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Dimorphism and inclusion compounds of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine

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Crystal structures of a new polymorph of *N*,*N*′-(*p*-phenylene)bis(benzenesulfonamide) ($C_{18}H_{16}N_2O_4S_2$) and of two inclusion compounds with acetone [$(CH_3)_2CO$] and dimethylsulfoxide [$2(CH_3)_2SO$], respectively, have been determined at 150 K. For a more reliable comparison, the structure of the already known polymorph of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine has been redetermined under identical conditions. In addition, the phase transformation behavior has been examined by differential scanning calorimetry and the crystallization conditions of both polymorphs including their formation by weathering of the inclusion compounds were investigated.

1. Introduction

Within chemistry, polymorphism is usually defined as the ability of a compound to crystallize in different modifications or, more precisely, that the respective compound should behave as one component with regard to the Phase Rule (Dunitz & Bernstein, 1995; Dunitz, 1995). The definition can be further specified to conformational polymorphism, when the molecules of polymorphs differ in their conformation (Bernstein & Hagler, 1978; Bernstein, 1987). A compound which crystallizes with its solvent molecules in varying ratios has often been classified as being pseudopolymorphic (Bernstein, 1987; Glusker *et al.*, 1994).

Among the first to show the phenomenon of polymorphism, calcite and aragonite were proven to possess identical chemical composition by Klaproth in 1798 (Buerger & Bloom, 1939). The historical development has been surveyed in the (presumably) first review article (Buerger & Bloom, 1939). Since then, the interest in polymorphism and its industrial importance has increased considerably: especially in pharmaceuticals, dyes and explosives. Details from the investigations of polymorphs have been summarized (Bernstein, 1993), thermodynamic and structural implications of data in the Cambridge Structural Database (Allen & Kennard, 1993) elaborated (Gavezzotti & Filippini, 1995) and kinetic aspects (Dunitz & Bernstein, 1995; Dunitz, 1995), including solvent effects (Khoshkhoo & Anwar, 1993), discussed.

The dimorphism of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine (1) has been discovered in investigations concerning the inclusion behavior of its derivatives (Bock *et al.*, 1998*a*–*d*, 2000*a*,*b*; Bock, Nagel & Näther, 2000). Other investigations of polymorphs by the Frankfurt group dealt with tetraalkyl-*p*-phenylenediamines (Bock *et al.*, 1993*a*,*b*), tetraalkoxythianthrenes (Bock *et al.*, 1995), diethyl-2,5-dihydroxyterephthalates (Näther, Nagel *et al.*, 1996; Näther, Bock *et al.*, 1996), hydrogen-bonded aggregates (Schödel *et al.*, 1996;

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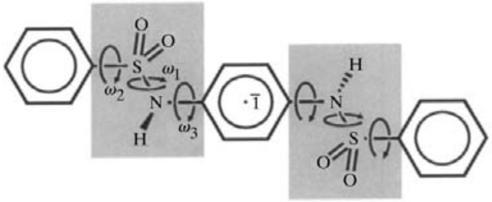
Table 1
Experimental details.

	Polymorph 1 from solution	Polymorph 2 from sublimation	Acetone solvate	DMSO adduct
Crystal data				
Chemical formula	$C_{18}H_{16}N_2O_4S_2$	$C_{18}H_{16}N_2O_4S_2$	$C_{18}H_{16}N_2O_4S_2\cdot(CH_3)_2CO$	$C_{18}H_{16}N_2O_4S_2\cdot 2[SO(CH_3)_2]$
Chemical formula weight	388.45	388.45	446.53	544.7
Cell setting	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	*Pbcn*	$P\overline{1}$
a (Å)	9.0603 (11)	10.6449 (6)	17.503 (2)	8.4277 (15)
b (Å)	10.6109 (13)	6.4510 (4)	7.7310 (9)	13.0779 (14)
c (Å)	9.4613 (14)	13.1061 (7)	15.188 (2)	13.401 (2)
α (°)	90	90	90	116.532 (6)
β (°)	101.893 (6)	96.195 (4)	90	97.10 (2)
γ (°)	90	90	90	90.425 (15)
V (Å^3)	890.1 (2)	894.74 (9)	2055.1 (4)	1308.1 (3)
Z	2	2	4	2
D_x (Mg m^{-3})	1.449	1.442	1.443	1.383
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	90	65	90	94
θ range (°)	7.5–20.5	8.5–21	10–19	8.5–21
μ (mm^{-1})	0.326	0.324	0.296	0.403
Temperature (K)	150 (2)	150 (2)	150 (2)	150 (2)
Crystal form	Block	Block	Block	Block
Crystal size (mm)	0.65 × 0.50 × 0.45	0.60 × 0.50 × 0.40	0.70 × 0.65 × 0.40	0.80 × 0.60 × 0.45
Crystal color	Colorless	Colorless	Colorless	Colorless
Data collection				
Diffractometer	Siemens *P*4 four circle	Siemens *P*4 four circle	Siemens *P*4 four circle	Siemens *P*4 four circle
Data collection method	ω scans	ω scans	ω scans	ω scans
No. of measured reflections	2712	2052	2658	6714
No. of independent reflections	2571	1949	2016	6312
No. of observed reflections	2214	1768	1564	5457
Criterion for observed ­reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.0143	0.0172	0.0202	0.0232
$\theta_{\rm max}$ (°)	30.00	27.00	26.00	29.00
Range of *h*, *k*, *l*	$0 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 14$ $-12 \rightarrow l \rightarrow 12$	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 8$ $-16 \rightarrow l \rightarrow 16$	$-1 \rightarrow h \rightarrow 21$ $-1 \rightarrow k \rightarrow 9$ $-1 \rightarrow l \rightarrow 18$	$0 \rightarrow h \rightarrow 11$ $-15 \rightarrow k \rightarrow 15$ $-18 \rightarrow l \rightarrow 18$
No. of standard reflections	4	4	4	4
Frequency of standard reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0377	0.0327	0.0422	0.0508
$wR(F^2)$	0.1010	0.0850	0.1007	0.1389
S	1.080	1.037	1.073	1.054
No. of reflections used in refinement	2571	1949	2013	6312
No. of parameters used	123	122	144	324
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.403P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.438P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 2.261P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 1.256P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$	0.000	0.000	0.000	0.000
$\Delta\rho_{\rm max}$ (e Å^{-3})	0.407	0.410	0.386	0.761
$\Delta\rho_{\rm min}$ (e Å^{-3})	−0.334	−0.324	−0.331	−0.494
Extinction method	*SHELXL*93	None	*SHELXL*93	*SHELXL*93
Extinction coefficient	0.0076 (25)	–	0.0071 (7)	0.0070 (17)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C , Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs				
Data collection	*XSCANS* (Siemens, 1992)	*XSCANS* (Siemens, 1992)	*XSCANS* (Siemens, 1992)	*XSCANS* (Sheldrick, 1992)
Structure solution	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)

Table 2
Selected geometry (Å, °).

