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Crystal structure of *N*-allyl-4-methylbenzenesulfonamide

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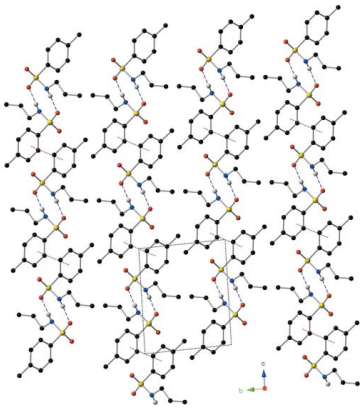
The title compound, $C_{10}H_{13}NO_2S$, was synthesized by a nucleophilic substitution reaction between allyl amine and *p*-toluenesulfonyl chloride. The sulfonate S—O bond lengths are 1.4282 (17) and 1.4353 (17) Å, and the C—N—S—C torsion angle involving the sulfonamide moiety is −61.0 (2)°. In the crystal, centrosymmetric dimers of the title compound are present *via* intermolecular N—H···O hydrogen bonds between sulfonamide groups. These dimers are linked into ribbons along the *c*-axis direction through offset π–π interactions.

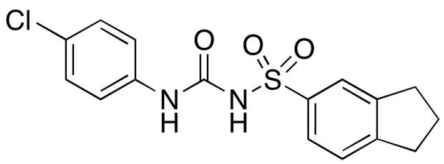
1. Chemical context

The sulfonamide moiety has been widely studied and its application in drug design has been reported (Qadir *et al.*, 2015; Rehman *et al.*, 2017; Gul *et al.*, 2018). Sulfa drugs, which incorporate the sulfonamide moiety, have found applications as antibacterial, anticancer, antifungal, anti-inflammatory, and antiviral agents (Alaoui *et al.*, 2017).

The synthesis of sulfonamides generally relies on the use of sulfonyl chlorides as electrophilic partners that react with nucleophilic amines. According to the current state of knowledge in the field, the use of sulfonyl chlorides as electrophilic substrates in the synthesis of sulfonamides suffers from some drawbacks. One such drawback is the difficulty in handling and storage (Caddick *et al.*, 2004). Other alternatives to sulfonyl chlorides have been reported (Parumala & Peddinti, 2016; Yang & Tian, 2017). Nucleophilic acyl substitution is the mechanism that describes the reaction between a carboxylic acid derivative such as acid chloride with an amine to form the corresponding amide. The mechanism of the reaction between sulfonyl chlorides and amines is analogous to nucleophilic acyl substitution, except that it occurs at the sulfonyl group and not the carbonyl group (Um *et al.*, 2013).

Recently, we have been particularly interested in the structural motif of sulfonamide compounds that are known to





Sulefonur

Figure 1
The structure of Sulefonur.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.83 (1)	2.07 (1)	2.900 (3)	174 (3)

Symmetry code: (i) $-x, -y, -z+1$.

modulate 5-HT$_6$ receptor activity and are used for the treatment of CNS diseases and disorders (Blass, 2016). We are also interested in the therapeutic application of sulfonamide molecules used for chondrogenic differentiation (Choi *et al.*, 2016), and for the treatment of cancer (Gul *et al.*, 2018). Fig. 1 shows the structure of Sulefonur, which has been reported as a potent anticancer sulfonamide drug candidate and is under anticancer clinical trials (Gul *et al.*, 2018). As part of our ongoing effort to synthesize small sulfonamide molecules that mimic the structural motifs of known sulfonamide drug candidates, we synthesized the title compound, $C_{10}H_{13}NO_2S$, (I) and determined its crystal structure from single crystal X-ray diffraction data.

2. Structural commentary

The molecular structure of compound (I), which was solved in the triclinic space group $P\overline{1}$, is shown in Fig. 2. The S—O bond lengths of 1.4282 (17) and 1.4353 (17) Å and the O1—S1—O2 bond angle of 118.87 (11)° are typical for sulfonamide moieties. The S1—N1 bond length is 1.617 (2) Å, and the C1—N1—S1—C4 torsion angle is −61.0 (2)°.

