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

Charles R. Ojala,[a] William H. Ojala[b] and Doyle Britton[c]*

[a]Department of Chemistry, Normandale Community College, Bloomington, MN 55431, USA, [b]Department of Chemistry, University of St Thomas, St Paul, MN 55105, USA, and [c]Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA
Correspondence e-mail: britton@chem.umn.edu

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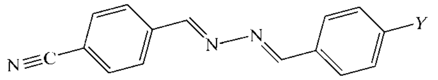
4-Cyano-4′-chlorobenzalazine [systematic name: 4-(4-chlorobenzylidenehydrazonomethyl)benzonitrile], $C_{15}H_{10}ClN_3$, occurs in two polymorphs. Polymorph *A* is isostructural with the corresponding dichloro compound. Polymorph *B* is isostructural with the bromo and iodo analogs, *viz*. $C_{15}H_{10}BrN_3$ 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*-(*p*-halobenzylidene)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), (CH_3/CH_3), (CH_3/Cl) and (Cl/CH_3) 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 $–CN\cdots X–$ interactions were found, but $–X\cdots X–$ 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.



(CN//Cl) *Y*=Cl
(CN//Br) *Y*=Br
(CN//I) *Y*=I

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

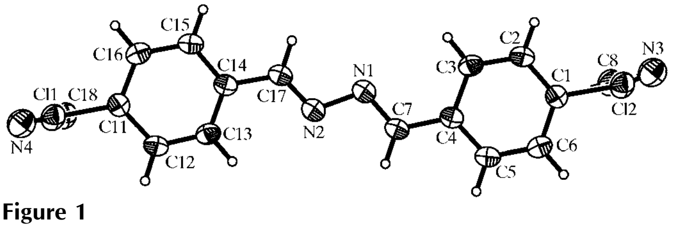


Figure 1
A view of the molecule of (CN//Cl-*A*). Displacement ellipsoids are shown at the 50% probability level. The molecule is disordered: atoms Cl1, N3 and C8 have 59.0 (4)% occupancy, and atoms Cl2, N4 and C18 have 41.0 (4)% occupancy.

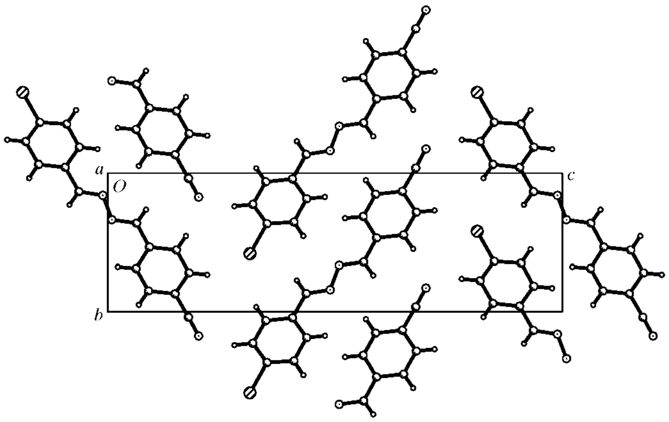


Figure 2
The packing in (CN//Cl-*A*), viewed along the *b* axis. The compound is isostructural with (Cl//Cl).

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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*⋯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⋯Br distances about the same and the N⋯I distances slightly shorter. However, the orientation of the contacts is the same in all three structures.

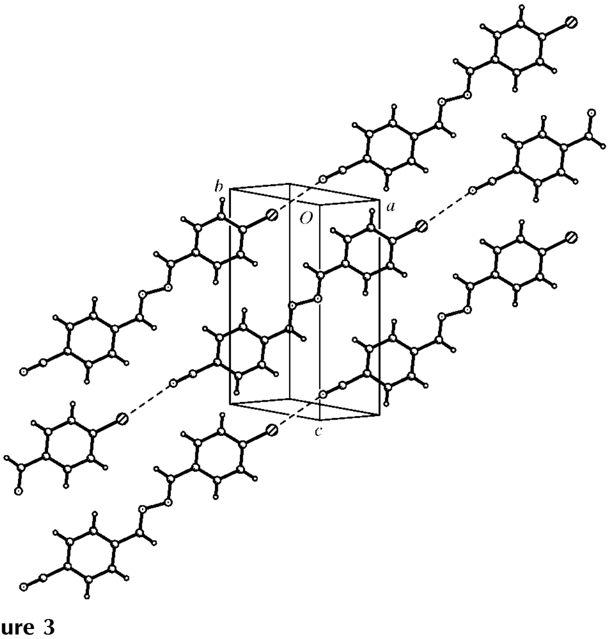

Figure 3
The packing in (CN//Cl-*B*), viewed perpendicular to the (221) plane. The CN⋯Cl contacts are shown as dashed lines. Polymorphs (CN//Br) and (CN//I) are virtually the same.