	Polymorph 1 from solution	Polymorph 2 by sublimation	Acetone solvate	DMSO adduct
S(1)—O(2)	1.4218 (11)	1.430 (1)	1.421 (2)	1.427 (2)
S(1)—O(1)	1.4367 (10)	1.439 (1)	1.432 (2)	1.426 (2)
S(1)—N(1)	1.6259 (13)	1.639 (1)	1.631 (2)	1.628 (2)
S(1)—C(10)	1.755 (2)	1.761 (2)	1.754 (3)	1.760 (2)
N(1)—C(1)	1.426 (2)	1.441 (2)	1.427 (3)	1.425 (3)
C(1)—C(3)	1.386 (2)	1.391 (2)	1.382 (3)	1.391 (3)
C(1)—C(2)	1.392 (2)	1.385 (2)	1.379 (3)	1.390 (3)
C(10)—C(11)	1.378 (2)	1.388 (2)	1.383 (4)	1.380 (3)
C(10)—C(15)	1.384 (2)	1.389 (2)	1.380 (4)	1.388 (3)
C(11)—C(12)	1.388 (3)	1.394 (3)	1.377 (4)	1.384 (4)
O(2)—S(1)—O(1)	119.18 (7)	119.9 (1)	119.30 (7)	119.84 (12)
O(1)—S(1)—N(1)	104.38 (7)	104.9 (1)	104.44 (10)	108.11 (11)
O(2)—S(1)—N(1)	108.29 (7)	108.0 (1)	108.87 (10)	105.29 (11)
O(2)—S(1)—C(10)	108.68 (8)	109.1 (1)	108.05 (11)	108.63 (11)
C(1)—N(1)—S(1)	121.44 (10)	117.7 (1)	123.8 (2)	120.60 (14)
C(3)—C(1)—C(2)	120.08 (13)	120.6 (1)	119.0 (2)	119.3 (2)
C(3)—C(1)—N(1)	118.99 (12)	120.6 (1)	122.7 (2)	121.5 2)
C(2)—C(1)—N(1)	120.83 (13)	118.8 (1)	118.2 (2)	119.2 (2)
C(11)—C(10)—S(1)	119.78 (14)	120.5 (1)	119.9 (2)	120.0 (2)
C(15)—C(10)—S(1)	118.73 (12)	117.8 (1)	118.9 (2)	119.1 (2)
C(11)—C(10)—C(15)	121.5 (2)	121.6 (1)	121.2 (3)	121.0 (2)

Bock *et al.*, 1997) and alkali metal contact ions (Näther *et al.*, 1997).



(I)

In the crystal structures of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine and its derivatives the molecules are located around crystallographic centers of inversion and adopt different conformations (Bock *et al.*, 1998*a*), which can be characterized by three torsion angles [see (I): ω_1, ω_2 and ω_3]. The title compound crystallizes in two different solvent-free modifications and, in addition, with one equivalent of acetone and two equivalents of dimethyl sulfoxide (DMSO), respectively. The three unknown crystal structures are presented together with a redetermined one of the known polymorph (Nesterov *et al.*, 1986) under comparable conditions. The phase transformation behavior of the dimorphs is investigated by differential scanning calorimetry and the crystallization conditions of both polymorphs including their formation by weathering of the inclusion compounds as well as by seeding with crystals of its dimethyl derivative *N*,*N*′-ditosyl-*p*-phenylenediamine are examined.

2. Experimental

2.1. Preparation and crystallization

The synthesis is analogous to the known one for similar compounds (Stetter & Roos, 1954; Adams & Anderson, 1950). To a solution of 36.2 g (200 mmol) of 1,4-phenylenediamine dihydrochloride in 400 ml of demineralized water, a solution of 79.5 g (450 mmol) of benzenesulfonyl chloride in 350 ml of diethyl ether and 600 ml of an aqueous sodium hydroxide solution (10%) were added. The mixture was stirred for 5 h to intermix both phases, acidified with hydrochloric acid (15%), filtered and the residue washed three times with 80 ml of diethyl ether. Recrystallization from ethanolic solution yielded 63.8 g (76%) of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine with melting point 528 K. Elemental analysis: exp. C 55.44, H 4.26, N 7.18%; calc. C 55.66, H 4.15, N 7.21%.

One polymorph crystallizes on cooling of a saturated ethanolic solution, while single crystals of the second polymorph are best obtained by slow sublimation at temperatures above 423 K under reduced pressure below 10^{-2} bar. The inclusion compound with one equivalent of acetone crystallizes on isothermal diffusion of *n*-hexane into a saturated solution of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine in acetone and crystals of the hydrogen-bond adduct with two equivalents of DMSO form on diffusion of water into a nearly saturated solution in DMSO.

2.2. X-ray crystal structure determination

Details of the crystal data, data collection and refinement are given in Table 1[1] for all four compounds.

Corrections for Lorentz and polarization effects but not for absorption were applied (Siemens, 1992). All H atoms bound to carbon were positioned according to standard geometrical criteria and refined with fixed isotropic displacement parameters [$U_{\rm iso}(\rm H_{phenyl})$ = $1.2{*}U_{\rm eq}(\rm C_{phenyl})$, $U_{\rm iso}(\rm H_{methyl})$ = $1.2{*}U_{\rm eq}(\rm C_{methyl})$] using a riding model. The position and the isotropic displacement parameter of the H(—N) atom has been refined in all four crystal structures. The carbon centers of the acetone molecule as well as the sulfur centers of the DMSO molecules were refined as disordered on two positions with site occupation factors of 0.5/0.5 (general positions) and 0.8/0.2, respectively.

2.3. Powder diffraction

The powder diffraction measurements were carried out on a HUBER Guinier diffractometer 642 system with Cu *Kα* radiation (λ = 1.540561 Å, scan range: $6 \leq 2\theta \leq 40°$, step width 0.01°, scan speed 10 s per step).

2.4. Calculations

Density functional theory calculations on sulfonamide conformations were performed with the program *GAUSSIAN*94 (Frisch *et al.*, 1995) using suitable model compounds (*cf.* Bock *et al.*, 1998*a*). Packing coefficients C_K

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SE0270). Services for accessing these data are described at the back of the journal.

(Kitaigorodskii, 1961) and packing energies PE (Gavezzotti, 1994) were estimated from crystal data with hydrogen bond lengths C—H and N—H normalized to 1.08 and 1.00 Å using the program *OPEC* (Gavezzotti & Filippini, 1994). The packing energy calculations based on the atom/atom-potential method (Pertsin & Kitaigorodskii, 1986) yielded the following values: PE (polymorph 1 from solution) = −213 kJ mol^{-1} and PE (polymorph 2 by sublimation) = −209 kJ mol^{-1}.

2.5. Thermochemical measurements and optical microscopy

For the thermochemical measurements a Mettler thermoanalytical system TA3000 with TC10A processor was used. Optical microscopy was performed using a Kofler heating unit from Wagner and Munz.

3. Results

3.1. Crystallization and crystal structures

3.1.1. Polymorph 1 from ethanol solution. *N*,*N*′-Di(benzenesulfonyl)-*p*-phenylenediamine crystallizes from ethanolic solution in the monoclinic space group $P2_1/c$ with two molecules in the unit cell (Fig. 1*a*). The sulfonamide subunits of adjacent molecules form hydrogen bonds N—H···O═S of the cyclic dimer type (Figs. 1*a* and *c* (shaded), *cf*. Bock *et al.*, 1998*a*) classified by the graph set R_2^2 (Bernstein *et al.*, 1995; Etter *et al.*, 1990).

