Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4,4′-Sulfonylbis[*N*-(4-nitrophenylmethylene)benzenamine]: whole-molecule disorder

Philip J. Cox[a]* and James L. Wardell[b]

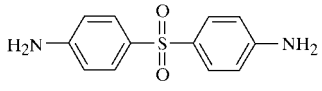
[a]School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen AB10 1FR, Scotland, and [b]Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: p.j.cox@rgu.ac.uk

Received 29 September 2003
Accepted 31 October 2003
Online 30 November 2003

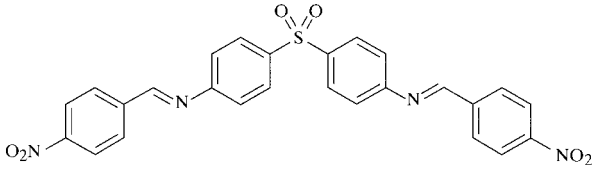
The crystal structure of the title compound, $C_{26}H_{18}N_4O_6S$, determined from synchrotron data with a small crystal, is characterized by the presence of whole-molecule disorder. In each molecule, the two planar portions are approximately perpendicular to one another and there are short intermolecular contacts between the nitro groups.

Comment

Dapsone [bis(4-aminophenyl) sulfone], (I), is an antibiotic that is used in combination with other drugs to treat leprosy. It is also used to help control dermatitis herpetiformis and to prevent pneumocystis carinii pneumonia in people infected with HIV (British National Formulary, 2003). The crystal form of (I) has been reported at room temperature by various authors (*e.g.* Dickinson *et al.*, 1970; Bocelli & Cantoni, 1990; Bertolasi *et al.*, 1993).



(I)



(II)

4,4′-Sulfonylbis[*N*-(4-nitrophenylmethylene)benzenamine], (II), has been synthesized from dapsone, and the unusual crystal structure of (II) is now reported. The molecules in the crystal are disordered such that each atom occupies two sites. A view of a resolved single molecule is shown in Fig. 1, and the two overlapping molecules are shown in Fig. 2. There is a very small separation between the coordinates for each of the atom pairs, but atom positions for the two molecules are resolved.

Essentially, the molecule consists of two planar portions that are inclined to one another by 87.6 (1)° for the minor conformer [population parameter = 0.430 (5)] and 87.8 (1)° for the major conformer [population parameter = 0.570 (5)]. The disorder prevents a discussion of accurate molecular geometry, but values (Table 1) are similar to those found in other diphenyl sulfones (Sime & Woodhouse, 1974*a*,*b*; Bertolasi *et al.*, 1993; Glidewell *et al.*, 2001). There are close intermolecular interactions between the O and N atoms of the nitro groups, as shown in Table 2 and Fig. 3 (Platts *et al.*, 1995). While close O···N separations have been observed previously,

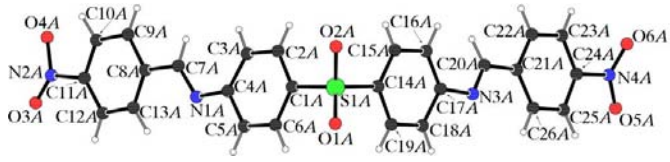


Figure 1
The atomic arrangement in the molecule of (II) (disorder excluded). Displacement ellipsoids are shown at the 50% probability level.

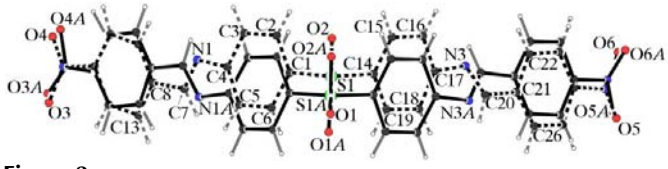


Figure 2
The atomic arrangement in the molecule of (II) (disorder included). Displacement ellipsoids are shown at the 50% probability level.

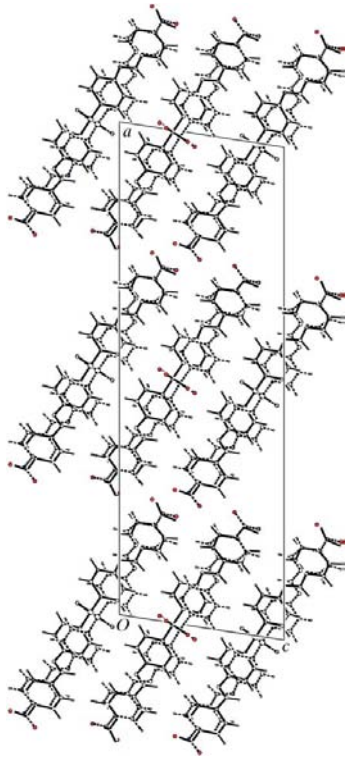


Figure 3
A view of the crystal packing.

