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4-Methyl-3,5-dinitrobenzoic acid–dimethyl sulfoxide (1/1)

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Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.102
Data-to-parameter ratio = 15.7

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

The title complex, $C_8H_6N_2O_6\cdot C_2H_6OS$, was predicted to illustrate an intermolecular hydrogen-bond motif between the carboxylic acid and the sulfoxide funtionalities, based upon a previously published structure of an analogous complex. The predicted hydrogen-bond motif was observed, thereby indicating a certain robustness of this intermolecular interaction for crystal engineering purposes.

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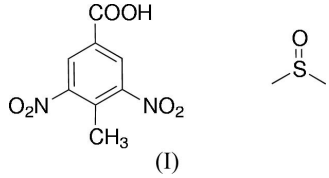
Comment

The asymmetric unit of the title crystal structure, (I), consists of one molecule each of 4-methyl-3,5-dinitrobenzoic acid and dimethyl sulfoxide (DMSO) (Fig. 1).



(I)

The crystallization was performed to evaluate the robustness of an intermolecular hydrogen bond involving an O—H···O=S contact between a carboxylic acid and a sulfoxide. This interaction was recently observed in the crystal structure of an analogous complex involving 3,5-dinitrobenzoic acid and DMSO (Abthorpe *et al.*, 2005). This interaction also is found in 29 of a possible 37 instances in the Cambridge Structural Database (CSD Version 5.25 Update 3; Allen, 2002), when searching for structures which contain both a carboxyl group and a DMSO molecule among all organic structures for which three-dimensional coordinates have been determined. The hydrogen-bond interaction in the crystal structure is presented in Fig. 2.

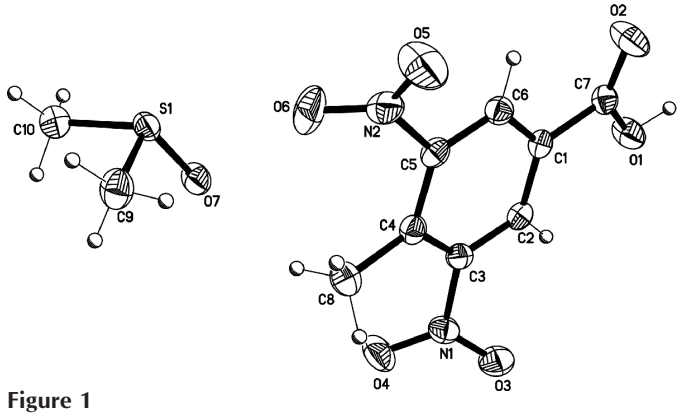


Figure 1
The asymmetric unit (*XP*; Sheldrick, 1993) of (I), showing displacement ellipsoids at the 50% probability level.

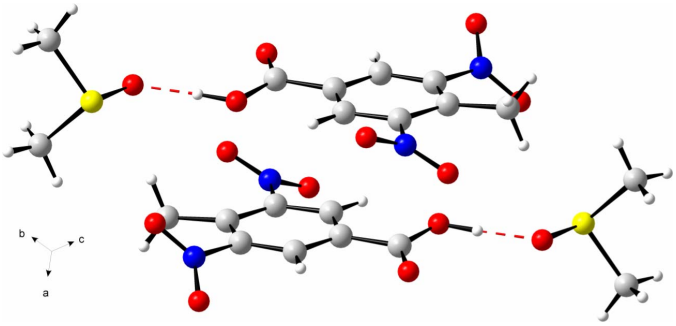


Figure 2
Part of the crystal packing (*DIAMOND*; Brandenburg, 1999), showing intermolecular hydrogen-bond interactions as dashed lines.

