Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

3-(Dimethylhydrazino)-2-(methylsulfonyl)propenenitrile

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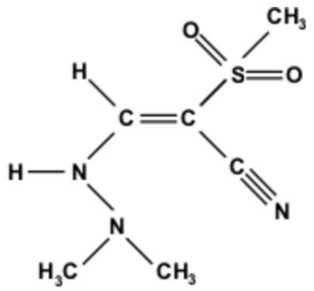
Received 17 April 2007; accepted 30 April 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.057; wR factor = 0.152; data-to-parameter ratio = 14.2.

In the title compound, $C_6H_{11}N_3O_2S$, which is an example of a push–pull olefin, a network of N—H$\cdots$O, C—H$\cdots$O and C—H$\cdots$N interactions help to establish the crystal packing.

Related literature

For background literature, see: Cook (1969); Dyke (1973); Chemla & Zyss (1987); Nalwa *et al.* (1997).



Experimental

Crystal data

$C_6H_{11}N_3O_2S$
M_r = 189.24
Monoclinic, $P2_1/c$
a = 11.526 (2) Å
b = 6.881 (1) Å
c = 11.577 (2) Å
β = 106.06 (3)°
V = 882.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 100 K
0.28 × 0.24 × 0.04 mm

Data collection

Oxford Diffraction GEMINI R diffractometer
Absorption correction: analytical (Clark & Reid, 1995)
$T_{\min}$ = 0.935, $T_{\max}$ = 0.987
14473 measured reflections
1606 independent reflections
1310 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.152
S = 1.14
1606 reflections
113 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.65 e Å^{-3}
$\Delta\rho_{\min}$ = −0.43 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$A\cdots$O1	0.93	2.51	2.922 (4)	107
C5—H5$C\cdots$N1$^{\rm i}$	0.96	2.68	3.449 (5)	138
C6—H6$A\cdots$N1$^{\rm ii}$	0.96	2.60	3.475 (2)	152
C4—H4$B\cdots$O1$^{\rm iii}$	0.96	2.62	3.415 (4)	141
C3—H3$A\cdots$O1$^{\rm iii}$	0.93	2.73	3.482 (5)	139
C5—H5$A\cdots$O1$^{\rm iv}$	0.96	2.65	3.392 (3)	135
N2—H2$A\cdots$O2$^{\rm ii}$	0.86	2.19	2.944 (2)	147
C4—H4$C\cdots$O2$^{\rm v}$	0.96	2.50	3.399 (4)	156

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXS97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

The authors thank the Grant Agency of the Slovak Republic, grant Nos. 1/2449/05, 1/1379/04 and APVT-20–007304, as well as the Structural Funds, Interreg IIIA, for financial support in purchasing the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2380).

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doi:10.1107/S1600536807021381

supplementary materials

Acta Cryst. (2007). E**63**, o2820 [**doi:10.1107/S1600536807021381**]

3-(Dimethylhydrazino)-2-(methylsulfonyl)propenenitrile

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Comment

3-*N*,*N*-dimethylhydrazino-2-methylsulfonyl propenenitrile (Fig. 1) belongs to the so-called push-pull olefins. Push-pull alkenes are substituted ethylenes containing electron- donor groups (D) at one end and electron-acceptor groups (A) at the other end of the general formula $D^1D^2C{=}CA^1A^2$. These compounds very often contain alkoxy, amino, alkylamino, dialkylamino or (hetero)aryl groups as electron-donor groups and cyano, acetyl, alkylester, methylsulfonyl or NO_2 groups as electron-acceptor groups. They are useful as starting reactants or intermediates for a lot of pharmaceutical, polymer and other syntheses (Cook, 1969, Dyke, 1973).

Due to the opposite character of the substituents, the olefinic C=C double bond order is reduced and accompanied by the increased bond orders of the bonds between the olefinic carbon atoms and their electron donor and electron acceptor groups, respectively. This leads to the substantial decrease of the rotational barrier about the C=C double bond and to the increase of an analogues barrier about the adjecent bonds. These changes are connected with the separation of the possitive and negative charges and electron delocalization within the π-electron system. Such compounds belong to the most developed structures in the search for new compounds with non-linear optics responses (Nalwa *et al.*, 1997, Chemla & Zyss, 1987).

