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# Three polymorphs of 4-4′-diiodobenzalazine, and 4-chloro-4′-iodobenzalazine

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

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

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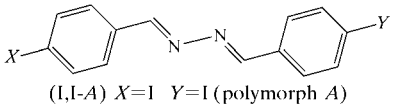
Three polymorphs of 4,4′-diiodobenzalazine (systematic name: 4-iodobenzaldehyde azine), $C_{14}H_{10}I_2N_2$, have crystallographically imposed inversion symmetry. 4-Chloro-4′-iodobenzalazine [systematic name: 1-(4-chlorobenzylidene)-2-(4-iodobenzylidene)diazane], $C_{14}H_{10}ClIN_2$, has a partially disordered pseudocentrosymmetric packing and is not isostructural with any of the polymorphs of 4,4′-diiodobenzalazine. All structures pack utilizing halogen–halogen interactions; some also have weak $\pi$ (benzene ring) interactions. A comparison with previously published methylphenylketalazines (which differ by substitution of methyl for H at the azine C atoms) shows a fundamentally different geometry for these two classes, namely planar for the alazines and twisted for the ketalazines. Density functional theory calculations confirm that the difference is fundamental and not an artifact of packing forces.

## Comment

In this paper, the descriptor (*X*,*Y*) is used as an abbreviation for 4-*X*-4′-*Y*-benzalazine, with the three title polymorphs designated as (I,I-*A*), (I,I-*B*) and (I,I-*C*). Crystals of the dichloro and dibromo analogs, *viz*. (Cl,Cl) and (Br,Br), of the title compound, (I,I), are not isostructural (Zheng *et al.*, 2005;




(I,I-*A*) *X*=I *Y*=I (polymorph *A*)
(I,I-*B*) *X*=I *Y*=I (polymorph *B*)
(I,I-*C*) *X*=I *Y*=I (polymorph *C*)
(I,Cl) *X*=I *Y*=Cl

Marignan *et al.*, 1972). The determination of the structure of (I,I) was undertaken to compare the packing with that of (Br,Br). When three polymorphs of (I,I) were found, the study was expanded to include (Br,Cl), (I,Cl) and (I,Br) to see if these were isostructural with one or another of the (*X*,*X*) compounds.

Fig. 1 shows the atom labeling and the anisotropic displacement ellipsoid plots for (I,I-*A*) and (I,Cl). Molecules of

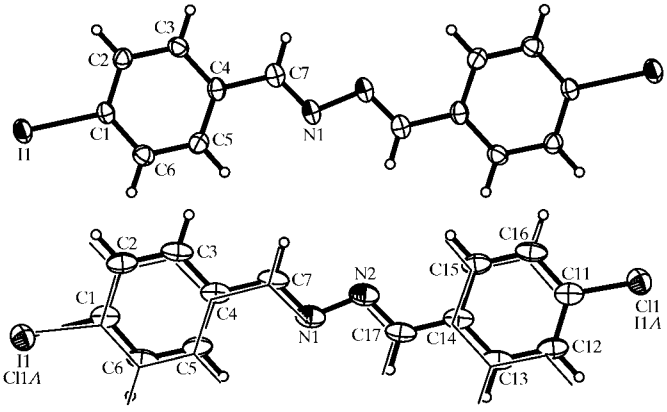



**Figure 1**
Top: the molecular structure of (I,I-*A*). Displacement ellipsoids are shown at the 50% probability level. Only the crystallographically unique atoms are labeled. The labelings for (I,I-*B*) and (I,I-*C*) are the same and the displacement ellipsoids are similar. Bottom: the molecular structure of (I,Cl). Only the major component of the disorder [fraction equal to 0.586 (2)] is shown in full, with displacement ellipsoids at the 50% probability level. The minor component is shown only in outline. The ellipsoids in the minor component are constrained to be identical to those of the overlapping atoms in the major component. The two components lie on a pseudosymmetry center in the space group *Pc*.

