

(2S)-Methyl 2-(p-toluenesulfonamido)-propanoate

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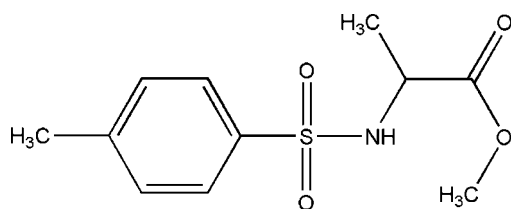
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.022; wR factor = 0.063; data-to-parameter ratio = 26.6.

The enantiomerically pure title compound, $\text{C}_{11}\text{H}_{15}\text{NO}_4\text{S}$, contains a pyramidal N atom with an S—N bond length of 1.6262 (8) Å. In the crystal, molecules are linked to form chains parallel to the *a* axis by the hydrogen bond from NH to the carbonyl oxygen. C—H...O interactions are also present.

Related literature

For the applications of esters in the food and cosmetics industries, see: Soni *et al.* (2002). For their use as intermediates in the synthesis of heterocyclic compounds, see: Akhtar *et al.* (2007); Chen *et al.* (2007); Kucukguzel *et al.* (2007). For their use in the pharmaceutical industry, see: Iqbal & Chaudhry (2008). For the pharmacological activity of sulfonamides, see: Akhtar *et al.* (2008); Zareef *et al.* (2007). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_{15}\text{NO}_4\text{S}$
 $M_r = 257.30$

 Orthorhombic, $P2_12_12_1$
 $a = 7.1948$ (2) Å

 $b = 11.2552$ (3) Å

 $c = 15.3311$ (4) Å

 $V = 1241.50$ (6) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.26$ mm⁻¹
 $T = 100$ K

 $0.35 \times 0.30 \times 0.20$ mm

Data collection

Oxford Diffraction Xcalibur E diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{\min} = 0.972$, $T_{\max} = 1.000$
(expected range = 0.922–0.949)
55416 measured reflections
4284 independent reflections
4060 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.063$
 $S = 1.05$

4284 reflections

161 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Absolute structure: Flack (1983),

1818 Friedel pairs

Flack parameter: 0.01 (4)

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N—H01...O1 ⁱ	0.865 (16)	2.057 (16)	2.9097 (10)	168.6 (14)
C10—H10...O1 ⁱ	0.95	2.62	3.3696 (11)	136
C9—H9...O2 ⁱⁱ	0.95	2.63	3.4065 (11)	140
C7—H7...O3 ⁱⁱⁱ	0.95	2.67	3.6167 (11)	172
C4—H4C...O4 ^{iv}	0.98	2.49	3.3453 (13)	145

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2507).

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supplementary materials

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(2S)-Methyl 2-(*p*-toluenesulfonamido)propanoate

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Comment

Because of their versatility and harmlessness, esters have found many applications in the food and cosmetics industries (Soni *et al.*, 2002). They have been reported as emulsifiers, dispersants, or thickeners. In addition to their use as intermediates in the synthesis of a large number of heterocyclic compounds (Chen *et al.*, 2007; Kucukguzel *et al.*, 2007; Akhtar *et al.*, 2007), esters have also been used in the pharmaceutical industry as nervous system depressants, intestinal antiseptics and antibacterials (Iqbal *et al.*, 2008). Sulfonamides, on the other hand, constitute an important class of drugs with several types of pharmacological activities (Akhtar *et al.*, 2008; Zareef *et al.*, 2007). The title compound (I) was synthesized in our laboratory as an intermediate for onward conversion to 1,3,4-oxadiazole derivatives, with a view to explore their anti-HIV and anti-HCV activities.

The molecule of (I) is shown in Fig. 1. Bond lengths and angles may be regarded as normal. In particular, the N—S bond length is 1.6262 (8) Å; a search of the Cambridge Database (Allen, 2002; Version 1.11) revealed 817 examples of the fragment Ph—SO₂—NH—C(*sp*³) (including substituted Ph rings) with a mean bond length of 1.614 Å. The nitrogen atom displays a pyramidal geometry, with N lying 0.293 (7) Å out of the plane of S, C2 and H01. The database hits showed a highly skewed distribution for this displacement, with many values of exactly zero; this is presumably attributable to fixing the hydrogen assuming planar geometry (AFIX 43 in the *SHELX* system), whereby the assumption of planarity is clearly not justified. Neglecting the zero values, the average deviation for 462 values is 0.24 Å. The sulfonyl group is oriented such that the bond S—O4 is approximately coplanar with the aromatic ring (torsion angle O4—S—C5—C6 - 6.70 (9)°).

