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Competing intermolecular interactions in some 'bridge-flipped' isomeric phenylhydrazones

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To examine the roles of competing intermolecular interactions in differentiating the molecular packing arrangements of some isomeric phenylhydrazones from each other, the crystal structures of five nitrile–halogen substituted phenylhydrazones and two nitro–halogen substituted phenylhydrazones have been determined and are described here: (*E*)-4-cyanobenzaldehyde 4-chlorophenylhydrazone, $C_{14}H_{10}ClN_3$, (I*a*); (*E*)-4-cyanobenzaldehyde 4-bromophenylhydrazone, $C_{14}H_{10}BrN_3$, (I*b*); (*E*)-4-cyanobenzaldehyde 4-iodophenylhydrazone, $C_{14}H_{10}IN_3$, (I*c*); (*E*)-4-bromobenzaldehyde 4-cyanophenylhydrazone, $C_{14}H_{10}BrN_3$, (II*b*); (*E*)-4-iodobenzaldehyde 4-cyanophenylhydrazone, $C_{14}H_{10}IN_3$, (II*c*); (*E*)-4-chlorobenzaldehyde 4-nitrophenylhydrazone, $C_{13}H_{10}ClN_3O_2$, (III); and (*E*)-4-nitrobenzaldehyde 4-chlorophenylhydrazone, $C_{13}H_{10}ClN_3O_2$, (IV). Both (I*a*) and (I*b*) are disordered (less than 7% of the molecules have the minor orientation in each structure). Pairs (I*a*)/(I*b*) and (II*b*)/(II*c*), related by a halogen exchange, are isomorphous, but none of the 'bridge-flipped' isomeric pairs, *viz.* (I*b*)/(II*b*), (I*c*)/(II*c*) or (III)/(IV), is isomorphous. In the nitrile–halogen structures (I*a*)–(I*c*) and (II*b*)–(II*c*), only the bridge N—H group and not the bridge C—H group acts as a hydrogen-bond donor to the nitrile group, but in the nitro–halogen structures (III) (with $Z' = 2$) and (IV), both the bridge N—H group and the bridge C—H group interact with the nitro group as hydrogen-bond donors, albeit *via* different motifs. The occurrence here of the bridge C—H contact with a hydrogen-bond acceptor suggests the possibility that other pairs of 'bridge-flipped' isomeric phenylhydrazones may prove to be isomorphous, regardless of the change from isomer to isomer in the position of the N—H group within the bridge.

Comment

The analysis of intermolecular interactions for their potential utility in crystal engineering is a topic of ongoing interest. These have included the varieties of hydrogen bond ranging from the strong conventional type to the weak nonconventional type, as well as halogen–halogen contacts, halogen–nitrogen contacts and π stacking. For our part, we have been examining the role of interactions between the nitrile group and nearby halogen and H atoms in defining the solid-state molecular packing motifs assumed by pairs of molecules we have designated 'bridge-flipped' isomers, molecules that differ only in the reversal of a bridge of atoms linking two major portions of the molecule (Ojala *et al.*, 2007). Examples are readily identified among the benzylideneanilines (Ar_1—CH═N—Ar_2 *versus* Ar_1—N═CH—Ar_2; Ar = aryl) and phenylhydrazones (Ar_1—CH═N—NH—Ar_2 *versus* Ar_1—NH—N═CH—Ar_2; Ar = aryl). Pairs of 'bridge-flipped' isomeric benzylideneanilines and phenylhydrazones may assume identical solid-state molecular packing arrangements by virtue of their closely similar space-filling requirements, although the number of reported isomorphous pairs is small (Ojala *et al.*, 2007; Ferguson *et al.*, 2005; Mocilak & Gallagher, 2011). 'Bridge-flipped' isomers that happen not to be isomorphous offer a useful context for the comparison and analysis of molecular conformations, intermolecular interactions and packing motifs that differentiate the packing arrangements. In our studies, we have attempted to facilitate isomorphism by placing substituents on the molecules that would engage in similar intermolecular interactions in the two isomers. Similar motifs generated by these interactions, if packed in similar ways in the two isomers, should favour the formation of similar overall molecular packing arrangements. To date, we have focused primarily on the potential intermolecular Lewis acid–base interaction between the nitrile group and a halogen atom on a neighbouring molecule in the crystal structure. Although this strategy in our own laboratory has yet to produce an isomorphous pair of 'bridge-flipped' isomers, it has allowed us to examine the variety of motifs in which nitrile groups and halogen atoms engage, whether separately or with each other. In previous reports, we have examined intermolecular interactions of this type primarily in 'bridge-flipped' nitrile–halogen substituted benzylideneanilines (Ojala *et al.*, 2009, 2001, 1999), where they play a significant role in defining the molecular packing arrangment. Here, we describe the interactions found in a group of 'bridge-flipped' nitrile–halogen substituted phenylhydrazones.