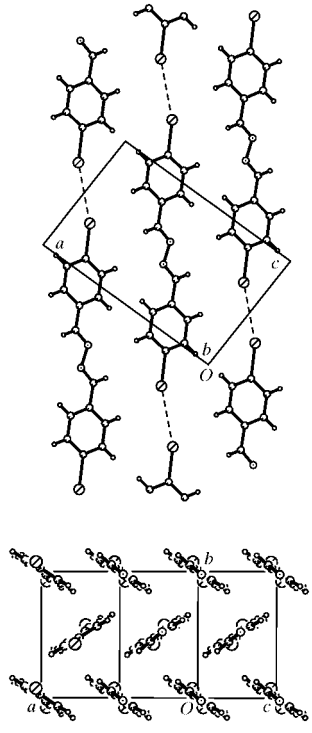



**Figure 2**
Top: one layer of the structure of (I,I-*A*), viewed normal to (100). The intermolecular I···I contacts are shown as dashed lines; these interactions lie across centers of symmetry. Bottom: three layers viewed along [102]. The middle layer in this view is the layer shown in the top view.

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(I,I-*A*) lie on a center of symmetry. (I,Cl) is disordered about a pseudo-center of symmetry, with 0.586 (2) as the fraction for the major component of the disorder. In both structures, the bond lengths and angles are normal. The labelings for all of the compounds described here are the same; the anisotropic displacement ellipsoids for (I,I-*B*) and (I,I-*C*) are similar to those of (I,I-*A*).

The packing of (I,I-*A*) is shown in Fig. 2. The molecules assemble in ribbons held together by I···I interactions and parallel to the [102] direction. The ribbons form sheets normal to the *b* axis, with the essentially planar molecules tilted by 33.4 (1)° away from the plane of the sheet. Adjacent sheets form a herring-bone pattern. Table 1 gives the geometric data for all of the I···I contacts.

The packing of (I,I-*B*) is shown in Fig. 3. The molecules assemble in layers held together by I···I interactions and parallel to the (103) plane. The molecules are tilted by 34.9 (1)° away from the mean plane of the layer; alternate molecules are tilted in opposite directions away from the plane.

The packing of (I,I-*C*) is shown in Fig. 4. The molecules assemble in layers held together by I···I interactions and parallel to the (10$\bar{4}$) plane. The molecules are tilted by 58.6 (1)° away from the mean plane of the layer; alternate molecules are tilted in opposite directions away from the plane. There are two kinds of I···I interactions, one lying across a $2_1$ axis and the other lying along the *b* axis.

The packing of (I,Cl) is shown in Fig. 5. The disordered molecules (as noted above) assemble in layers held together by I···I, I···Cl or Cl···Cl interactions. The molecules are tilted by 59.9 (1)° away from the mean plane. All of the molecules in a given layer have the same tilt; those in the adjacent layer tilt in the opposite sense. This leads to a herring-bone pattern between the layers. There are two kinds of I···I interactions, one lying across a $2_1$ axis and the other lying along the *b* axis. There is some similarity in this respect between the packing arrangements of (I,Cl) and (I,I-*C*).

Schmidt (1971) showed that dichloro aromatic compounds often crystallize with a short (approximately 4 Å) axis, presumably, in part, as a consequence of weak intermolecular Cl···Cl interactions. Sakurai *et al.* (1963) pointed out two other kinds of Cl···Cl interactions, *viz.* an approximately linear arrangement across a center of symmetry, and an angular arrangement across a $2_1$ axis or a glide plane. These interactions have been discussed by Desiraju (1987, 1989, 1995). Examples of all of these are shown in the four compounds reported here. (I,I-*A*) has the approximately linear arrangement across a center of symmetry. (I,I-*B*), (I,I-*C*) and (I,Cl) all adopt the angular arrangement across a $2_1$ axis. In addition, (I,Cl) and (I,I-*C*) have short axial contacts of the type described by Schmidt (1971). The distances and angles for all of the *X*···*X* interactions are listed in Table 1. Also included in Table 1 are the same data for the compounds (*X*,*X*)*, where *X* = Cl, Br or I and * denotes the analogous

