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Hydrogen bonding in C-substituted nitroanilines: sheets built from alternating $R_2^2(12)$ and $R_6^6(36)$ rings in 2-bromo-6-cyano-4-nitroaniline

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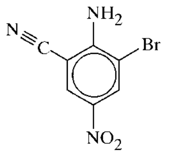
Molecules of the title compound (systematic name: 2-amino-3-bromo-5-nitrobenzonitrile), $C_7H_4BrN_3O_2$, are linked by N—H···N and N—H···O hydrogen bonds [H···N 2.19 Å, N···N 3.019 (4) Å and N—H···N 157°, and H···O 2.17 Å, N···O 2.854 (3) Å and N—H···O 134°] to form $(10\bar{3})$ sheets built from alternating $R_2^2(12)$ and $R_6^6(36)$ rings, both of which are centrosymmetric.

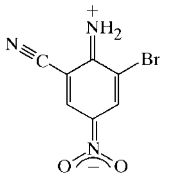
Comment

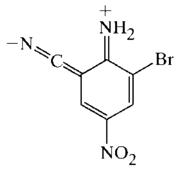
We have recently reported the striking differences which are induced in the hydrogen-bonding schemes in nitroanilines by the introduction of simple substituents elsewhere in the aryl ring (Cannon *et al.*, 2001; Ferguson *et al.*, 2001; Garden *et al.*, 2001; McWilliam *et al.*, 2001; Zakaria *et al.*, 2001). As part of this study, we have reported the structures of two polymorphs of 2-iodo-4-nitroaniline, where the I···NO_2 interactions provide an effective alternative to hard and soft hydrogen bonds as determinants of supramolecular aggregation (McWilliam *et al.*, 2001).

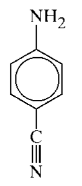
Seeking to introduce an additional hydrogen-bond acceptor as a potential alternative to the nitro group O atoms, we have now investigated the structure of 2-bromo-6-cyano-4-nitroaniline, (I), where the cyano group is potentially an effective acceptor of hydrogen bonds, as demonstrated by the structures of the isomeric cyanoanilines (Merlino & Sartori, 1982; Heine *et al.*, 1994; Laine *et al.*, 1996).

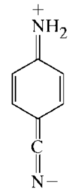
In compound (I) (Fig. 1), the amino group acts as a double donor of hydrogen bonds. The cyano atom N61 acts as a single acceptor, as does one of the nitro O atoms, O41, but atom O42 does not participate in the hydrogen bonding. These two hydrogen bonds (Table 2) link the molecules into sheets, within which each molecule is directly connected to three others.


(I)


(I*a*)


(I*b*)


(II)


(II*a*)

Amino atom N1 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* H11, to cyano N61 at $(2 - x, 1 - y, 1 - z)$, thereby generating a dimer unit centred at $(1, \frac{1}{2}, \frac{1}{2})$ and containing a centrosymmetric $R_2^2(12)$ ring. Atom N1 at (x, y, z) also acts as a donor, this time *via* H12, to nitro O41 at $(\frac{3}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, which is part of the dimeric unit centred at $(\frac{5}{2}, 0, 1)$. Propagation of these two hydrogen bonds thus generates a sheet, parallel to $(10\bar{3})$, built from alternating $R_2^2(12)$ and $R_6^6(36)$ rings arranged in a checkerboard fashion (Fig. 2). Three of these sheets are required to define the structure fully, but since the sheets are virtually planar, there is no possibility of any interweaving. If the individual molecules are regarded as the nodes of the resulting net, then this net is of the (6,3)-type (Batten & Robson, 1998), while if the $R_2^2(12)$ dimers are taken as the nodes, then the net is of the (4,4)-type. There are no aromatic π–π-stacking interactions, or other direction-specific interactions, between adjacent sheets, so that the supramolecular structure is strictly two-dimensional.