Whether the potential nitrile–halogen intermolecular interaction can actually encourage isomorphism in phenylhydrazones is complicated by the presence of the N—H group in the phenylhydrazone bridge. This strong conventional hydrogen-bond donor, not present in the bridge of benzylideneanilines, could be expected to cause nitrile–halogen substituted 'bridge-flipped' phenylhydrazones to assume different packing arrangements if the nitrile group were to hydrogen bond to it rather than engage in Lewis acid–base interactions with the halogen atom. Reversal of the bridge from one isomer to the other would cause a substantial and probably structure-differentiating change in the position of the hydrogen-bonded groups. On the other hand, isomorphous pairs of 'bridge-flipped' phenylhydrazones bearing

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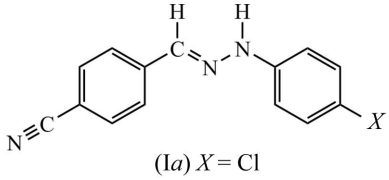
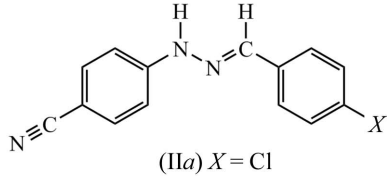
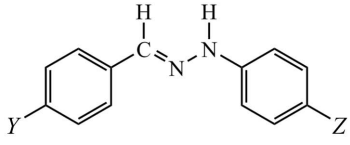
hydrogen-bond acceptors are known, including the pair (*E*)-2-nitrobenzaldehyde 3-nitrophenylhydrazone [Cambridge Structural Database (CSD; Allen, 2002) refcode LAWCOC] and (*E*)-3-nitrobenzaldehyde 2-nitrophenylhydrazone (LAWJAV) (Ferguson *et al.*, 2005), and the pair (*E*)-2-bromobenzaldehyde 4-cyanophenylhydrazone (RIFXOU) and (*E*)-4-cyanobenzaldehyde 2-bromophenylhydrazone (RIFXUA) (Ojala *et al.*, 2007). In both these pairs, the hydrogen-bond acceptor (the nitro or nitrile group) is in contact (within the sum of the van der Waals radii) with both the N—H and C—H donors within the bridge; no clear preference for the stronger donor is shown by the acceptor. To find out how general this might be, and to examine what other structural motifs might be preferred given a choice among potential nitrile–hydrogen, nitrile–halogen and halogen–halogen contacts in the solid state, we have determined and describe here the crystal structures of cyanobenzaldehyde halophenylhydrazones (I*a*)–(I*c*) and halobenzaldehyde cyanophenylhydrazones (II*b*) and (II*c*). [Regrettably, and in spite of our repeated efforts, we have not been successful in obtaining X-ray quality crystals of (II*a*).]



(I*a*) X = Cl
(I*b*) X = Br
(I*c*) X = I



(II*a*) X = Cl
(II*b*) X = Br
(II*c*) X = I



(III) Y = Cl, Z = NO_2
(IV) Y = NO_2, Z = Cl

Because one of the two previously published isomorphous pairs of 'bridge-flipped' phenylhydrazones cited above (Ferguson *et al.*, 2005) involves the nitro group rather than the nitrile group as the potential hydrogen-bond acceptor, we have extended our inquiry to nitro–halogen substituted phenylhydrazones in order to examine how discriminating the nitro group is as a potential acceptor of N—H *versus* C—H hydrogen bonds from phenylhydrazone bridges. We thus describe here, in addition to these nitrile–halogen substituted phenylhydrazones, the structures of the 'bridge-flipped' isomeric pair of nitro–halogen (chlorine) substituted phenylhydrazones, (III) and (IV). None of the 'bridge-flipped' isomeric pairs described here, whether nitrile- or nitro-

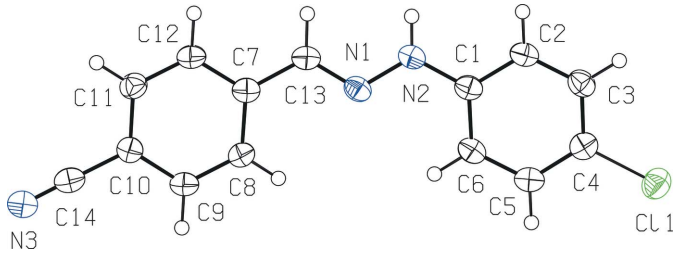


Figure 1
The molecular structure of (I*a*), showing the atom-numbering scheme in the major orientation of the disorder. Displacement ellipsoids are drawn at the 50% probability level.

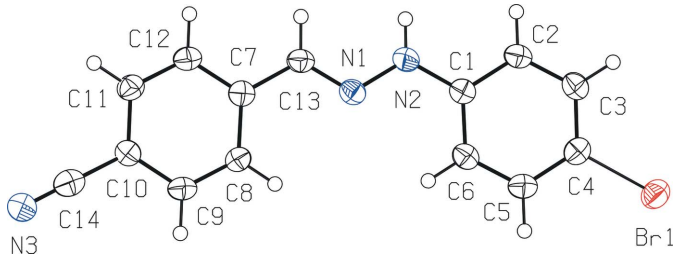


Figure 2
The molecular structure of (I*b*), showing the atom-numbering scheme in the major orientation of the disorder. Displacement ellipsoids are drawn at the 50% probability level.

