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4-(4-Chlorobenzylidenehydrazonomethyl)benzonitrile and the bromo and iodo analogs

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4-Cyano-4'-chlorobenzalazine [systematic name: 4-(4-chlorobenzylidenehydrazonomethyl)benzonitrile], $C_{15}H_{10}ClN_3$, occurs in two polymorphs. Polymorph *A* is isostructural with the corresponding dichloro compound. Polymorph *B* is isostructural with the bromo and iodo analogs, *viz*. $C_{15}H_{10}BrN_3$ and $C_{15}H_{10}IN_3$, respectively. The latter three structures all have approximately linear $C-N\cdots X-C$ intermolecular contacts in which the $N\cdots X$ contact distances are longer than those in the corresponding benzylideneanilines.

Comment

In earlier work (Ojala et al., 1999, 2001), the packings of p-halo-N-(p-cyanobenzylidene)anilines and p-cyano-N-(phalobenzylidene)anilines were reported for the chloro, bromo and iodo compounds. [Hereafter, we will use the descriptor (X/Y) to denote $X-C_6H_4-CH=N-C_6H_4-Y$.] This previous work was prompted by earlier work (Bernstein & Schmidt, 1972; Bernstein & Izak, 1976; Bernstein et al., 1976; Bar & Bernstein, 1977, 1982, 1983; Haller et al., 1995) in which it was shown that in (Cl/Cl), (CH₃/CH₃), (CH₃/Cl) and (Cl/ CH₃) there was extensive disorder among the orientations of the molecules. The disorder could be by inversion through the pseudo-center of symmetry in the molecule, or by rotation around the $X \cdots Y$ axis, or by both, leading in some cases to fourfold disorder. The purpose of the earlier work (Ojala et al., 1999, 2001) was to see whether a possible $-CN \cdots X$ - interaction could reduce the disorder. In (I/CN), (CN/I), (CN/Br) and (CN/Cl), such interactions did occur; the disorder was eliminated in (I/CN) and (CN/I) and reduced to only the inversion disorder in (CN/Br) and (CN/Cl). In (Br/CN) and (Cl/CN), no –CN···X– interactions were found, but –X···X– interactions removed the disorder completely. We report here the structures of the corresponding 4-(4-halobenzylidenehydrazonomethyl)benzonitriles, with the descriptor (CN/X). The -CH=N- bridges in benzylideneanilines are replaced by -CH = N - N = CH-bridges in benzalazines. Two polymorphs, *A* and *B*, were found for 4-(4-chlorobenzylidenehydrazonomethyl)benzonitrile, *viz*. (CN//Cl-*A*) and (CN//Cl-*B*). Polymorph (CN//Cl-*B*), 4-(4-bromobenzylidenehydrazonomethyl)benzonitrile, (CN//Br), and 4-(4-iodobenzylidenehydrazonomethyl)benzonitrile, (CN//I), are isostructural. All four structures show end-for-end disorder of the molecules.



The atom labeling and the anisotropic displacement parameters for (CN//Cl-A) are shown in Fig. 1. The displacement parameters are similar and the labeling scheme is the same for the other three polymorphs. In every case, there is partial disorder between the two ends; the major component of the disorder has 59.0 (4)% occupancy in (CN//Cl-A), 67.2 (2)% in (CN//Cl-B), 81.45 (8)% in (CN//Br) and 70.16 (4)% in (CN//I). Judging from the changes in these percentages over the course of the refinements, these s.u. values are very optimistic. If the disorder were 50/50, the average molecule, in every case, would lie on a center of symmetry. When the disorder is other than 50/50, there is only a pseudo-center of symmetry and the space group becomes noncentrosymmetric. There are no unusual bond lengths or angles in any of the structures although, again, the s.u. values seem low. The molecules





A view of the molecule of (CN//Cl-A). Displacement ellipsoids are shown at the 50% probability level. The molecule is disordered: atoms Cl1, N3 and C8 have 59.0 (4)% occupancy, and atoms Cl2, N4 and Cl8 have 41.0 (4)% occupancy.