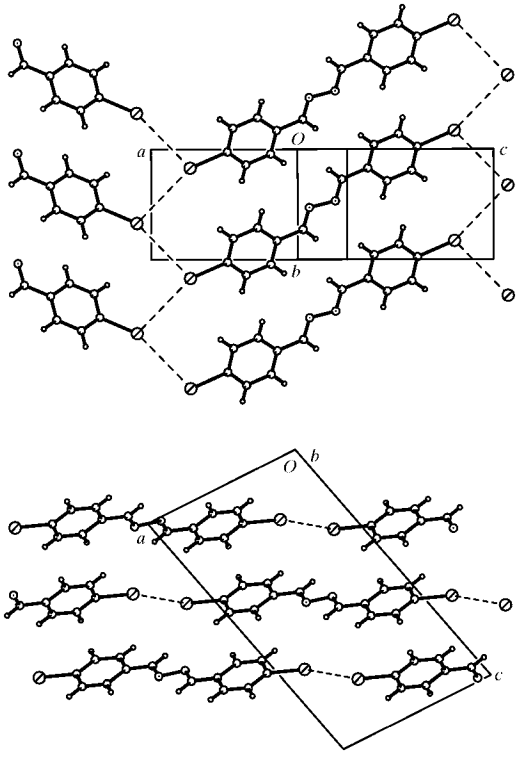


**Figure 3**
Top: one layer of the structure of (I,I-*B*), viewed normal to (103). The intermolecular I···I interactions are shown as dashed lines; they zigzag about a $2_1$ axis. Bottom: three layers viewed along *b*. The middle layer in this view is the layer shown in the top view.

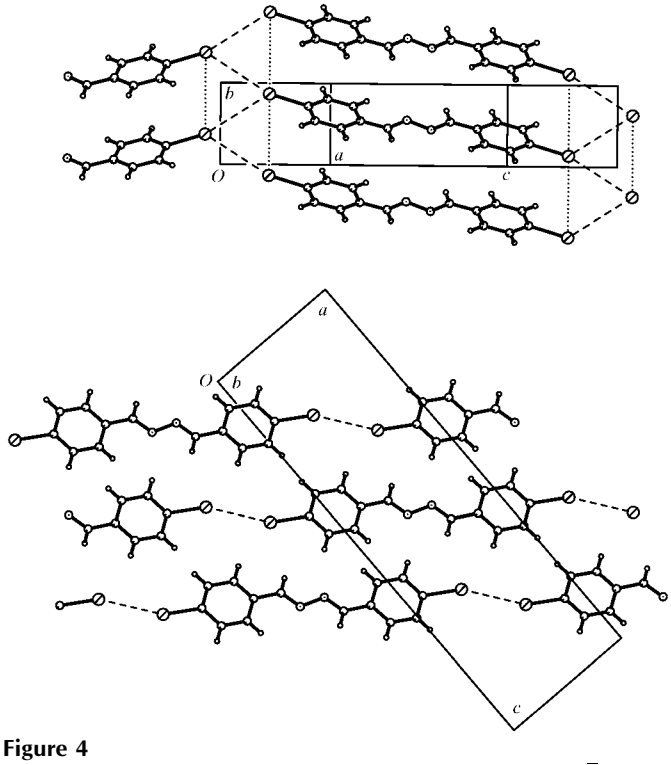


**Figure 4**
Top: one layer of the structure of (I,I-*C*), viewed normal to (10$\bar{4}$). There are two kinds of intermolecular I···I contacts: one, shown by dashed lines, zigzags about a $2_1$ axis, while the other, shown by dotted lines, lies along the *b* axis. Bottom: three layers viewed along *b*. The middle layer in this view is the layer shown in the top view.

molecules in which the aliphatic H atoms have been replaced by methyl groups (the methylphenylketalazines, hereafter referred to as simply ketalazines). In this latter series, the $X\cdots X$ distances are significantly shorter in every case apart from the (I,I) case.

The (*X*,*X*) and (*X*,*X*)* molecules differ in that the (*X*,*X*) molecules are all planar while the (*X*,*X*)* molecules are not, even though they all have *gauche* configurations around the N—N bonds. A comparison of benzalazine structures with ketalazine structures (Chen *et al.*, 1994; Bolte & Ton, 2003; Lewis *et al.*, 1999) confirms the fundamentally different geometry for the two systems. In the benzalazine structures, including the non-*para*-substituted parent system, the molecules are effectively planar with fully conjugated $\pi$ systems. By contrast, in the ketalazine structures, again including the parent system, the torsion angle about the central CNNC linkage is large, ranging from 50 to 100° depending on the *para* substitution.