Through these cyclic hydrogen bonds the molecules form chains parallel to the crystallographic *c* axis. The sulfonamide hydrogen-bond geometry corresponds to average values (Bock *et al.*, 1998*a*): the distances N···O and (N)H···O amount to 2.90 (1) and 2.10 (1) Å [N—H 0.80 (1) Å], the angles N—H···O and H···O═S to 175 (1) and 134 (1)°. The second sulfonamide O atom, which does not participate in the sulfonamide hydrogen bonding, forms a weak hydrogen bond C—H···O (Desiraju, 1991, 1996; Steiner & Desiraju, 1998) to the phenyl H atom of an adjacent molecule with distances C···O and (C)H···O of 3.36 (1) and 2.50 (1) Å (C—H 0.95 Å) and a C—H···O angle of 151 (1)°. In addition, each molecule exhibits intermolecular contacts C—H···π (Hobza *et al.*, 1994; Hunter, 1994; Nishio *et al.*, 1995; Chipot *et al.*, 1996) between phenyl rings. The central phenylene ring forms contacts to two phenyl rings with a centroid···centroid distance of 4.82 Å and an angle of 51° between the ring planes. Further contacts between phenyl rings exhibit centroid···centroid distances of 4.87 and 5.05 Å as well as dihedral angles of 24 and 0°. The packing coefficient, which represents the fraction of occupied volume within the crystal, was estimated as C_K = 0.698 (*OPEC*; Gavezzotti & Filippini, 1994), using the 'caps and spheres' method of Kitaigorodskii (1961).

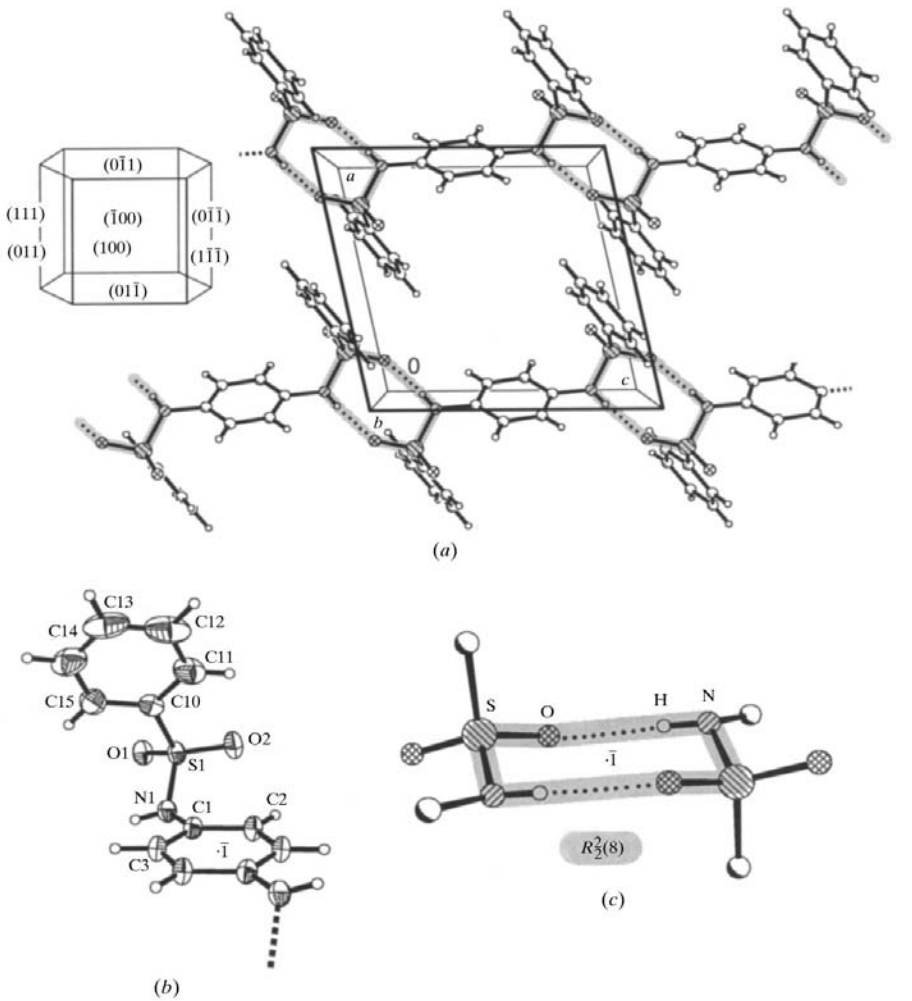


Figure 1
Crystal structure of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine polymorph (*T* = 150 K) obtained from ethanolic solution: (*a*) typical crystal shape with indexed faces and unit cell (monoclinic, $P2_1/c$, $Z = 2$) along the *b* axis, (*b*) molecule (50% probability displacement ellipsoids) with labeling and (*c*) hydrogen-bond motif between the sulfonamide units.

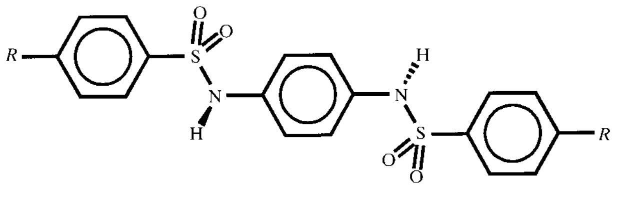
The *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine molecules are located around crystallographic centers of inversion (Wyckoff letter *a*) and the anisotropic displacement parameters of the ring C atoms indicate a weak libration or static disorder of the phenyl rings (Fig. 1*b*). The molecular geometry (see Table 2) corresponds to standard values (Orpen *et al.*, 1994) and the torsion angles ω_{1-3} (Figs. 2*a* and *b*) characterizing the conformation represent the energy minima estimated by density functional theory calculations on sulfonamide model compounds (Bock *et al.*, 1998*a*).

The sulfonamide H atom avoids contact with the *ortho*-phenylene H atom by a slight twist out of the phenylene plane, whereas the nitrogen lone pair, which is twisted out of that plane by 55 (1)°, can interact with the phenylene π-system (Bock *et al.*, 1993*a*,*b*). The two intramolecular contacts C—H···O=S show distances C···O and (C)H···O of 2.90 (1)/3.03 (1) and 2.53 (1)/2.48 (1) Å (Fig. 2*c*).

3.1.2. Polymorph 2 by sublimation. Single crystals of a second modification can be obtained by slow vacuum sublimation at 10^{-2} mbar and about 423 K. *N*,*N*′-Di(benzenesulfonyl)-*p*-phenylenediamine crystallizes in the monoclinic space group $P2_1/n$ with Z = 2 molecules in the unit cell (Fig. 3*a*).

The crystal structure is isomorphous with the crystal structures of *N*,*N*′-ditosyl-*p*-phenylenediamine (2*A*) and *N*,*N*′-di(4-ethylbenzosulfuryl)-*p*-phenylenediamine (2*B*) (Bock *et al.*, 1998*a*, 2000*a*).