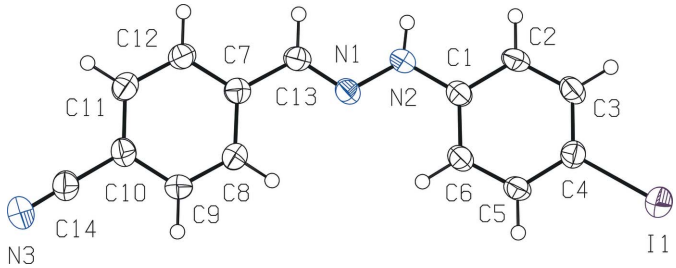


Figure 3
The molecular structure of (I*c*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

substituted, proved to be isomorphous in our study, although several of the compounds related simply by the exchange of one halogen for another did: (I*a*) and (I*b*) are isomorphous, as are (II*b*) and (II*c*). Our purpose here is thus to determine which intermolecular interactions from an array of competing possibilities, including C≡N···H—N, C≡N···H—C, O—N—O···H—N, O—N—O···H—C, C≡N···*X*—C and C—*X*···*X*—C, are preferred in these structures and how these preferences differentiate the structures of these 'bridge-flipped' isomers from each other.

Views of the isolated molecules of all seven title compounds are given in Figs. 1–7. All seven arylhydrazones possess the *E* conformation about the C=N bond. All are nearly planar, with dihedral angles between the six-membered rings ranging from 7.31 (6)° in (I*a*) to 25.38 (9)° in (IV). The conformational differences between the bridge-flipped isomers appear insufficient to explain completely the differences in their crystal structures. The nitro groups in (III) and (IV) are essentially coplanar with the rings to which they are attached.

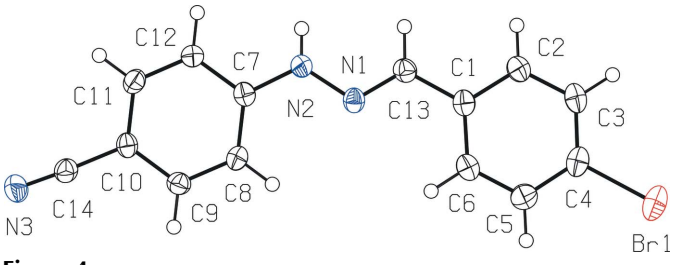


Figure 4
The molecular structure of (II*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

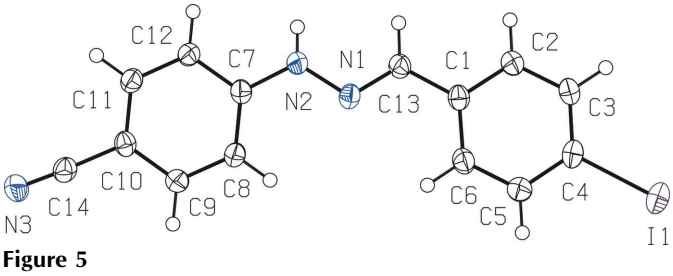


Figure 5
The molecular structure of (II*c*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

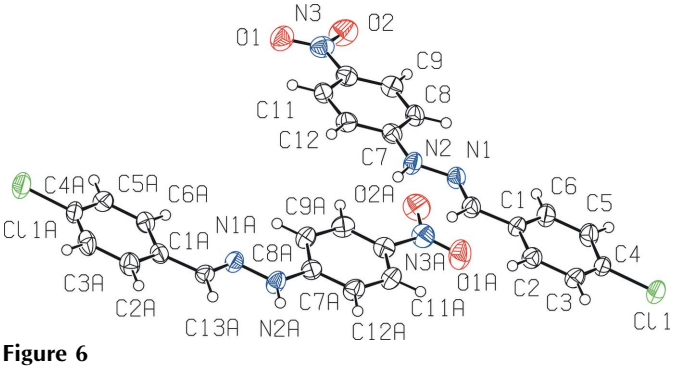


Figure 6
The two molecules in the asymmetric unit of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