Figure 2

The packing in (CN//Cl-A), viewed along the *b* axis. The compound is isostructural with (Cl//Cl).

deviate slightly from planarity; the benzene rings are twisted out of the plane of the C=N-N=C fragments, by 4.2 (2)° in (CN//Cl-A), 8.6 (2)° in (CN//Cl-B), 7.4 (1)° in (CN//Br) and 4.8 (2)° in (CN//I).

The packing for (CN//Cl-A) is shown in Fig. 2. Only the major component of the disorder is used in the figure. The compound is isostructural with (Cl//Cl) (Zheng et al., 2005; Glaser et al., 2006; Ojala et al., 2007). This packing arrangement has no short CN···CN, CN···Cl or Cl···Cl contacts except those arising from the *a*-axis distance of 3.828 Å.

The packing for (CN//Cl-B) is shown in Fig. 3. To the eye, the corresponding figures for (CN//Br) and (CN//I) are the same. The molecules form layers parallel to the (221) plane, and are tilted away from this plane, by 19.6 (1)° for (CN//Cl-B), 19.3 (1)° for (CN//Br) and 18.8 (1)° for (CN//I). In each of these compounds there are approximately linear $X \cdots NC$ contacts. The geometric details of these are listed in Table 1, where they are compared with similar data for the corresponding benzylideneanilines. The N···Cl distances are slightly longer than the usual van der Waals distances, the $N \cdots Br$ distances about the same and the $N \cdots I$ distances slightly shorter. However, the orientation of the contacts is the same in all three structures.



Figure 3

The packing in (CN//Cl-B), viewed perpendicular to the (221) plane. The CN···Cl contacts are shown as dashed lines. Polymorphs (CN//Br) and (CN//I) are virtually the same.



Figure 4

The π stacking in (CN//Cl-A), viewed normal to the mean molecular plane. The mean C_6-C_6 ring distance is 3.458 (8) Å.

In addition to the N···X contacts there is π stacking in all four polymorphs. Fig. 4 shows the stacking for (CN//Cl-A) and Fig. 5 that for (CN//Cl-B). The stacking in (CN//Br) and (CN//I) is essentially the same as that in (CN//CI-B). As a consequence of the disorder, the distance between adjacent C1-C6 rings is slightly different from the distance between adjacent C11-C16 rings. The average distances are as follows: (CN//Cl-A), 3.47 (2) Å; (CN//Cl-B), 3.402 (4) Å; (CN//Br), 3.425 (4) Å; (CN//I), 3.474 (10) Å.



Figure 5

The π stacking in (CN//Cl-B). The mean C₆-C₆ ring distance is 3.402 (4) Å. (CN//Br) and (CN//I) appear the same and have mean ring distances of 3.425 (4) and 3.474 (10) Å, respectively.

Experimental

For the preparation of 4-cyanobenzaldehyde hydrazone, a solution of 4-cyanobenzaldehyde (0.5 g, 4 mmol) dissolved in approximately 10 ml of ethanol was added dropwise with stirring to an aqueous 8% hydrazine solution (14.25 g, 4 mmol hydrazine). The milky solution was stirred for approximately 30 min after the completion of the addition and then was refrigerated overnight. The hydrazone (m.p. 336 K) was not recrystallized. For the preparation of the 4-cyano-4'halobenzalazines, 4-cyanobenzaldehyde hydrazone (0.1 g, 1 mmol) was added to a solution of 4-halobenzaldehyde (1 mmol) dissolved in 10 ml of absolute ethanol. The mixture was heated (lower than 323 K) with stirring for approximately 1 h, cooled and then refrigerated overnight. The crude benzalazine was recrystallized from carbon tetrachloride. Crystals of (CN//Cl-A) were grown from CH2Cl2/petroleum ether mixtures and crystals of (CN//Cl-B) were grown from either CH₂Cl₂ or CHCl₃.

