule at (x, y, z) acts as a donor to O2 at $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$, while N1 at $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$ in turn acts as a donor to O2 at $(x, 1+y, z)$: these interactions result in the formation of a $C(4)$ (Bernstein *et al.*, 1995) spiral, based on the N—H···O═S motif and generated by the 2_1 screw axis along $(0, y, \frac{3}{4})$. In addition, N1 at (x, y, z) also acts as a donor to O1 at $(-x, 1-y, 1-z)$, while N1 at $(-x, 1-y, 1-z)$ acts as a donor to O1 at (x, y, z), thus generating a cyclic $R_2^2(8)$ motif around the centre of inversion at $(0, \frac{1}{2}, \frac{1}{2})$ (Fig. 5). The N···O distances, 2.77 (1) Å in the spiral chains and 2.92 (1) Å in the $R_2^2(8)$ rings, are similar to the two independent N···O distances, 2.87 and 2.99 Å, found in the powder structure of 4-$CH_3C_6H_4SO_2NH_2$ (Lightfoot *et al.*, 1993): hydrogen-bonded N···O distances in sulfonamide structures determined from single-crystal X-ray data range from 2.854 (6) Å in $(PhSO_2)_2NH$ (Cotton & Stokely, 1970) to 3.24 Å in the γ modification of 4-$H_2NC_6H_4SO_2NH_2$ (Alléaume & Decap, 1965).

The $C(4)$ motif of N—H···O═S hydrogen bonds is extremely common in sulfonamides (Vorontsova, 1966; Cotton & Stokely, 1970; Klug, 1970; Brink & Mattes, 1986; Lightfoot *et al.*, 1993); the $R_2^2(8)$ motif has also been observed in sulfonamides (Klug, 1968; Blaschette

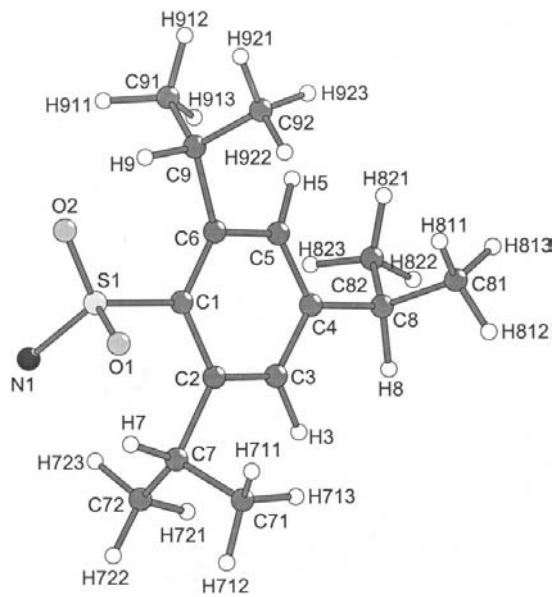

Fig. 3. The refined molecular structure of (I) showing the atom-labelling scheme.

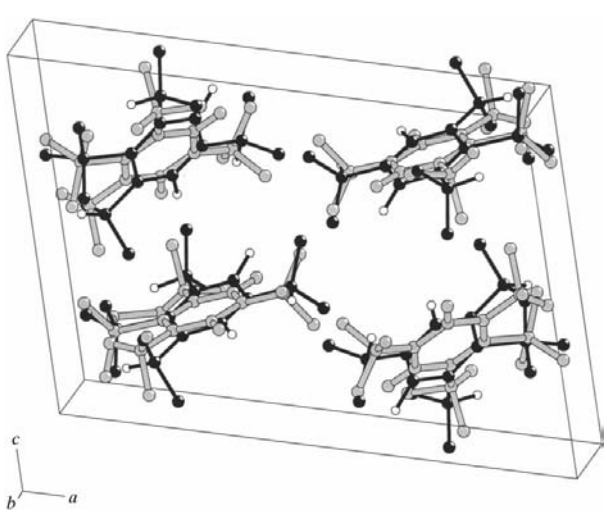

Fig. 4. Comparison between the position of the molecule obtained from the Monte Carlo structure solution calculation (hatched) and the corresponding atoms in the refined crystal structure of (I) (solid): in the refined structure non-methyl H atoms on C are shown as open circles.