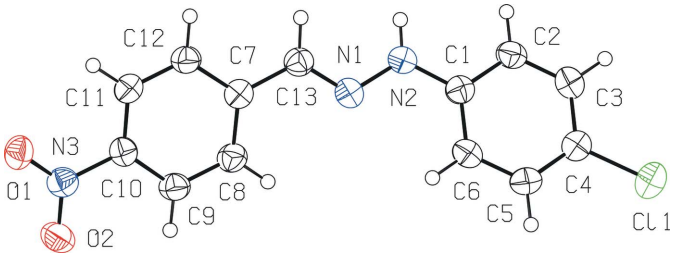


Figure 7
The molecular structure of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The packing arrangement assumed by both cyanobenzaldehyde chlorophenylhydrazone (I*a*) and cyanobenzaldehyde bromophenylhydrazone (I*b*) is shown in Fig. 8 for (I*a*). Both structures show a small proportion [approximately 3% of the molecules in (I*a*) and 6% in (I*b*)] of end-for-end disorder of the molecules; Fig. 8 shows the molecules as they are oriented in the major component of the disorder. The nitrile group in (I*a*) and (I*b*) is in contact with only the N—H group of the bridge and not with the C—H group (see Tables 1 and 2 for intermolecular N—H contact geometries). Even with this preference for the strong N—H donor over the weak C—H donor, the fact that the molecules are not locked into an entirely nondisordered pattern indicates that this particular interaction between the nitrile group and the bridge N—H group may be relatively weak compared with other conventional hydrogen bonds. This is consistent with the observed donor-H···acceptor angle in these structures (Tables 1 and 2), which is unfavourable for strong hydrogen-bond formation (Wood *et al.*, 2009). The nitrile group in (I*a*) and (I*b*) also engages in a centrosymmetric $R_2^2(10)$ motif (Bernstein *et al.*, 1995) defined by C—H···N≡C (a ring C—H as opposed to a bridge C—H) contacts between the cyanobenzylidene moieties: for (I*a*), H11···N3^{ii} = 2.67 Å and C11—H11···N3^{ii} = 144°; for (I*b*), H11···N3^{ii} = 2.66 Å and C11—H11···N3^{ii} = 144° [symmetry code: (ii) $-x, -y+2, -z+1$]. With respect to the halogen atoms (*X*), no close contacts of either the C—*X*···N≡C type or the C—*X*···*X*—C type are found. Instead, neighbouring molecules are connected by centrosymmetric interactions composed of C—H···*X*—C (a ring C—H) contacts involving the halophenylhydrazone moieties, defining an $R_2^2(8)$ motif: for (I*a*), H3···Cl1^{iii} = 2.95 Å and C3—H3···Cl1^{iii} = 160°; for (I*b*), H3···Br1^{iii} = 3.08 Å and C3—H3···Br1^{iii} = 160° [symmetry code: (iii) $-x+2, -y+2, -z$]. This halogen–hydrogen approach in (I*a*) is closer than that in (I*b*), which lies just outside the sum of the van der Waals radii (3.05 Å; Bondi, 1964) even though the Br atom is larger than the Cl atom. Our analysis has not revealed whether individual molecules assume disordered positions that would feature mixed cyclic motifs composed of both C—H···*X*—C and C—H···N≡C contacts, or whether instead entire chains of molecules are reversed and each cyclic motif is composed of only one kind of contact.

The hydrogen-bonded chain packing motif assumed by cyanobenzaldehyde iodophenylhydrazone (I*c*) is shown in Fig. 9. As in (I*a*) and (I*b*), molecules of (I*c*) are linked by an N—H···N≡C interaction, and no appreciable hydrogen bonding exists between the nitrile group and the bridge C—H group. Iodine, as the strongest Lewis acid of the halogen atoms, might have offered the best opportunity for C—*X*···N≡C contacts, but these are excluded in (I*c*) in favour of a strong N—H···N≡C contact that is more nearly linear than those in (I*a*) and (I*b*) (Table 3). In accord with this, the structure of (I*c*) is ordered. Notably absent from the packing arrangement of (I*c*) are the $R_2^2(10)$ motif defined by ring C—H···N≡C contacts and the $R_2^2(8)$ motif defined by ring C—H···*X*—C contacts present in (I*a*) and (I*b*), as are any C—*X*···*X*—C interactions involving the I atoms. Present instead are C—H···*X*—C approaches (3.24 Å) just beyond the van der Waals contact distance (3.18 Å; Bondi, 1964) between centrosymmetrically related molecules, the I atom of one molecule being directed toward the cyanobenzylidene C—H group *ortho* to the bridge of its neighbour.

The hydrogen-bonded chain packing motif assumed by both the bromobenzaldehyde cyanophenylhydrazone, (II*b*), and

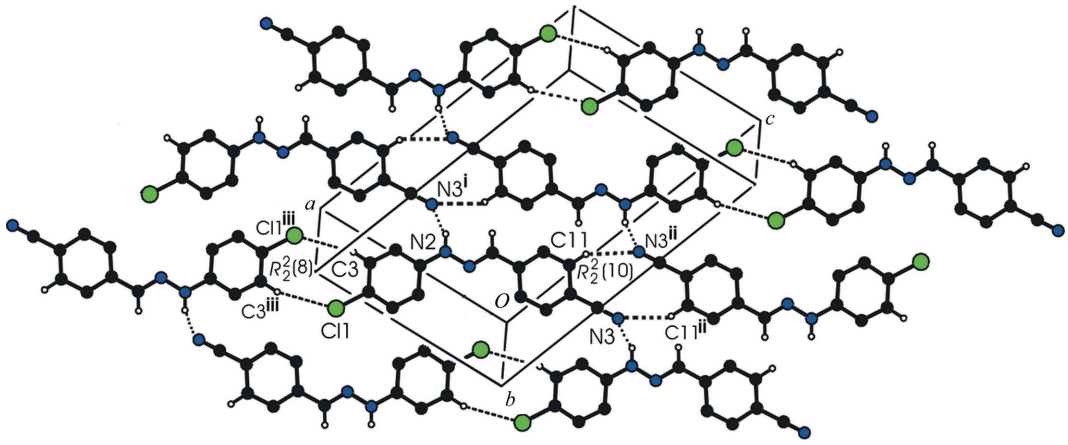


Figure 8
The molecular packing in (I*a*) and (I*b*), shown for the major component of disordered (I*a*). For clarity, only the H atoms in the bridge and others involved in intermolecular contacts are shown. Dashed lines indicate contacts at or shorter than the sum of the van der Waals radii. The bridge N—H group participates in a weak hydrogen bond, but the bridge C—H group does not participate in hydrogen bonding (see Tables 1 and 2 for N—H contact geometries). Centrosymmetric close-contact motifs shown here are defined by paired C—$X\cdots$H—C interactions, where X = Cl in (I*a*) and X = Br in (I*b*) [the $R_2^2(8)$ motif], and paired C≡N$\cdots$H—C interactions [the $R_2^2(10)$ motif]; see *Comment* for contact geometries. [Symmetry codes: (i) $x+1, y, z$; (ii) $-x, -y+2, -z+1$; (iii) $-x+2, -y+2, -z$.]