To better understand this difference, we carried out density functional structure calculations using the M06 density functional (Zhao & Truhlar, 2007) and the MIDI! basis set (Easton *et al.*, 1996). For the case of 4,4′-dichloro substitution, both the benzalazine and ketalazine systems were subjected to constrained optimizations where the C═N—N═C torsion angle was varied and held fixed in increments of 15° (Fig. 6). Interestingly, while the ketalazine is predicted to have a double-well potential characterized by a minimum-energy geometry with a C═N—N═C angle of 105.3° (in very good agreement with the experimental value of 103.1°), the benzalazine has a triple-well potential, with very shallow minima predicted for the symmetrically related twisted geometries and a more stable planar minimum predicted for the fully planar geometry (*i.e.* having a CNNC torsion angle of 180°). In each instance, the torsional potential is relatively flat over the range 75–285°; the total variation in energy is only about 2 kcal mol$^{-1}$. The methyl groups in the ketalazine experience unfavorable steric repulsion that causes the energy in this system to rise steeply outside this range. A full rotational coordinate for the benzalazine system was computed; the energy of the system having a C═N—N═C torsion angle of 0° is predicted to be about 15 kcal mol$^{-1}$ above the *trans* planar minimum.

The relatively flat potentials are associated with a balance between full $\pi$ conjugation, available to the planar geometry, and a push–pull resonance available to the rotated system; the rotation also minimizes NN lone-pair–lone-pair repulsions analogous to those in hydrazine, which also adopts a twisted minimum-energy geometry (Fig. 7). The deeper well for the twisted geometry of the ketalazine compared with the benzalazine, relative to the planar structure, is associated with improved hyperconjugative interactions for the nitrogen lone pairs delocalizing into the eclipsed $\pi$ system when the methyl groups are present. Thus, natural bond orbital analysis (Reed *et al.*, 1988) quantifies the $n_N \rightarrow \pi^*$ delocalization for each nitrogen lone pair as 16.5 kcal mol$^{-1}$ in the ketalazine system but only 13.5 kcal mol$^{-1}$ in the benzalazine system. This is the largest difference in the filled/empty delocalization energies between the two systems. A consequence of this delocalization is that the NN bond should be shorter (because of some double-bond character) in the twisted systems than in the planar systems, and this is indeed borne out by the experimental structural data (see Table 2).

A second aspect of the packing in the azalazines is the $\pi$ interaction between the benzene rings. The geometric aspects are given in Table 3, where the perpendicular distances between the rings and the overlap are given. The overlap is given as the percentage overlap of the areas in the adjacent $C_6$ rings. The overlap for (I,I-*C*) is shown in Fig. 8; the molecules assemble in stacks along the short axis. With two exceptions, the others are similar; in (I,I-*A*) there is no overlap, and in

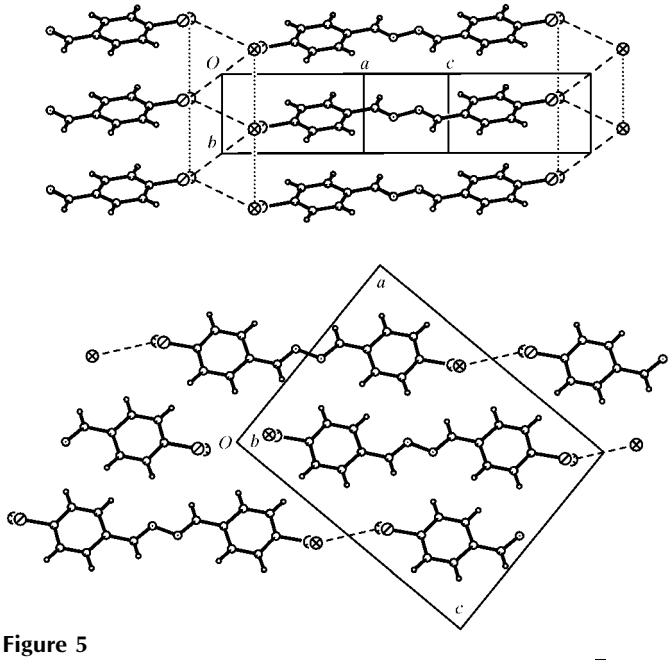


**Figure 5**
Top: one layer of the structure of (I,Cl), viewed normal to $(10\bar{1})$. As a reminder of the disorder, both Cl and I atoms are shown at all positions; the rest of the disordered positions are not shown. Only the I$\cdots$I contacts are shown. The conventions are the same as in Fig. 4. Bottom: three layers viewed along *b*. The middle layer in this view is the layer shown in the top view.