The molecules are linked by classical hydrogen bonds from the NH group to the carbonyl oxygen (and not, as might have been expected, to a sulfonyl oxygen); the packing diagram (Fig. 2) shows chains of molecules parallel to the **a** axis. The four "weak" hydrogen bonds crosslink these chains to a three-dimensional pattern.

Experimental

Alanine (0.02 mol) was dissolved in an aqueous solution of potassium carbonate (0.06 mol, 50 ml) and a solution of 4-methylbenzenesulfonyl chloride (0.027 mol) in toluene (30 ml) was added. On completion of the reaction, the organic layer was separated and the aqueous layer acidified using dilute hydrochloric acid. The 2-(4-methylphenylsulfonylamino)propanoic acid thus obtained was filtered off and recrystallized from aqueous ethanol.

2-(4-Methylphenylsulfonylamino)propanoic acid (0.02 mol) was dissolved in methanol (30 ml), sulfuric acid (0.5 ml) was added and the mixture subjected to reflux while the reaction was monitored by TLC at regular intervals. After completion of the reaction, the reaction mixture was concentrated on the rotary evaporator to remove excess methanol. The product thus obtained was poured into water, neutralized with sodium bicarbonate and extracted with ethyl acetate (3 × 50 ml). The combined organic extracts were dried over anhydrous sodium sulfate and the solvent evaporated on a rotary evaporator. The product was recrystallized from acetone/water.

Refinement

The NH hydrogen was refined freely. Methyl H atoms were located in difference syntheses, idealized to C—H 0.98 Å and H—C—H 109.5°, and refined as rigid groups allowed to rotate but not tip. Other H atoms were placed in calculated positions and refined using a riding model with C—H 0.95 Å for aromatic H and 1.00 Å for methine CH. Hydrogen U values were fixed at $1.5 \times U(\text{eq})$ of the parent atom for methyl H and $1.2 \times U(\text{eq})$ of the parent atom for other H. The compound is enantiomerically pure and its absolute configuration (S at C2) was confirmed by the Flack (1983) parameter.

Figures

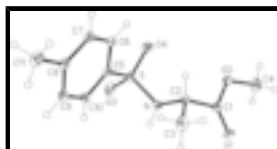


Fig. 1. The molecule of the title compound. Ellipsoids correspond to 50% probability levels.

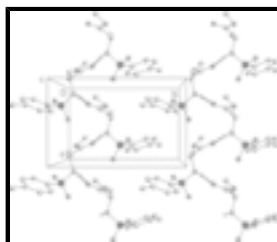


Fig. 2. Packing diagram of the title compound, showing classical hydrogen bonds (dashed lines).

(2S)-Methyl 2-(*p*-toluenesulfonamido)propanoate

Crystal data

$\text{C}_{11}\text{H}_{15}\text{NO}_4\text{S}$

$M_r = 257.30$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.1948$ (2) Å

$b = 11.2552$ (3) Å

$c = 15.3311$ (4) Å

$V = 1241.50$ (6) Å³

$Z = 4$

$F_{000} = 544$

$D_x = 1.377$ Mg m⁻³

Melting point = 363–365 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 40101 reflections

$\theta = 2.2$ – 32.6°

$\mu = 0.26$ mm⁻¹

$T = 100$ K

Irregular block, colourless

$0.35 \times 0.30 \times 0.20$ mm

Data collection

Oxford Diffraction Xcalibur E
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 16.1419 pixels mm⁻¹

4284 independent reflections

4060 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\text{max}} = 32.0^\circ$

$T = 100$ K $\theta_{\min} = 2.2^\circ$
 ω -scan $h = -10 \rightarrow 10$
 Absorption correction: multi-scan
 (CrysAlis RED; Oxford Diffraction, 2008) $k = -16 \rightarrow 16$
 $T_{\min} = 0.972$, $T_{\max} = 1.000$ $l = -22 \rightarrow 22$
 55416 measured reflections