Experimental

2.5 mmol (150 mg) of 1,1-dimethylhydrazine was added at room temperature to 2.5 mmol (438 mg) of 3-ethoxy-2-methylsulfonylpropenenitrile (acrylonitrile) without any solvent. The reaction mixture became hot and after 10 min. of stirring ethanol (formed by the reaction) was removed and the crude product was recrystallized from ethyl acetate-hexane (1:4 v/v), to yield a light yellow powder (86%). Recrystallisation from chloroform gave pink blocks of (I).

Refinement

The H atoms were geometrically placed (C—H = 0.93-0.96 Å, N—H = 0.86 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(methyl C). The methyl groups were allowed to rotate, but not to tip, to best fit the electron density.

Figures

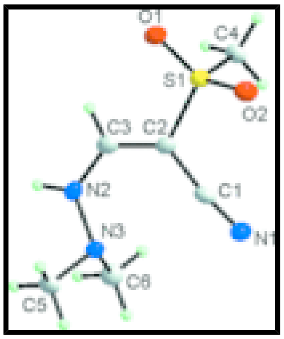

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level (arbitrary spheres for the H atoms).

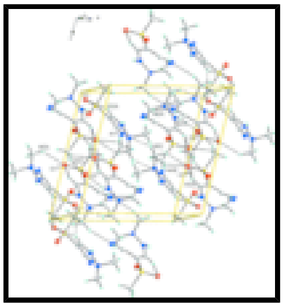

Fig. 2. Packing diagram of (I). Hydrogen-bond interactions are indicated by dashed lines.

3-*N*,*N*-dimethylhydrazino-2-methylsulfonyl propenenitrile

Crystal data

$C_6H_{11}N_3O_2S$	$F_{000} = 400$
$M_r = 189.24$	$D_x = 1.425$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 421 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 11.526$ (2) Å	Cell parameters from 5328 reflections
$b = 6.881$ (1) Å	$\theta = 3.5$–27.9°
$c = 11.577$ (2) Å	$\mu = 0.33$ mm^{-1}
$\beta = 106.06$ (3)°	$T = 100$ K
$V = 882.4$ (3) Å^3	Slab, pink
$Z = 4$	0.28 × 0.24 × 0.04 mm

Data collection

Oxford Diffraction GEMINI R diffractometer	1606 independent reflections
Radiation source: fine-focus sealed tube	1310 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.038$
$T = 100$ K	$\theta_{\text{max}} = 25.3$°
Rotation method data acquisition using ω and phi scans	$\theta_{\text{min}} = 4.2$°
Absorption correction: analytical	$h = -13 \rightarrow 13$

(Clark & Reid, 1995)	
T_{min} = 0.935, T_{max} = 0.987	$k = -8\rightarrow 8$
14473 measured reflections	$l = -13\rightarrow 13$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 1.0681P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$(\Delta/\sigma)_{max} = 0.003$
$wR(F^2) = 0.152$	$\Delta\rho_{max} = 0.65$ e Å^{-3}
$S = 1.14$	$\Delta\rho_{min} = -0.43$ e Å^{-3}
1606 reflections	Extinction correction: none
113 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Experimental. face-indexed (CrysAlis RED; Oxford Diffraction, 2006)

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.

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 > 2sigma(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_{iso}*/U_{eq}
S1	0.90922 (6)	0.76365 (10)	0.88325 (6)	0.0210 (3)
N1	0.6238 (2)	0.8154 (4)	0.6634 (2)	0.0294 (6)
N3	0.6663 (2)	0.3452 (3)	0.6091 (2)	0.0226 (6)
N2	0.7653 (2)	0.2899 (4)	0.7060 (2)	0.0239 (6)
H2A	0.7844	0.1691	0.7171	0.029*
C2	0.8065 (2)	0.6173 (4)	0.7816 (2)	0.0221 (6)
C1	0.7039 (3)	0.7189 (4)	0.7119 (2)	0.0213 (6)
C6	0.5527 (3)	0.3072 (5)	0.6390 (3)	0.0280 (7)
H6C	0.4860	0.3464	0.5731	0.034*
H6B	0.5514	0.3794	0.7096	0.034*
H6A	0.5464	0.1709	0.6539	0.034*
C3	0.8286 (3)	0.4217 (4)	0.7794 (2)	0.0223 (6)

