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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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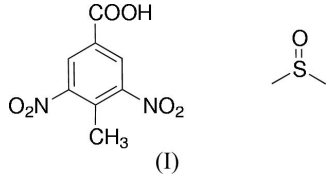
Comment

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.

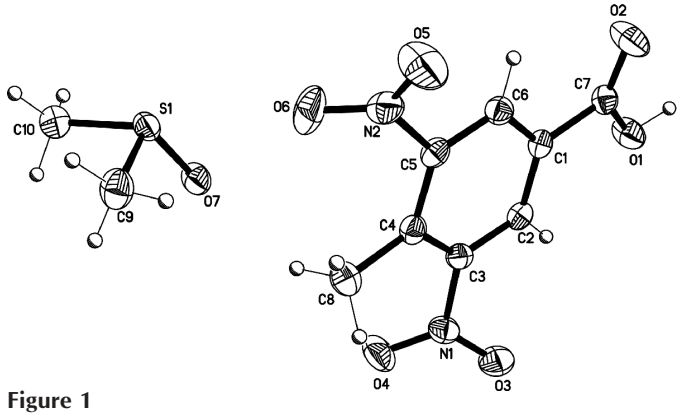


Figure 1
The asymmetric unit (*XP*; Sheldrick, 1993) of (I), showing displacement ellipsoids at the 50% probability level.

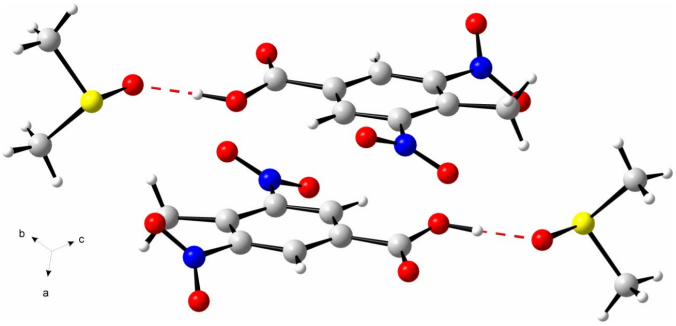


Figure 2
Part of the crystal packing (*DIAMOND*; Brandenburg, 1999), showing intermolecular hydrogen-bond interactions as dashed lines.

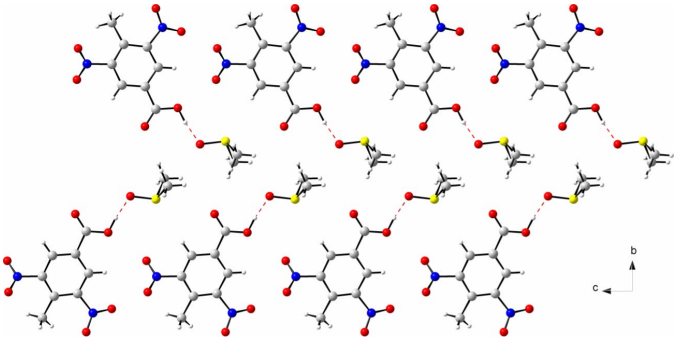


Figure 3
The crystal packing (*DIAMOND*; Brandenburg, 1999), viewed along [100], showing sheets stacking along [010].

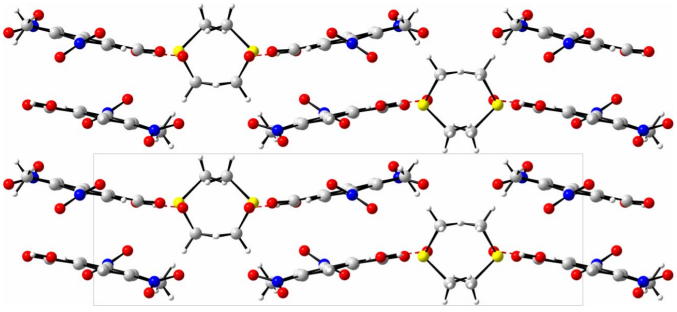


Figure 4
The crystal packing (*DIAMOND*; Brandenburg, 1999), viewed along [001], showing sheets stacking along [010].

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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supporting information

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

A. V. Trask, M. Abthorpe and W. Jones

3,5-dinitro-4-methylbenzoic acid dimethyl sulfoxide

Crystal data

$C_8H_6N_2O_6·C_2H_6OS$
M_r = 304.28
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 6.9483 (2) Å
b = 22.4844 (5) Å
c = 8.2364 (2) Å
β = 92.765 (1)°
V = 1285.26 (6) Å^3
Z = 4
$F(000)$ = 632
D_x = 1.572 Mg m^{-3}
Melting point: not measured K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7863 reflections
θ = 1.0–27.5°
μ = 0.29 mm^{-1}
T = 180 K
Plate, colourless
0.35 × 0.32 × 0.10 mm

Data collection

Nonius Kappa CCD diffractometer
Radiation source: fine-focus sealed tube
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
θ_{max} = 27.5°, θ_{min} = 3.6°
h = −9→9
k = −29→29
l = −7→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.102
S = 1.06
2930 reflections
187 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
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}

Special details

Experimental. The –COOH hydrogen atom was located and its position was refined satisfactorily.