  DOI: 10.1107/S0108270103025149

for example in 1-chloro-3-nitrobenzene (Sharma *et al.*, 1985) and 4,5-spirobi(adamantyl)-*N*-(3,5-dinitrophenyl)-1,3,2-dioxazolidine (Okada *et al.*, 1992), close O···O separations, in the absence of hydrogen bonding, are unusual. The N—O bond lengths indicate that the negative charge distribution between the two O atoms in each nitro group may be unequal. The 16 O—N—C_{ar}—C_{ar} torsion angles range from 21.5 (13) to −159.2 (7)° and indicate that some of the nitro groups are twisted slightly from the planes of the aromatic rings. There is some evidence that molecules *A* are held together by C—H···O bonding, but the disorder prevents an accurate description of the geometries involved.

The percentage of disordered organic structures in the Cambridge Structural Database (Allen, 2002) rose from 3.9% in 1970 to 15.0% in 1999 (Flippen-Anderson *et al.*, 2001). The April 2003 release of the database contains 49 743 structures with some form of disorder out of a total of 296 427, *i.e.* 16.8%. Although whole-molecule disorder is unusual, two crystal structures that exhibit this phenomenon, *viz.* 2-(2-thienyl)-1-(pyrazinyl)ethene and 2-(2-thienyl)-1-(quinoxalinyl)ethene, have been reported (Ichharam & Boeyens, 2001).

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.435 (7)	S1*A*—O1*A*	1.384 (7)
S1—O2	1.497 (7)	S1*A*—O2*A*	1.482 (7)
S1—C14	1.768 (9)	S1*A*—C1*A*	1.768 (9)
S1—C1	1.770 (10)	S1*A*—C14*A*	1.792 (8)
O3—N2	1.305 (17)	O3*A*—N2*A*	1.194 (17)
O4—N2	1.148 (17)	O4*A*—N2*A*	1.362 (17)
O5—N4	1.103 (11)	O5*A*—N4*A*	1.256 (10)
O6—N4	1.343 (13)	O6*A*—N4*A*	1.195 (8)
O1—S1—O2	118.4 (4)	O1*A*—S1*A*—O2*A*	122.7 (4)

Table 2
Intermolecular contacts (Å) between nitro group atoms.

Atom *A*	Atom *B*	*A*···*B*	Symmetry applied to atom *B*
O3	O5	2.937 (10)	$\frac{1}{2}+x, \frac{1}{2}+y, 1+z$
O3	O6	2.718 (12)	$\frac{1}{2}+x, -\frac{3}{2}-y, \frac{1}{2}+z$
O4	N4	2.816 (13)	$\frac{1}{2}+x, -\frac{1}{2}+y, 1+z$
O3*A*	O5*A*	2.926 (8)	$\frac{1}{2}+x, \frac{1}{2}+y, 1+z$
O4*A*	O6*A*	2.885 (9)	$\frac{1}{2}+x, -\frac{1}{2}+y, 1+z$
O4*A*	N4*A*	2.959 (9)	$\frac{1}{2}+x, -\frac{1}{2}+y, 1+z$
O5*A*	N2*A*	2.815 (15)	$-\frac{1}{2}+x, -\frac{1}{2}+y, -1+z$

Experimental

To a solution of dapsone (1 mmol) in methanol (30 ml) was added a solution of 4-nitrobenzaldehyde (2 mmol) in methanol (10 ml). The mixture was refluxed for 3 h and then cooled, and all the volatiles were removed under vacuum. The resulting solid was recrystallized from toluene (m.p. 504–506 K). IR (KBr, cm^{-1}): ν 3099, 3079, 3061, 2998, 2946, 2885, 1627, 1602, 1579, 1541, 1491, 1412, 1350, 1324, 1296, 1282, 1185, 1151, 1105, 1071, 1005, 954, 854, 748, 735, 706, 683, 663, 642, 633, 584, 560, 503. A data set was collected with synchrotron radiation at the Daresbury synchrotron radiation source, station 9.8 (Cernik *et al.*, 1997; Clegg *et al.*, 1998).