In the crystal, the molecules are linked by sulfonamide hydrogen bonds of the catemer type and the resulting chains

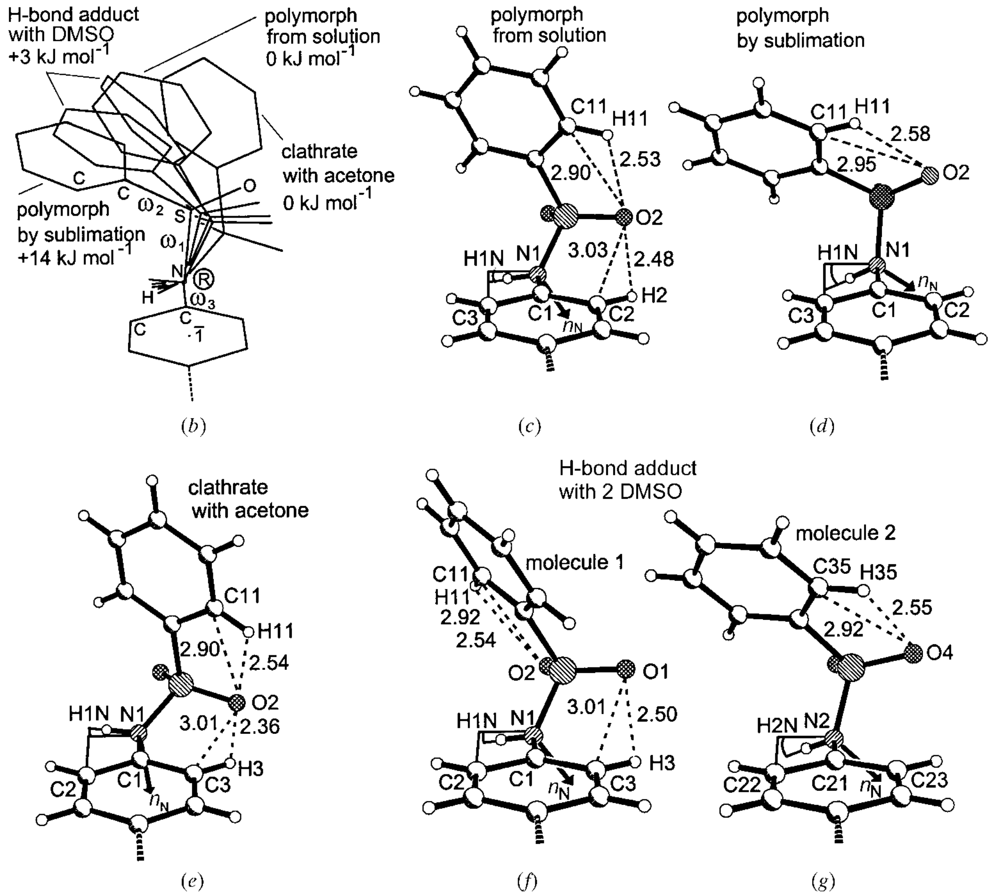


(2*A*) $R = CH_3$
(2*B*) $R = CH_2CH_3$

run parallel to the crystallographic *b* axis, twisted round the crystallographic 2_1-screw axis [Figs. 3*a* and *c* (shaded)]. The sulfonamide hydrogen-bond distances N···O and (N)H···O of 2.87 (1) and 1.99 (1) Å [N—H 0.88 (1) Å] are only slightly shorter than in the first polymorph and the N—H···O and H···O=S angles amount to 170 (1) and 145 (1)°. The second sulfonamide O atom, which does not participate in the sulfonamide hydrogen bonding, forms a C—H···O hydrogen bond to a phenyl H atom of an adjacent molecule with distances C···O and (C)H···O of 3.41 (1) and 2.56 (1) Å (C—H 0.95 Å) and a C—H···O angle of 149 (1)°. The phenyl rings of the molecule exhibit altogether eight short and two longer contacts to six-membered rings of neighbor molecules. Short contacts with centroid··· centroid distances of 4.07 (1) Å are detected between coplanar phenyl rings and additional short contacts with distances of 5.33 (1) Å and dihedral angles between the ring planes of 69 (1)° are present between the central phenylene ring and two phenyl rings. The longer contacts between phenylene and phenyl rings with centroid···centroid distances of 5.97 (1) Å exhibit a dihedral angle of 96 (1)°. The packing coefficient $C_K = 0.697$ is only slightly smaller than that calculated for polymorph 1 crystallized from ethanol solution, in agreement with the rather small density difference between the two polymorphs (Table 1).

	polymorph from solution	polymorph by sublimation	clathrate with acetone	H-bond adduct with 2 DMSO
ω_1(C-S-N-C)	−60	−66	−61	−61 /−56
ω_2(C-C-S-N)	109	107	104	74 / 97
ω_3(S-N-C-C)	123	96	143	119 / 108
ω(C-C-N-H)	−13	−35	2	−15 /−25
ω(C-C-N-n_N)	55	31	73	52 / 42

(*a*)



(*b*) (*c*) (*d*)

(*e*) (*f*) (*g*)

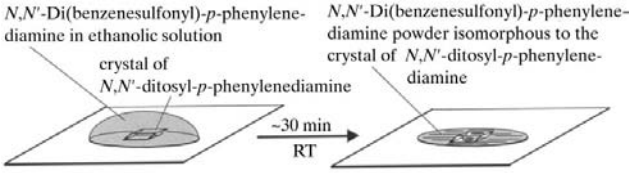
Figure 2
Conformations and intramolecular interactions of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine within the four crystal structures presented: (*a*) survey of the torsion angles (°) within the sulfonamide subunits, (*b*) comparision of conformations determined for the five unique molecules within four crystal structures and (*c*)–(*g*) intramolecular interactions (Å) resulting from the five different conformations.

Altogether, the intermolecular interactions within both polymorphs are comparable, both in number as well as in their geometry: each molecule exhibits four sulfonamide hydrogen bonds with contact distances N···O and (N)H···O of approximately 2.90 and 2.00 Å, as well as four weaker hydrogen bonds C—H···O with contact distances C···O and (C)H···O of approximately 3.40 and 2.50 Å, and eight phenyl···phenyl contacts with centroid···centroid distances below 5.40 Å. Atom/atom-potential calculations (Pertsin & Kitaigorodskii, 1986) with the *OPEC* (Gavezzotti & Filippini, 1994) program which predict the intermolecular interactions in the first polymorph are more favorable by only 4 kJ mol^{-1}.

The *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine molecule is located again around a crystallographic center of inversion (Wyckoff position *a*) and the anisotropic displacement parameters of the phenyl rings indicate weak libration or static disorder (Fig. 3*b*). Bond lengths and angles (Table 2) correspond to standard values (Orpen *et al.*, 1994), but the molecular conformation around the N—C bond deviates from the preferred orientation (Figs. 2*a* and *b*). The torsional angle ω_3(S—N—C—C) = 96 (1)° indicates the phenyl ring to be less twisted out of the phenylene plane and according to density functional theory calculations on sulfonamide model compounds (Bock *et al.*, 1998*a*) this conformation should be less favorable by approximately 14 kJ mol^{-1}. One of the reasons for this energy difference should be the orientation of the nitrogen lone pair, which is twisted out of the phenylene plane by 31 (1)° (Figs. 2*a*, *b* and *d*) and, therefore, hardly delocalizes into the phenylene *p*-system (Bock *et al.*, 1993*a*,*b*). The one intramolecular contact C—H···O═S found in this crystal structure exhibits C···O and (C)H···O distances of 2.95 (1) and 2.58 (1) Å (Fig. 2*d*).

The total energy difference ΔE between both polymorphs can be estimated by adding the energy difference of the intermolecular interactions $\Delta E^{\rm PE}$ to the energy difference of both molecular conformations $\Delta E^{\rm DFT}$. This predicts the sublimed polymorph to be less favorable at room temperature by $\Delta E = \Delta E^{\rm PE} + \Delta E^{\rm DFT} = 14 + 4 = 18$ kJ mol^{-1} and indicates, together with the differences in densities and packing coefficients, that the polymorph crystallized from ethanolic solution should be the more stable one at room temperature. Temperature-dependent crystallizations from solutions in ethanol or *n*-octane from 293 K up to 448 K yield precipitates, the powder diffraction patterns of which correspond to that of polymorph 1 (Fig. 4).