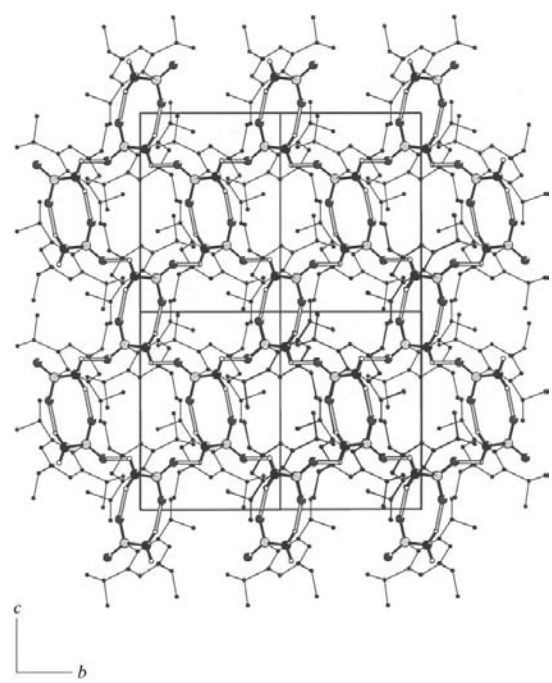

Fig. 5. View of part of the crystal structure of (I), showing the $C(4)$ N—H···O═S chains parallel to [010] and the alternation of $R_2^2(8)$ and $R_6^6(20)$ hydrogen-bonded rings in the (100) plane: thin lines represent bonds to carbon, lines of intermediate thickness represent covalent S—N or S═O bonds, and thick lines represent N—H···O═S hydrogen bonds. The H atoms shown are for the purposes of this diagram only, and are placed in calculated positions (see text). These atoms were not included in the Rietveld refinement. All other H atoms are omitted for the sake of clarity.

et al., 1986), but these two motifs do not normally occur together in a single sulfonamide.

The $R_2^2(8)$ rings have the effect of linking together two adjacent, but antiparallel $C(4)$ spirals. The propagation of these two hydrogen-bond motifs by means of the combined action of 2_1 screw axes and centres of inversion leads to the generation of a continuous two-dimensional sheet parallel to (100) in which $R_2^2(8)$ and $R_6^6(20)$ rings alternate in a checkerboard pattern (Fig. 5). The triisopropylphenyl units lie on either side of the hydrogen-bonded sheet (Fig. 6), so that the overall structure is that of a sandwich: a polar layer containing only S, O, N and H atoms lies between two non-polar hydrocarbon layers. This three-layer sandwich occupies the entire domain $-\frac{1}{2} < x < +\frac{1}{2}$, and there are only van der Waals contacts between adjacent sandwiches.

5. General comments

This study demonstrates the structure determination from powder diffraction data of a molecular compound containing 19 non-H atoms in which the molecule was permitted considerable torsional flexibility in structure solution by the Monte Carlo method. Comparison of the structure found for (I) with those of a range of other systems containing the 2,4,6-triisopropylphenyl fragment has revealed a common conformation, within which there is, in fact, just one twofold choice, the orientation of the 4-substituent.

While the information in the CSD has been extensively analysed in terms of both bond distances and a wide range of intermolecular interactions, it has been mined rather less frequently for conformational information, despite the fact that this may well be the richest vein within the CSD. Clearly, significant economy in the Monte Carlo structure solution could have been attained by incorporation of prior conformational information regarding the intramolecular rotation of the isopropyl groups in this structure. This type of performance enhancement has been illustrated recently elsewhere (Shankland *et al.*, 1998). It is clear that the use of appropriate conformational probabilities derived from exhaustive analysis of the information in the CSD will greatly benefit direct-space structure techniques as they are applied to larger molecular systems of ever-greater complexity.

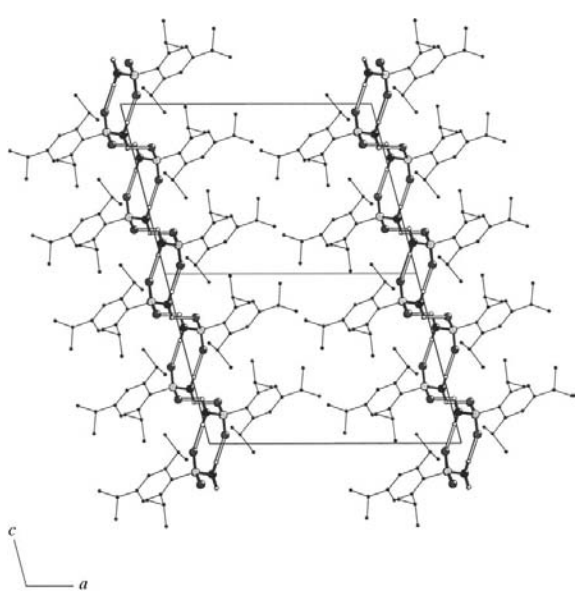

Fig. 6. View of part of the crystal structure of (I) showing the three-layer sandwich structure: atoms and bonds are depicted as in Fig. 5.

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