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DL-Methionine DL-methioninium picrate

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The asymmetric unit of the title compound, $C_5H_{11}NO_2S\cdot C_5H_{12}NO_2S^+\cdot C_6H_2N_3O_7^-$, is composed of two crystallographically independent methionine residues and a picrate anion. The methionine and protonated methioninium residues are bonded through a strong O—H···O hydrogen bond, and an inversion-related DL1 head-to-tail sequence along the *a* axis is observed in the zwitterion. The amino groups of two residues connect to the lone oxygen of two inversion-related picrate anions. Hydrophobic layers are observed in the *y* = 0 plane.

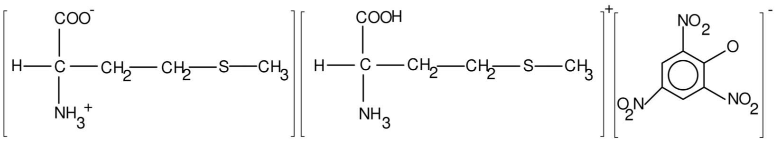
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.072
wR factor = 0.237
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Methionine, an essential amino acid, is one of the two sulfur-containing amino acids. The side chain is quite hydrophobic and methionine is usually found buried within proteins. Methionine reacts with adenosine triphosphate to form *S*-adenosyl methionine, a potent donor of methyl groups in the body (Jain, 1994) and contributes to the synthesis of many important substances, such as choline. The crystal structures of L-methionine (Torii & Iitaka, 1973), DL-methionine (α-form) (Mathieson, 1952), bis(DL-methionine) dihydrogen phosphate (Bahadur, 1992), L-methionine L-methioninium perchlorate monohydrate (Sridhar *et al.*, 2002), bis(L-methioninium) sulfate (Srinivasan *et al.*, 2001), L-methioninium nitrate (Pandiarajan *et al.*, 2002) and bis(DL-methioninium) sulfate (Ramaswamy *et al.*, 2004) have been reported. As part of a study of hydrogen bonding of picrate complexes of amino acids, a complex of DL-methionine with picric acid is reported.



(I)

The asymmetric unit of the title compound, (I), contains two crystallographically independent methionine residues and a picrate anion (Fig. 1). The S^δ atom in both methionine residues and the C^β atom of residue A are disordered. The backbone conformation angles $\psi^1$and ψ^2 are *cis* and *trans*, respectively, for both the residues. The side-chain conformation angles $\chi^1/\chi^2/\chi^3$ are *trans*/*trans*/*gauche* I and *gauche* II/*gauche* I/*gauche* I for residues A and B, respectively.

The picrate anion plays an important role in forming hydrogen bonds. In the picrate anion, removal of a proton leads to a shortening of the C—O bond and lengthening of adjacent C—C bond distances as in many other picrate complexes. In most picrates the *ortho*-related nitro groups are rotated further out of the molecular plane than the *para*-nitro substituent (Anitha *et al.*, 2004; Smith *et al.*, 2004). These nitro groups are commonly involved in hydrogen bonding. In the present case, one of the *ortho*-nitro groups is twisted from the plane of the ring. Such twisting of these nitro groups is independent of C—N bond distances (Soriano-Garcia *et al.*, 1978; Srikrishnan *et al.*, 1980). The nitro O atoms, not involved in hydrogen bonding, have large U_{eq} values.

The two methionine residues are linked through a strong asymmetric O—H···O hydrogen bond forming a dimer (Table 2 and Fig. 2). For residue A, two two-centered and one chelated three-centered hydrogen bonds are observed, leading to a class II hydrogen-bonding pattern in addition to an inversion-related DL1 head-to-tail sequence. The amino groups of two residues are connected through the lone oxygen of a picrate anion and the amino group of residue A connects to O atoms of the same picrate, leading to a chelated three-centered hydrogen bond. Three two-centered hydrogen bonds are observed in residue B, leading to a class I hydrogen-bonding pattern. The amino group of residue B connects two different picrate anions. It also connects to the carboxylate oxygen of inversion-related residue A and the amino group of residue A connects the O atom of residue B, leading to a ring. Hydrophobic layers are observed in the $y = 0$ plane.

Experimental

The title compound was crystallized from a mixture of DL-methionine and picric acid in the stoichiometric ratio of 2:1 at room temperature by the technique of slow evaporation.

Crystal data

$C_5H_{11}NO_2S{\cdot}C_5H_{12}NO_2S^+{\cdot}$-$C_6H_2N_3O_7^-$
$M_r = 527.53$
Triclinic, $P\bar{1}$
$a = 7.076$ (1) Å
$b = 12.102$ (1) Å
$c = 14.895$ (2) Å
$\alpha = 103.90$ (1)°
$\beta = 97.04$ (2)°
$\gamma = 101.73$ (2)°
$V = 1192.4$ (3) Å^3
$Z = 2$
$D_x = 1.469$ Mg m^{-3}
$D_m = 1.460$ Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 6.8$–14.2°
$\mu = 0.29$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.20 × 0.15 × 0.10 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.943$, $T_{max} = 0.975$
4940 measured reflections
4217 independent reflections
2516 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.237$
$S = 1.03$
4217 reflections
331 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1091P)^2 + 0.8526P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