Refinement

Refinement on F^2 Hydrogen site location: inferred from neighbouring sites
 Least-squares matrix: full H atoms treated by a mixture of independent and constrained refinement
 $R[F^2 > 2\sigma(F^2)] = 0.022$ $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.0628P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.063$ $(\Delta/\sigma)_{\max} = 0.001$
 $S = 1.05$ $\Delta\rho_{\max} = 0.37 \text{ e } \text{Å}^{-3}$
 4284 reflections $\Delta\rho_{\min} = -0.31 \text{ e } \text{Å}^{-3}$
 161 parameters Extinction correction: none
 Primary atom site location: structure-invariant direct methods Absolute structure: Flack (1983), 1818 Friedel pairs
 Secondary atom site location: difference Fourier map Flack parameter: 0.01 (4)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.77287 (3)	0.499255 (18)	0.576519 (12)	0.01308 (5)
O1	0.26383 (10)	0.24453 (5)	0.58832 (5)	0.01963 (14)
O2	0.29792 (10)	0.39044 (5)	0.68639 (4)	0.01622 (12)
O3	0.95092 (9)	0.44220 (6)	0.58061 (5)	0.02115 (14)
O4	0.70626 (11)	0.56695 (6)	0.64934 (4)	0.02111 (14)
C1	0.31824 (12)	0.34256 (7)	0.60812 (5)	0.01252 (14)
C2	0.42632 (12)	0.42436 (7)	0.54745 (5)	0.01322 (14)
H2	0.4070	0.5085	0.5662	0.016*
C3	0.36297 (14)	0.41083 (10)	0.45331 (6)	0.0239 (2)
H3A	0.4314	0.4668	0.4164	0.036*

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H3B	0.2295	0.4275	0.4493	0.036*
H3C	0.3872	0.3295	0.4336	0.036*
C4	0.19070 (16)	0.32121 (10)	0.74852 (7)	0.0258 (2)
H4A	0.0614	0.3160	0.7288	0.039*
H4B	0.1950	0.3598	0.8058	0.039*
H4C	0.2433	0.2411	0.7529	0.039*
C5	0.77229 (12)	0.59314 (7)	0.48448 (5)	0.01268 (14)
C6	0.69566 (12)	0.70659 (7)	0.48923 (5)	0.01463 (14)
H6	0.6427	0.7348	0.5421	0.018*
C7	0.69813 (12)	0.77808 (7)	0.41487 (6)	0.01543 (15)
H7	0.6459	0.8555	0.4174	0.019*
C8	0.77573 (13)	0.73814 (7)	0.33690 (5)	0.01487 (15)
C9	0.84746 (13)	0.62251 (8)	0.33331 (6)	0.01649 (16)
H9	0.8974	0.5933	0.2801	0.020*
C10	0.84653 (12)	0.55006 (7)	0.40655 (6)	0.01525 (15)
H10	0.8959	0.4719	0.4037	0.018*
C11	0.78446 (17)	0.81761 (9)	0.25811 (6)	0.02262 (18)
H11A	0.6738	0.8683	0.2564	0.034*
H11B	0.7893	0.7689	0.2052	0.034*
H11C	0.8960	0.8674	0.2614	0.034*
N	0.62422 (10)	0.39329 (6)	0.55827 (5)	0.01262 (13)
H01	0.661 (2)	0.3437 (14)	0.5189 (10)	0.032 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.01306 (9)	0.01406 (8)	0.01212 (8)	-0.00207 (7)	-0.00239 (6)	0.00121 (7)
O1	0.0243 (3)	0.0136 (3)	0.0210 (3)	-0.0038 (2)	-0.0008 (3)	-0.0026 (2)
O2	0.0175 (3)	0.0183 (3)	0.0129 (3)	-0.0021 (2)	0.0007 (2)	-0.0013 (2)
O3	0.0131 (3)	0.0248 (3)	0.0256 (3)	-0.0009 (2)	-0.0058 (3)	0.0072 (3)
O4	0.0310 (4)	0.0199 (3)	0.0125 (3)	-0.0053 (3)	0.0004 (3)	-0.0036 (2)
C1	0.0109 (3)	0.0130 (3)	0.0137 (3)	0.0008 (3)	-0.0016 (3)	0.0000 (3)
C2	0.0113 (3)	0.0137 (3)	0.0146 (3)	0.0008 (3)	-0.0005 (3)	0.0020 (3)
C3	0.0167 (4)	0.0388 (5)	0.0163 (4)	-0.0023 (4)	-0.0046 (3)	0.0078 (4)
C4	0.0269 (5)	0.0319 (5)	0.0187 (4)	-0.0047 (4)	0.0050 (4)	0.0060 (4)
C5	0.0123 (3)	0.0128 (3)	0.0129 (3)	-0.0013 (3)	-0.0004 (3)	0.0003 (2)
C6	0.0141 (3)	0.0140 (3)	0.0158 (3)	0.0005 (3)	0.0016 (3)	-0.0013 (3)
C7	0.0145 (3)	0.0128 (3)	0.0190 (4)	0.0006 (3)	-0.0003 (3)	0.0004 (3)
C8	0.0150 (3)	0.0153 (3)	0.0143 (3)	-0.0032 (3)	-0.0031 (3)	0.0019 (3)
C9	0.0194 (4)	0.0164 (4)	0.0137 (4)	-0.0014 (3)	0.0022 (3)	-0.0011 (3)
C10	0.0167 (4)	0.0129 (3)	0.0162 (4)	0.0009 (3)	0.0014 (3)	-0.0012 (3)
C11	0.0299 (5)	0.0199 (4)	0.0180 (4)	-0.0044 (4)	-0.0027 (4)	0.0050 (3)
N	0.0112 (3)	0.0109 (3)	0.0157 (3)	0.0003 (2)	-0.0002 (2)	-0.0002 (2)

