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2-Cyano-4-iodoacetanilide: a hydrogen-bonded chain of $R_2^2(12)$ and $R_2^2(14)$ rings

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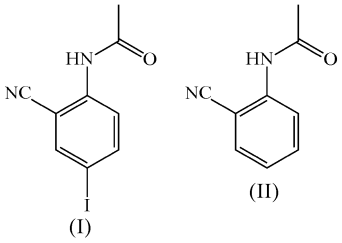
The molecules of 2-cyano-4-iodoacetanilide, $C_9H_7IN_2O$, are linked by N—H···N and C—H···O hydrogen bonds into chains of alternating $R_2^2(12)$ and $R_2^2(14)$ rings.

Comment

We report here the molecular and supramolecular structures of 2-cyano-4-iodoacetanilide, (I) (Fig. 1), and compare the structure of (I) with that of the simpler analogue 2-cyanoacetanilide, (II), for which we have re-interpreted the recently published structure (Arslan *et al.*, 2005). The present study is a continuation of our extended programme on the supramolecular structures of substituted iodoaniline derivatives (Ferguson *et al.*, 2005; Garden *et al.*, 2002, 2004, 2005, 2006; Garden, Glidewell *et al.*, 2001; Glidewell *et al.*, 2004; McWilliam *et al.*, 2001).



In (I), the C6—C1—N1, C1—N1—C11 and N1—C11—O1 angles are all significantly larger than 120° (Table 1), suggesting that the short intramolecular H6···O1 contact (Table 2) may be repulsive rather than attractive. Despite this, the molecule of (I) is almost planar, as indicated by the leading torsion angles, and it is thus possible that the overall molecular conformation results from a balance between repulsive intramolecular contacts and attractive intermolecular hydrogen bonds. The remaining bond lengths and angles show no unusual features.

Two intermolecular hydrogen bonds link the molecules of (I) into chains of fused rings. Atoms N1 and C5 in the molecule at (x, y, z) act as hydrogen-bond donors, respectively, to atoms N2 in the molecule at $(2-x, 1-y, 1-z)$ and O1 in the molecule at $(-x, 2-y, 1-z)$. Propagation by inversion of these two interactions generates a chain of rings running parallel to the $[2\bar{1}0]$ direction, with centrosymmetric $R_2^2(12)$ rings (Bernstein *et al.*, 1995) containing N—H···N hydrogen bonds and centred at $(2n+1, \frac{1}{2}-n, \frac{1}{2})$ (where n represents zero or an integer) alternating with centrosymmetric $R_2^2(14)$ rings containing C—H···O hydrogen bonds and centred at $(2n, 1-n, \frac{1}{2})$ (where n represents zero or an integer) (Fig. 2).

The structure of the related compound (II) has recently been reported (Arslan *et al.*, 2005). The structure was described as forming sheets parallel to (100) generated by a combination of N—H···N and C—H···O hydrogen bonds. The formation of a two-dimensional supramolecular structure in the space group $P2_12_12_1$ is somewhat unexpected, and reanalysis of the published structure shows that the hydrogen-bonded structure of (II) is, in fact, three-dimensional. The N—H···N and C—H···O hydrogen bonds, acting individually, form chains running parallel to the [100] and [010] directions, of $C(6)$ and $C(8)$ types, respectively, while in combination they form a $C_2^2(10)$ chain running parallel to the [001] direction, so completing the three-dimensional framework. The original report on (II) (Arslan *et al.*, 2005) showed the structure in projection along [100], and the published packing diagram appears to show the formation of $R_2^2(12)$ rings containing pairs of N—H···N hydrogen bonds, when in fact this hydrogen bond forms $C(6)$ chains along the direction of the projection and thus normal to the plane of the supposed hydrogen-bonded sheet.

Although the iodine substituent in (I) plays no direct role in the supramolecular aggregation, its presence leads to an

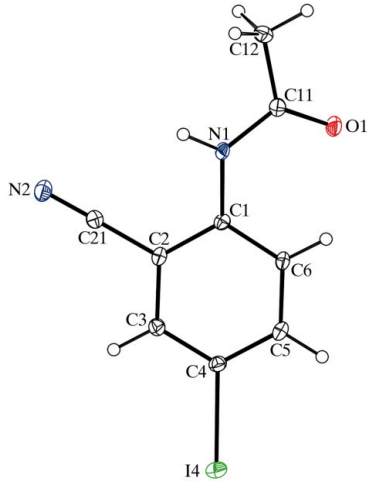


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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entirely different supramolecular structure in (I) as compared with (II), even though the structures of (I) and (II) are each built from the combination of one N—H···N hydrogen bond and one C—H···O hydrogen bond.