Crystal data

$C_{26}H_{18}N_4O_6S$
M_r = 514.5
Monoclinic, *Cc*
a = 36.706 (3) Å
b = 4.9130 (4) Å
c = 12.364 (5) Å
β = 98.808 (4)°
V = 2203.4 (9) Å^3
Z = 4
D_x = 1.551 Mg m^{-3}
Synchrotron radiation
λ = 0.6934 Å
Cell parameters from 1948 reflections
θ = 3.3–25.2°
μ = 0.20 mm^{-1}
T = 120 (2) K
Lozenge, yellow
0.15 × 0.05 × 0.02 mm

Data collection

Bruker SMART 1K CCD diffractometer
ω rotation with narrow frame scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.970, T_{max} = 0.996
9138 measured reflections
4141 independent reflections
3069 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.7°
h = −45 → 45
k = −5 → 6
l = −15 → 15

Refinement

Refinement on F^2
$R(F)$ = 0.042
$wR(F^2)$ = 0.107
S = 1.01
4141 reflections
299 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Absolute structure: Flack (1983), 1907 Friedel parameters
Flack parameter = 0.3 (2)

Following structure elucidation, refinement was impeded by non-positive definite anisotropic displacement parameters for several atoms. Because of the disorder, all atoms were refined with isotropic displacement parameters using *SHELXL*97-2 (Sheldrick, 1998). The C_{ar}—C_{ar} bond lengths were restrained to 1.395 Å before each refinement cycle. Atom population parameters of the two molecules were refined and converged to 0.430 (5) and 0.570 (5). The H atoms were initially placed in calculated positions (C—H = 0.95 Å) and thereafter were allowed to ride on their attached atoms, with a common isotropic displacement parameter that refined to 0.026 (2) Å^2. The N—O bond lengths ranged from 1.103 (11) to 1.362 (17) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97-2 (Sheldrick, 1998); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank Professor W. Clegg for collecting the synchrotron data at CLRC Daresbury Laboratory and Dr Simon Parsons for useful discussions on twinning and disorder.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1545). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bertolasi, V., Ferretti, V., Gilli, P. & Debenedetti, P. G. (1993). *J. Chem. Soc. Perkin Trans.* 2, pp. 213–219.
Bocelli, G. & Cantoni, A. (1990). *Acta Cryst.* C**46**, 2257–2259.

British National Formulary (2003). BNF-45. Joint Formulary Committee, British Medical Association and Royal Pharmaceutical Society of Great Britain, London. (URL: http://www.BNF.org.)
Bruker (1998). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SADABS* (Version 2.03) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
Cernik, R. J., Clegg, W., Catlow, C. R. A., Bushnell-Wye, G., Flaherty, J. V., Greaves, G. N., Burrows, I., Taylor, D. J., Teat, S. J. & Hamichi, M. (1997). *J. Synchrotron Rad.* **4**, 279–286.
Clegg, W., Elsegood, M. R. J., Teat, S. J., Redshaw, C. & Gibson, V. C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3037–3039.
Dickinson, C., Stewart, T. M. & Ammon, H. L. (1970). *J. Chem. Soc. D*, pp. 920–921.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flippen-Anderson, J. L., Deschamps, J. R., Gilardi, R. D. & George, C. (2001). *Cryst. Eng.* **4**, 131–139.
Glidewell, C., Harrison, W. T. A., Low, J. N., Sime, J. G. & Wardell, J. L. (2001). *Acta Cryst.* B**57**, 190–200.
Ichharam, V. & Boeyens, J. C. A. (2001). *Cryst. Eng.* **4**, 171–178.
Okada, K., Saito, Y. & Oda, M. (1992). *J. Chem. Soc. Chem. Commun.* **23**, 1731–1732.
Platts, J. A., Howard, S. T. & Woźniak, K. (1995). *Chem. Phys. Lett.* **232**, 479–485.
Sharma, S., Paulus, H., Weiden, N. & Weiss, A. (1985). *Z. Kristallogr.* **171**, 101–112.
Sheldrick, G. M. (1998). *SHELXL*97-2. University of Göttingen, Germany.
Sime, J. G. & Woodhouse, D. I. (1974*a*). *J. Cryst. Mol. Struct.* **4**, 269–285.
Sime, J. G. & Woodhouse, D. I. (1974*b*). *J. Cryst. Mol. Struct.* **4**, 287–303.
Spek, A. L. (2002). *PLATON*. Version 80702. University of Utrecht, The Netherlands.