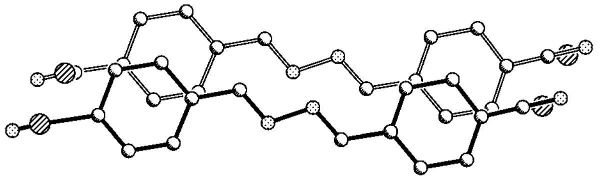

Figure 4
The π stacking in (CN//Cl-*A*), viewed normal to the mean molecular plane. The mean C_6–C_6 ring distance is 3.458 (8) Å.

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//Cl-*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.

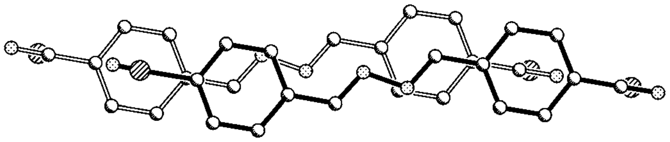

Figure 5
The π stacking in (CN//Cl-*B*). The mean C_6–C_6 ring distance is 3.402 (4) Å. (CN//Br) and (CN//I) appear the same and have mean ring distances of 3.425 (4) and 3.474 (10) Å, respectively.

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 CH_2Cl_2/petroleum ether mixtures and crystals of (CN//Cl-*B*) were grown from either CH_2Cl_2 or $CHCl_3$.

Polymorph (CN//Cl-*A*)

Crystal data

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

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{min} = 0.93$, $T_{max} = 0.98$
7125 measured reflections
2818 independent reflections
2207 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.162$
$S = 1.06$
2818 reflections
129 parameters
10 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}
Absolute structure: Flack (1983), 1380 Friedel pairs
Flack parameter: 0.4 (2)

Polymorph (CN//Cl-*B*)

Crystal data

$C_{15}H_{10}ClN_3$
$M_r = 267.72$
Triclinic, $P1$
$a = 4.6904$ (7) Å
$b = 5.9498$ (7) Å
$c = 11.4426$ (16) Å
$\alpha = 98.361$ (2)°
$\beta = 93.317$ (2)°
$\gamma = 96.823$ (1)°
$V = 312.78$ (7) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.29$ mm^{-1}
$T = 174$ (2) K
0.50 × 0.40 × 0.05 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{\min} = 0.87$, $T_{\max} = 0.99$
3127 measured reflections
2191 independent reflections
2131 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.116$
$S = 1.09$
2191 reflections
124 parameters
11 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.60$ e Å^{-3}
Absolute structure: Flack (1983), 1081 Friedel pairs
Flack parameter: 0.42 (12)

Polymorph (CN//Br)

Crystal data

$C_{15}H_{10}BrN_3$
$M_r = 312.18$
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)°
$\gamma = 96.629$ (9)°
$V = 318.74$ (14) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 3.21$ mm^{-1}
$T = 174$ (2) K
0.45 × 0.40 × 0.25 mm

Data collection

Bruker SMART 1K CCD area-detecctor diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{\min} = 0.25$, $T_{\max} = 0.45$
3142 measured reflections
2189 independent reflections
2188 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.05$
2189 reflections
124 parameters
11 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Absolute structure: Flack (1983), 1066 Friedel pairs
Flack parameter: 0.236 (10)

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)°
$\gamma = 96.038$ (3)°
$V = 335.13$ (4) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 2.38$ mm^{-1}
$T = 173$ (2) K
0.50 × 0.20 × 0.15 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{\min} = 0.59$, $T_{\max} = 0.70$
3922 measured reflections
2879 independent reflections
2879 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$

Refinement

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

Table 1
Distances and angles (Å, °) in the CN$\cdots X$ 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$\cdots$Cl1	161	3.49	164
N4$\cdots$Cl2	149	3.61	154
(CN/Cl)[b]			
N2$\cdots$Cl1	162	3.25	169
N2′$\cdots$Cl1′	160	3.27	168
N2$\cdots$Cl1′	162	3.23	159
N2′$\cdots$Cl1	166	3.31	168
N2A$\cdots$Cl1*A*	171	3.30	171
(CN//Br)[a]			
N3$\cdots$Br1	159	3.36	160
N4$\cdots$Br2	158	3.35	161
(CN/Br)[c]			
N2$\cdots$Br1	162	3.17	169
N2*A*$\cdots$Br1*A*	165	3.22	170
(CN//I)[a]			
N3$\cdots$I1	161	3.32	164
N4$\cdots$I2	163	3.23	170
(CN/I)[c]			
N2$\cdots$I1	179	3.15	178
(I/CN)[c]			
N2$\cdots$I1	176	3.26	176
(I//CN)[d]			
N1*A*$\cdots$I1*A*	171	3.19	167
N1*B*$\cdots$I1*B*	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$\equiv$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 $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

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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