At higher temperatures *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine starts to decompose and the solutions turn black. Solid samples of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine can be heated to the melting point at 524 K without decomposition, but the melt rapidly turns black. The powder diffraction pattern of the solidified black melt corresponds to that of polymorph 2, which obviously is the only crystalline component (Fig. 5)



Polymorph 2 can also be obtained by seeding an ethanolic solution with isomorphous crystals of *N*,*N*′-ditosyl-*p*-phenylenediamine (2*A*). On placing a small single crystal in an almost saturated ethanolic solution of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine and evaporating the solvent, a crystalline powder of polymorph 2 precipitates.

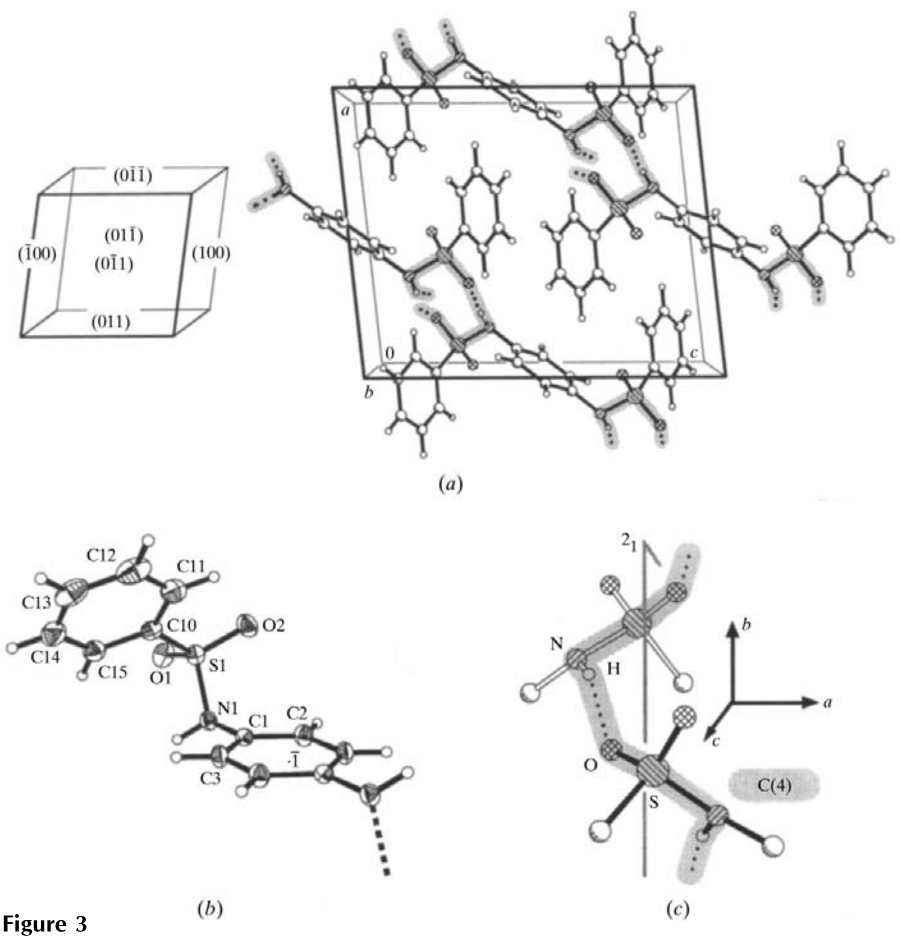


Figure 3

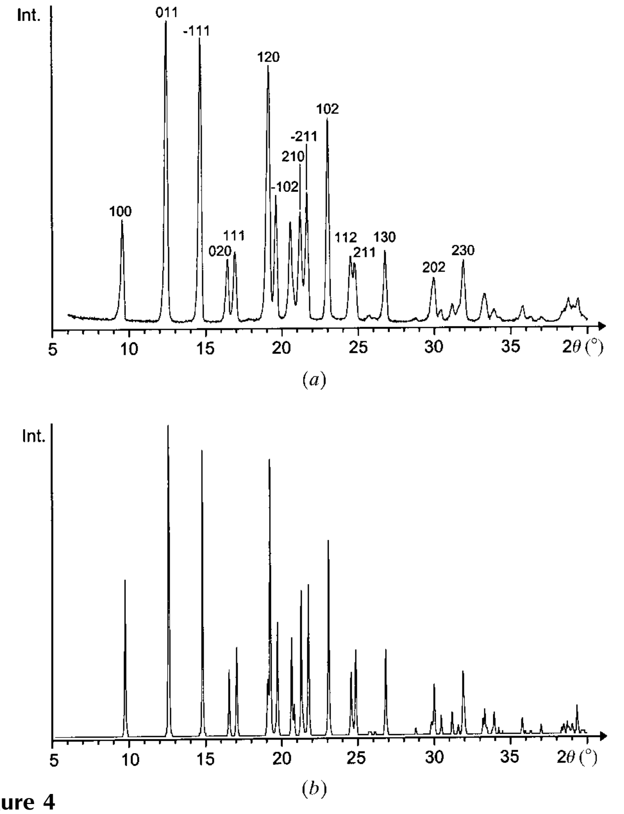
Crystal structure of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine polymorph (*T* = 150 K) obtained by sublimation: (*a*) typical crystal shape with indexed faces and unit cell (monoclinic, $P2_1/n$, $Z = 2$) along the *b* axis, (*b*) molecule (50% probability displacement ellipsoids) with labeling and (*c*) hydrogen-bond motif between the sulfonamide units.

The crystalline powder obtained is not significantly polluted by the seeding crystal, because *N*,*N*′-ditosyl-*p*-phenylenediamine is almost insoluble in ethanol.

3.1.3. Clathrate with one equivalent of acetone. *N*,*N*′-Di(benzenesulfonyl)-*p*-phenylenediamine crystallizes on isothermal diffusion of *n*-hexane into a saturated solution in acetone with one equivalent of the solvent. The clathrate crystallizes in the orthorhombic space group *Pbcn* with $Z = 4$ formula aggregates in the unit cell (Fig. 6).

The acetone molecules [Fig. 6*a* (shaded)] are enclosed in cages of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine host matrix and the host molecules are linked by sulfonamide hydrogen bonds of the catemer type (Fig. 6*c*). The sulfonamide hydrogen-bond chains are aligned parallel to the crystallographic *b* axis and neighboring sulfonamide units within these chains are symmetry related by the *b* glide plane perpendicular to the *a* axis (Fig. 6*c*). The hydrogen-bond geometry is comparable to those in the two polymorphs: the contact distances $\mathrm{N}\cdots\mathrm{O}$ and $\mathrm{(N)H}\cdots\mathrm{O}$ of 3.06 (1) and 2.25 (1) Å are slightly longer and exhibit $\mathrm{N-H}\cdots\mathrm{O}$ and $\mathrm{H}\cdots\mathrm{O{=}S}$ angles of 165 (1) and 137 (1)°. The sulfonamide O atom already involved in the sulfonamide hydrogen bonding forms two additional $\mathrm{C-H}\cdots\mathrm{O}$ hydrogen bonds to adjacent molecules with $\mathrm{C}\cdots\mathrm{O}$ and $\mathrm{(C)H}\cdots\mathrm{O}$ distances of 3.38 (1)/3.34 (1) Å and $\mathrm{C-H}\cdots\mathrm{O}$ angles of 143 (1) and 135 (1)°. The three phenyl rings of the host molecules exhibit altogether six contacts to phenyl rings of neighbor host molecules: the phenylene unit shows two contacts to perpendicular phenyl rings with centroid$\cdots$centroid distances of 5.98 (1) Å and each phenyl ring exhibits a shorter contact with a centroid$\cdots$centroid distance of 4.70 (1) Å and an angle between the ring planes of 60 (1)°.

