The structure of the α-form was solved by a combination of Patterson and direct methods. The Cl atom is disordered over two sites; both sites were refined anisotropically, with their occupancies constrained to sum to unity (55 and 45%). All H atoms were included in calculated positions, with both sets of sites for the H atoms on the chloromethyl group included at the appropriate occupancies. An attempt was made to determine the chirality of the crystal studied, but refinement of the two enantiomorphs showed no significant differences in agreement factors. The high R factors probably result from the large overall thermal motion, which may be rationalized as a consequence of the disorder of the heaviest atom.

The structure of the γ-form was solved by direct methods. There are two molecules per asymmetric unit; one of the molecules exhibits disorder of one ester group.

For both compounds, data collection: *TEXSAN* (Molecular Structure Corporation, 1985); cell refinement: *TEXSAN*; data reduction: *TEXSAN*; program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN*; molecular graphics: *TEXSAN*.

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1-Amino-2-nitro-4,5-bis(p-toluenesulfonamido)benzene

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Abstract

The crystal structure of the title compound [alternative name: N,N'-(5-amino-4-nitrobenzene-1,2-diyl)bis(p-

toluenesulfonamide)], $C_{20}H_{20}N_4O_6S_2$, has been determined. An intramolecular hydrogen bond between the amino and nitro groups keeps these groups nearly coplanar with the benzene ring.

Comment

The long-standing interest in substituted nitroanilines (Panunto, Urbanczyk-Lipowska, Johnson & Etter, 1987; Butcher, Gilardi, Flippen-Anderson & George, 1992) stems mainly from their large hyperpolarizabilities (Ledoux, Zyss, Siegel, Brienne & Lehn, 1990; Verbiest, Clays, Samyn, Wolff, Reinhoudt & Persoons, 1994), which makes them good candidates for non-linear optical studies. In the course of a study of 1,2,4,5-benzenetetramine derivatives, partial reduction of 1,2-dinitro-4,5-bis(p-tosylamido)benzene led to the title compound, (I), as a precursor of 1,2-diamino-4,5-bis(p-tosylamido)-benzene.

(I)
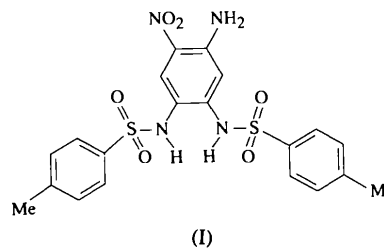
Similar to most nitroanilines, the C—N bond length C(5)—N(8), involving the amino group, is shortened from a normal value of 1.428 Å to a value of 1.346 (4) Å, indicating significant double-bond character. However, a survey of *ortho*-nitroaniline structures in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed that the presence of tosylamido substituents causes this effect to be less pronounced than that observed for most other similar compounds [mean value of 1.325 (2) Å for 49 observed C—N$_{amino}$ distances]. The amine proton H(82) is involved in intramolecular hydrogen bonding to the nitro O(72) atom with an O(72)···H(82) distance of 2.02 (4) Å. This keeps the nitro group in the benzene plane with an angle of rotation of 8.3°. The expected rotation angle for a nitro group having one substituent in an *ortho* position without hydrogen bonding is about 40° (Holden & Dickinson, 1969). For one of the tosylamido groups, the N(10) lone-pair direction is nearly perpendicular to the plane of the benzene ring (angle *ca* 74°), whereas for the other group, the N(20) lone pair is nearly parallel to this plane (angle *ca* 15°). This geometry increases the double-bond character of C(1)—N(10) as opposed to C(2)—N(20), with bond lengths of 1.401 (3) and 1.427 (3) Å, respectively. This effect is also reflected in the intracyclic C—C distances, the longest bonds, C(5)—C(4), C(5)—C(6) and C(1)—C(2), being those involving the C atoms

which are closely bonded to N atoms. An intermolecular hydrogen bond between atoms N(10) and O(21) [N(10)···O(21) 2.911 (3) and O(21)···H(10) 2.09 (4) Å] links the molecules in pairs. A weaker intermolecular hydrogen bond between atoms N(20) and O(11) [N(20)···O(11) 3.148 (3) and O(11)···H(20) 2.39 (4) Å] links the molecules to form chains.
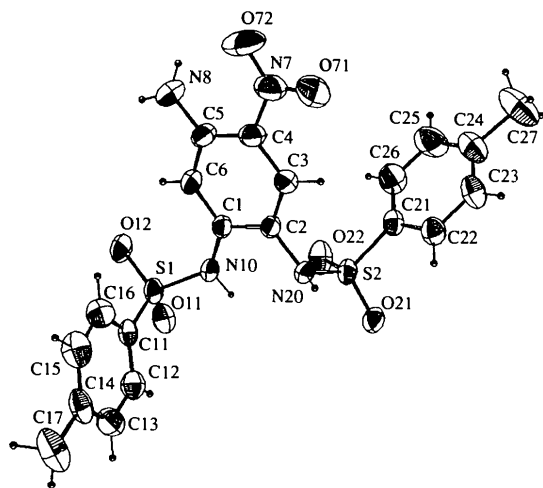