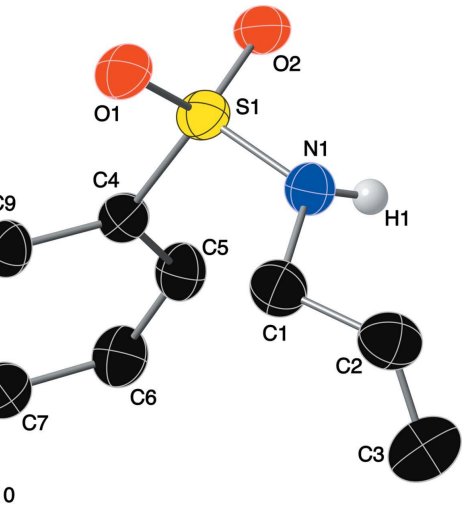


Figure 2
The molecular structure of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

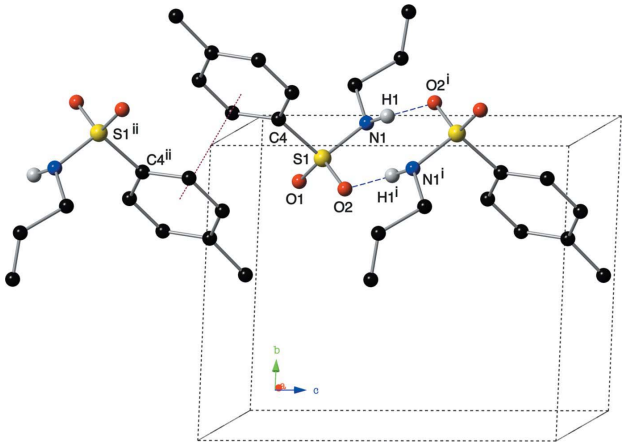


Figure 3
A depiction of the intermolecular hydrogen bonds and offset π–π interactions present in the crystal, viewed down the *a* axis, using a ball and stick model with standard CPK colors. [Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x, -y, -z$.]

3. Supramolecular features

Molecules of the title compound are linked to one another *via* hydrogen bonds and π–π interactions. Centrosymmetric

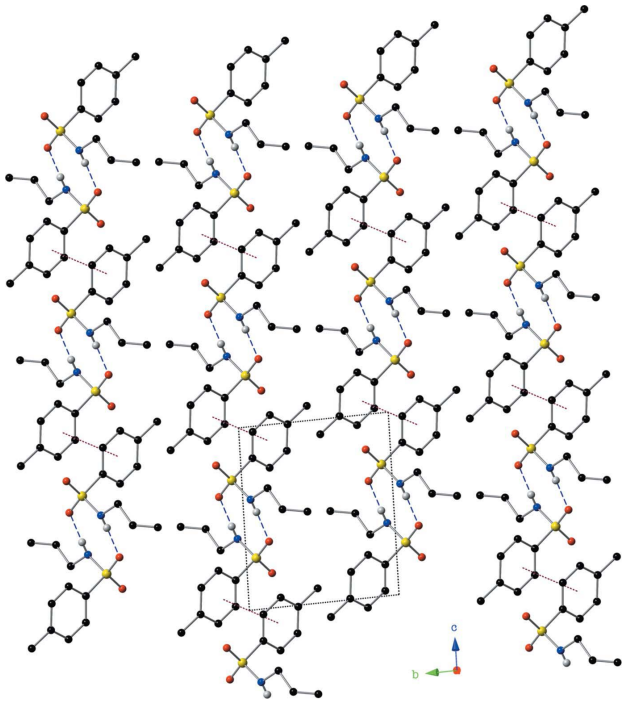


Figure 4
A view along the *a* axis of the title compound showing the supramolecular ribbons assembled *via* N—H···O hydrogen bonds (blue, dashed lines) and π–π interactions (red, dotted lines).