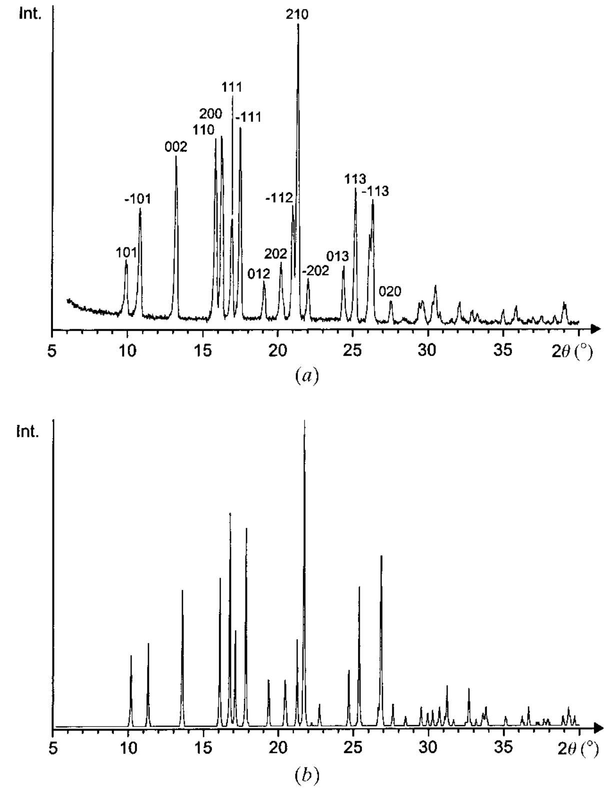
Within the crystal, *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine is located around a crystallographic center of inversion (Wyckoff position *a*) and the anisotropic displacement parameters of the phenyl rings are slightly enlarged, relative to those of the central phenylene ring (Fig. 6*b*). Bond lengths and angles of the host molecule (Table 2) correspond to standard values (Orpen *et al.*, 1994) and also those of the acetone guest molecule, which is found disordered on the twofold symmetry axis parallel to the crystallographic *b* axis (Fig. 6*b*). The host conformation differs from those found in both polymorphs, but is more closely related to that in polymorph 1 (Figs. 2*a* and *b*). Density functional theory calculations on sulfonamide model compounds (Bock *et al.*, 1998*a*) suggest this conformation to be energetically as favorable as the one in polymorph 1 (Fig. 2*b*). The orientation of the nitrogen lone pair n_{N} almost perpendicular to the phenylene ring plane allows n_{N}–π interactions with the six-membered ring (Figs. 2*a* and *e*). Two intramolecular $\mathrm{C-H}\cdots\mathrm{O}$ contacts are found with $\mathrm{C}\cdots\mathrm{O}$ and $\mathrm{(C)H}\cdots\mathrm{O}$ distances of 2.90 (1)/3.01 (1) Å and 2.54 (1)/2.36 (1) Å, respectively (Fig. 2*e*).



(*a*)

(*b*)

Figure 4
Powder diffraction pattern of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine polymorph obtained from ethanolic solution: (*a*) measured pattern with indexed reflections and (*b*) pattern calculated from single-crystal structural data (Cu *Kα* radiation).



(*a*)

(*b*)

Figure 5
Powder diffraction pattern of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine polymorph obtained by sublimation: (*a*) measured pattern with indexed reflections and (*b*) pattern calculated from single-crystal structural data (Cu *Kα* radiation).

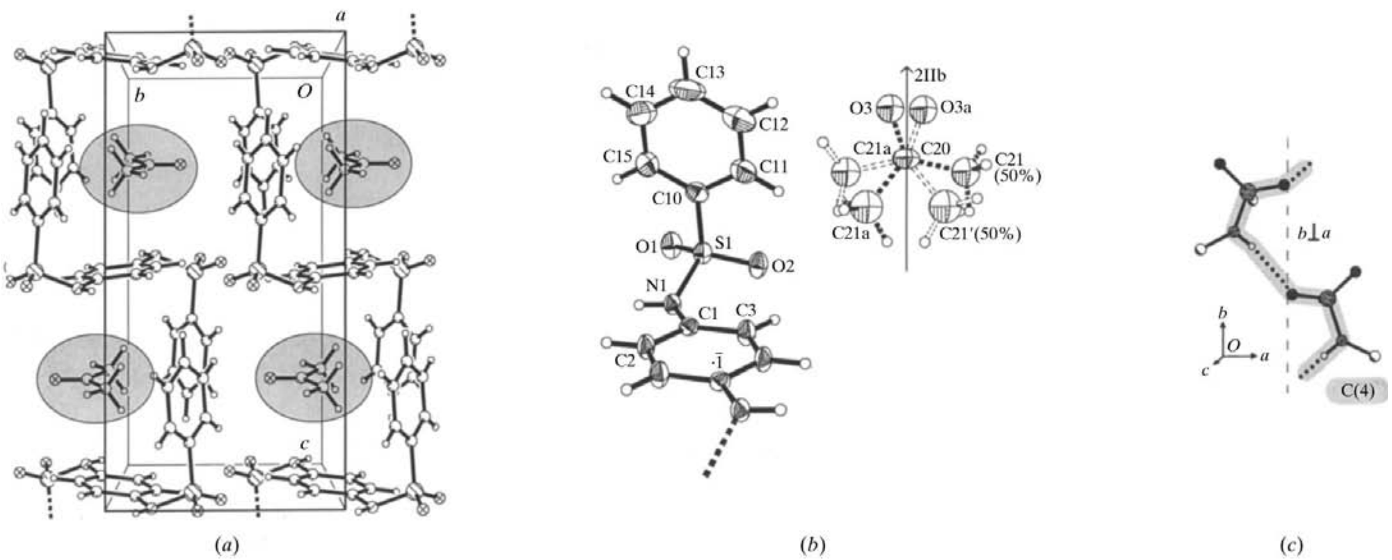


Figure 6
Crystal structure of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine clathrate with one equivalent of acetone ($T = 150$ K): (*a*) unit cell (orthorhombic, *Pbcn*, $Z = 4$) along the *a* axis, (*b*) host and guest molecule (50% probability displacement ellipsoids) with labeling and (*c*) hydrogen-bond motif between the sulfonamide units of the host molecule.