Fig. 1. View of title molecule showing the atom-numbering scheme. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn with an artificial $B = 0.2$ Å^2 for clarity.
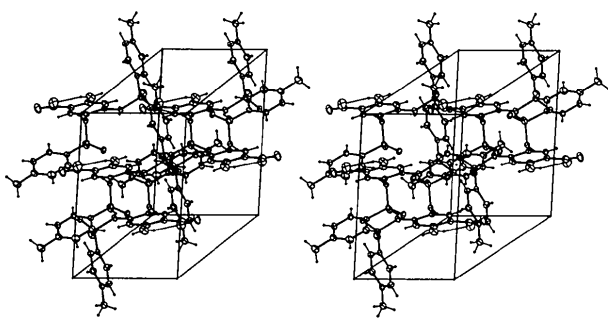

Fig. 2. Stereoscopic packing diagram with the b axis vertical and the a axis horizontal.

Experimental

The title compound was prepared by the reduction of 1,2-dinitro-4,5-bis(p-tosylamido)benzene by NaSH in water–dimethylacetamide solution. The experimental conditions were similar to those used for the preparation of 1,2-diamino-4,5-bis(p-tosylamido)benzene (Arnold, 1970). The raw product was purified by column chromatography on silica gel using chloroform as eluent. Slow evaporation of this solution gave X-ray quality crystals. NMR spectrum (250 MHz, DMSO-d_6): δ 2.49 (6H, s), 6.97 (1H, s), 7.37 (1H, s), 7.48 (2H, d, J = 8.5 Hz), 7.51 (2H, d, J = 8.5 Hz), 7.65 (2H, d, J = 8.5 Hz), 7.95 (2H, d, J = 8.5 Hz), 9.40 (1H, s), 9.54 (1H, s) p.p.m.

Crystal data

$C_{20}H_{20}N_4O_6S_2$	Mo $K\alpha$ radiation
$M_r = 476.522$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 7.643 (1)$ Å	$\theta = 13–16°$
$b = 11.578 (2)$ Å	$\mu = 0.2807$ mm^{-1}
$c = 13.117 (2)$ Å	$T = 297$ K
$\alpha = 69.69 (5)°$	Prism
$\beta = 80.57 (6)°$	$0.50 \times 0.40 \times 0.15$ mm
$\gamma = 86.87 (5)°$	Yellow
$V = 1074 (1)$ Å^3	
$Z = 2$	
$D_x = 1.474$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.010$
$\theta/2\theta$ scans	$\theta_{max} = 25°$
Absorption correction: none	$h = -9 \rightarrow 9$
	$k = -13 \rightarrow 13$
3962 measured reflections	$l = 0 \rightarrow 15$
3762 independent reflections	2 standard reflections
2994 observed reflections	frequency: 60 min
$[I > 3\sigma(I)]$	intensity decay: none

Refinement

Refinement on F	$\Delta\rho_{max} = 0.29$ e Å^{-3}
$R = 0.034$	$\Delta\rho_{min} = -0.26$ e Å^{-3}
$wR = 0.034$	Extinction correction:
$S = 2.13$	Zachariansen (1967)
2994 reflections	Gaussian
350 parameters	Extinction coefficient: 75 (7)
Only coordinates of H atoms refined	Atomic scattering factors from *International Tables*
Unit weights applied	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} = 0.001$	(1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0.3099 (3)	0.2478 (2)	0.2889 (2)	0.0315
C(2)	0.4883 (3)	0.2869 (2)	0.2747 (2)	0.0299
C(3)	0.5781 (4)	0.2485 (2)	0.3627 (2)	0.0368
C(4)	0.4983 (4)	0.1729 (2)	0.4657 (2)	0.0411
C(5)	0.3198 (4)	0.1365 (3)	0.4833 (2)	0.0428
C(6)	0.2301 (4)	0.1769 (3)	0.3917 (2)	0.0409
N(7)	0.6057 (4)	0.1333 (2)	0.5524 (2)	0.0563
O(71)	0.7660 (4)	0.1553 (3)	0.5291 (2)	0.0713
O(72)	0.5338 (4)	0.0765 (3)	0.6468 (2)	0.0765
N(8)	0.2306 (5)	0.0668 (3)	0.5809 (2)	0.0620
N(10)	0.2227 (3)	0.2882 (2)	0.1966 (2)	0.0345
S(1)	0.05747 (8)	0.22257 (6)	0.17130 (6)	0.0346
O(11)	-0.0271 (2)	0.3191 (2)	0.0942 (2)	0.0434
O(12)	-0.0440 (2)	0.1546 (2)	0.2746 (2)	0.0477
C(11)	0.1460 (3)	0.1182 (2)	0.1071 (2)	0.0338
C(12)	0.1639 (4)	0.1512 (3)	-0.0053 (3)	0.0457
C(13)	0.2307 (4)	0.0672 (3)	-0.0549 (3)	0.0521
C(14)	0.2794 (4)	-0.0494 (3)	0.0057 (3)	0.0450
C(15)	0.2605 (4)	-0.0799 (3)	0.1181 (3)	0.0547
C(16)	0.1949 (4)	0.0016 (3)	0.1696 (3)	0.0509
C(17)	0.3501 (5)	-0.1394 (4)	-0.0489 (4)	0.0642
N(20)	0.5704 (3)	0.3649 (2)	0.1691 (2)	0.0306