H3A	0.8966	0.3766	0.8369	0.027*
C5	0.6735 (3)	0.2423 (4)	0.5005 (3)	0.0256 (7)
H5C	0.6078	0.2823	0.4338	0.031*
H5B	0.6685	0.1048	0.5124	0.031*
H5A	0.7487	0.2724	0.4842	0.031*
O1	1.02390 (17)	0.6673 (3)	0.91967 (17)	0.0247 (5)
O2	0.90420 (19)	0.9546 (3)	0.82968 (18)	0.0287 (5)
C4	0.8543 (3)	0.7845 (4)	1.0102 (3)	0.0248 (7)
H4C	0.9053	0.8710	1.0673	0.030*
H4B	0.8542	0.6588	1.0462	0.030*
H4A	0.7736	0.8350	0.9864	0.030*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0198 (4)	0.0233 (4)	0.0185 (4)	−0.0014 (3)	0.0031 (3)	0.0009 (3)
N1	0.0256 (14)	0.0259 (13)	0.0308 (14)	0.0016 (12)	−0.0021 (11)	−0.0010 (11)
N3	0.0220 (12)	0.0246 (13)	0.0186 (12)	0.0045 (10)	0.0011 (10)	−0.0013 (10)
N2	0.0258 (13)	0.0223 (12)	0.0215 (13)	0.0062 (10)	0.0029 (10)	0.0018 (10)
C2	0.0199 (14)	0.0256 (15)	0.0186 (14)	0.0013 (12)	0.0020 (11)	0.0018 (12)
C1	0.0206 (15)	0.0246 (14)	0.0175 (14)	−0.0047 (12)	0.0030 (11)	−0.0033 (11)
C6	0.0265 (16)	0.0295 (16)	0.0277 (16)	−0.0008 (13)	0.0071 (13)	0.0000 (13)
C3	0.0212 (14)	0.0273 (15)	0.0177 (13)	0.0003 (12)	0.0041 (11)	0.0014 (12)
C5	0.0255 (16)	0.0286 (16)	0.0204 (15)	0.0016 (12)	0.0026 (12)	−0.0047 (12)
O1	0.0213 (11)	0.0276 (11)	0.0234 (10)	0.0002 (9)	0.0030 (8)	0.0022 (9)
O2	0.0302 (12)	0.0242 (11)	0.0275 (11)	−0.0044 (9)	0.0011 (9)	0.0041 (9)
C4	0.0241 (15)	0.0287 (15)	0.0201 (15)	−0.0011 (12)	0.0036 (12)	−0.0052 (12)

Geometric parameters (Å, °)

S1—O1	1.434 (2)	C2—C1	1.418 (4)
S1—O2	1.447 (2)	C6—H6C	0.9600
S1—C2	1.740 (3)	C6—H6B	0.9600
S1—C4	1.759 (3)	C6—H6A	0.9600
N1—C1	1.150 (4)	C3—H3A	0.9300
N3—N2	1.413 (3)	C5—H5C	0.9600
N3—C5	1.465 (4)	C5—H5B	0.9600
N3—C6	1.468 (4)	C5—H5A	0.9600
N2—C3	1.317 (4)	C4—H4C	0.9600
N2—H2A	0.8600	C4—H4B	0.9600
C2—C3	1.371 (4)	C4—H4A	0.9600
O1—S1—O2	118.04 (13)	N3—C6—H6A	109.5
O1—S1—C2	109.30 (13)	H6C—C6—H6A	109.5
O2—S1—C2	107.24 (13)	H6B—C6—H6A	109.5
O1—S1—C4	107.89 (13)	N2—C3—C2	128.0 (3)
O2—S1—C4	107.64 (14)	N2—C3—H3A	116.0
C2—S1—C4	106.12 (14)	C2—C3—H3A	116.0
N2—N3—C5	109.0 (2)	N3—C5—H5C	109.5

N2—N3—C6	110.0 (2)	N3—C5—H5B	109.5
C5—N3—C6	112.5 (2)	H5C—C5—H5B	109.5
C3—N2—N3	120.5 (2)	N3—C5—H5A	109.5
C3—N2—H2A	119.7	H5C—C5—H5A	109.5
N3—N2—H2A	119.7	H5B—C5—H5A	109.5
C3—C2—C1	127.1 (3)	S1—C4—H4C	109.5
C3—C2—S1	119.0 (2)	S1—C4—H4B	109.5
C1—C2—S1	113.8 (2)	H4C—C4—H4B	109.5
N1—C1—C2	173.4 (3)	S1—C4—H4A	109.5
N3—C6—H6C	109.5	H4C—C4—H4A	109.5
N3—C6—H6B	109.5	H4B—C4—H4A	109.5
H6C—C6—H6B	109.5		