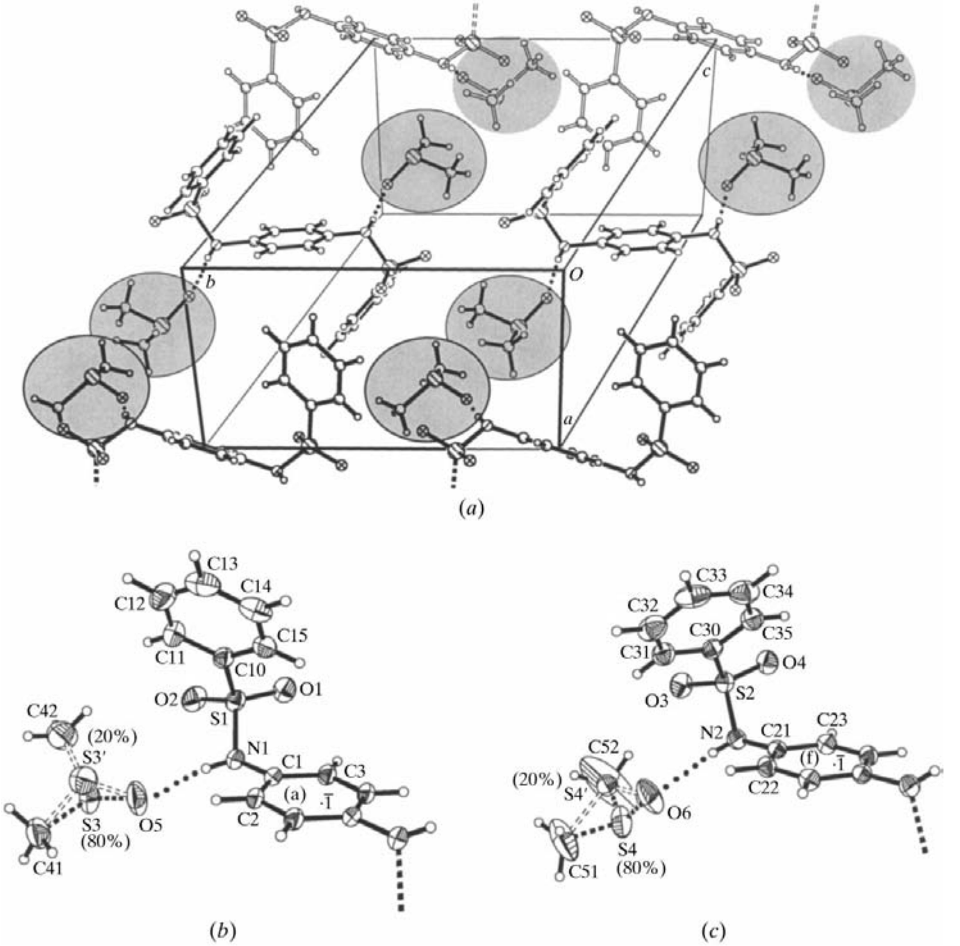


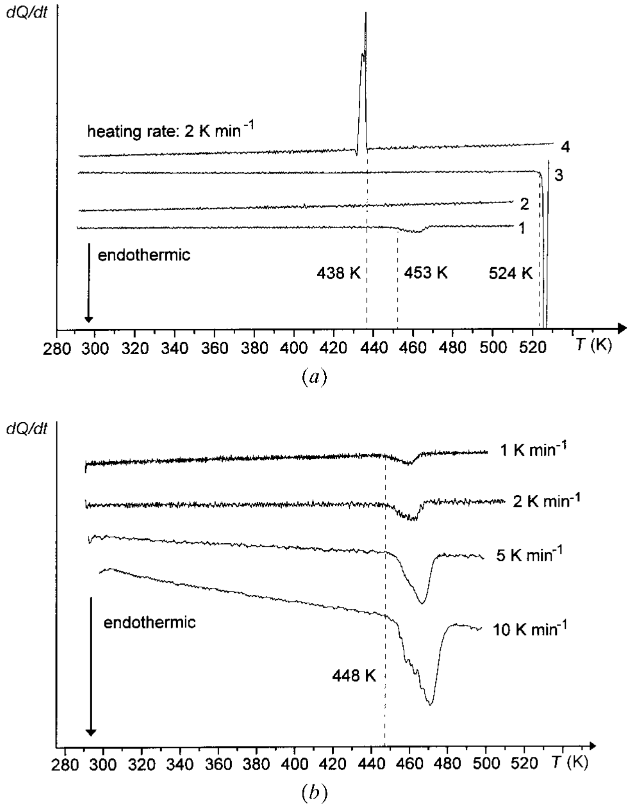
Figure 7
Crystal structure of the hydrogen-bond adduct of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine with two equivalents of dimethyl sulfoxide ($T = 150$ K): (*a*) unit cell (triclinic, $P\bar{1}$, $Z = 2$) in the *c*-axis direction, (*b*) first and (*c*) second host and guest molecule (50% probability displacement ellipsoids) with labeling.

Single crystals of this host–guest compound, when taken out of the mother liquor, turn rapidly from clear to pale. Samples, which are stored at room temperature under a vacuum of about 10^{-2} mbar for 6 h, lose all acetone host molecules. The powder diffraction pattern of the microcrystalline residue corresponds to that of polymorph 2, resulting on sublimation (*cf*. Fig. 5), and no other reflections are detected.

3.1.4. Hydrogen-bond adduct with two equivalents of dimethyl sulfoxide. *N*,*N*′-Di(benzenesulfonyl)-*p*-phenylenediamine crystallizes from a nearly saturated solution in DMSO after adding a layer of water, which slowly diffuses into the solution. The resulting crystals contain two equivalents of DMSO, the oxygen centers of which form hydrogen bonds *via* the sulfonamide H atoms of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine (Fig. 7*a*).

The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ formula aggregates in the unit cell (Fig. 7*a*). The asymmetric unit contains two half host molecules around crystallographic centers of inversion (Wyckoff positions *a* and *f*) and two DMSO molecules in general positions (Figs. 7*b* and *c*). The host–guest hydrogen bonds [Figs. 7*b* and *c* (···)] are slightly shorter than the sulfonamide hydrogen bonds in the other crystal structures of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine with distances N···O of 2.78 (1)/2.80 (1) Å and (N)H···O of 1.98 (1)/2.07 (1) Å [N—H 0.80 (1) and 0.74 (1) Å] and N—H···O angles of 168 (1) and 174 (1)°. Additional short C—H···O contacts from phenyl H atoms to the dimethylformamide O5 atom and to the sulfonamide O2 atom (Figs. 2*f* and *g*) exhibit H···O distances of 2.56 (1)/2.48 (1) Å, C(H)···O distances of 3.27 (1)/3.33 (1) Å and C—H···O angles of 132 (1) and 149 (1)°. The phenyl rings of adjacent molecules again form additional C—H···π contacts and the shortest centroid···centroid distance of 5.12 (1) Å is found between the phenyl rings of the two unique host molecules with a dihedral angle of 68 (1)°.

The anisotropic displacement parameters of the phenyl rings are again larger than those of the phenylene rings (Figs. 7*b* and *c*) and the DMSO molecules are slightly disordered despite their connection to the hosts *via* strong hydrogen bonds (Figs. 7*b* and *c*, see §2 for a detailed description of the disorder). Bond lengths and angles of the host (Table 2) and even of the disordered guest molecules agree fairly well with standard values (Orpen *et al.*, 1994). The conformation around the S—C and N—C bonds of both crystallographically unique molecules differs by $\Delta\omega_2$(N—S—C—C) = −23 (1)° and $\Delta\omega_3$(S—N—C—C) = 11 (1)°, whereas that around the S—N bond is almost equal with $\Delta\omega_1$(C—S—N—C) = −5 (1)° (Figs. 2*a*, *f* and *g*). Density functional theory calculations on model compounds (Bock *et al.*, 1998*a*) suggest that both conformations should be rather similar in energy and less favorable by about 3 kJ mol^{-1} than those in the polymorph 1 and in the acetone clathrate (Fig. 2*b*). In the other host molecule (Fig. 2*g*), the sulfonamide hydrogen is twisted more strongly out of the phenylene plane and the orientation of the nitrogen lone pair n_N should allow a stronger delocalization into the phenylene π-system (Figs. 2*a* and *f*). Short intramolecular contacts C—H···O between phenyl H atoms and sulfonamide O atoms are found in both molecular conformations (Figs. 2*f* and *g*).