Geometric parameters (\AA , $^\circ$)

S—O4	1.4341 (7)	C9—C10	1.3878 (12)
S—O3	1.4344 (7)	C2—H2	1.0000
S—N	1.6262 (8)	C3—H3A	0.9800

S—C5	1.7628 (8)	C3—H3B	0.9800
O1—C1	1.2094 (10)	C3—H3C	0.9800
O2—C1	1.3235 (10)	C4—H4A	0.9800
O2—C4	1.4525 (11)	C4—H4B	0.9800
C1—C2	1.5223 (11)	C4—H4C	0.9800
C2—N	1.4755 (11)	C6—H6	0.9500
C2—C3	1.5213 (13)	C7—H7	0.9500
C5—C6	1.3929 (11)	C9—H9	0.9500
C5—C10	1.3956 (11)	C10—H10	0.9500
C6—C7	1.3955 (11)	C11—H11A	0.9800
C7—C8	1.3938 (12)	C11—H11B	0.9800
C8—C9	1.4012 (12)	C11—H11C	0.9800
C8—C11	1.5043 (12)	N—H01	0.865 (16)
O4—S—O3	120.15 (5)	C2—C3—H3B	109.5
O4—S—N	107.69 (4)	H3A—C3—H3B	109.5
O3—S—N	105.46 (4)	C2—C3—H3C	109.5
O4—S—C5	107.69 (4)	H3A—C3—H3C	109.5
O3—S—C5	107.79 (4)	H3B—C3—H3C	109.5
N—S—C5	107.48 (4)	O2—C4—H4A	109.5
C1—O2—C4	115.78 (7)	O2—C4—H4B	109.5
O1—C1—O2	124.28 (8)	H4A—C4—H4B	109.5
O1—C1—C2	124.32 (8)	O2—C4—H4C	109.5
O2—C1—C2	111.35 (7)	H4A—C4—H4C	109.5
N—C2—C3	111.84 (7)	H4B—C4—H4C	109.5
N—C2—C1	106.32 (7)	C5—C6—H6	120.6
C3—C2—C1	111.48 (7)	C7—C6—H6	120.6
C6—C5—C10	120.98 (7)	C8—C7—H7	119.3
C6—C5—S	120.57 (6)	C6—C7—H7	119.3
C10—C5—S	118.43 (6)	C10—C9—H9	119.6
C5—C6—C7	118.74 (7)	C8—C9—H9	119.6
C8—C7—C6	121.32 (7)	C9—C10—H10	120.3
C7—C8—C9	118.74 (7)	C5—C10—H10	120.3
C7—C8—C11	120.90 (8)	C8—C11—H11A	109.5
C9—C8—C11	120.36 (8)	C8—C11—H11B	109.5
C10—C9—C8	120.81 (8)	H11A—C11—H11B	109.5
C9—C10—C5	119.37 (8)	C8—C11—H11C	109.5
C2—N—S	118.70 (6)	H11A—C11—H11C	109.5
N—C2—H2	109.0	H11B—C11—H11C	109.5
C3—C2—H2	109.0	C2—N—H01	111.8 (10)
C1—C2—H2	109.0	S—N—H01	113.1 (10)
C2—C3—H3A	109.5		
C4—O2—C1—O1	-4.64 (13)	C5—C6—C7—C8	-0.17 (13)
C4—O2—C1—C2	177.89 (8)	C6—C7—C8—C9	1.82 (13)
O1—C1—C2—N	-87.54 (10)	C6—C7—C8—C11	-177.58 (9)
O2—C1—C2—N	89.93 (8)	C7—C8—C9—C10	-1.88 (13)
O1—C1—C2—C3	34.58 (12)	C11—C8—C9—C10	177.52 (9)
O2—C1—C2—C3	-147.95 (8)	C8—C9—C10—C5	0.29 (13)
O4—S—C5—C6	-6.70 (9)	C6—C5—C10—C9	1.42 (13)

