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Hydrogen bonding in C-substituted nitroanilines: π-stacked sheets of $R_4^4(20)$ and $R_4^4(28)$ rings in 2-cyano-4-nitroaniline

Christopher Glidewell,[a]* John N. Low,[b] Janet M. S. Skakle[b] and James L. Wardell[c]

[a]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: cg@st-andrews.ac.uk

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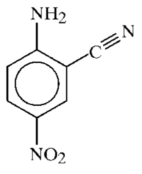
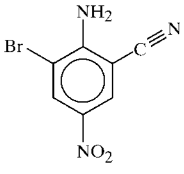
In the title compound, $C_7H_5N_3O_2$, which crystallizes with $Z' = 2$ in space group $P2_1/c$, the two independent molecules both exhibit positional disorder, with refined site-occupancy factors of 0.947 (2) and 0.053 (2) for the major and minor components, respectively. The major components have polarized molecular electronic structures. The two major components are linked into sheets of alternating $R_4^4(20)$ and $R_4^4(28)$ rings by two N—H···O hydrogen bonds [H···O = 2.18 and 2.21 Å, N···O = 3.022 (2) and 3.043 (2) Å and N—H···O both 159°] and two N—H···N hydrogen bonds [H···N = 2.14 and 2.17 Å, N···N = 2.990 (2) and 3.001 (2) Å, and N—H···N = 162 and 158°]. The sheets are linked into a three-dimensional framework by a single aromatic π–π stacking interaction.

Comment

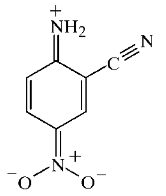
We report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1), which provides an interesting comparison with the bromo-substituted analogue, (II) (Glidewell *et al.*, 2002). In compound (II), the molecules are linked *via* paired N—H···N hydrogen bonds, in which the cyano N atom acts as the acceptor, into centrosymmetric dimers characterized by an $R_2^2(12)$ motif (Bernstein *et al.*, 1995), and these dimers are linked by a single N—H···O hydrogen bond into essentially planar sheets built from alternating $R_2^2(12)$ and $R_6^6(36)$ rings, where both ring types are centrosymmetric (Glidewell *et al.*, 2002). Within the larger of these rings, there are centrosymmetrically related pairs of fairly short intermolecular Br···O contacts, involving the nitro O atom which is not engaged in the hydrogen bonding, and this raises the possibility that these Br and O atoms may be acting as an effective template for the formation of the $R_6^6(36)$ rings. It is thus of interest to investigate the analogue, (I), from which the Br substituent is absent.



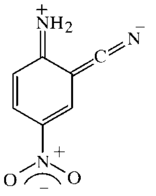
(I)



(II)



(I*a*)



(I*b*)

The molecules of (I) exhibit positional disorder (see *Experimental*). In both the major components, molecules *A* and *B* (Fig. 1), the bond distances (Table 1) provide evidence for polarized molecular electronic structures. The C—NH_2 and C—NO_2 distances are both short for their types (Allen *et al.*, 1987) while the N—O distances are all long, and the bonds C2*X*—C3*X*, C3*X*—C4*X* and C5*X*—C6*X* (*X* is *A* or *B*) are all significantly shorter than the remaining ring bonds, consistent with quinonoid bond fixation. These values thus indicate a contribution to the overall molecular electronic structure from the canonical forms (I*a*) and (I*b*). Entirely similar forms also contribute to the molecular electronic structure of (II) (Glidewell *et al.*, 2002).