dimers of compound (I) are formed through intermolecular hydrogen bonds between the sulfonamide N—H group and an O atom of a neighbouring sulfonamide group (Fig. 3). The N1···O2^{i} distance of 2.900 (3) Å suggests interactions of medium strength with a nearly linear N—H···O hydrogen bond of 174 (3)° (Table 1). These dimers are then linked through offset π–π interactions into ribbons that lie along the c axis (Figs. 3, 4). The intercentroid distance $Cg\cdots Cg^{ii}$ is 3.8340 (17) Å, with a slippage of 1.320 Å and a plane-to-plane distance between phenyl rings of 3.600 Å [symmetry code (ii) = $-x, -y, -z$].

4. Database survey

The Cambridge Structural Database (CSD, Version 5.39, February 2018; Groom *et al.*, 2016) contains 17 structures of *p*-tolylsulfonamides where there is a –CH_2—C≡C group bonded to the sulfonamide-N atom. The alkene group in these structures is a part of, for example, furan rings (DERTIE and DERTOK, Hashmi *et al.*, 2006), an allene (XUDNEP, Lan & Hammond, 2002), and various acyclic systems (BUXYUQ, Kiyokawa *et al.*, 2015; KIHMIY, Lee *et al.*, 2007). While all of the structures listed here display intermolecular hydrogen bonds between sulfonamide groups, none of them display π–π interactions between the *p*-tolylsulfonamide rings as seen in the title compound.

5. Synthesis and crystallization

Allylamine (1.31 ml, 18 mmol) was added in 20 ml of degassed dichloromethane. This was followed by the addition of pyridine (1.42 ml, 18 mmol). The resulting solution was stirred under an atmosphere of N_2, followed by the portion-wise addition of *p*-toluenesulfonyl chloride (3.05 g, 16 mmol). The mixture was stirred at room temperature for 24 h. Reaction completion was verified by using TLC analysis. The mixture was acidified to pH 2–3 using concentrated HCl. After dilution with 20 ml of CH_2Cl_2, the organic phase was washed with H_2O (3 × 20 ml) and the aqueous layer was back-extracted with CH_2Cl_2 (20 ml). The combined organic extracts were dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was obtained as a yellow solid which was recrystallized in cold ethanol to afford pale-yellow crystals (56%; m.p. 332–333 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms bonded to carbon atoms were placed in calculated positions and refined as riding: Csp^3—H = 0.95–1.00 Å with U_{iso}(H) = 1.2U_{eq}(C) for methine and methylene groups, and U_{iso}(H) = 1.5U_{eq}(C) for methyl groups. The hydrogen atom bonded to the nitrogen atom (H1) was located using electron-density difference maps, and the N—H bond length was restrained to 0.84±0.01 Å using the DFIX command as executed in *SHELXL* (Sheldrick, 2015).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{13}NO_2S$
M_r	211.27
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	7.5538 (10), 8.2591 (11), 9.7145 (13)
α, β, γ (°)	85.9415 (16), 72.9167 (16), 67.6989 (15)
V (Å^3)	535.42 (12)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.28
Crystal size (mm)	0.28 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.672, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6472, 1963, 1564
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.604
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.156, 1.09
No. of reflections	1963
No. of parameters	132
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.60, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009; Bourhis *et al.*, 2015) and *CrystalMaker* (Palmer, 2007).

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009; Bourhis *et al.*, 2015); software used to prepare material for publication: *CrystalMaker* (Palmer, 2007).