supplementary materials

O3—S—C5—C6	-137.70 (7)	S—C5—C10—C9	-179.99 (7)
N—S—C5—C6	109.07 (7)	C3—C2—N—S	108.25 (8)
O4—S—C5—C10	174.70 (7)	C1—C2—N—S	-129.86 (6)
O3—S—C5—C10	43.70 (8)	O4—S—N—C2	52.67 (7)
N—S—C5—C10	-69.53 (8)	O3—S—N—C2	-177.90 (6)
C10—C5—C6—C7	-1.48 (13)	C5—S—N—C2	-63.10 (7)
S—C5—C6—C7	179.97 (6)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N—H01 \cdots O1 ⁱ	0.865 (16)	2.057 (16)	2.9097 (10)	168.6 (14)
C10—H10 \cdots O1 ⁱ	0.95	2.62	3.3696 (11)	136
C9—H9 \cdots O2 ⁱⁱ	0.95	2.63	3.4065 (11)	140
C7—H7 \cdots O3 ⁱⁱⁱ	0.95	2.67	3.6167 (11)	172
C4—H4C \cdots O4 ^{iv}	0.98	2.49	3.3453 (13)	145

Symmetry codes: (i) $x+1/2, -y+1/2, -z+1$; (ii) $-x+3/2, -y+1, z-1/2$; (iii) $x-1/2, -y+3/2, -z+1$; (iv) $-x+1, y-1/2, -z+3/2$.

Fig. 1

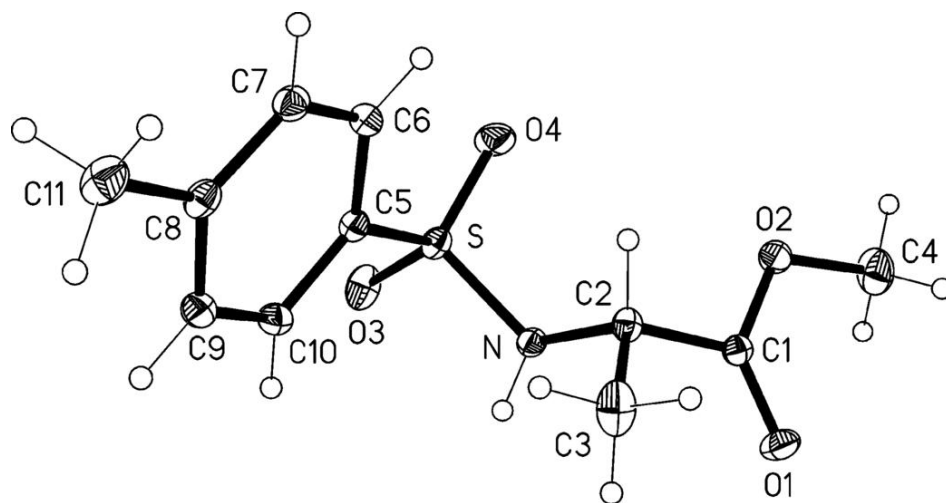


Fig. 2