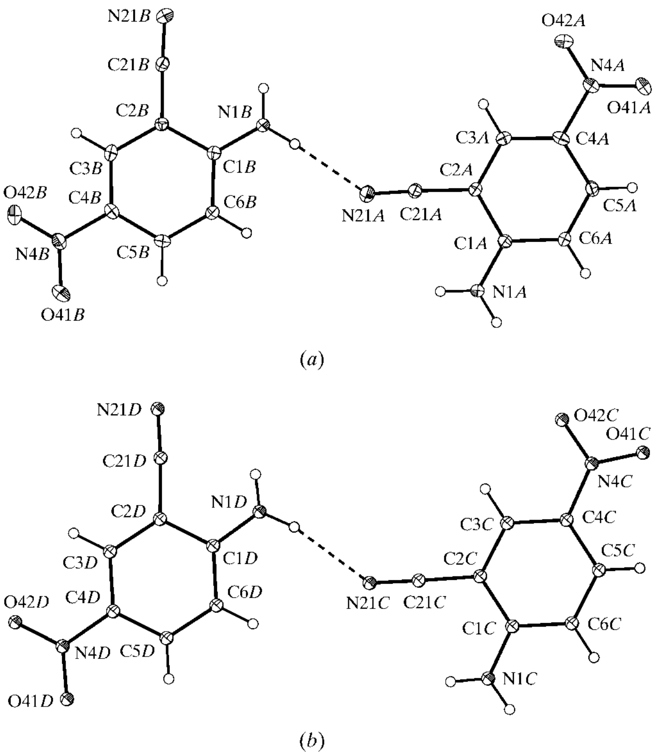


Figure 1
The independent molecular components of compound (I), showing the atom-labelling schemes. (*a*) The major components, molecules *A* and *B*, and (*b*) the minor components, molecules *C* and *D* (see text). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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However, the supramolecular structure of (I) is entirely different from that of (II). Since the pattern of hydrogen bonds linking the major components, molecules *A* and *B*, is identical to that linking the minor components, molecules *C* and *D* (Table 2), we discuss in detail only the supramolecular aggregation of the major components. Each of the N—H$\cdots$O hydrogen bonds involves only a single type of molecule, *A*–*D* respectively, while the N—H$\cdots$N hydrogen bonds link molecules either of types *A* and *B*, or of types *C* and *D*.

Amino atom N1*A* in the type *A* molecule at (x, y, z), acts as hydrogen-bond donor, *via* atom H11*A*, to atom O41*A* in the type *A* molecule at $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, so producing a $C(8)$ spiral chain of type *A* molecules only, running parallel to the [010] direction and generated by the 2_1 screw axis along $(0, y, \frac{1}{4})$ (Fig. 2). Similarly, atom N1*B* in the type *B* molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H11*B*, to atom O41*B* in the type *B* molecule at $(1-x, y-\frac{1}{2}, \frac{3}{2}-z)$, so producing a second $C(8)$ chain parallel to [010], this time of type *B* molecules only and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ (Fig. 2).

These independent $C(8)$ chains built from N—H$\cdots$O hydrogen bonds are linked into $(10\overline{1})$ sheets by the N—H$\cdots$N hydrogen bonds. Amino atom N1*B* acts as hydrogen-bond donor, *via* atom H12*B*, to cyano atom N21*A* within the asymmetric unit (Fig. 1), while atom N1*A* in the type *A* molecule at (x, y, z) similarly acts as donor, *via* atom H12*A*, to cyano atom N21*B* in the type *B* molecule at $(x-1, y, z-1)$. The combination of these two N—H$\cdots$N hydrogen bonds generates by translation a $C_2^2(12)$ chain running parallel to the [101] direction, and the combination of this chain and the two independent [010] chains generates a $(10\overline{1})$ sheet built of $R_4^4(20)$ and $R_4^4(28)$ rings, alternating in a chess-board fashion (Fig. 2).