(*a*)

(*b*)

Figure 8
Differential scanning calorimetry measurements on samples of the *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine polymorph 1 obtained from ethanolic solution: [(*a*) line 1] heating curve to 510 K with endothermic peak at 453 K, indicating the phase transition to the second polymorph, [(*a*) line 2] cooling curve of the same sample to 293 K without transformation back to the first polymorph, [(*a*) line 3] repeated heating of the sample until melting at 524 K, [(*a*) line 4] repeated cooling curve with the melt solidifying at 438 K and (*b*) heating curves with phase transition peak at different heating rates.

The host matrix binds the DMSO guest molecules obviously tighter than the acetone molecules and the crystals can be stored at room temperature outside the mother liquor without any significant loss of solvent. A sample of the hydrogen-bonded adduct, from which the guest molecules have been removed in vacuum (10^{-2} mbar) at 333 K over 6 h shows a powder diffraction pattern corresponding to a superposition of the powder diffraction patterns of both *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine polymorphs.

3.2. Phase transitions and thermochemical measurements

Crystals of polymorph 1 from ethanolic solution turned pale when heated to temperatures above 453 K on a Kofler heating unit and wavefronts moving through the crystals were visible through the microscope above 448 K. During the cooling-off period no further change was observed and the powder diffraction pattern proves that a transformation to polymorph 2, previously crystallized by sublimation, took place. Differential scanning calorimetry of a sample of polymorph 1 exhibited an endothermic phase transition peak beginning at 448–453 K on heating the sample to 510 K [Figs. 8*a* (lines 1 and 8) and *b* (different heating rates)].

On cooling back to room temperature, no back-transformation was observed [Fig. 8*a* (line 2)] and repeated heating to temperatures above 510 K resulted in a single endothermic melting peak at 524 K [Fig. 8*a* (line 3)]. Cooling down the melt yielded polymorph 1, previously crystallized by sublimation. The solidifying peak began at 438 K and was the only thermic effect detected during cooling back to room temperature [Fig. 8*a* (line 4)].

4. Summary

The crystallization and phase-transformation behavior of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine was investi-

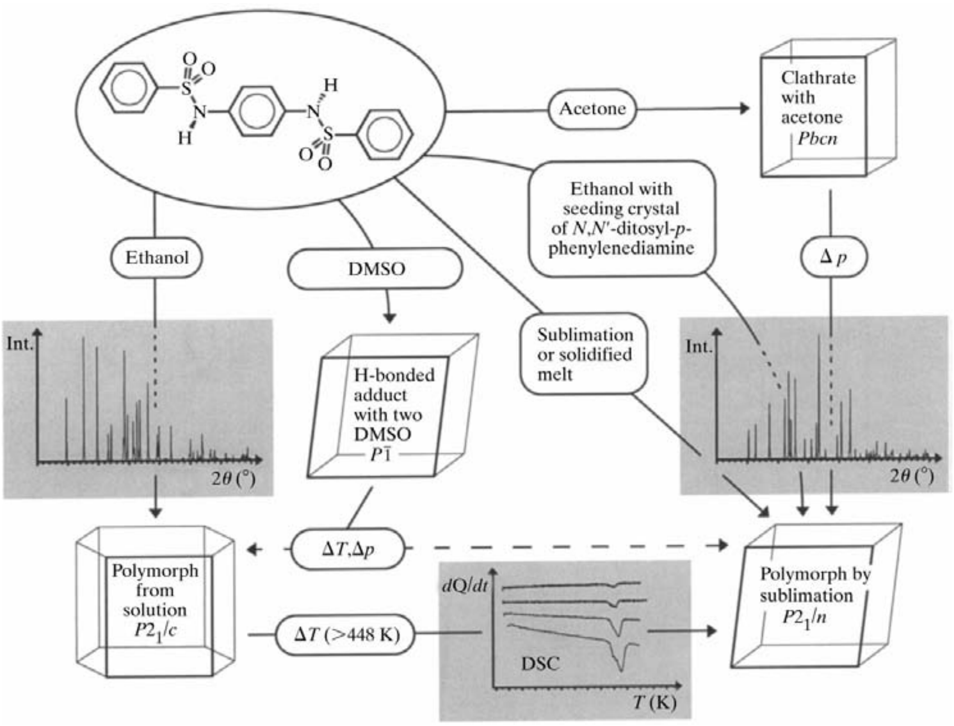


Figure 9
Investigation scheme for *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine polymorphs 1 and 2, the clathrate with acetone and the hydrogen-bonded dimethyl sulfoxide adduct, indicating crystal shapes, varying crystallization conditions and representative measurements.

gated by crystallization experiments, single-crystal structure determinations, powder diffraction, thermomicroscopy and differential scanning calorimetry. The title compound exhibits dimorphism (Figs. 1 and 3) and, in addition, forms inclusion compounds with acetone and dimethyl sulfoxide, respectively, as guest molecules (Figs. 6 and 7). Polymorph 1 was obtained by crystallization from ethanolic solution and the second one resulted on sublimation (Fig. 9). Further crystallization experiments show that polymorph 2 also forms on solidification of the melt and even on crystallization from ethanolic solution, if isomorphous crystals of *N*,*N*′-ditosyl-*p*-phenylenediamine are used as seedings (Fig. 9). In addition, polymorph 2 is formed on weathering of the acetone clathrate, whereas weathering of the hydrogen-bonded adduct with dimethyl sulfoxide yields a microcrystalline mixture of both polymorphs (Fig. 9).

Above 448 K single crystals of polymorph 1 transform to a microcrystalline material of polymorph 2 (Fig. 9), and no back-transformation is observed on cooling to room temperature. The conformation of *N*,*N*′-di(benzenesulfonyl)-*p*-phenylenediamine differs in all four crystal structures (Fig. 2). Density functional theory calculations on sulfonamide model compounds (Bock *et al.*, 1998*a*) predict the conformation in polymorph 1, obtained from solution, and in the acetone clathrate, to be energetically comparable and more favorable than the conformation in the hydrogen-bonded adduct with dimethylsulfoxide. The conformation of polymorph 2 should be the least favorable one (Fig. 2*b*). Atom/atom-potential calculations (Pertsin & Kitaigorodskii, 1986) suggest that the packing energies of both polymorphs are close to identical and, therefore, their total energy difference is due predominantly to their different conformations.

The results obtained complement those of investigations on the crystallization and guest-inclusion behavior of *N*,*N*′-ditosyl-*p*-phenylenediamine (Bock *et al.*, 1998*a*–*d*; Bock, Nagel & Näther, 2000) and its derivatives *N*,*N*′-di(4-ethylbenzenesulfonyl)-*p*-phenylenediamine (Bock *et al.*, 2000*a*) and *N*,*N*′-di(4-nitrobenzenesulfonyl)-*p*-phenylenediamine (Bock *et al.*, 2000*b*).

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