

3,5-Dinitrobenzoic acid–dimethyl sulfoxide (1/1)

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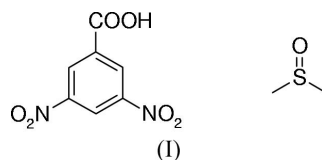
Key indicators

Single-crystal X-ray study
 $T = 260$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.045
 wR factor = 0.134
Data-to-parameter ratio = 16.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $\text{C}_7\text{H}_4\text{N}_2\text{O}_6 \cdot \text{C}_2\text{H}_6\text{OS}$, involves an intermolecular hydrogen-bond motif between the carboxyl and the sulfoxide groups. This motif has precedence in the Cambridge Structural Database, and is shown here to be more favourable than a possible carboxylic acid homodimer.

Comment

As part of ongoing research into the crystallization preferences of crystalline complexes, the growth of a previously reported three-component crystalline complex (Pedireddi *et al.*, 1996) was attempted. The solvent dimethyl sulfoxide (DMSO) was used to aid dissolution of the components. In several instances, the crystallization unexpectedly resulted in single crystals of the title adduct, (I). The asymmetric unit consists of one molecule each of 3,5-dinitrobenzoic acid (3,5-DNBA) and DMSO (Fig. 1).



Previously reported crystallizations of 3,5-DNBA indicate a dimorphic nature for this substance. Two monoclinic polymorphs have been reported (Prince *et al.*, 1991) and both exhibit the common carboxylic acid dimer hydrogen-bond motif. The interaction between 3,5-DNBA and DMSO described here involves a hydrogen bond between the carboxyl moiety of the acid and the sulfoxide group of the

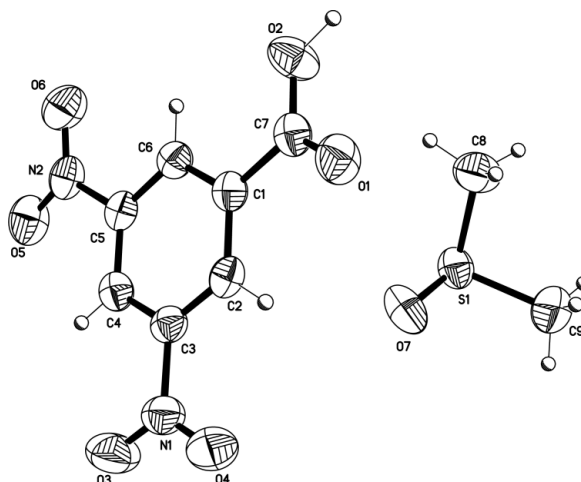


Figure 1
The asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level (*XP*; Sheldrick, 1993).

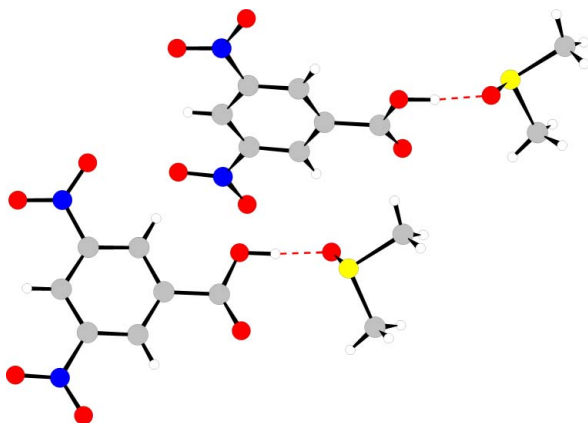


Figure 2
Crystal packing diagram, showing the intermolecular hydrogen-bonding interactions as dashed lines.

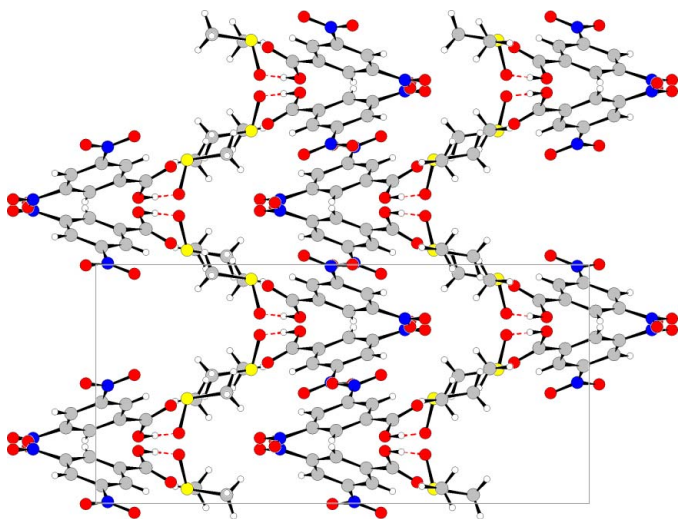


Figure 3
Crystal packing diagram, showing sheets stacking along [001], as viewed along [010]. Dashed lines indicate hydrogen bonds.