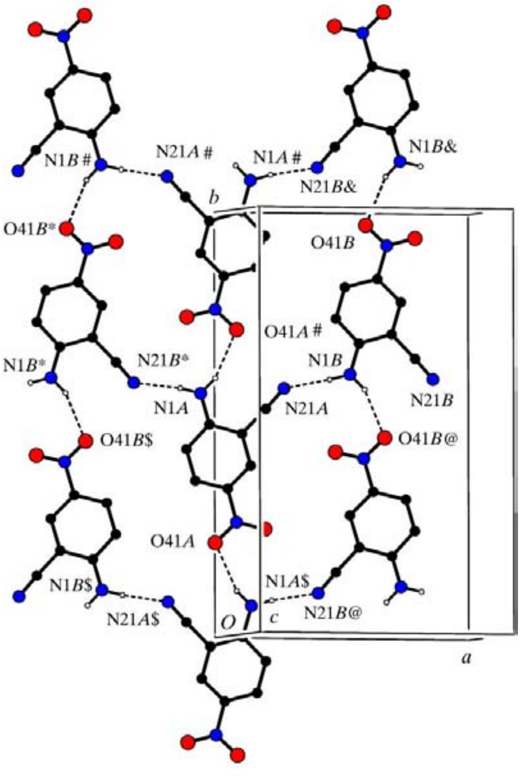

Figure 2
Part of the crystal structure of (I), showing the formation of a $(10\overline{1})$ sheet of $R_4^4(20)$ and $R_4^4(28)$ rings built from molecules of types *A* and *B* only (see text). For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or 'at' sign (@) are at the symmetry positions $(x-1, y, z-1)$, $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $(-x, y-\frac{1}{2}, \frac{1}{2}-z)$, $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$ and $(1-x, y-\frac{1}{2}, \frac{3}{2}-z)$, respectively.

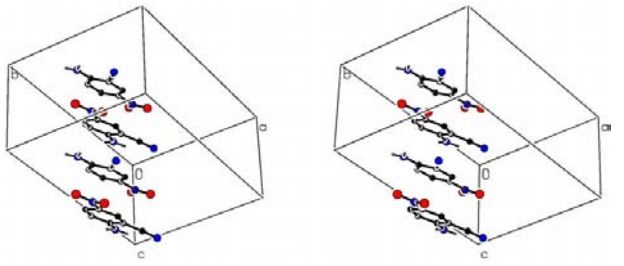

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a π-stacked chain of type *B* molecules along [001]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Two sheets of this type pass through each unit cell and each sheet is weakly linked to the two adjacent sheets by means of a single aromatic π–π stacking interaction involving the type *B* molecules only. The aryl ring of the type *B* molecule at (x, y, z) makes angles of only *ca* 0.5° with those of the type *B* molecules at $(x, \frac{3}{2}-y, \frac{1}{2}+z)$ and $(x, \frac{3}{2}-y, z-\frac{1}{2})$. The corresponding interplanar spacings are *ca* 3.295 Å, with centroid separations of 3.574 (2) Å, corresponding to centroid offsets of *ca* 1.384 Å. Propagation of this interaction forms a π-stacked chain of type *B* molecules running parallel to the [001] direction, generated by the *c*-glide plane at $y = \frac{3}{4}$ (Fig. 3). The absence of an analogous interaction involving the type *A* molecules is sufficient to preclude the possibility of any additional symmetry in the structure.

The supramolecular structure of (I) thus differs from that of (II) in a number of significant respects. There are no centrosymmetric dimer motifs present in (I) of the type found in (II), although such motifs are, in fact, absent from the structure of 2-cyanoaniline (Laine *et al.*, 1996). The hydrogen-bonded sheets exhibit different chess-board patterns in the two structures, with $R_4^4(20)$ and $R_4^4(28)$ rings present in (I) and $R_2^2(12)$ and $R_6^6(36)$ rings present in (II), and, in particular, the absence of a Br substituent in (I) is accompanied by the absence of the large rings found in (II). Finally, adjacent sheets in (I) are linked by an aromatic π–π stacking interaction, whereas such interactions are absent from the structure of (II), where the aggregation dependent upon direction-specific interactions is strictly two-dimensional.

Experimental

A sample of (I) was obtained from Bayer and purified by preparative thin-layer chromatography on alumina using ethyl acetate as eluant.

Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

$C_7H_5N_3O_2$
$M_r = 163.14$
Monoclinic, $P2_1/c$
$a = 11.2316\ (4)$ Å
$b = 17.7275\ (7)$ Å
$c = 7.1078\ (2)$ Å
$\beta = 94.630\ (3)^\circ$
$V = 1410.60\ (9)$ Å^3
$Z = 8$

$D_x = 1.536$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3216 reflections
$\theta = 2.9$–27.5°
$\mu = 0.12$ mm^{-1}
$T = 120\ (2)$ K
Block, orange
$0.30 \times 0.30 \times 0.30$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.928$, $T_{\max} = 0.958$
19 532 measured reflections

3216 independent reflections
2067 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.059$
$\theta_{\max} = 27.5^\circ$
$h = -14 \rightarrow 14$
$k = -22 \rightarrow 23$
$l = -9 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.126$
$S = 1.00$
3216 reflections
267 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected bond lengths (Å).

C1*A*—C2*A*	1.419 (2)	C1*B*—C2*B*	1.419 (2)
C2*A*—C3*A*	1.386 (2)	C2*B*—C3*B*	1.389 (2)
C3*A*—C4*A*	1.369 (4)	C3*B*—C4*B*	1.384 (2)
C4*A*—C5*A*	1.404 (4)	C4*B*—C5*B*	1.402 (2)
C5*A*—C6*A*	1.368 (2)	C5*B*—C6*B*	1.365 (2)
C6*A*—C1*A*	1.412 (2)	C6*B*—C1*B*	1.415 (2)
C1*A*—N1*A*	1.345 (2)	C1*B*—N1*B*	1.338 (2)
C2*A*—C21*A*	1.432 (2)	C2*B*—C21*B*	1.428 (2)
C21*A*—N21*A*	1.144 (2)	C21*B*—N21*B*	1.147 (2)
C4*A*—N4*A*	1.442 (2)	C4*B*—N4*B*	1.443 (2)
N4*A*—O41*A*	1.242 (2)	N4*B*—O41*B*	1.240 (2)
N4*A*—O42*A*	1.232 (2)	N4*B*—O42*B*	1.232 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1*A*—H11*A*···O41*A*$^{\rm i}$	0.88	2.21	3.043 (2)	159
N1*B*—H11*B*···O41*B*$^{\rm ii}$	0.88	2.18	3.022 (2)	159
N1*C*—H11*C*···O41*C*$^{\rm i}$	0.88	2.04	2.86 (5)	155
N1*D*—H11*D*···O41*D*$^{\rm ii}$	0.88	2.17	2.95 (3)	152
N1*A*—H12*A*···N21*B*$^{\rm iii}$	0.88	2.14	2.990 (2)	162
N1*B*—H12*B*···N21*A*	0.88	2.17	3.001 (2)	158
N1*C*—H12*C*···N21*D*$^{\rm iii}$	0.88	2.12	2.96 (3)	160
N1*D*—H12*D*···N21*C*	0.88	2.21	3.06 (3)	163

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

Space group $P2_1/c$ was assigned from the systematic absences. At an early stage of the refinement it became apparent that both independent molecules, labelled *A* and *B* (Fig. 1), exhibited a modest degree of positional disorder, giving rise to two further independent molecules, labelled *C* and *D*. The $h0l$ reflections having l even are all weak to very weak when h is odd, and in (010) projection the coordinates of molecules *A* and *B* are approximately related by the transformation ($\frac{1}{2}+x, \frac{1}{2}+z$). Those of molecules *C* and *D* are similarly related, implying an approximate *n*-glide present only in the (010) projection. The disorder was satisfactorily modelled by assigning one common site-occupancy factor to molecules *A* and *B*, and a second common factor to molecules *C* and *D*; the refined values are 0.947 (2) and 0.053 (2), respectively. Because of the very low occupancy of the *C* and *D* sites, the non-H atoms in these sites were assigned a common isotropic displacement parameter and their phenyl rings were constrained to be rigid planar hexagons with a C—C distance of 1.39 Å. In addition, the remaining intramolecular parameters for molecules *C* and *D* were all restrained, using DFIX commands, to values based upon the average values of the corresponding parameters in molecules *A* and *B*; attempted free refinement of molecules *C* and *D* led to some unrealistic geometric parameters for these molecules. All the H atoms of the major components were located from difference maps, and all H atoms were included in the refinements as riding atoms, with C—H distances of 0.95 Å 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: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1684). Services for accessing these data are described at the back of the journal.

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