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Hydrogen bonding in C-substituted nitroanilines: a chain of $R^3_3(12)$ rings in 2-methanesulfonyl-4-nitroaniline

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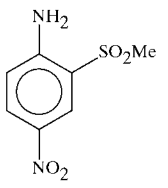
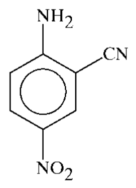
The title compound, $C_7H_8N_2O_4S$, exhibits a markedly polarized molecular–electronic structure. The molecules are linked into a chain of edge-fused $R^3_3(12)$ rings by two N—H···O=S hydrogen bonds [H···O = 2.10 and 2.21 Å, N···O = 2.900 (2) and 2.878 (2) Å, and N—H···O = 152 and 133°].

Comment

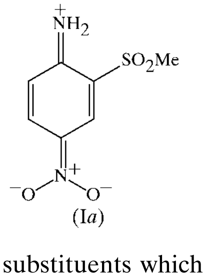
The supramolecular structure of 4-nitroaniline (Tonogaki *et al.*, 1993) consists of a hydrogen-bonded (4,4)-sheet (Batten & Robson, 1998) built from a single type of $R^4_4(22)$ ring (Bernstein *et al.*, 1995). This essentially straightforward mode of aggregation can be modified in a variety of ways by the introduction of simple C-substituents. These can be simple space-filling substituents which do not themselves participate in the supramolecular aggregation, but which nonetheless affect the hydrogen-bonding possibilities. Thus, a 2-methyl substituent generates a three-dimensional hydrogen-bonded framework structure (Ferguson *et al.*, 2001), while 2- or 3-trifluoromethyl substituents generate, respectively, molecular ladders, or sheets containing alternating $R^4_4(12)$ and $R^4_4(32)$ rings (Glidewell *et al.*, 2002*a*). Alternatively, the additional substituents can themselves participate in the hydrogen bonding, as with a 3-amino substituent, where (4,4)-nets of $R^4_4(24)$ rings are formed (Glidewell *et al.*, 2001), or with a 6-cyano substituent, where the sheets contain alternating $R^2_2(12)$ and $R^6_6(36)$ rings (Glidewell *et al.*, 2002*b*). Finally, if iodo substituents are present, there is the possibility of iodo–nitro interactions, as in the triclinic and orthorhombic polymorphs of 2-iodo-4-nitroaniline (McWilliam *et al.*, 2001).



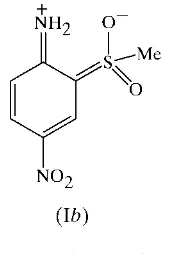
(I)



(II)



(I*a*)



(I*b*)

Continuing this study, we have now investigated the molecular and supramolecular structure of the title compound, (I). The supramolecular structure is again dominated by two N—H···O hydrogen bonds, but in both of these the acceptor is one of the sulfone O atoms. The nitro group does not participate in the intermolecular hydrogen bonding.

Within the molecule of (I), the nitro group is nearly coplanar with the aryl ring, as shown by the torsion angles (Table 1), and the C—NH_2 and C—NO_2 bonds (Table 1) are both short for their types. The corresponding mean and lower-quartile reference values (Allen *et al.*, 1987) are, respectively, 1.355 and 1.340 Å for C—NH_2, and 1.468 and 1.460 Å for C—NO_2. At the same time, the N—O bonds are both longer than the upper-quartile reference value of 1.215 Å for aromatic nitro groups, suggesting a significant contribution from the *p*-quinonoid form, (I*a*). However, the C3—C4 and C5—C6 ring bonds are somewhat shorter than the analogous C4—C5 and C2—C3 bonds, respectively (Table 1), indicating a contribution also from the *o*-quinonoid form, (I*b*), although the S—C and S—O distances, at their lower- and upper-quartile reference values, respectively, do not offer significant support for this.