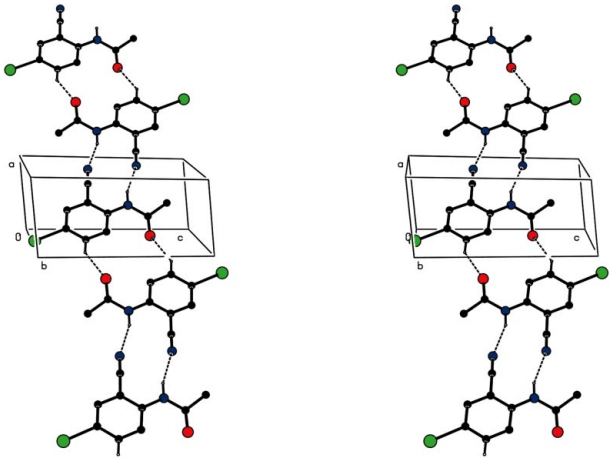

Figure 2
A stereoview of part of the crystal structure of (I), showing a chain of alternating $R_2^2(12)$ and $R_2^2(14)$ rings running parallel to [2$\bar{1}$0]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

Experimental

Compound (I) was prepared by the acetylation of 2-amino-5-iodobenzonitrile, prepared as follows. K(ICl_2) (Garden, Torres *et al.*, 2001) (3 ml of a 2 mol dm^{-3} solution in water) was added to a methanol solution (15 ml) of 2-aminobenzonitrile (0.510 g, 5.0 mmol). The reaction mixture was stirred at room temperature. After 2 h, the product had precipitated and the benzonitrile substrate had been completely consumed. The reaction mixture was diluted with water (50 ml) and the product was collected by filtration and dried in air (yield 93%). Recrystallization from aqueous ethanol (97:3 *v*/*v*) gave pale-brown plates [m.p. 356–357 K; literature (Harris *et al.*, 1992) 358 K]. NMR ($CDCl_3$): δ_H 6.20 (2H, *s*, NH_2), 6.62 (1H, *d*, *J* = 8.8 Hz), 7.52 (1H, *dd*, *J* = 8.8 and 2.0 Hz), 7.65 (1H, *d*, *J* = 2.0 Hz); δ_C: 74.9, 96.0, 116.8, 117.8, 139.7, 142.2, 151.2. IR (KBr disk, cm^{-1}): 3456, 3359, 2224, 1643, 1552, 1483, 1402, 1155, 899, 820. The product (0.500 g, 2.0 mmol) was treated with acetic anhydride (1 ml) and acetic acid (2 ml). The reaction mixture was warmed gently for a few minutes then hydrolyzed with water (20 ml). The product, (I), was collected by filtration and recrystallized from aqueous ethanol (97:3 *v*/*v*) (yield 79%, m.p. 449–451 K). NMR ($CDCl_3$): δ_H 2.27 (3H, *s*, CH_3), 7.69 (1H, *br*, *s*, NH), 7.85 (1H, *dd*, *J* = 10 and 1.9 Hz, H-5), 7.87 (1H, *d*, *J* = 1.9 Hz, H-3), 8.19 (1H, *d*, *J* = 10 Hz, H-6); δ_C 24.4, 85.5, 103.2, 114.5, 122.4, 139.7, 139.9, 142.7, 168.2. IR (KBr disk, cm^{-1}): 3344, 3054, 2225, 1689, 1577, 1516, 1383, 1369, 1295, 1258, 1182, 1122, 884, 842.

Crystal data

$C_9H_7IN_2O$
M_r = 286.07
Triclinic, $P\bar{1}$
a = 4.6657 (2) Å
b = 9.4172 (4) Å
c = 11.6841 (4) Å
α = 109.7520 (17)°
β = 98.598 (2)°
γ = 90.926 (2)°
V = 476.51 (3) Å^3
Z = 2
Mo *K*α radiation
μ = 3.32 mm^{-1}
T = 120 (2) K
0.24 × 0.06 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.503, T_{max} = 0.937
7314 measured reflections
2160 independent reflections
2047 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.058
S = 1.04
2160 reflections
119 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Selected bond angles (°).

C6—C1—N1	122.5 (3)	N1—C11—O1	122.6 (3)
C1—N1—C11	126.8 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2^{i}	0.86	2.54	3.309 (4)	149
C5—H5···O1^{ii}	0.95	2.38	3.214 (4)	147
C6—H6···O1	0.95	2.24	2.815 (4)	118

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x, -y+2, -z+1$.

Crystals of (I) are triclinic; the space group $P\bar{1}$ was selected and confirmed by the subsequent structure analysis. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.95 (aromatic) or 0.98 Å (methyl), N—H distances of 0.86 Å and $U_{iso}(H) = kU_{eq}(C,N)$, where k = 1.5 for the methyl group and k = 1.2 for all other H atoms.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3136). Services for accessing these data are described at the back of the journal.

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