Polymorph (CN//Cl-A)

Crystal data

$C_{15}H_{10}ClN_3$	$V = 631.76 (14) \text{ Å}^3$
$M_r = 267.71$	Z = 2
Monoclinic, Pc	Mo $K\alpha$ radiation
a = 3.8276 (5) Å	$\mu = 0.29 \text{ mm}^{-1}$
b = 7.1042 (9) Å	T = 173 (2) K
c = 23.238 (3) Å	$0.50 \times 0.20 \times 0.07 \text{ mm}$
$\beta = 91.151 \ (2)^{\circ}$	

Data collection

Bruker SMART 1K CCD areadetector diffractometer Absorption correction: multi-scan (SADABS; Sheldrick, 2003; Blessing, 1995) $T_{\min} = 0.93, \ T_{\max} = 0.98$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.066$ $wR(F^2) = 0.162$ S = 1.062818 reflections 129 parameters 10 restraints

7125 measured reflections 2818 independent reflections 2207 reflections with $I > 2\sigma(I)$ $R_{\rm int} = 0.025$

H-atom parameters constrained $\Delta \rho_{\rm max} = 0.53 \text{ e } \text{\AA}^ \Delta \rho_{\rm min} = -0.60 \text{ e } \text{\AA}^{-3}$ Absolute structure: Flack (1983), 1380 Friedel pairs Flack parameter: 0.4 (2)

3922 measured reflections

 $R_{\rm int} = 0.017$

2879 independent reflections

2879 reflections with $I > 2\sigma(I)$

Polymorph (CN//Cl-B)

Crystal data

 $\begin{array}{l} C_{15}H_{10}ClN_3\\ M_r = 267.72\\ \text{Triclinic, }P1\\ a = 4.6904 \ (7) \text{ Å}\\ b = 5.9498 \ (7) \text{ Å}\\ c = 11.4426 \ (16) \text{ Å}\\ a = 98.361 \ (2)^{\circ}\\ \beta = 93.317 \ (2)^{\circ} \end{array}$

Data collection

Bruker SMART 1K CCD areadetector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003; Blessing, 1995)
T_{min} = 0.87, T_{max} = 0.99

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.116$ S = 1.092191 reflections 124 parameters 11 restraints

Polymorph (CN//Br)

Crystal data

C₁₅H₁₀BrN₃ $M_r = 312.18$ Triclinic, P1 a = 4.6963 (12) Å b = 6.0023 (15) Å c = 11.585 (3) Å $\alpha = 99.493$ (10)° $\beta = 93.767$ (10)° Data collection Bruker SMART 1K CCD area-

detector diffractometer Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995) $T_{min} = 0.25, T_{max} = 0.45$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.064$ S = 1.052189 reflections 124 parameters 11 restraints

Polymorph (CN//I)

Crystal data

 $C_{15}H_{10}IN_3$ $M_r = 359.16$ Triclinic, P1 a = 4.7165 (3) Å b = 6.1524 (4) Å c = 11.9054 (8) Å $\alpha = 101.271$ (2)° $\beta = 94.588$ (2)°
$$\begin{split} \gamma &= 96.823 \ (1)^{\circ} \\ V &= 312.78 \ (7) \ \text{\AA}^3 \\ Z &= 1 \\ \text{Mo } K\alpha \text{ radiation} \\ \mu &= 0.29 \ \text{mm}^{-1} \\ T &= 174 \ (2) \ \text{K} \\ 0.50 \ \times \ 0.40 \ \times \ 0.05 \ \text{mm} \end{split}$$

3127 measured reflections 2191 independent reflections 2131 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.015$

H-atom parameters constrained $\Delta \rho_{max} = 0.31 \text{ e} \text{ Å}^{-3}$ $\Delta \rho_{min} = -0.60 \text{ e} \text{ Å}^{-3}$ Absolute structure: Flack (1983), 1081 Friedel pairs Flack parameter: 0.42 (12)

$$\begin{split} \gamma &= 96.629 \ (9)^{\circ} \\ V &= 318.74 \ (14) \text{ Å}^3 \\ Z &= 1 \\ \text{Mo } K\alpha \text{ radiation} \\ \mu &= 3.21 \text{ mm}^{-1} \\ T &= 174 \ (2) \text{ K} \\ 0.45 \times 0.40 \times 0.25 \text{ mm} \end{split}$$

3142 measured reflections 2189 independent reflections 2188 reflections with $I > 2\sigma(I)$ $R_{int} = 0.021$

