

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

M. Abthorpe,^a A. V. Trask^{b*} and
W. Jones^b^aDepartment of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England, and ^bPfizer Institute for Pharmaceutical Materials Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

Correspondence e-mail: avt21@cam.ac.uk

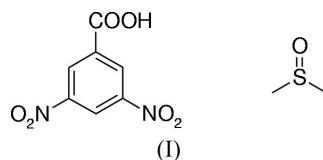
Key indicators

Single-crystal X-ray study
T = 260 K
Mean σ (C–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, $C_7H_4N_2O_6 \cdot C_2H_6OS$, 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

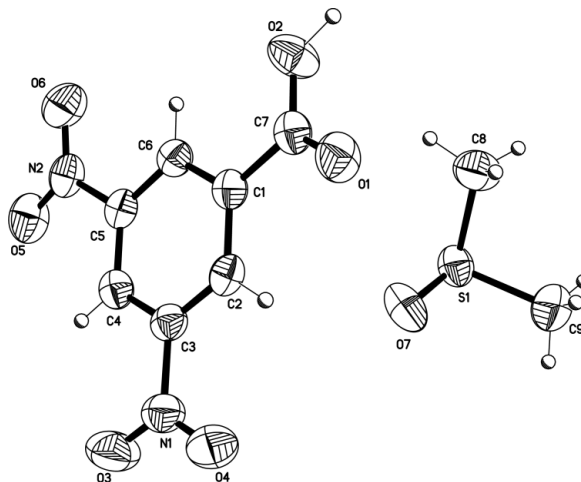


Figure 1
The asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level (*XP*; Sheldrick, 1993).

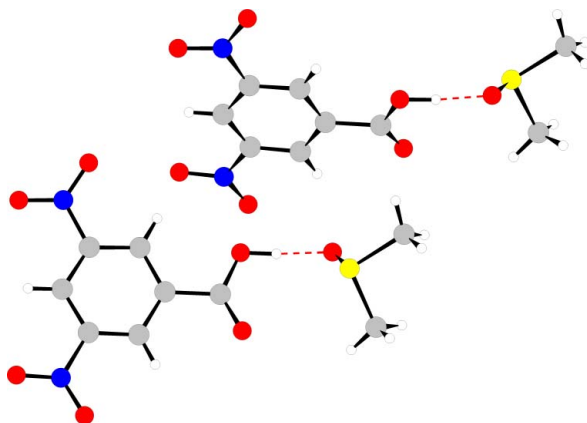


Figure 2
Crystal packing diagram, showing the intermolecular hydrogen-bonding interactions as dashed lines.

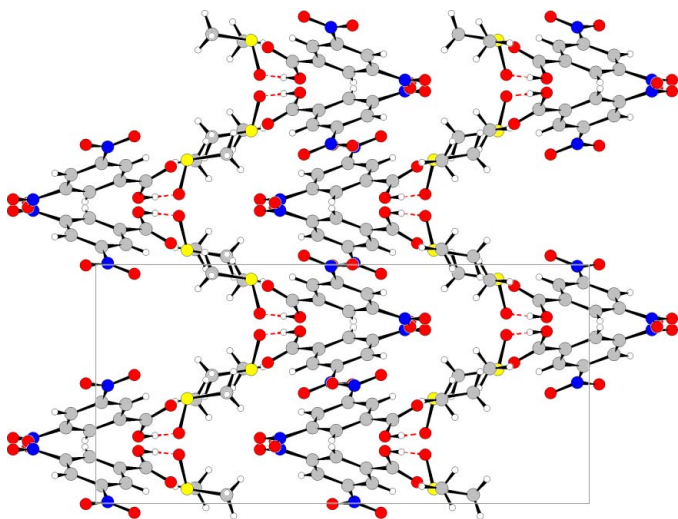


Figure 3
Crystal packing diagram, showing sheets stacking along [001], as viewed along [010]. Dashed lines indicate hydrogen bonds.

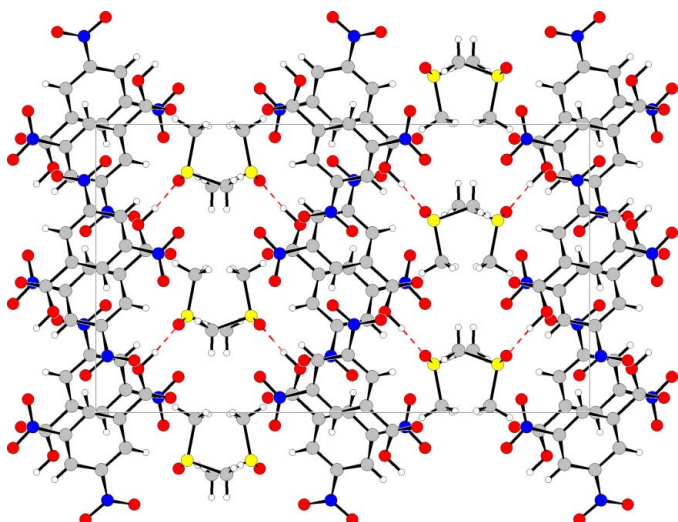


Figure 4
Crystal packing diagram showing sheets stacking along [001], as viewed along [100].

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, $Pbca$
 $a = 10.0156 (2) \text{ \AA}$
 $b = 12.0767 (2) \text{ \AA}$
 $c = 20.6483 (5) \text{ \AA}$
 $V = 2497.52 (9) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.544 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 11 611 reflections
 $\theta = 1.0\text{--}27.5^\circ$
 $\mu = 0.29 \text{ mm}^{-1}$
 $T = 260 (2) \text{ K}$
 Plate, yellow
 $0.23 \times 0.23 \times 0.12 \text{ mm}$

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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.60 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e \AA}^{-3}$

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*.

We are grateful for funding from the Pfizer Institute for Pharmaceutical Materials Science (AVT and WJ). We thank Dr J. E. Davies for data collection and structure determination.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Casciaro, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Brandenburg, K. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Pedireddi, V. R., Jones, W., Chorlton, A. P. & Docherty, R. (1996). *Chem. Commun.* p. 987.
- Prince, P., Fronczek, F. R. & Gandour, R. D. (1991). *Acta Cryst.* **C47**, 895–898.
- Sheldrick, G. M. (1993). *XP*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.