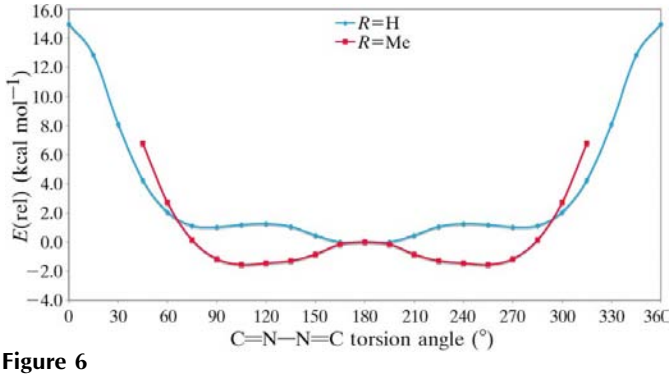


**Figure 6**
The energies of the 4,4-dichlorobenzalazine (diamonds, upper line) and 4,4-dichloromethylphenylketalazine (squares, lower line) geometries relative to the planar structure having a C═N—N═C torsion angle of 180°.

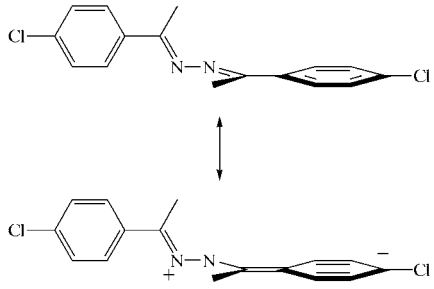

**Figure 7**
Push–pull resonance in the twisted ketalazine geometry.

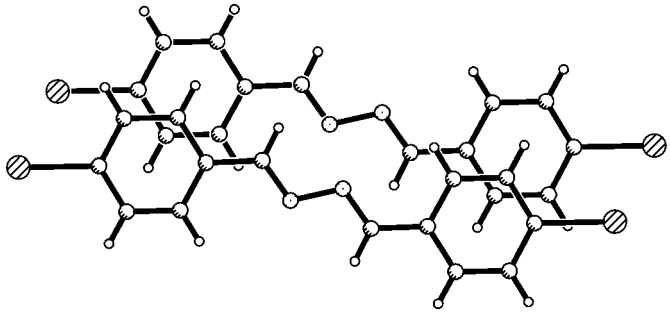

**Figure 8**
The overlap between (I,I-*C*) molecules (view normal to the molecular plane). The area of the overlap between the $C_6$ rings is 5.7 (3)% of the area of either ring.

(I,I-*B*) the molecules assemble in chains rather than stacks. (Br,Cl) and (Br,Br) appear to be isostructural with each other, as do (I,Cl) and (I,Br). These similarities would require disorder in (Br,Cl) and (I,Br). In view of the disorder in all of the (*X*,*Y*) structures, no data are included here for their $\pi$ overlap. However, they all appear to be similar to that shown in Fig. 8.

The unit-cell dimensions for all of the (*X*,*X*) and (*X*,*Y*) structures are given in Table 4. The (Cl,Cl) structure is unique. (Br,Cl) and (Br,Br) are isostructural with (I,I-*C*). (I,Cl) and (I,Br) are isostructural only with each other. Thus, there are five different structural types in this series of compounds. When three polymorphs of (I,I) were found, all the remaining compounds in Table 4 were examined to see if other polymorphs could be found. Each compound was recrystallized from acetone, benzene, dichloromethane, chloroform, tetrachloromethane and acetonitrile. Although a variety of crystal habits were found for each compound, in no case were other polymorphs found.