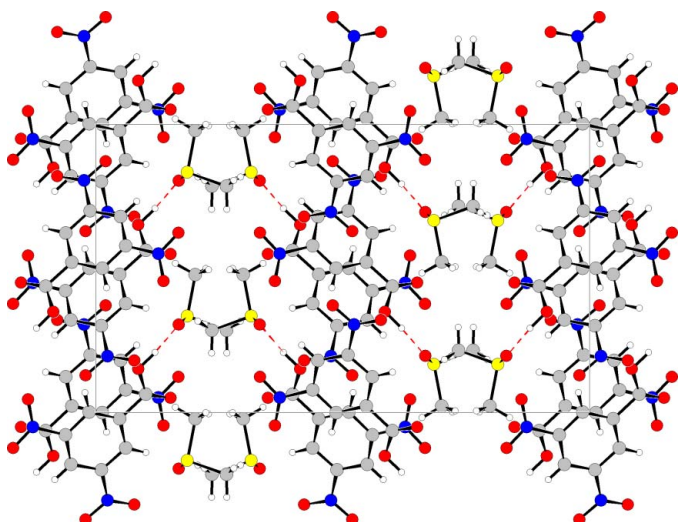


Figure 4
Crystal packing diagram showing sheets stacking along [001], as viewed along [100].

solvent (Fig. 2). It is interesting, therefore, that the title complex represents the disruption of the carboxylic acid dimer by the introduction of the sulfoxide moiety upon complexation.

A search of the Cambridge Structural Database (CSD, Version 5.25, Update 3; Allen, 2002) reveals precedence for this acid–DMSO interaction. Searching for structures which contain both a carboxyl moiety and a DMSO molecule among all organic structures for which three-dimensional coordinates have been determined resulted in 37 hits. Of those, 29 complexes exhibit an O–H···O=S hydrogen bond which is shorter than the sum of the van der Waals radii of the two O atoms. The apparent substantial likelihood of the formation of this motif indicates a potential utility for crystal engineering experimental design.

Crystal packing results in what may be perceived as alternating sheets of 3,5-DNBA and DMSO stacking along [001] (Figs. 3 and 4).

Experimental

All starting components were obtained from Sigma Aldrich Ltd. 3,5-Dinitrobenzoic acid (357 mg) and 0.5 equivalents of anthracene (150 mg) were heated to reflux in benzene (*ca* 50 ml). To dissolve the solids fully, a small quantity of DMSO (*ca* 2 ml) was added to the slurry. The resulting solution was allowed to cool and evaporate slowly over a period of 24 h. Crystals were observed before all the solvent had evaporated; a single crystal was harvested from this saturated solution for X-ray diffraction analysis.

Crystal data

$C_7H_4N_2O_6 \cdot C_2H_6OS$
 $M_r = 290.25$
 Orthorhombic, $Pbca$
 $a = 10.0156$ (2) Å
 $b = 12.0767$ (2) Å
 $c = 20.6483$ (5) Å
 $V = 2497.52$ (9) Å³
 $Z = 8$
 $D_x = 1.544$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 11 611 reflections
 $\theta = 1.0$ – 27.5°
 $\mu = 0.29$ mm⁻¹
 $T = 260$ (2) K
 Plate, yellow
 $0.23 \times 0.23 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.873$, $T_{\max} = 0.970$
 16 897 measured reflections
 2856 independent reflections

2114 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 27.5^\circ$
 $h = -12 \rightarrow 13$
 $k = -15 \rightarrow 15$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.134$
 $S = 1.03$
 2856 reflections
 178 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 1.1187P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.60$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

All H atoms bonded to C atoms were placed geometrically and refined using a riding model. The U_{iso} values for methyl H atoms were taken as $1.5U_{\text{eq}}$ of the carrier atom. For all other H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$. The C–H distances of the methyl groups were

fixed at 0.96 Å; all other C–H distances were fixed at 0.93 Å. The O–H H atom was located from difference Fourier maps and fixed at an O–H bond distance of 1.00 Å.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); 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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 $c = 20.6483$ (5) Å
 $V = 2497.52$ (9) Å³
 $Z = 8$
 $F(000) = 1200$

$D_x = 1.544$ Mg m⁻³
 Melting point: not measured K
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 11611 reflections
 $\theta = 1.0$ – 27.5°
 $\mu = 0.29$ mm⁻¹
 $T = 260$ K
 Plate, yellow
 $0.23 \times 0.23 \times 0.12$ 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)
 $T_{\min} = 0.873$, $T_{\max} = 0.970$
 16897 measured reflections