The shorter of the two N—H···O=S hydrogen bonds (Table 1) links the molecules of (I) into chains generated by translation. Amino atom N1 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H1*A*, to sulfone atom O21 in the molecule at (x, y − 1, z), so forming a *C*(6) chain running parallel to the [010] direction. Eight of these chains pass through each unit cell and they are linked in pairs by the second, weaker, N—H···O=S hydrogen bond. In this, atom N1 at (x, y, z) acts as hydrogen-bond donor, *via* atom H1*B*, to

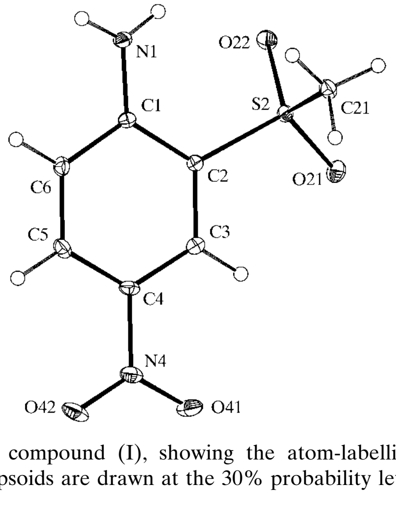


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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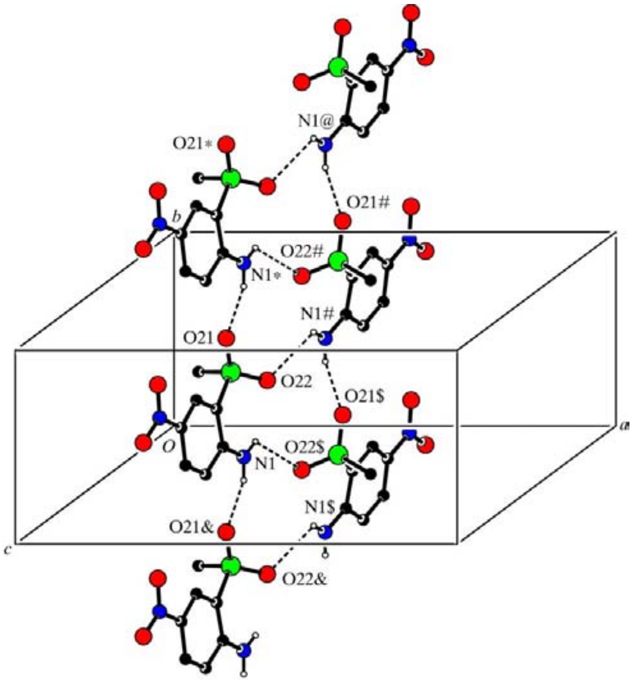

Figure 2
Part of the crystal structure of (I), showing the formation of a chain of edge-fused $R_3^3(12)$ rings along [010]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or 'at' sign (@) are at the symmetry positions $(x, 1 + y, z)$, $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$, $(\frac{1}{2} - x, y - \frac{1}{2}, -z)$, $(x, y - 1, z)$ and $(\frac{1}{2} - x, \frac{3}{2} + y, -z)$, respectively.

atom O22 in the molecule at $(\frac{1}{2} - x, y - \frac{1}{2}, -z)$, so producing a second $C(6)$ chain motif parallel to [010], this time generated by the 2_1 screw axis along $(\frac{1}{4}, y, 0)$. The combination of these two independent $C(6)$ motifs generates a chain of edge-fused $R_3^3(12)$ rings. There are four chains of rings passing through each unit cell, but there are no direction-specific interactions between adjacent chains. It is perhaps surprising that both aromatic π–π stacking interactions and dipolar nitro–nitro interactions are absent. Indeed, the nitro O atoms play no role whatsoever in the supramolecular aggregation of (I).

The one-dimensional supramolecular structure of (I) may be contrasted with the two-dimensional structure of the analogous 2-cyano-4-nitroaniline, (II), where the cyano N and one of the nitro O atoms act as hydrogen-bond acceptors (Glidewell *et al.*, 2004).