N-Allyl-4-methylbenzenesulfonamide

Crystal data

$C_{10}H_{13}NO_2S$
$M_r = 211.27$
Triclinic, $P\overline{1}$
$a = 7.5538$ (10) Å
$b = 8.2591$ (11) Å
$c = 9.7145$ (13) Å
$\alpha = 85.9415$ (16)°
$\beta = 72.9167$ (16)°
$\gamma = 67.6989$ (15)°
$V = 535.42$ (12) Å^3
$Z = 2$
$F(000) = 224$
$D_x = 1.310$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2805 reflections
$\theta = 2.2$–25.3°
$\mu = 0.28$ mm^{-1}
$T = 173$ K
Chunk, pale yellow
0.28 × 0.25 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
$T_{min} = 0.672$, $T_{max} = 0.745$
6472 measured reflections
1963 independent reflections
1564 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.4°$, $\theta_{min} = 2.2°$
$h = -9\rightarrow9$
$k = -9\rightarrow9$
$l = -11\rightarrow11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.156$
$S = 1.09$
1963 reflections
132 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0902P)^2 + 0.112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.23035 (9)	−0.06592 (8)	0.28093 (6)	0.0355 (3)
O1	0.4258 (2)	−0.1649 (2)	0.19086 (19)	0.0423 (5)
O2	0.1100 (3)	−0.1576 (2)	0.36436 (18)	0.0407 (5)
N1	0.2532 (3)	0.0508 (3)	0.3966 (2)	0.0352 (5)
H1	0.153 (3)	0.085 (4)	0.468 (2)	0.048 (8)*
C1	0.3608 (4)	0.1687 (4)	0.3441 (3)	0.0436 (7)
H1A	0.2923	0.2565	0.2830	0.052*
H1B	0.4984	0.1006	0.2847	0.052*
C2	0.3677 (4)	0.2590 (4)	0.4684 (3)	0.0483 (7)
H2	0.4323	0.1874	0.5339	0.058*
C3	0.2948 (6)	0.4239 (5)	0.4948 (4)	0.0705 (10)
H3A	0.2289	0.5005	0.4322	0.085*
H3B	0.3063	0.4703	0.5770	0.085*
C4	0.0966 (3)	0.0803 (3)	0.1729 (3)	0.0318 (6)
C5	−0.1007 (4)	0.1904 (3)	0.2347 (3)	0.0390 (6)
H5	−0.1655	0.1827	0.3334	0.047*
C6	−0.2011 (4)	0.3105 (4)	0.1516 (3)	0.0424 (7)
H6	−0.3363	0.3849	0.1937	0.051*
C7	−0.1092 (4)	0.3257 (3)	0.0072 (3)	0.0397 (6)
C8	0.0869 (4)	0.2125 (4)	−0.0528 (3)	0.0423 (7)
H8	0.1509	0.2187	−0.1520	0.051*
C9	0.1909 (4)	0.0909 (4)	0.0291 (3)	0.0380 (6)
H9	0.3258	0.0156	−0.0130	0.046*
C10	−0.2180 (5)	0.4608 (4)	−0.0817 (3)	0.0506 (7)
H10A	−0.1212	0.4891	−0.1614	0.076*
H10B	−0.3076	0.5669	−0.0212	0.076*
H10C	−0.2964	0.4147	−0.1205	0.076*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0316 (4)	0.0323 (4)	0.0372 (4)	−0.0107 (3)	−0.0031 (3)	−0.0010 (3)
O1	0.0323 (10)	0.0378 (10)	0.0444 (10)	−0.0067 (8)	−0.0007 (8)	−0.0047 (8)
O2	0.0425 (10)	0.0322 (10)	0.0428 (10)	−0.0158 (9)	−0.0034 (8)	0.0010 (8)
N1	0.0325 (11)	0.0363 (12)	0.0333 (11)	−0.0124 (10)	−0.0049 (9)	0.0010 (9)
C1	0.0464 (16)	0.0444 (16)	0.0430 (15)	−0.0237 (13)	−0.0087 (12)	0.0036 (12)
C2	0.0484 (17)	0.0476 (18)	0.0550 (17)	−0.0218 (14)	−0.0196 (14)	0.0063 (14)
C3	0.084 (3)	0.056 (2)	0.073 (2)	−0.0282 (19)	−0.020 (2)	−0.0084 (18)
C4	0.0280 (12)	0.0331 (13)	0.0346 (13)	−0.0140 (11)	−0.0058 (10)	−0.0009 (10)