Each of the five structure types in Table 4 gives a plausible packing arrangement for all of the benzalazine compounds, so this system, which involves only planar molecules, could provide a reasonable test for programs that predict crystal packing. It is surprising that in five of the six compounds no polymorphs were found, even though the search for polymorphs was not exhaustive.

## Experimental

For the preparation of 4-chlorobenzaldehyde hydrazone, a solution of 4-chlorobenzaldehyde (0.5 g, 3.6 mmol) dissolved in approximately 10 ml of ethanol was added dropwise with stirring to an aqueous 8% hydrazine solution (14.25 g, 3.6 mmol hydrazine). The milky solution was stirred for approximately 30 min after the completion of the addition and then cooled in a refrigerator overnight (at 277 K). The solid hydrazone was removed by filtration and used without recrystallization.

For the preparation of 4-chloro-4′-iodobenzalazine, 4-chlorobenzaldehyde hydrazone (0.15 g, 1.0 mmol) was added to a solution of 4-iodobenzaldehyde (0.2 g, 0.9 mmol) dissolved in 10 ml of absolute ethanol. The mixture was heated to 323 K with stirring for approximately 1 h, cooled, and then placed in a refrigerator overnight. The crude azine was recrystallized from chloroform.

For the preparation of 4-iodobenzaldehyde azine, a solution of 4-iodobenzaldehyde (0.1 g, 0.4 mmol) dissolved in approximately 5 ml of ethanol was added dropwise with stirring to an aqueous 8%

**Table 1**
Distances and angles (Å, °) for the $X\cdots X$ contacts in (*X*,*X*) and (*X*,*X*)*[a].

For comparison, the van der Waals contact distances (Bondi, 1964; Rowland & Taylor, 1996) are Cl$\cdots$Cl = 3.50 Å, Br$\cdots$Br = 3.70 Å and I$\cdots$I = 3.96 Å.

| Compound | Temperature (K) | *X* | *X*′ | C—*X*$\cdots$*X*′ | *X*$\cdots$*X*′ | *X*$\cdots$*X*′—C | Reference |
|---|---|---|---|---|---|---|---|
| (Cl,Cl) | 173 | Cl1 | Cl1$^{i}$ | 74.1 (1) | 3.887 (1) | 105.9 (1) | *b* |
| (Cl,Cl) | 173 | Cl1 | Cl1 | 73.8 (1) | 3.892 (1) | 105.9 (1) | *c* |
| (Cl,Cl) | 294 | Cl1 | Cl1 | 74.1 (1) | 3.958 (1) | 106.2 (1) | *d* |
| (Br,Br) | 173 | Br1 | Br1$^{ii}$ | 127.1 (1) | 3.812 (2) | 152.6 (1) | *b* |
| | 173 | Br1 | Br1$^{iii}$ | 74.2 (1) | 3.977 (1) | 105.8 (1) | *b* |
| (Br,Br) | 294 | Br1 | Br1 | 126.3 (3) | 3.861 (4) | 153.4 (3) | *e* |
| | 294 | Br1 | Br1 | 73.3 (3) | 4.051 (4) | 106.7 (3) | *e* |
| (I,I-*A*) | 173 | I1 | I1$^{iv}$ | 147.0 (2) | 3.781 (1) | 147.0 (2) | *f* |
| (I,I-*B*) | 173 | I1 | I1$^{v}$ | 109.9 (3) | 3.965 (2) | 154.5 (3) | *f* |
| (I,I-*C*) | 173 | I1 | I1$^{vi}$ | 127.1 (5) | 3.960 (4) | 154.9 (5) | *f* |
| | 173 | I1 | I1$^{iii}$ | 73.2 (5) | 4.154 (1) | 106.8 (5) | *f* |
| (Cl,Cl)* | 294 | Cl1 | Cl2 | 163.4 (2) | 3.340 (1) | 163.6 (2) | *g* |
| (Br,Br)* | 294 | Br1 | Br2 | 168.8 (2) | 3.560 (1) | 97.0 (2) | *g* |
| (I,I)* | 173 | I1 | I1′ | 155.3 (3) | 4.122 (1) | 101.8 (3) | *h* |

