Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen bonding in C-substituted nitroanilines: simple *C*(8) chains in 2-bromo-6-chloro-4-nitroaniline

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Received 29 March 2005
Accepted 30 March 2005
Online 30 April 2005

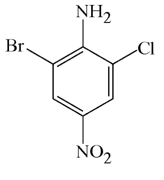
In the title compound, $C_6H_4BrClN_2O_2$, the Br and Cl substituents are disordered over two sites, and the intramolecular dimensions provide evidence for charge polarization. The molecules are linked into *C*(8) chains by a single N—H$\cdots$O hydrogen bond.

Comment

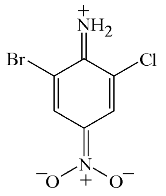
We report here the structure of the title compound, (I), which we compare with the structures of four other closely related 2,6-substituted 4-nitroanilines, namely 2,6-dichloro-4-nitroaniline, (II) (Hughes & Trotter, 1971), 2,6-dibromo-4-nitroaniline, (III) (Bryant *et al.*, 1998), 2-bromo-6-cyano-4-nitroaniline, (IV) (Glidewell *et al.*, 2002), and 2-iodo-6-methoxy-4-nitroaniline, (V) (Garden *et al.*, 2005).

In molecules of (I) (Fig. 1), the Br and Cl substituents are disordered between the 2- and 6-positions in the aryl ring. Refinement of the site occupancies showed that position 2 is occupied equally by the two substituents, whereas there is slight preponderance of Cl at position 6, corresponding to co-crystallization of (I) with 10% of the dichloro analogue (II); compound (II) is isomorphous with (I) but not strictly isostructural. The sample of (I) originated in an industrial preparation using bromination of 2-chloro-4-nitroaniline and it seems likely that the 2,6-dichloro compound (II) may have been present as an impurity before the bromination step.

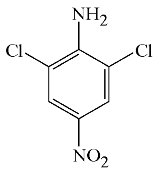
The C—C bond distances in (I) show marked bond fixation (Table 1), with the C2—C3 and C5—C6 distances significantly shorter than the rest; correspondingly, the two C—N distances are both short for their types (Allen *et al.*, 1987), while the N—O distances are both long. These observations taken all together point to the importance of the charge-separated form (I*a*) (see scheme) as an important contributor to the overall molecular–electronic structure, as commonly found in 4-nitroanilines. Consistent with the contribution of form (I*a*), the dihedral angle between the nitro group and the aryl ring is only 6.6 (2)°.



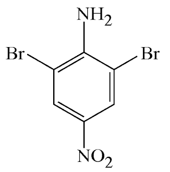
(I)



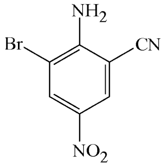
(I*a*)



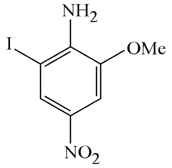
(II)



(III)



(IV)



(V)

The molecules of (I) are linked into simple chains by a single N—H$\cdots$O hydrogen bond (Table 2). Amine atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H1*A*, to nitro atom O41 in the molecule at $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, so forming a *C*(8) chain (Bernstein *et al.*, 1995) running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ (Fig. 2). Two antiparallel chains of this type, related to one another by inversion, pass through each unit cell, but there are no direction specific interactions between adjacent chains; in particular, there are no potential acceptors in other chains within hydrogen-bonding distance of H1*B*.

In (II), the molecules are again linked by a single N—H$\cdots$O hydrogen bond into *C*(8) chains virtually identical to those in (I) (Hughes & Trotter, 1971). Hence, the presence of a small proportion of (II) co-crystallized with (I) appears to have no significant influence on the supramolecular structure adopted by (I), which in addition retains the sharp melting point of the pure compound (Körner & Contardi, 1914). In contrast to the very simple aggregation in (I) and (II), the molecules of (III),

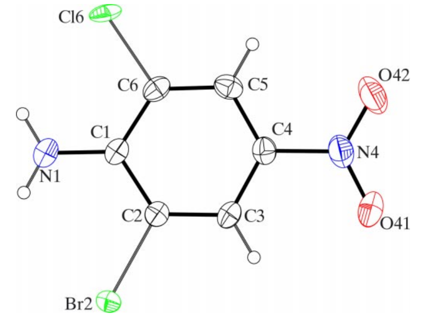


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only one substituent is drawn bonded to C2 and to C6.