C5	0.0337 (14)	0.0439 (16)	0.0344 (13)	−0.0135 (12)	−0.0032 (11)	−0.0019 (12)
C6	0.0334 (14)	0.0474 (17)	0.0421 (15)	−0.0113 (12)	−0.0086 (12)	−0.0027 (13)
C7	0.0431 (15)	0.0423 (16)	0.0433 (15)	−0.0228 (13)	−0.0173 (12)	0.0013 (12)
C8	0.0415 (15)	0.0546 (17)	0.0312 (13)	−0.0227 (14)	−0.0045 (11)	0.0008 (12)
C9	0.0339 (14)	0.0442 (15)	0.0337 (13)	−0.0169 (12)	−0.0022 (11)	−0.0038 (11)
C10	0.0553 (18)	0.0505 (18)	0.0528 (17)	−0.0216 (15)	−0.0242 (14)	0.0076 (14)

Geometric parameters (Å, º)

S1—O1	1.4282 (17)	C4—C9	1.383 (3)
S1—O2	1.4353 (17)	C5—H5	0.9500
S1—N1	1.617 (2)	C5—C6	1.373 (4)
S1—C4	1.760 (3)	C6—H6	0.9500
N1—H1	0.831 (10)	C6—C7	1.390 (4)
N1—C1	1.468 (3)	C7—C8	1.388 (3)
C1—H1A	0.9900	C7—C10	1.501 (4)
C1—H1B	0.9900	C8—H8	0.9500
C1—C2	1.487 (4)	C8—C9	1.383 (4)
C2—H2	0.9500	C9—H9	0.9500
C2—C3	1.273 (4)	C10—H10A	0.9800
C3—H3A	0.9500	C10—H10B	0.9800
C3—H3B	0.9500	C10—H10C	0.9800
C4—C5	1.390 (3)		
O1—S1—O2	118.87 (11)	C9—C4—C5	120.4 (2)
O1—S1—N1	107.94 (11)	C4—C5—H5	120.3
O1—S1—C4	108.08 (11)	C6—C5—C4	119.3 (2)
O2—S1—N1	105.56 (11)	C6—C5—H5	120.3
O2—S1—C4	108.64 (11)	C5—C6—H6	119.3
N1—S1—C4	107.21 (11)	C5—C6—C7	121.5 (2)
S1—N1—H1	112 (2)	C7—C6—H6	119.3
C1—N1—S1	119.02 (17)	C6—C7—C10	121.1 (3)
C1—N1—H1	118 (2)	C8—C7—C6	118.2 (2)
N1—C1—H1A	109.7	C8—C7—C10	120.7 (2)
N1—C1—H1B	109.7	C7—C8—H8	119.4
N1—C1—C2	109.8 (2)	C9—C8—C7	121.2 (2)
H1A—C1—H1B	108.2	C9—C8—H8	119.4
C2—C1—H1A	109.7	C4—C9—C8	119.3 (2)
C2—C1—H1B	109.7	C4—C9—H9	120.3
C1—C2—H2	117.1	C8—C9—H9	120.3
C3—C2—C1	125.7 (3)	C7—C10—H10A	109.5
C3—C2—H2	117.1	C7—C10—H10B	109.5
C2—C3—H3A	120.0	C7—C10—H10C	109.5
C2—C3—H3B	120.0	H10A—C10—H10B	109.5
H3A—C3—H3B	120.0	H10A—C10—H10C	109.5
C5—C4—S1	119.60 (19)	H10B—C10—H10C	109.5
C9—C4—S1	119.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.83 (1)	2.07 (1)	2.900 (3)	174 (3)

Symmetry code: (i) −*x*, −*y*, −*z*+1.