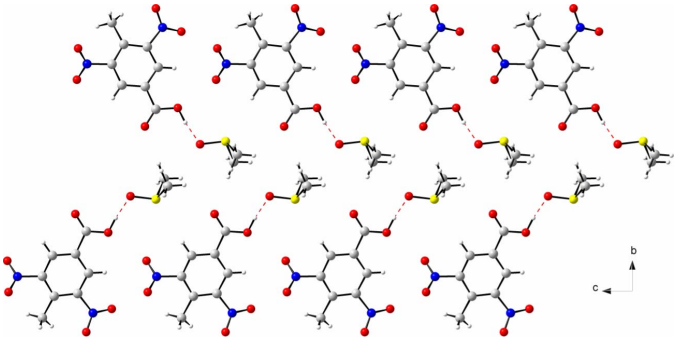


Figure 3
The crystal packing (*DIAMOND*; Brandenburg, 1999), viewed along [100], showing sheets stacking along [010].

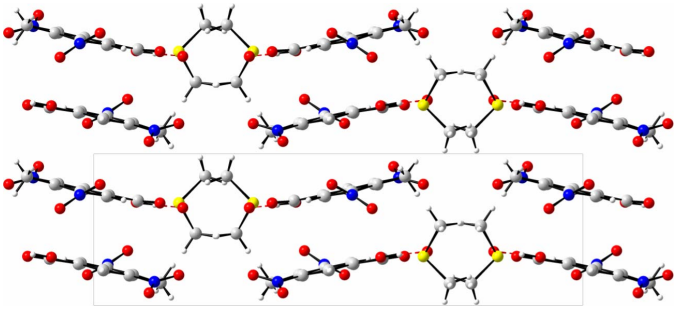


Figure 4
The crystal packing (*DIAMOND*; Brandenburg, 1999), viewed along [001], showing sheets stacking along [010].

The title complex packs in a monoclinic unit cell in the space group $P2_1/c$. Crystal packing results in alternating sheets of acid and DMSO molecules stacking along [010]. (Figs. 3 and 4).

The experiment reported here represents a successful demonstration of the methodological approach of crystal engineering: observation of a particular heteromolecular hydrogen-bonding interaction, evaluation of the abundance of the interaction in the CSD, and application of this information to the design of a novel crystalline molecular complex. The demonstrated robustness of this hydrogen-bond motif indicates a potential utility for future crystal engineering experiment design.

Experimental

All starting components were obtained from Sigma Aldrich Ltd. 4-Methyl-3,5-dinitrobenzoic acid (64 mg) was dissolved in excess DMSO with gentle heating. The resulting solution was allowed to cool and evaporate slowly over a period of one week. From the solids that precipitated, a single crystal was harvested for subsequent XRD analysis.

Crystal data

$C_8H_6N_2O_6\cdot C_2H_6OS$
$M_r = 304.28$
Monoclinic, $P2_1/c$
$a = 6.9483\ (2)$ Å
$b = 22.4844\ (5)$ Å
$c = 8.2364\ (2)$ Å
$\beta = 92.765\ (1)^\circ$
$V = 1285.26\ (6)$ Å^3
$Z = 4$
$D_x = 1.572$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7863 reflections
$\theta = 1.0$–27.5°
$\mu = 0.29$ mm^{-1}
$T = 180\ (2)$ K
Plate, colourless
0.35 × 0.32 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.901$, $T_{max} = 0.976$
9790 measured reflections
2930 independent reflections
2263 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 27.5^\circ$
$h = -9 \rightarrow 9$
$k = -29 \rightarrow 29$
$l = -7 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.102$
$S = 1.06$
2930 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.6419P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

All H atoms bonded to carbon were positioned geometrically and refined using a riding model, with $U_{iso} = 1.5U_{eq}$ for methyl H atoms and $U_{iso}(H) = 1.2U_{eq}$(carrier atom) for all other H atoms. The C—H distances of the methyl groups were fixed at 0.98 Å; all other C—H distances were fixed at 0.95 Å. The O—H H atom was located in a difference Fourier map and refined isotropically.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1993) and *DIAMOND* (Brandenburg, 1999)(software used to prepare material for publication: *SHELXL97*.

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