Although the nitro atom O42 plays no role in the hydrogen bonding, it does participate in a fairly short intermolecular

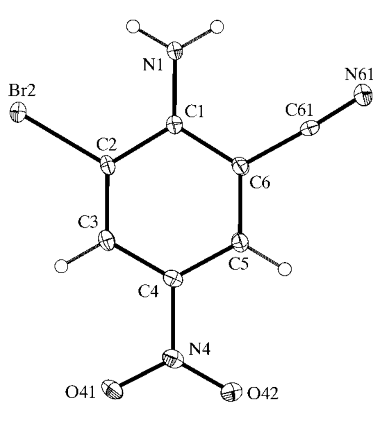


Figure 1
A view of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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Br···O contact. Atom Br2 in the molecule at (x, y, z) makes a short contact with O42 in the molecule at ($\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$), part of the dimer unit centred at ($-\frac{1}{2}$, 0, 0) (Fig. 2), and there are thus centrosymmetrically related pairs of such interactions within each of the $R_6^6(36)$ rings. The Br2···O42$^{\rm i}$ distance is 3.247 (2) Å and the C2—Br2···O42$^{\rm i}$ angle is 163.0 (2)° [symmetry code: (i) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$]. However, this Br···O distance is comparable with the shortest intermolecular I···O distances in 2-iodo-4-nitroaniline, *viz.* 3.266 (5) Å in the triclinic polymorph and 3.153 (7) Å in the orthorhombic polymorph (McWilliam *et al.*, 2001), and hence this contact is more likely to be an adventitious consequence of the ring structure generated by the hydrogen bonds than to be structurally significant in itself. There are no short Br···Br contacts nor any C—H···O hydrogen bonds in the structure.

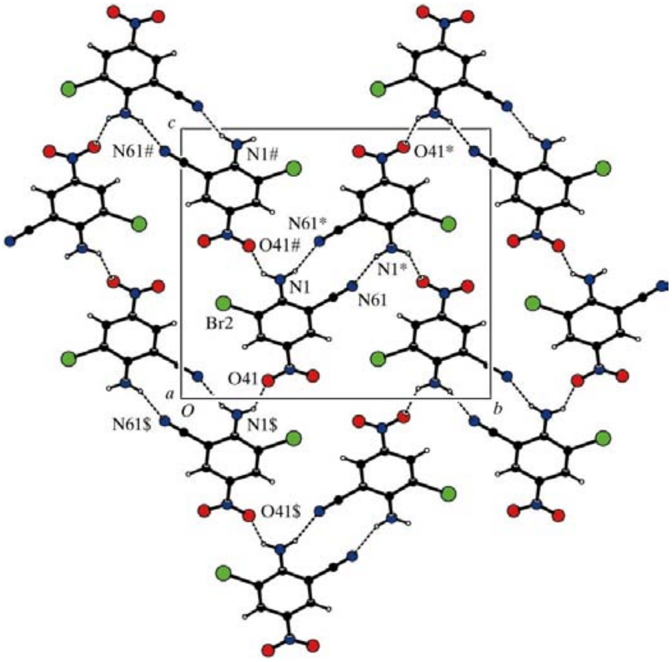

Figure 2
A projection of part of the crystal structure of (I) showing the formation of a $(10\bar{3})$ sheet built from $R_2^2(12)$ and $R_6^6(36)$ rings. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($2 - x$, $1 - y$, $1 - z$), ($\frac{3}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$) and ($x - \frac{3}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$), respectively.

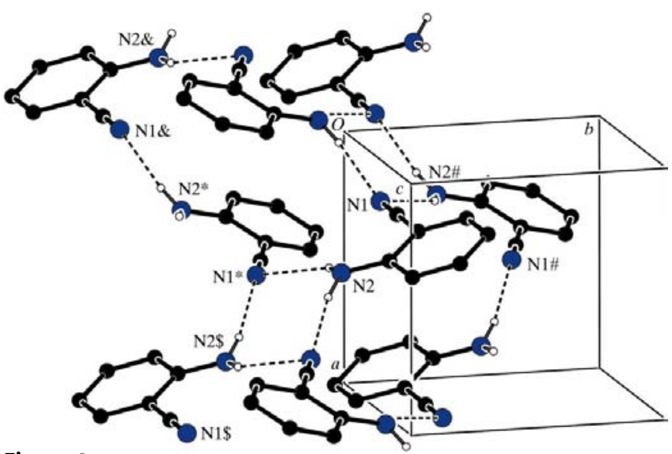

Figure 3
Part of the crystal structure of 2-cyanoaniline (Laine *et al.*, 1996), showing the formation of a $(10\bar{1})$ sheet of $R_4^2(8)$ and $R_4^4(24)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions ($\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$), ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), ($\frac{1}{2} + x$, $-\frac{1}{2} - y$, $\frac{1}{2} + z$) and ($x - \frac{1}{2}$, $-\frac{1}{2} - y$, $z - \frac{1}{2}$), respectively.