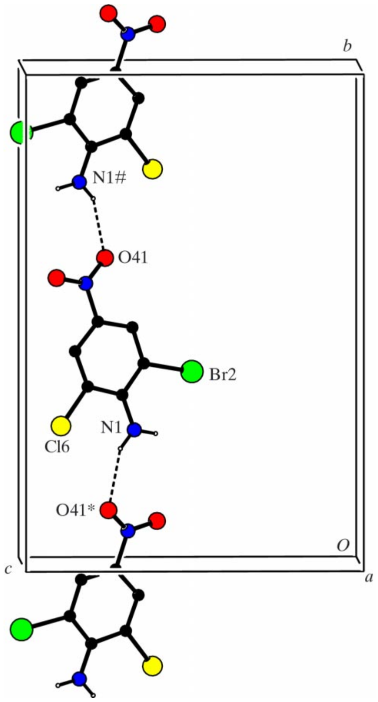


Figure 2
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded *C*(8) chain along [010]. For clarity, only one substituent is drawn bonded to C2 and to C6, and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

which lie across mirror planes in space group $P2_1/m$, are linked by paired N—H···O hydrogen bonds into $C(8)[R_2^2(6)]$ chains of rings, further linked into sheets by bromo–nitro interactions (Bryant *et al.*, 1998). In compound (IV), the molecules are linked by a combination of one N—H···O and one N—H···N hydrogen bond into sheets of alternating $R_2^2(12)$ and $R_6^6(36)$ rings (Glidewell *et al.*, 2002), while in compound (V), hydrogen-bonded $C(8)C(8)[R_2^2(6)]$ chains of rings are linked into quite complex ribbons by two-centre iodo–nitro interactions (Garden *et al.*, 2005). In each of (III)–(V), the two N—H bonds of the amine group both participate in the hydrogen bonding, in contrast to the situation in (I) and (II), where one of the N—H bonds plays no role in the supramolecular aggregation.

Experimental

The sample of (I) employed was a gift from ICI; crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol [m.p. 450–452 K; literature m.p. 450 K (Körner & Contardi, 1914)].

Crystal data

$C_6H_4Br_{0.90}Cl_{1.10}N_2O_2$
$M_r = 247.02$
Monoclinic, $P2_1/c$
$a = 3.8052$ (3) Å
$b = 17.9667$ (13) Å
$c = 12.0417$ (9) Å
$\beta = 93.224$ (2)°
$V = 821.95$ (11) Å^3
$Z = 4$
$D_x = 1.996$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1863 reflections
$\theta = 2.0$–27.5°
$\mu = 4.83$ mm^{-1}
$T = 298$ (2) K
Plate, red
0.49 × 0.16 × 0.06 mm

Data collection

Bruker SMART 1000 CCD area detector diffractometer
φ–ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.201$, $T_{\max} = 0.749$
5904 measured reflections
1863 independent reflections
1357 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 27.5°$
$h = -4 \rightarrow 4$
$k = -23 \rightarrow 16$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.087$
$S = 1.02$
1863 reflections
129 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

C1—C2	1.408 (4)	C6—C1	1.404 (5)
C2—C3	1.373 (4)	C1—N1	1.345 (4)
C3—C4	1.387 (5)	C4—N4	1.456 (5)
C4—C5	1.387 (5)	N4—O41	1.241 (4)
C5—C6	1.364 (5)	N4—O42	1.228 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O41$^{\rm i}$	0.86	2.25	3.026 (4)	151

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

The space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.93 Å and N—H distances of 0.86 Å, and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C,N). It was apparent from an early stage that the Cl and Br substituents were disordered between the sites bonded to C2 and C6. Refinement of the site-occupancy factors for the substituents at C2 led to values of 0.503 (6) and 0.497 (6) for Cl and Br, respectively; these were thereafter fixed at 0.50. Refinement of the site-occupancy factors for the substituents at C6 led to values of 0.603 (5) and 0.397 (5) for Cl and Br, respectively; these were thereafter fixed at 0.60 and 0.40, respectively. Refinements with the occupancy factors for all the halogen sites fixed at 0.50 (to force equal populations of Cl and Br) led to significantly higher *R* values and hence this model was decisively rejected. Because of the fairly close similarity between the C—Cl and C—Br distances, it was necessary to apply DFIX restraints to the four independent C—*X* (*X* = Cl and Br) distances.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Aberdeen; the authors thank the university for funding the purchase of the diffractometer.

Acta Cryst. (2005). C**61**, o336–o338 Glidewell *et al.* • $C_6H_4Br_{0.90}Cl_{1.10}N_2O_2$ **o337**

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1832). Services for accessing these data are described at the back of the journal.

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