the iodobenzaldehyde cyanophenylhydrazone, (II*c*), is shown in Fig. 10 for (II*c*). The structure is ordered and the intermolecular approach distances indicate a preference for the N—H group over the bridge C—H group as the hydrogen-bond donor to the cyano group (Tables 4 and 5). The bridge flip relating (I*b*) and (I*c*) to (II*b*) on the one hand and to (II*c*) on the other is accompanied by sharp differences in packing motifs. The $R_2^2(10)$ motif defined by ring C—H$\cdots$N≡C contacts and the $R_2^2(8)$ motif defined by ring C—H$\cdots X$—C contacts present in (I*b*) [and in (I*a*) but not in (I*c*)] are absent from (II*b*) and (II*c*), but also absent from (II*b*) and (II*c*) are the rather long C—H$\cdots X$—C approaches to the *ortho* C—H groups present in (I*c*). Intermolecular contacts involving the Br atom of (II*b*) and the I atom of (II*c*) are not obvious C—

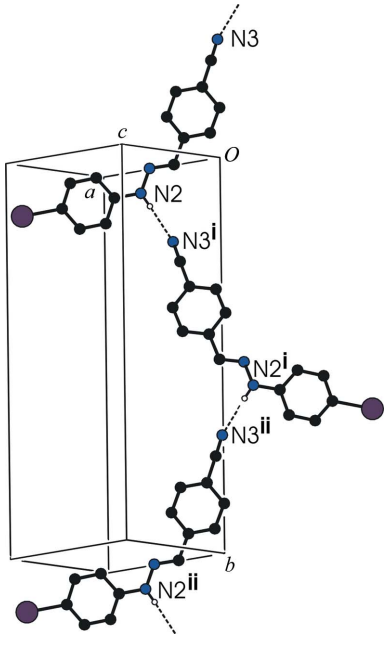


Figure 9
The hydrogen-bonded chain motif (dashed lines) defined by the N—H$\cdots$N≡C interaction in cyanobenzaldehyde iodophenylhydrazone (I*c*); see Table 3 for contact geometry. For clarity, only the H atom involved in hydrogen bonding, the N—H atom, is shown; the bridge C—H group is not involved in any hydrogen-bonding motifs. [Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, y+1, z$.]

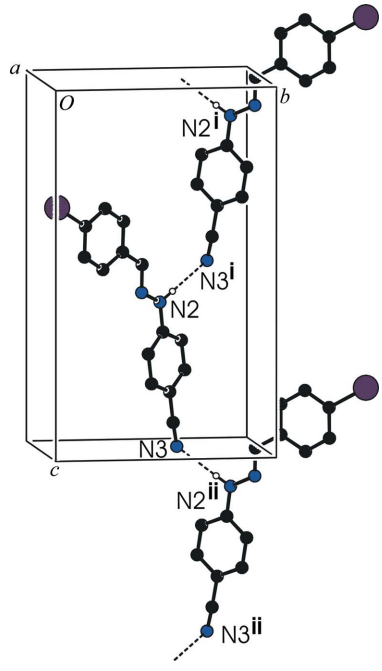


Figure 10
The hydrogen-bonded chain motif (dashed lines) defined by the N—H$\cdots$N≡C interaction in iodobenzaldehyde cyanophenylhydrazone (II*c*); see Table 5 for contact geometry. A corresponding hydrogen-bonded chain motif is observed in the bromo analogue (II*b*) (contact geometry given in Table 4). For clarity, only the H atom involved in hydrogen bonding, the N—H atom, is shown; as in (I*c*) (Fig. 9), the bridge C—H group is not involved in any hydrogen-bonding motifs. [Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.]

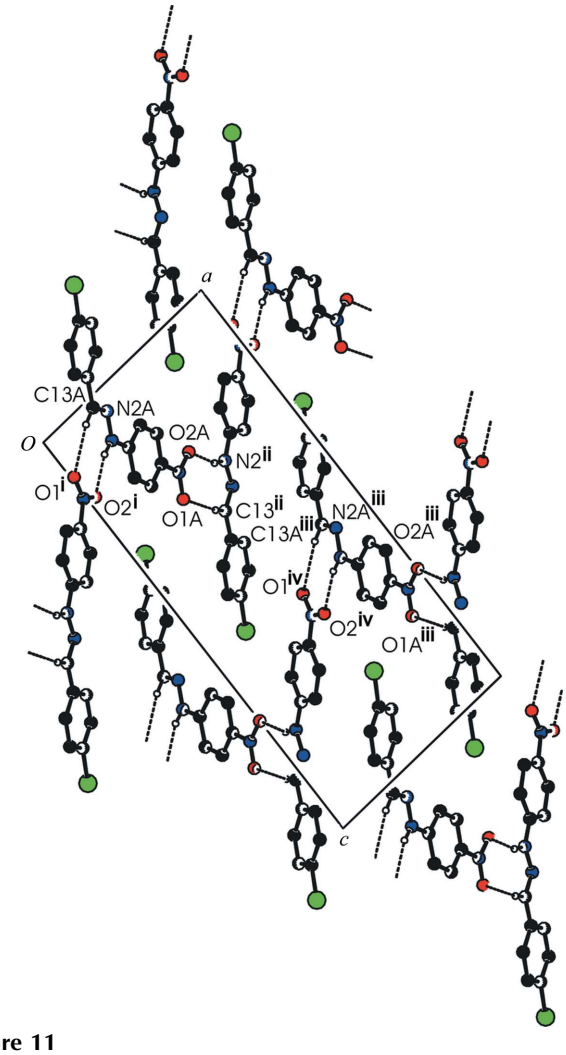


Figure 11
The molecular packing in (III), showing the $R_2^2(8)$ hydrogen-bonding interaction (dashed lines) between the nitro group and the bridge N—H and C—H groups. For clarity, only the H atoms of the bridge are shown. See Table 6 for contact geometries. [Symmetry codes: (i) $x-1, y+1, z$; (ii) $x, y-1, z$; (iii) $x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+2, z+\frac{1}{2}$.]