2856 independent reflections
 2114 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.5^\circ$
 $h = -12 \rightarrow 13$
 $k = -15 \rightarrow 15$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.134$
 $S = 1.03$
 2856 reflections
 178 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
 $w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 1.1187P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.60$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.41031 (17)	-0.05040 (14)	0.15161 (8)	0.0526 (4)
O2	0.28020 (17)	-0.15088 (14)	0.08622 (9)	0.0553 (5)
H2A	0.284 (4)	-0.208 (3)	0.1197 (15)	0.117 (14)*
O3	0.5018 (2)	0.37105 (15)	-0.02034 (10)	0.0713 (6)
O4	0.5381 (2)	0.31999 (16)	0.07821 (10)	0.0642 (5)
O5	0.27367 (19)	0.12356 (17)	-0.16760 (8)	0.0618 (5)
O6	0.2394 (2)	-0.04496 (16)	-0.13742 (9)	0.0643 (5)
C1	0.35291 (19)	0.02206 (16)	0.04847 (10)	0.0354 (4)
N1	0.49347 (19)	0.30483 (16)	0.02397 (11)	0.0478 (5)
N2	0.27320 (18)	0.05110 (18)	-0.12700 (9)	0.0456 (5)
C2	0.41434 (19)	0.12320 (18)	0.06069 (10)	0.0375 (5)
H2	0.4482	0.1391	0.1016	0.045*
C3	0.42432 (19)	0.19929 (17)	0.01149 (10)	0.0375 (5)
C4	0.3761 (2)	0.17989 (17)	-0.05049 (10)	0.0385 (5)
H4	0.3828	0.2327	-0.0831	0.046*
C5	0.31788 (19)	0.07820 (17)	-0.06102 (10)	0.0367 (5)
C6	0.30450 (19)	-0.00084 (18)	-0.01318 (10)	0.0369 (5)
H6	0.2637	-0.0684	-0.0221	0.044*
C7	0.3500 (2)	-0.06314 (18)	0.10160 (10)	0.0398 (5)
S1	0.06085 (6)	0.16639 (5)	0.18509 (3)	0.04586 (19)
O7	0.20480 (17)	0.19557 (15)	0.16814 (9)	0.0581 (5)
C8	0.0644 (3)	0.0223 (2)	0.20131 (15)	0.0641 (7)
H8A	0.0720	-0.0177	0.1613	0.096*
H8B	-0.0165	0.0011	0.2230	0.096*
H8C	0.1395	0.0055	0.2284	0.096*
C9	0.0355 (3)	0.2154 (3)	0.26485 (14)	0.0688 (8)
H9A	0.0434	0.2946	0.2654	0.103*
H9B	0.1014	0.1837	0.2931	0.103*
H9C	-0.0520	0.1944	0.2793	0.103*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0591 (10)	0.0608 (10)	0.0378 (9)	-0.0014 (8)	-0.0088 (7)	0.0056 (8)
O2	0.0572 (10)	0.0523 (10)	0.0563 (10)	-0.0128 (8)	-0.0177 (8)	0.0165 (8)
O3	0.0949 (15)	0.0464 (10)	0.0726 (13)	-0.0167 (10)	-0.0046 (11)	0.0084 (9)
O4	0.0642 (11)	0.0684 (12)	0.0600 (12)	-0.0216 (9)	-0.0089 (9)	-0.0114 (9)
O5	0.0707 (12)	0.0784 (12)	0.0362 (9)	0.0107 (10)	-0.0072 (8)	0.0069 (9)
O6	0.0764 (13)	0.0694 (12)	0.0471 (10)	-0.0071 (10)	-0.0109 (9)	-0.0148 (9)
C1	0.0285 (9)	0.0418 (11)	0.0360 (11)	0.0047 (8)	0.0006 (8)	0.0007 (8)

N1	0.0428 (10)	0.0434 (10)	0.0571 (12)	-0.0025 (8)	0.0025 (9)	-0.0058 (9)
N2	0.0401 (10)	0.0602 (12)	0.0364 (10)	0.0068 (9)	-0.0032 (8)	-0.0037 (9)
C2	0.0335 (10)	0.0460 (11)	0.0329 (10)	0.0052 (9)	0.0001 (8)	-0.0050 (9)
C3	0.0329 (10)	0.0378 (10)	0.0418 (11)	0.0026 (8)	0.0020 (8)	-0.0042 (9)
C4	0.0357 (10)	0.0415 (11)	0.0384 (11)	0.0065 (9)	0.0023 (8)	0.0044 (9)
C5	0.0318 (9)	0.0469 (11)	0.0313 (10)	0.0053 (9)	-0.0013 (8)	-0.0037 (9)
C6	0.0315 (9)	0.0405 (10)	0.0386 (11)	0.0015 (8)	-0.0001 (8)	-0.0022 (9)
C7	0.0347 (10)	0.0465 (12)	0.0382 (11)	0.0044 (9)	0.0014 (9)	0.0036 (9)
S1	0.0476 (3)	0.0501 (3)	0.0399 (3)	0.0041 (2)	0.0004 (2)	0.0081 (2)
O7	0.0498 (10)	0.0589 (10)	0.0656 (11)	0.0066 (8)	0.0140 (8)	0.0232 (9)
C8	0.0721 (18)	0.0475 (14)	0.0727 (18)	-0.0040 (13)	0.0059 (14)	0.0033 (13)
C9	0.0781 (19)	0.0703 (18)	0.0581 (17)	-0.0043 (15)	0.0164 (14)	-0.0099 (14)