C5—N3—N2—C3	134.3 (3)	O2—S1—C2—C1	−32.2 (2)
C6—N3—N2—C3	−101.9 (3)	C4—S1—C2—C1	82.6 (2)
O1—S1—C2—C3	21.2 (3)	N3—N2—C3—C2	5.4 (4)
O2—S1—C2—C3	150.3 (2)	C1—C2—C3—N2	6.4 (5)
C4—S1—C2—C3	−94.9 (3)	S1—C2—C3—N2	−176.5 (2)
O1—S1—C2—C1	−161.3 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3A···O1	0.93	2.51	2.922 (4)	107
C5—H5C···N1^{i}	0.96	2.68	3.449 (5)	138
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C5—H5A···O1^{iv}	0.96	2.65	3.392 (3)	135
N2—H2A···O2^{ii}	0.86	2.19	2.944 (2)	147
C4—H4C···O2^{v}	0.96	2.50	3.399 (4)	156

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Fig. 1

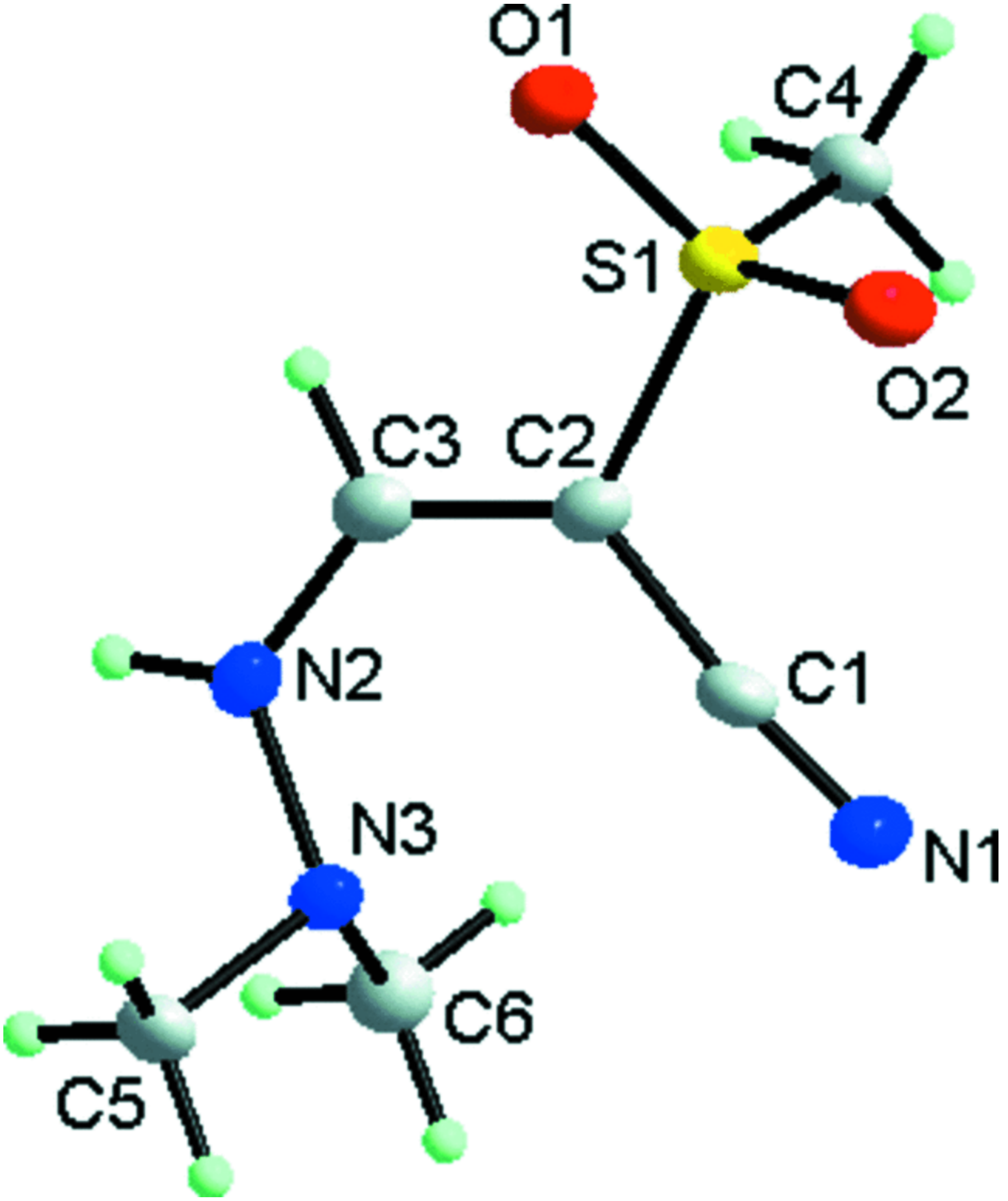
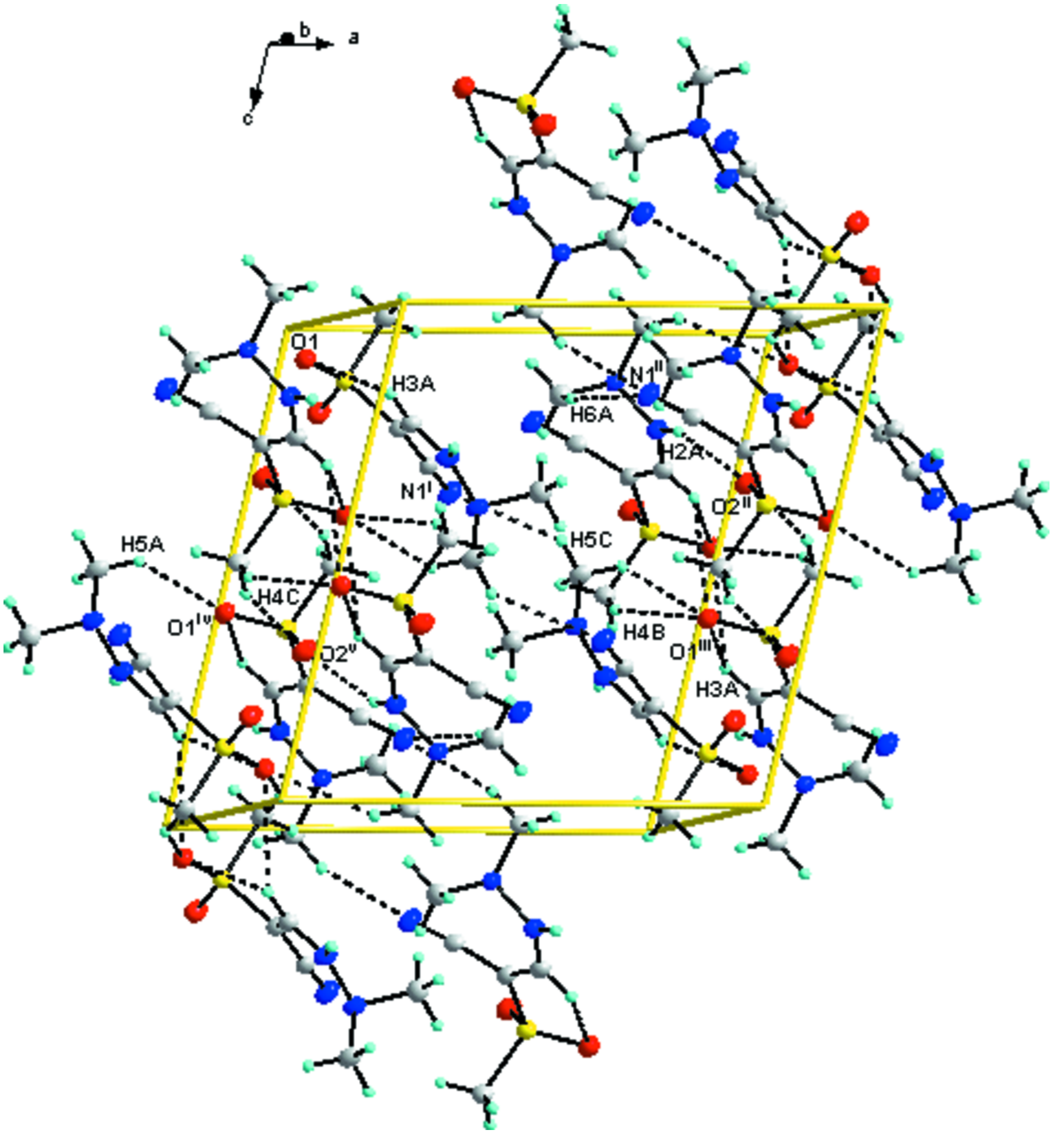


Fig. 2


b
a
c
O1
H3A
N1ⁱⁱ
H6A
H2A
N1ⁱ
O2ⁱⁱ
H5A
H5C
H4C
O1ⁱᵛ
O2ᵛ
H4B
O1ⁱⁱⁱ
H3A