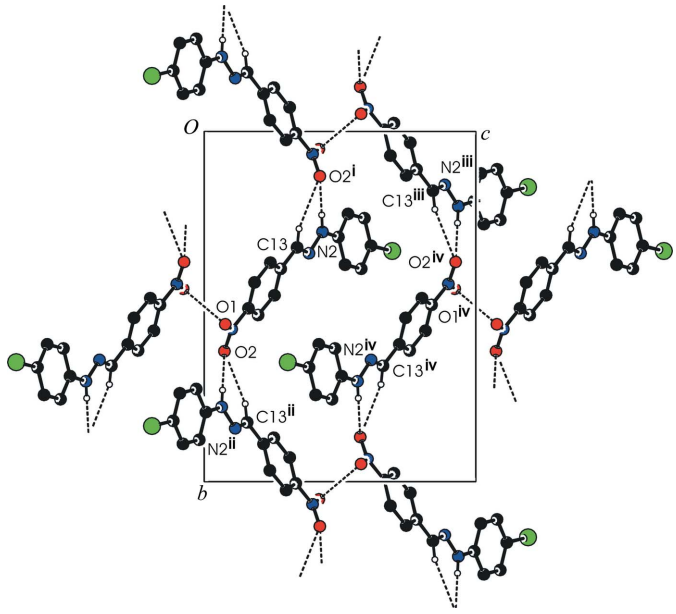


Figure 12
The molecular packing in (IV), showing the $R_2^1(6)$ interaction (dashed lines) between one O atom of the nitro group and both the bridge N—H and C—H groups of a neighbouring molecule. Also shown as a dashed line is the 3.002 (2) Å approach between atom O1 and the N atom of the nitro group of a neighbouring molecule, an interaction in which O1 engages instead of hydrogen bonding with the molecular bridge. For clarity, only the H atoms of the bridge are shown. See Table 7 for contact geometries. [Symmetry codes: (i) $-x+\frac{5}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{5}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $-x+2, -y+1, -z+1$.]

H···*X*—C interactions but simply point the C—*X* bond towards the π cloud of the cyanophenylhydrazone ring of a neighbouring molecule, an interaction that may arise simply as a consequence of space-filling considerations, rather than as a directional interaction that would influence the packing pattern. Given the non-equivalence of the N—H and C—H groups as potential hydrogen-bond donors in (I*a*)–(I*c*) and (II*b*)–(II*c*), and the different positions of the N—H groups within the bridges of the bridge-flipped isomeric pairs (I*b*)/(II*b*) and (I*c*)/(II*c*), it is not surprising that these isomers assume different molecular packing arrangements.

Figs. 11 and 12 show the two different packing arrangements assumed by the bridge-flipped isomers (III) and (IV), respectively. In both chlorobenzaldehyde nitrophenylhydrazone (III) and nitrobenzaldehyde chlorophenylhydrazone (IV), and in contrast with the nitrile-substituted phenylhydrazones discussed above, the geometries of the intermolecular approach indicate that both the N—H and C—H groups of the bridge act as hydrogen-bond donors. Although this equivalence might be expected to permit isomorphism between (III) and (IV), the packing arrangements of (III) and (IV) differ at least in part because the equivalence is expressed in the form of two different cyclic motifs. In (III), both molecules in the asymmetric unit engage in bridging interactions of the $R_2^2(8)$ type, involving both bridge hydrogen-bond donors and both nitro-group O atoms (Fig. 11), but in (IV) the bridging interactions are of the $R_2^1(6)$ type and involve only one of the two nitro-group O atoms (Fig. 12). In (III), the nitro O atom in contact with the bridge N—H group is also in contact with the neighbouring *ortho* C—H group of the nitrophenylhydrazone ring; this motif is followed by both molecules in the asymmetric unit of (III). Contacts involving the Cl atom in (III) are exclusively of the C—H···*X*—C type, where the C—H group is part of the nitrophenylhydrazone ring. In (IV), the O atom not involved in the bridge interaction is in contact with a nitro group from a neighbouring molecule; this centrosymmetric nitro–nitro stacking interaction is not present in (III). The Cl atoms in (IV) are not involved in any contacts sufficiently directional to be noteworthy in terms of determining the molecular packing.