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.424 (4)	C1—N1	1.342 (4)
C2—C3	1.365 (4)	C4—N4	1.456 (4)
C3—C4	1.388 (4)	C6—C61	1.439 (4)
C4—C5	1.385 (4)	C61—N61	1.140 (4)
C5—C6	1.382 (4)	N4—O41	1.236 (3)
C6—C1	1.416 (4)	N4—O42	1.224 (3)
C2—Br2	1.888 (3)		
C3—C4—N4—O41	−1.5 (4)	C5—C4—N4—O42	−1.9 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···N61$^{\rm i}$	0.88	2.19	3.019 (4)	157
N1—H12···O41$^{\rm ii}$	0.88	2.17	2.854 (3)	134

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

It is of interest to compare the hydrogen-bonding pattern in (I), arising from the cyano and amino groups acting as the acceptors, with those in the isomers of cyanoaniline itself. In 2-cyanoaniline, where the original report (Laine *et al.*, 1996) gave no analysis of the supramolecular structure, the amino group acts as a double donor of hydrogen bonds and the cyano N atom acts as a double acceptor, and the molecules are thereby linked into deeply puckered sheets of alternating $R_4^2(8)$ and $R_4^4(24)$ rings (Fig. 3). Within these sheets, no dimer motif can be identified analogous to that in (I). By contrast, 3-cyanoaniline (Merlino & Sartori, 1982) forms a three-dimensional framework structure in which both N atoms act as acceptors in N—H···N hydrogen bonds. 4-Cyanoaniline crystallizes in both monoclinic (Merlino & Sartori, 1982) and orthorhombic (Heine *et al.*, 1994) polymorphs, at ambient and reduced temperatures, respectively, and in both forms the supramolecular aggregation takes the form of simple $C(8)$ chains, generated by a glide plane in $P2_1/c$ and a screw axis in $P2_12_12_1$, respectively. In both these polymorphs, only one N—H bond of the amino group is engaged in the hydrogen bonding.

The bond distances in (I) (Table 1) provide some evidence for a contribution to the overall electronic structure from the canonical forms (I*a*) and (I*b*). In particular, the C—NH$_2$ and C—NO$_2$ bonds are both short for their types (Allen *et al.*, 1987). The C2—C3 bond is the shortest of the ring bonds, and C1—C2 and C6—C1 are the longest. For 4-cyanoaniline, (II), and a range of methylated derivatives (Heine *et al.*, 1994), the quinonoid form (II*a*), analogous to (I*b*), was found to be significant.

Experimental

A sample of (I) was obtained from Bayer, and crystals suitable for single-crystal X-ray diffraction were grown from a solution in ethanol.

Crystal data

$C_7H_4BrN_3O_2$
$M_r = 242.04$
Monoclinic, $P2_1/n$
$a = 4.2494$ (2) Å
$b = 14.9094$ (7) Å
$c = 13.0958$ (7) Å
$\beta = 96.138$ (2)°
$V = 824.94$ (7) Å^3
$Z = 4$
$D_x = 1.949$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1894 reflections
$\theta = 3.1$–27.5°
$\mu = 4.95$ mm^{-1}
$T = 150$ (2) K
Needle, colourless
$0.25 \times 0.07 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.647$, $T_{\max} = 0.820$
6073 measured reflections
1894 independent reflections
1413 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 27.5°$
$h = -5 \rightarrow 5$
$k = -19 \rightarrow 19$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.081$
$S = 1.01$
1894 reflections
118 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ was uniquely assigned from the systematic absences. H atoms were treated as riding, with C—H = 0.95 Å and N—H = 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, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1529). Services for accessing these data are described at the back of the journal.

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