Geometric parameters (Å, °)

O1—C7	1.206 (3)	C3—C4	1.388 (3)
O2—C7	1.309 (3)	C4—C5	1.377 (3)
O2—H2A	0.974 (19)	C4—H4	0.9300
O3—N1	1.218 (3)	C5—C6	1.380 (3)
O4—N1	1.220 (3)	C6—H6	0.9300
O5—N2	1.212 (3)	S1—O7	1.5249 (18)
O6—N2	1.228 (3)	S1—C9	1.768 (3)
C1—C6	1.390 (3)	S1—C8	1.772 (3)
C1—C2	1.391 (3)	C8—H8A	0.9600
C1—C7	1.504 (3)	C8—H8B	0.9600
N1—C3	1.473 (3)	C8—H8C	0.9600
N2—C5	1.471 (3)	C9—H9A	0.9600
C2—C3	1.373 (3)	C9—H9B	0.9600
C2—H2	0.9300	C9—H9C	0.9600
C7—O2—H2A	112 (2)	C5—C6—C1	118.95 (19)
C6—C1—C2	119.68 (19)	C5—C6—H6	120.5
C6—C1—C7	121.67 (19)	C1—C6—H6	120.5
C2—C1—C7	118.49 (18)	O1—C7—O2	125.4 (2)
O3—N1—O4	124.5 (2)	O1—C7—C1	121.8 (2)
O3—N1—C3	118.0 (2)	O2—C7—C1	112.78 (18)
O4—N1—C3	117.6 (2)	O7—S1—C9	105.79 (13)
O5—N2—O6	124.2 (2)	O7—S1—C8	104.57 (12)
O5—N2—C5	118.6 (2)	C9—S1—C8	98.93 (15)
O6—N2—C5	117.17 (19)	S1—C8—H8A	109.5
C3—C2—C1	119.06 (19)	S1—C8—H8B	109.5
C3—C2—H2	120.5	H8A—C8—H8B	109.5
C1—C2—H2	120.5	S1—C8—H8C	109.5
C2—C3—C4	122.94 (19)	H8A—C8—H8C	109.5
C2—C3—N1	118.92 (19)	H8B—C8—H8C	109.5
C4—C3—N1	118.10 (19)	S1—C9—H9A	109.5
C5—C4—C3	116.34 (19)	S1—C9—H9B	109.5
C5—C4—H4	121.8	H9A—C9—H9B	109.5

C3—C4—H4	121.8	S1—C9—H9C	109.5
C4—C5—C6	123.02 (19)	H9A—C9—H9C	109.5
C4—C5—N2	118.28 (19)	H9B—C9—H9C	109.5
C6—C5—N2	118.65 (19)		
C6—C1—C2—C3	0.9 (3)	O5—N2—C5—C4	-9.2 (3)
C7—C1—C2—C3	176.37 (18)	O6—N2—C5—C4	169.85 (19)
C1—C2—C3—C4	-0.2 (3)	O5—N2—C5—C6	173.41 (19)
C1—C2—C3—N1	-177.95 (17)	O6—N2—C5—C6	-7.6 (3)
O3—N1—C3—C2	179.7 (2)	C4—C5—C6—C1	-0.7 (3)
O4—N1—C3—C2	-0.5 (3)	N2—C5—C6—C1	176.65 (17)
O3—N1—C3—C4	1.9 (3)	C2—C1—C6—C5	-0.4 (3)
O4—N1—C3—C4	-178.4 (2)	C7—C1—C6—C5	-175.80 (17)
C2—C3—C4—C5	-0.8 (3)	C6—C1—C7—O1	168.0 (2)
N1—C3—C4—C5	176.96 (17)	C2—C1—C7—O1	-7.5 (3)
C3—C4—C5—C6	1.2 (3)	C6—C1—C7—O2	-9.9 (3)
C3—C4—C5—N2	-176.09 (17)	C2—C1—C7—O2	174.69 (18)