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.6815 (2)	−0.08681 (6)	1.20349 (17)	0.0350 (3)
H1	0.664 (3)	−0.1248 (8)	1.257 (3)	0.042*
O2	0.6761 (3)	−0.13533 (6)	0.96732 (18)	0.0454 (4)
O3	0.9171 (2)	0.11314 (7)	1.22899 (18)	0.0390 (4)
O4	0.8000 (2)	0.17390 (6)	1.0462 (2)	0.0426 (4)
O5	0.7981 (3)	−0.01287 (8)	0.4786 (2)	0.0610 (5)
O6	0.6390 (2)	0.06916 (8)	0.4873 (2)	0.0501 (4)
N1	0.8439 (2)	0.12389 (7)	1.0941 (2)	0.0278 (4)
N2	0.7299 (3)	0.02850 (8)	0.5517 (2)	0.0334 (4)
C1	0.7264 (2)	−0.03097 (8)	0.9698 (2)	0.0213 (4)
C2	0.7674 (2)	0.01946 (8)	1.0625 (2)	0.0214 (4)
H2	0.7716	0.0174	1.1778	0.026*
C3	0.8021 (2)	0.07289 (8)	0.9847 (2)	0.0221 (4)
C4	0.7989 (3)	0.07983 (8)	0.8157 (2)	0.0238 (4)
C5	0.7521 (2)	0.02758 (8)	0.7310 (2)	0.0237 (4)
C6	0.7207 (2)	−0.02672 (8)	0.8024 (2)	0.0241 (4)
H6	0.6954	−0.0609	0.7371	0.029*
C7	0.6912 (3)	−0.09025 (8)	1.0459 (2)	0.0239 (4)
C8	0.8514 (3)	0.13656 (9)	0.7308 (3)	0.0340 (5)
H8A	0.9031	0.1270	0.6253	0.051*
H8B	0.9488	0.1581	0.7976	0.051*
H8C	0.7363	0.1614	0.7142	0.051*
S1	0.32344 (7)	0.17405 (2)	0.45368 (6)	0.02639 (14)
O7	0.3552 (2)	0.18195 (6)	0.63648 (16)	0.0319 (3)
C9	0.5251 (3)	0.20847 (10)	0.3685 (3)	0.0368 (5)
H9A	0.6407	0.1846	0.3934	0.055*
H9B	0.5429	0.2484	0.4147	0.055*
H9C	0.5029	0.2115	0.2504	0.055*
C10	0.1463 (3)	0.22803 (9)	0.3945 (3)	0.0350 (5)
H10A	0.0234	0.2176	0.4408	0.052*
H10B	0.1300	0.2290	0.2757	0.052*
H10C	0.1878	0.2673	0.4344	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0579 (9)	0.0267 (7)	0.0208 (7)	−0.0060 (7)	0.0045 (6)	0.0032 (6)
O2	0.0836 (12)	0.0235 (8)	0.0293 (9)	−0.0053 (7)	0.0061 (8)	−0.0017 (6)
O3	0.0488 (9)	0.0370 (8)	0.0305 (9)	−0.0036 (7)	−0.0061 (7)	−0.0084 (7)
O4	0.0565 (10)	0.0216 (7)	0.0497 (10)	0.0047 (7)	0.0024 (8)	−0.0023 (7)
O5	0.1171 (16)	0.0419 (10)	0.0243 (9)	−0.0021 (10)	0.0078 (9)	−0.0072 (7)
O6	0.0561 (10)	0.0609 (11)	0.0323 (9)	0.0060 (8)	−0.0078 (7)	0.0193 (8)
N1	0.0285 (8)	0.0258 (9)	0.0294 (9)	−0.0013 (7)	0.0036 (7)	−0.0045 (7)
N2	0.0421 (10)	0.0379 (10)	0.0201 (9)	−0.0112 (8)	−0.0003 (7)	0.0032 (8)
C1	0.0195 (8)	0.0243 (9)	0.0201 (9)	0.0030 (7)	0.0013 (7)	0.0022 (7)
C2	0.0194 (8)	0.0275 (9)	0.0174 (9)	0.0024 (7)	0.0012 (6)	−0.0004 (7)
C3	0.0194 (8)	0.0223 (9)	0.0245 (10)	0.0010 (7)	0.0009 (7)	−0.0034 (7)
C4	0.0213 (9)	0.0254 (10)	0.0248 (10)	0.0016 (7)	0.0004 (7)	0.0019 (7)
C5	0.0245 (9)	0.0305 (10)	0.0160 (9)	−0.0002 (7)	0.0004 (7)	0.0016 (7)
C6	0.0249 (9)	0.0245 (10)	0.0227 (10)	0.0012 (7)	0.0005 (7)	−0.0018 (7)
C7	0.0262 (9)	0.0247 (9)	0.0210 (10)	0.0021 (7)	0.0026 (7)	0.0017 (8)
C8	0.0390 (11)	0.0287 (10)	0.0341 (12)	−0.0042 (9)	0.0005 (9)	0.0083 (9)
S1	0.0386 (3)	0.0196 (2)	0.0209 (3)	−0.00201 (19)	0.00083 (19)	0.00087 (18)
O7	0.0510 (9)	0.0263 (7)	0.0185 (7)	−0.0026 (6)	0.0034 (6)	0.0016 (5)
C9	0.0389 (12)	0.0421 (13)	0.0297 (12)	0.0006 (9)	0.0054 (9)	0.0085 (9)
C10	0.0364 (11)	0.0317 (11)	0.0363 (12)	−0.0017 (9)	−0.0025 (9)	0.0039 (9)