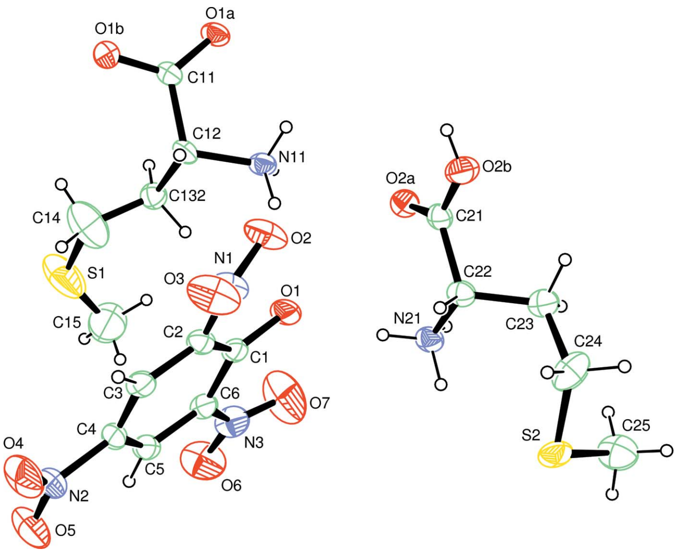


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level. Only the major disorder components are shown.

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.236 (5)	O2*A*—C21	1.218 (5)
O1*B*—C11	1.263 (5)	O2*B*—C21	1.276 (5)
O1*A*—C11—O1*B*	125.3 (4)	O2*A*—C21—O2*B*	126.1 (4)
O1*A*—C11—C12	120.1 (4)	O2*A*—C21—C22	121.3 (4)
O1*B*—C11—C12	114.6 (3)	O2*B*—C21—C22	112.6 (4)
O1*A*—C11—C12—N11	13.2 (6)	C23—C24—S2—C25	74.4 (11)
O1*B*—C11—C12—N11	−166.7 (4)	O3—N1—C2—C3	19.9 (7)
N11—C12—C132—C14	145.1 (6)	O2—N1—C2—C1	23.2 (7)
C132—C14—S1—C15	42.8 (14)	O4—N2—C4—C3	−1.5 (7)
O2*A*—C21—C22—N21	−2.4 (5)	O5—N2—C4—C5	−2.6 (7)
O2*B*—C21—C22—N21	176.6 (3)	O6—N3—C6—C5	6.8 (8)
N21—C22—C23—C24	−80.0 (6)	O7—N3—C6—C1	10.8 (9)
C22—C23—C24—S22	69.9 (15)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*B*—H2*B*···O1*B*^{i}	0.82	1.66	2.457 (5)	163
N11—H11*A*···O1*A*^{i}	0.89	2.11	2.901 (5)	147
N11—H11*B*···O2*A*^{ii}	0.89	2.06	2.868 (4)	151
N11—H11*C*···O1	0.89	2.06	2.861 (5)	149
N11—H11*C*···O2	0.89	2.26	2.928 (5)	131
N21—H21*A*···O4^{iii}	0.89	2.57	3.062 (5)	115
N21—H21*B*···O1*A*^{ii}	0.89	2.07	2.955 (4)	174
N21—H21*C*···O1	0.89	1.97	2.820 (5)	160

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

The S atom of both residues and the Cβ of the methionine residue were found to be disordered. Hence two more sets of data, with two different crystals selected from different crops, were collected. Disorder was also observed from these two data sets. During refinement with isotropic displacement parameters, the occupancy of

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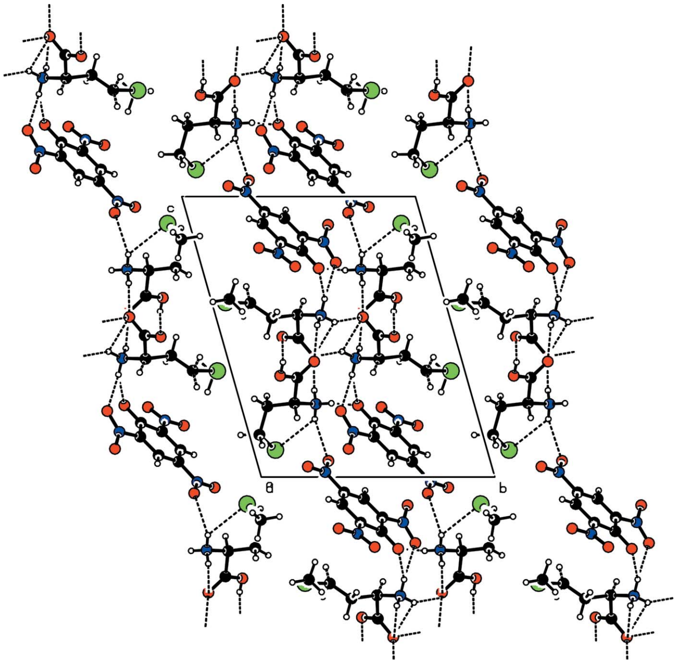

Figure 2
Packing diagram of (I) viewed down the *a* axis. Hydrogen bonds are drawn as dashed lines. Only the major disorder components are shown.

disordered atoms in both residues were refined. These site-occupancy factors were then fixed as S1 0.55, S11 0.21, S12 0.24, C131 0.35, C132 0.65, S2 0.55, S21 0.10 and S22 0.35 during anisotropic refinement. The final refinements were performed with only one set of data. All H atoms were placed in geometrically calculated positions [0.89 (NH), 0.82 (OH), 0.93 and 0.98 (CH), 0.97 (CH_2) and 0.96 Å (CH_3)] and constrained to ride on their parent atoms with $U_{iso}(H) = 1.5(1.2$ for CH and CH_2) U_{eq}(C,N,O).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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