H-atom parameters constrained $\Delta \rho_{\text{max}} = 0.38 \text{ e} \text{ Å}^{-3}$ $\Delta \rho_{\text{min}} = -0.78 \text{ e} \text{ Å}^{-3}$ Absolute structure: Flack (1983), 1066 Friedel pairs Flack parameter: 0.236 (10)

 $\gamma = 96.038 \ (3)^{\circ}$

Z = 1

V = 335.13 (4) Å³

Mo Ka radiation

 $0.50 \times 0.20 \times 0.15 \text{ mm}$

 $\mu = 2.38 \text{ mm}^{-1}$

T = 173 (2) K

Data collection

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Bruker SMART 1K CCD area-
detector diffractometer
Absorption correction: multi-scan
(SADABS; Sheldrick, 2003;
Blessing, 1995)
T<sub>min</sub> = 0.59, T<sub>max</sub> = 0.70
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Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	H-atom parameters constrained
$wR(F^2) = 0.059$	$\Delta \rho_{\rm max} = 0.52 \text{ e } \text{\AA}^{-3}$
S = 0.99	$\Delta \rho_{\rm min} = -0.78 \ {\rm e} \ {\rm \AA}^{-3}$
2879 reflections	Absolute structure: Flack (1983),
123 parameters	1383 Friedel pairs
11 restraints	Flack parameter: 0.41 (2)

Table 1

Distances and angles (Å, $^{\circ}$) in the CN···X contacts.

For comparison, the van der Waals contact distances (Bondi, 1964; Rowland & Taylor, 1996) are $N \cdots Cl = 3.30$ Å, $N \cdots Br = 3.40$ Å and $N \cdots I = 3.53$ Å. All structures were determined at 173 K, except (I//CN), which was determined at 183 K.

Compound	$C-N\cdots X$	$CN \cdots X$	$N \cdots X - C$
$(CN//Cl-B)^a$			
N3···Cl1	161	3.49	164
N4···Cl2	149	3.61	154
$(CN/Cl)^{b}$			
$N2 \cdot \cdot \cdot C11$	162	3.25	169
$N2' \cdots Cl1'$	160	3.27	168
$N2 \cdot \cdot \cdot Cl1'$	162	3.23	159
$N2' \cdots Cl1$	166	3.31	168
$N2A \cdot \cdot \cdot Cl1A$	171	3.30	171
$(CN//Br)^a$			
N3···Br1	159	3.36	160
$N4 \cdots Br2$	158	3.35	161
(CN/Br) ^c			
N2···Br1	162	3.17	169
$N2A \cdots Br1A$	165	3.22	170
$(CN//I)^a$			
N3· · · Í1	161	3.32	164
$N4 \cdot \cdot \cdot I2$	163	3.23	170
$(CN/I)^{c}$			
N2···I1	179	3.15	178
$(I/CN)^c$			
$N2 \cdot \cdot \cdot I1$	176	3.26	176
$(I//CN)^d$			
$N1A \cdots I1A$	171	3.19	167
$N1B \cdot \cdot \cdot I1B$	172	3.14	175

Notes: the distances and angles have been rounded to 0.01 Å and 1°, respectively, to make the comparison simpler; the s.u. values vary but are smaller than these limits. References: (a) this work; (b) Ojala *et al.* (2001); (c) Ojala *et al.* (1999); (d) 4-cyano-4'-iodobiphenyl (Britton & Gleason, 1991).

All of the four structures show disorder about a pseudo-center of symmetry. In order to refine the structures, the following distances were restrained: C-CN = 1.445 (1) Å; C=N = 1.142 (1) Å; C-Cl = 1.746 (1) Å; C-Br = 1.903 (1) Å; C-I = 2.095 (1) Å. In addition, the pairs of atoms that would be overlapping if the center were real were constrained to have identical displacement parameters. H atoms were placed at geometrically idealized positions and constrained to ride on their parent atoms, with C-H distances of 0.95 Å and $U_{iso}(H)$ values of $1.2U_{eq}(C)$.

organic compounds

For all polymorphs, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3028). Services for accessing these data are described at the back of the journal.

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