Notes: (*a*) the (*X*,*X*)* structures are for analogous compounds where the azine H atoms have been replaced by methyl groups; (*b*) Ojala *et al.* (2007*a*); (*c*) Glaser *et al.* (2006); (*d*) Zheng *et al.* (2005); (*e*) Marignan *et al.* (1972); (*f*) this work; (*g*) Chen *et al.* (1994); (*h*) Lewis *et al.* (1999). Symmetry codes: (i) $x+1, y, z$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y-1, z$; (iv) $-x, -y+1, -z-1$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x-1, y-\frac{1}{2}, -z+\frac{1}{2}$.

hydrazine solution (3 g, 8 mmol hydrazine). The milky solution was heated (lower than 323 K) with stirring for approximately 1 h and was then allowed to stand at room temperature overnight. The solution was refrigerated and the crude azine was recrystallized from chloroform. All three polymorphs were obtained in the original recrystallization.

### Polymorph (I,I-*A*)

*Crystal data*

$C_{14}H_{10}I_2N_2$
$M_r$ = 460.04
Monoclinic, $P2_1/c$
$a$ = 11.854 (2) Å
$b$ = 7.7308 (13) Å
$c$ = 7.6827 (13) Å
$\beta$ = 92.407 (3)°
$V$ = 703.5 (2) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 4.45 mm$^{-1}$
$T$ = 174 (2) K
0.45 × 0.35 × 0.06 mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{min}$ = 0.32, $T_{max}$ = 0.77
7773 measured reflections
1602 independent reflections
1442 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.054
$S$ = 1.11
1602 reflections
83 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.86 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.55 e Å$^{-3}$

### Polymorph (I,I-*B*)

*Crystal data*

$C_{14}H_{10}I_2N_2$
$M_r$ = 460.04
Monoclinic, $P2_1/n$
$a$ = 8.4303 (17) Å
$b$ = 5.6453 (12) Å
$c$ = 15.248 (3) Å
$\beta$ = 104.346 (3)°
$V$ = 703.0 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 4.46 mm$^{-1}$
$T$ = 174 (2) K
0.30 × 0.06 × 0.03 mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{min}$ = 0.54, $T_{max}$ = 0.87
7699 measured reflections
1600 independent reflections
1189 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.052

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.061
$S$ = 1.02
1600 reflections
83 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.61 e Å$^{-3}$

### Polymorph (I,I-*C*)

*Crystal data*

$C_{14}H_{10}I_2N_2$
$M_r$ = 460.04
Monoclinic, $P2_1/c$
$a$ = 7.2077 (17) Å
$b$ = 4.1543 (10) Å
$c$ = 23.317 (6) Å
$\beta$ = 90.314 (4)°
$V$ = 698.2 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 4.49 mm$^{-1}$
$T$ = 174 (2) K
0.45 × 0.10 × 0.04 mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{min}$ = 0.24, $T_{max}$ = 0.84
7115 measured reflections
1601 independent reflections
1290 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.085

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.122
$S$ = 1.05
1601 reflections
82 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 3.00 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.34 e Å$^{-3}$

### Compound (I,Cl)

*Crystal data*

$C_{14}H_{10}ClIN_2$
$M_r$ = 368.59
Monoclinic, $Pc$
$a$ = 11.499 (2) Å
$b$ = 4.0006 (7) Å
$c$ = 14.717 (3) Å
$\beta$ = 90.900 (3)°
$V$ = 676.9 (2) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 2.55 mm$^{-1}$
$T$ = 174 (2) K
0.20 × 0.20 × 0.05 mm

*Data collection*

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)
$T_{min}$ = 0.42, $T_{max}$ = 0.88
7262 measured reflections
3089 independent reflections
2308 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.072
$S$ = 1.05
3089 reflections
164 parameters
109 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.33 e Å$^{-3}$
Absolute structure: Flack (1983), 1476 Friedel pairs
Flack parameter: 0.17 (7)