Geometric parameters (Å, º)

O1—C7	1.305 (2)	C4—C8	1.508 (3)
O1—H1	0.972 (16)	C5—C6	1.377 (3)
O2—C7	1.204 (2)	C6—H6	0.9500
O3—N1	1.224 (2)	C8—H8A	0.9800
O4—N1	1.225 (2)	C8—H8B	0.9800
O5—N2	1.217 (2)	C8—H8C	0.9800
O6—N2	1.218 (2)	S1—O7	1.5215 (14)
N1—C3	1.479 (2)	S1—C9	1.775 (2)
N2—C5	1.478 (2)	S1—C10	1.780 (2)
C1—C6	1.380 (2)	C9—H9A	0.9800
C1—C2	1.389 (2)	C9—H9B	0.9800
C1—C7	1.498 (2)	C9—H9C	0.9800
C2—C3	1.388 (2)	C10—H10A	0.9800
C2—H2	0.9500	C10—H10B	0.9800
C3—C4	1.399 (3)	C10—H10C	0.9800
C4—C5	1.397 (3)		
C7—O1—H1	114.4 (14)	O2—C7—O1	125.24 (17)
O3—N1—O4	124.04 (17)	O2—C7—C1	122.39 (17)
O3—N1—C3	117.46 (16)	O1—C7—C1	112.37 (16)
O4—N1—C3	118.48 (16)	C4—C8—H8A	109.5
O5—N2—O6	124.34 (19)	C4—C8—H8B	109.5

O5—N2—C5	117.38 (17)	H8A—C8—H8B	109.5
O6—N2—C5	118.22 (18)	C4—C8—H8C	109.5
C6—C1—C2	119.19 (17)	H8A—C8—H8C	109.5
C6—C1—C7	118.82 (16)	H8B—C8—H8C	109.5
C2—C1—C7	121.99 (16)	O7—S1—C9	105.10 (9)
C3—C2—C1	119.23 (17)	O7—S1—C10	104.89 (9)
C3—C2—H2	120.4	C9—S1—C10	98.23 (10)
C1—C2—H2	120.4	S1—C9—H9A	109.5
C2—C3—C4	124.11 (17)	S1—C9—H9B	109.5
C2—C3—N1	115.04 (16)	H9A—C9—H9B	109.5
C4—C3—N1	120.86 (16)	S1—C9—H9C	109.5
C5—C4—C3	113.27 (16)	H9A—C9—H9C	109.5
C5—C4—C8	122.37 (17)	H9B—C9—H9C	109.5
C3—C4—C8	124.27 (17)	S1—C10—H10A	109.5
C6—C5—C4	124.78 (17)	S1—C10—H10B	109.5
C6—C5—N2	115.35 (16)	H10A—C10—H10B	109.5
C4—C5—N2	119.86 (16)	S1—C10—H10C	109.5
C5—C6—C1	119.36 (17)	H10A—C10—H10C	109.5
C5—C6—H6	120.3	H10B—C10—H10C	109.5
C1—C6—H6	120.3		

C6—C1—C2—C3	−0.2 (2)	C3—C4—C5—N2	175.91 (16)
C7—C1—C2—C3	178.84 (15)	C8—C4—C5—N2	−7.4 (3)
C1—C2—C3—C4	0.0 (3)	O5—N2—C5—C6	−42.7 (2)
C1—C2—C3—N1	179.89 (15)	O6—N2—C5—C6	134.65 (19)
O3—N1—C3—C2	27.8 (2)	O5—N2—C5—C4	138.3 (2)
O4—N1—C3—C2	−150.75 (16)	O6—N2—C5—C4	−44.4 (2)
O3—N1—C3—C4	−152.29 (17)	C4—C5—C6—C1	3.0 (3)
O4—N1—C3—C4	29.2 (2)	N2—C5—C6—C1	−175.97 (16)
C2—C3—C4—C5	1.5 (3)	C2—C1—C6—C5	−1.2 (3)
N1—C3—C4—C5	−178.39 (15)	C7—C1—C6—C5	179.72 (16)
C2—C3—C4—C8	−175.10 (17)	C6—C1—C7—O2	7.2 (3)
N1—C3—C4—C8	5.0 (3)	C2—C1—C7—O2	−171.82 (18)
C3—C4—C5—C6	−3.1 (3)	C6—C1—C7—O1	−173.54 (16)
C8—C4—C5—C6	173.63 (18)	C2—C1—C7—O1	7.4 (2)