S(2)	0.56435 (8)	0.51396 (6)	0.14181 (6)	0.0350
O(21)	0.6551 (3)	0.5658 (2)	0.0322 (2)	0.0468
O(22)	0.3840 (2)	0.5447 (2)	0.1701 (2)	0.0504
C(21)	0.6893 (3)	0.5487 (2)	0.2288 (2)	0.0358
C(22)	0.8728 (4)	0.5439 (3)	0.2064 (2)	0.0418
C(23)	0.9711 (4)	0.5774 (3)	0.2706 (3)	0.0511
C(24)	0.8935 (5)	0.6154 (3)	0.3552 (3)	0.0571
C(25)	0.7108 (5)	0.6163 (4)	0.3779 (3)	0.0661
C(26)	0.6081 (4)	0.5835 (3)	0.3145 (3)	0.0567
C(27)	1.0065 (8)	0.6575 (5)	0.4197 (5)	0.0819

Table 2. Selected geometric parameters (Å, °)

C(1)—C(2)	1.422 (3)	C(5)—N(8)	1.346 (4)
C(1)—C(6)	1.371 (4)	N(7)—O(71)	1.231 (4)
C(1)—N(10)	1.401 (3)	N(7)—O(72)	1.232 (3)
C(2)—C(3)	1.368 (3)	N(10)—S(1)	1.643 (2)
C(2)—N(20)	1.427 (3)	S(1)—O(11)	1.429 (2)
C(3)—C(4)	1.389 (4)	S(1)—O(12)	1.428 (2)
C(4)—C(5)	1.408 (4)	S(2)—O(21)	1.424 (2)
C(4)—N(7)	1.443 (4)	S(2)—O(22)	1.426 (2)
C(5)—C(6)	1.407 (4)		

N—H distances	0.80 (3)–0.84 (3)	C—H distances	0.82 (3)–0.99 (3)
C(6)—C(1)—C(2)	119.0 (2)	N(8)—C(5)—C(4)	124.7 (3)
N(10)—C(1)—C(2)	117.6 (2)	N(8)—C(5)—C(6)	118.4 (3)
N(10)—C(1)—C(6)	123.4 (2)	C(5)—C(6)—C(1)	122.7 (3)
C(3)—C(2)—C(1)	119.3 (2)	O(71)—N(7)—C(4)	118.9 (3)
N(20)—C(2)—C(1)	119.5 (2)	O(72)—N(7)—C(4)	118.6 (3)
N(20)—C(2)—C(3)	121.2 (2)	O(72)—N(7)—O(71)	122.5 (3)
C(4)—C(3)—C(2)	121.3 (3)	O(11)—S(1)—N(10)	105.7 (1)
C(5)—C(4)—C(3)	120.8 (2)	O(12)—S(1)—N(10)	107.6 (1)
N(7)—C(4)—C(3)	117.3 (3)	O(21)—S(2)—N(20)	105.3 (1)
N(7)—C(4)—C(5)	121.9 (3)	O(22)—S(2)—N(20)	106.7 (1)
C(6)—C(5)—C(4)	116.9 (2)	O(22)—S(2)—O(21)	120.9 (1)

Data collection and cell refinement used *CAD*-4 *Software* (Enraf–Nonius, 1989). The structure was solved with *SHELXS*86 (Sheldrick, 1985). Most calculations were performed with the *CRYSTALS* package (Watkin, Carruthers & Betteridge, 1985). The drawings were prepared with *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2′-Methoxy-5′-methoxycarbonylspiro[acridine-9(10H),4′(5′H)-thiazole]

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Abstract

The structure of the title ester, methyl 2′-methoxyspiro[acridine-9(10H),4′(5′H)-thiazole]-5′-carboxylate, $C_{18}H_{16}N_2O_3S$, is described. The compound is of spiro type. The acridine molecule is not planar, but adopts an arch-like conformation. The thiazole ring is in an envelope form. One of the C—C bonds exhibits an unusual value of 1.610 (3) Å. A C=O···H—N-type intermolecular hydrogen bond takes part in the packing of the molecules.

Comment

Isothiocyanates are at present extensively studied as they are used as synthones of various heterocycles (Mukerjee & Ashare, 1991), fluorescence reagents for labelling of biomolecules (Russel & Boron, 1976), and important chemotherapeutics (Zhang & Talalay, 1994). Our interest lies in the study of such new functionalized 9-acridinyl derivatives (Mazagová *et al.*, 1994).

Our goal was to prepare a three-membered heterocycle by the reaction of sodium *O*-methyl-*N*-(9-acridinyl)-iminothiocarbonate with methyl bromoacetate. As the ¹H NMR, ¹³C NMR and IR spectra of the obtained compound were not in line with the expected composi-