Experimental

A sample of (I) was obtained many years ago from ICI Dyestuffs Division. Crystals suitable for single-crystal X-ray diffraction were grown from a solution in 2-ethoxyethanol.

Crystal data

$C_7H_8N_2O_4S$
M_r = 216.21
Monoclinic, $I2/c$
a = 15.8657 (5) Å
b = 7.2366 (1) Å
c = 16.4224 (5) Å
β = 110.304 (1)°
V = 1768.36 (8) Å^3
Z = 8
D_x = 1.624 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2026 reflections
θ = 3.1–27.5°
μ = 0.36 mm^{-1}
T = 120 (2) K
Block, orange
0.40 × 0.35 × 0.30 mm

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.421 (2)	C4—N4	1.444 (2)
C2—C3	1.380 (2)	N4—O41	1.232 (2)
C3—C4	1.377 (2)	N4—O42	1.230 (2)
C4—C5	1.397 (2)	C2—S2	1.7592 (14)
C5—C6	1.368 (2)	S2—O21	1.4402 (11)
C6—C1	1.420 (2)	S2—O22	1.4443 (11)
C1—N1	1.341 (2)	S2—C21	1.7568 (15)
C1—C2—S2—C21	75.0 (2)	C3—C4—N4—O41	−5.7 (2)
C1—C2—S2—O21	−170.2 (2)	C5—C4—N4—O42	−4.1 (2)
C1—C2—S2—O22	−40.9 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O21^{i}	0.88	2.10	2.900 (2)	152
N1—H1$B\cdots$O22^{ii}	0.88	2.21	2.878 (2)	133

Symmetry code: (i) $x, y - 1, z$; (ii) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$.

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.871, $T_{\max}$ = 0.901
11 417 measured reflections
2026 independent reflections
1781 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.005
$\theta_{\max}$ = 27.5°
$h = -17 \rightarrow 20$
$k = -9 \rightarrow 9$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.086
S = 1.10
2026 reflections
128 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 1.6784P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.30 e Å^{-3}
$\Delta\rho_{\min}$ = −0.54 e Å^{-3}

The systematic absences permitted $C2/c$ and Cc as possible space groups; $C2/c$ was selected and confirmed by the successful structure analysis. Because the unit cell in $C2/c$ has a β value of 123.4295 (12)°, the cell was transformed to the non-standard setting $I2/c$ in order to reduce the value of β. All H atoms were located in difference maps and were then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.98 Å (methyl), and N—H distances of 0.88 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Acta Cryst. (2004). C**60**, o84–o86 R. Alan Howie *et al.* • $C_7H_8N_2O_4S$ **o85**

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1687). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Ferguson, G., Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 315–316.

Glidewell, C., Cannon, D., Quesada, A., Low, J. N., McWilliam, S. A., Skakle, J. M. S. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 455–458.

Glidewell, C., Low, J. N., McWilliam, S. A., Skakle, J. M. S. & Wardell, J. L. (2002*a*). *Acta Cryst.* C**58**, o97–o99.

Glidewell, C., Low, J. N., McWilliam, S. A., Skakle, J. M. S. & Wardell, J. L. (2002*b*). *Acta Cryst.* C**58**, o100–o102.

Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2004). *Acta Cryst.* C**60**, o35–o37.

McWilliam, S. A., Skakle, J. M. S., Low, J. N., Wardell, J. L., Garden, S. J., Pinto, A. C., Torres, J. C. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 942–945.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. 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.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Tonogaki, M., Kawata, T., Ohba, S., Iwata, Y. & Shibuya, I. (1993). *Acta Cryst.* B**49**, 1031–1039.

o86 R. Alan Howie *et al.* • $C_7H_8N_2O_4S$ *Acta Cryst.* (2004). C**60**, o84–o86