**Table 2**
Comparison of N—N distances (Å) between (*X*,*X*) and (*X*,*X*)*.

| *X* | (*X*,*X*) | Reference | (*X*,*X*)* | Reference |
|---|---|---|---|---|
| H | 1.418 (3) | *a* | 1.403 (3) | *b* |
| | 1.412 (10) | *c* | 1.396 (2) | *d* |
| Cl | 1.412 (2) | *e* | 1.398 (3) | *b* |
| | 1.414 (3) | *f* | – | – |
| | 1.409 (2) | *g* | – | – |
| Br | 1.45 (2) | *h* | 1.383 (6) | *b* |
| | 1.411 (4) | *g* | – | – |
| I | 1.411 (4) | *i* | 1.396 (6) | *j* |
| | 1.418 (6) | *i* | – | – |
| | 1.400 (12) | *i* | – | – |

Notes: (*a*) Mom & de With (1978); (*b*) Chen *et al.* (1994); (*c*) Burke-Laing & Laing (1976); (*d*) Bolte & Ton (2003); (*e*) Glaser *et al.* (2006); (*f*) Zheng *et al.* (2005); (*g*) Ojala *et al.* (2007*a*); (*h*) Marignan *et al.* (1972); this work; (*j*) Lewis *et al.* (1999).

**Table 3**
The inter-ring distances (Å) and ring overlaps (%) of the $\pi$ contacts.

| Compound | Distance (Å) | Overlap (%) | Reference |
|---|---|---|---|
| (Cl,Cl) | 3.459 (4) | 17.8 (2) | *a* |
| (Br,Br) | 3.479 (6) | 12.8 (2) | *a* |
| (I,I-*A*) | No overlap | | *b* |
| (I,I-*B*) | 3.584 (8) | 12.7 (2) | *b* |
| (I,I-*C*) | 3.522 (3) | 5.7 (2) | *b* |

Notes: (*a*) Ojala *et al.* (2007*a*); (*b*) this work.

**Table 4**
Cell constants (Å, °, Å$^3$) for all (*X*,*X*) and (*X*,*Y*) structures at 173 K.

| Compound | *a* | *b* | *c* | *β* | *V* | Reference |
|---|---|---|---|---|---|---|
| (Cl,Cl) | 3.887 (1) | 6.990 (1) | 22.980 (2) | 90.77 (1) | 624.3 (1) | *a* |
| (Br,Cl) | 6.995 (1) | 3.945 (1) | 22.971 (4) | 92.72 (1) | 633.1 (2) | *b* |
| (Br,Br) | 7.027 (1) | 3.977 (1) | 23.141 (3) | 91.72 (1) | 646.5 (1) | *a* |
| (I,Cl) | 11.499 (2) | 4.001 (1) | 14.717 (3) | 90.90 (1) | 676.9 (2) | *c* |
| (I,Br) | 11.513 (5) | 4.044 (2) | 14.719 (4) | 90.34 (2) | 685.3 (3) | *b* |
| (I,I-*A*) | 11.854 (2) | 7.731 (1) | 7.683 (1) | 92.41 (1) | 703.5 (2) | *c* |
| (I,I-*B*) | 8.430 (2) | 5.645 (1) | 15.248 (3) | 104.35 (1) | 703.0 (3) | *c* |
| (I,I-*C*) | 7.208 (2) | 4.154 (1) | 23.317 (6) | 90.31 (1) | 698.2 (3) | *c* |

Notes: (*a*) Ojala *et al.* (2007*a*); (*b*) Ojala *et al.* (2007*b*); (*c*) this work.

The solutions and refinements were straightforward except for (I,Cl). This structure was solved as an end-for-end disordered molecule in $P2_1/c$; the refinement converged with $R[F^2 > 2\sigma(F^2)] = 0.043$ and $wR(F^2) = 0.084$. To test whether the disorder was complete, the structure was solved and partially refined in *P*1. At this point, it appeared that the disorder was not 50/50 and that *Pc* was the correct space group; the final *R* and *wR*2 values were 0.038 and 0.072, with 0.586 (2)/0.414 (2) disorder of the Cl and I atoms. In all of the refinements, C—Cl distances were constrained to 1.746 (1) Å and C—I to 2.095 (1) Å; all of the $C_6H_4$—CH—N fragments were constrained to be the same within 0.001 Å. The atoms that would have overlapped in the pseudo-centric arrangement were constrained to have the same anisotropic 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).

For all determinations, 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: GA3056). Services for accessing these data are described at the back of the journal.

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