The four arylhydrazone structures published to date (Version 5.32 of the CSD) in which a nitrile group is present (other than the RIFXOU and RIFXUA structures already noted) bear no halogen atoms and thus lend no further insight into potential nitrile–halogen or halogen–halogen interactions in substituted phenylhydrazones, but three of them bear nitro

groups and are relevant with respect to competition between nitrile and nitro groups as potential bridge hydrogen-bond acceptors. These structures show either a preference for the bridge N—H group as the hydrogen-bond donor or no interaction with the bridge atoms at all. Of the latter type, two are acetonitrile solvates that also bear nitro groups: 4-[(2,4-dinitrophenyl)hydrazonomethyl]phenol (BAFHIA; Szczesna & Urbanczyk-Lipkowska, 2002) and (*E*)-1-[3-(benzyloxy)-4-methoxybenzylidene]-2-(2,4-dinitrophenyl)hydrazine (DAYSOM; Shi, 2005). In BAFHIA, any hydrogen-bonding contact between the acetonitrile molecule and the bridge appears to be excluded in favour of a tight centrosymmetric hydrogen-bonding interaction in which a nitro group spans the HC=N—NH group of the bridge. One of the nitro O atoms is within the van der Waals contact distance of both the C—H and N—H groups, while the other nitro O atom is within the van der Waals contact distance of only the C—H group. In DAYSOM, in contrast, no close contacts between the bridge atoms and either the acetonitrile molecule or either of the nitro groups are found. On the other hand, in the acetonitrile solvate (*E*)-1-[3-ethoxy-4-(4-methylbenzenesulfonyloxy)benzylidene]-2-(4-nitrophenyl)hydrazine (NEQKEA; Chen & Yu, 2006), it is the nitrile group rather than the nitro group that acts as the hydrogen-bond acceptor toward the bridge atoms, the acetonitrile molecule interacting at hydrogen-bonding distance with only the bridge N—H group and not with the bridge C—H group. A clear preference by the nitrile group for the bridge N—H group over the bridge C—H group is also shown by the close approach between the nitrile group and the bridge N—H group of 4-(phenylhydrazonomethyl)benzonitrile (CIQKOD; Wang & Ye, 2007), a system in which competition from a nitrile–halogen, halogen–halogen or any type of nitro interaction is impossible. This preference for the bridge N—H group in CIQKOD suggests that the as yet unreported 'bridge-flipped' isomer of CIQKOD will ultimately be found to assume a different molecular packing arrangement.

Of the various nitro–halogen substituted structures published thus far, that most closely related in molecular structure to (III) and (IV) is 4-iodobenzaldehyde 4-nitrophenylhydrazone (OMOLIL; Glidewell *et al.*, 2004), although it is not isomorphous with either (III) or (IV). In OMOLIL, which differs from (III) only in the replacement of the Cl atom with an I atom, one of the nitro O atoms is in contact with both N—H and C—H groups, while the other O atom is in contact with only an iodobenzylidene ring C—H group *ortho* to the bridge N—H group. The differences between this motif and those observed in (III) and (IV) are subtle. In (III), one of the nitro O atoms is in contact with both the bridge N—H group and the ring C—H group *ortho* to it, but the O atom making only a single contact forms that contact with the bridge C—H group. In (IV), as in OMOLIL and (III), one of the nitro O atoms is in contact with both the N—H and C—H groups of the bridge, but only in (IV) is the other O atom not in close van der Waals contact with any neighbouring atom. No directional contacts involving the I atom are apparent in OMOLIL.

In none of our structures do we observe a situation in which a hydrogen-bond acceptor in contact with the phenylhydrazone bridge C—H group is not also in contact with the bridge N—H group. The nitrile–halogen compounds show a preference for the N—H donor, while the nitro–halogen compounds treat the N—H and C—H donors equally. Hydrogen-bonding interactions with the bridge appear to be preferred over nitrile–halogen interactions. The limited number of examples we have examined here does not permit any firm conclusions to be drawn regarding how nitrile or nitro groups interact with the two potential hydrogen-bond donor groups of the phenylhydrazone bridge. On the other hand, the frequency with which no clear choice between these donor groups is made by potential hydrogen-bond acceptors may point towards the future identification of more isomorphous 'bridge-flipped' phenylhydrazones than the two pairs identified thus far.

Experimental

All of the phenylhydrazones described here were prepared by standard methods, *i.e.* reaction of a substituted benzaldehyde with a substituted phenylhydrazine (or the phenylhydrazine hydrochloride in the presence of a base) by brief heating of an ethanol solution. Obtained by this method were: (I*a*) as yellow plates, m.p. 451–456 K; (I*b*) as yellow prisms, m.p. 443–446 K; (I*c*) as red needles, m.p. 421–422 K; (II*b*) as brown prisms, m.p. 464–465 K; (II*c*) as brown needles, m.p. 477–479 K; (III) as orange needles, m.p. 498–499 K; and (IV) as red needles, m.p. 423–427 K. In each case, crystals were grown by slow evaporation from an ethanol solution.

Compound (I*a*)

Crystal data

$C_{14}H_{10}ClN_3$
M_r = 255.70
Monoclinic, $P2_1/n$
a = 10.7246 (10) Å
b = 7.1767 (6) Å
c = 16.3492 (15) Å
β = 104.779 (1)°
V = 1216.72 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 173 K
0.50 × 0.50 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.894, T_{max} = 1.000
11510 measured reflections
2154 independent reflections
1952 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.080
S = 1.13
2154 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I*a*).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···N3^{i}	0.871 (17)	2.471 (17)	3.1345 (19)	133.5 (14)

Symmetry code: (i) $x+1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °) for (I*b*).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···N3^{i}	0.87 (3)	2.54 (3)	3.129 (3)	126 (2)

Symmetry code: (i) $x+1, y, z$.

Table 3
Hydrogen-bond geometry (Å, °) for (I*c*).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···N3^{i}	0.82 (2)	2.21 (2)	3.035 (4)	177 (3)

Symmetry code: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.

Compound (I*b*)

Crystal data

$C_{14}H_{10}BrN_3$
M_r = 300.16
Monoclinic, $P2_1/n$
a = 10.6804 (8) Å
b = 7.3150 (6) Å
c = 16.5427 (13) Å
β = 105.500 (1)°
V = 1245.43 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.28 mm^{-1}
T = 173 K
0.40 × 0.30 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.778, T_{max} = 1.000
8153 measured reflections
2205 independent reflections
1975 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.068
S = 1.13
2205 reflections
172 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Compound (I*c*)

Crystal data

$C_{14}H_{10}IN_3$
M_r = 347.15
Monoclinic, $P2_1/c$
a = 8.9757 (11) Å
b = 20.547 (2) Å
c = 7.3703 (9) Å
β = 95.137 (2)°
V = 1353.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.35 mm^{-1}
T = 173 K
0.50 × 0.15 × 0.13 mm

Table 4
Hydrogen-bond geometry (Å, °) for (II*b*).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···N3^{i}	0.82 (2)	2.19 (2)	3.006 (2)	173 (2)

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

Table 5
Hydrogen-bond geometry (Å, °) for (II*c*).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···N3^{i}	0.80 (2)	2.22 (2)	3.021 (3)	177 (3)

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

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.801, T_{max} = 1.000
13201 measured reflections
2405 independent reflections
2164 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.058
S = 1.12
2405 reflections
167 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Compound (II*b*)

Crystal data

$C_{14}H_{10}BrN_3$
M_r = 300.16
Monoclinic, $P2_1/c$
a = 7.7963 (6) Å
b = 9.8952 (8) Å
c = 16.5695 (13) Å
β = 91.070 (1)°
V = 1278.05 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.20 mm^{-1}
T = 173 K
0.35 × 0.25 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.778, T_{max} = 1.000
12087 measured reflections
2250 independent reflections
2050 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.058
S = 1.06
2250 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Compound (II*c*)

Crystal data

$C_{14}H_{10}IN_3$
M_r = 347.15
Monoclinic, $P2_1/c$
a = 7.9108 (8) Å
b = 10.0376 (11) Å
c = 16.6958 (18) Å
β = 90.871 (2)°
V = 1325.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.40 mm^{-1}
T = 173 K
0.50 × 0.25 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.775, T_{max} = 1.000
15523 measured reflections
3047 independent reflections
2735 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N2A—H2NA···O2^{i}	0.84 (2)	2.11 (2)	2.930 (4)	164 (4)
N2—H2N···O2A^{ii}	0.87 (2)	2.09 (2)	2.911 (3)	159 (3)
C13A—H13A···O1^{i}	0.95	2.64	3.583 (4)	170
C13—H13···O1A^{ii}	0.95	2.62	3.559 (4)	169

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.068$
$S = 1.05$
3047 reflections
167 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Compound (III)

Crystal data

$C_{13}H_{10}ClN_3O_2$
$M_r = 275.69$
Monoclinic, Pn
$a = 9.7426$ (8) Å
$b = 6.1015$ (5) Å
$c = 21.7139$ (18) Å
$\beta = 96.175$ (1)°
$V = 1283.28$ (18) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}
$T = 173$ K
0.50 × 0.20 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.877$, $T_{max} = 1.000$
11862 measured reflections
5458 independent reflections
4595 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.126$
$S = 1.06$
5458 reflections
350 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Absolute structure: Flack (1983), with 2560 Friedel pairs
Flack parameter: 0.59 (6)

Compound (IV)

Crystal data

$C_{13}H_{10}ClN_3O_2$
$M_r = 275.69$
Monoclinic, $P2_1/n$
$a = 6.1260$ (7) Å
$b = 16.404$ (2) Å
$c = 12.9510$ (16) Å
$\beta = 101.091$ (2)°
$V = 1277.1$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}
$T = 173$ K
0.50 × 0.23 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.869$, $T_{max} = 1.000$
13035 measured reflections
2426 independent reflections
1730 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$

Table 7
Hydrogen-bond geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···O2^{i}	0.86 (3)	2.17 (3)	3.021 (3)	170 (2)
C13—H13···O2^{i}	0.95	2.72	3.510 (3)	141

Symmetry code: (i) $-x+\frac{5}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.118$
$S = 1.07$
2426 reflections
176 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

After initial refinement of (I*a*), the presence of residual electron density near the nitrile group and (as a result) an anomalously short C≡N bond suggested a small amount of end-for-end disorder of the molecule. Attempts to refine the occupancy of the Cl atom over the two possible positions while applying geometric restraints to the nitrile group failed to yield a satisfactory geometry for that group, so only the two positions of the Cl atom were included in the final model, which refined with a final occupation factor of the minor component of 0.0331 (12). A similar procedure was followed for (I*b*), in which the occupation factor of the minor component refined to 0.0648 (13) and the C10—Br1*A* bond length in the minor component was restrained to 1.90 (2) Å. In all structures, C-bound H atoms were placed in calculated positions and refined using a riding model, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). N-bound H atoms were refined isotropically without constraints in (I*a*), (I*b*), (II*b*) and (IV); in (I*c*), (II*c*) and (III), the N—H distance was restrained to 0.83 (2) Å.

For all compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3255). Services for accessing these data are described at the back of the journal.

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