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C—halogen···π dimer and C—H···π interactions in 1-(2-bromo-4,5-dimethoxybenzyl)-2-butyl-4-chloro-1*H*-imidazole-5-carbaldehyde and 2-butyl-4-chloro-1-(6-methyl-1,3-benzodioxol-5-ylmethyl)-1*H*-imidazole-5-carbaldehyde

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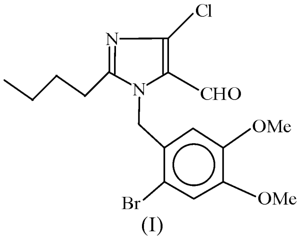
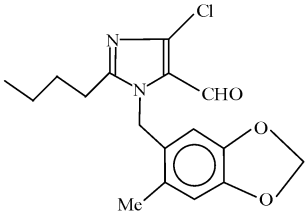
The structures of the title compounds, $C_{17}H_{20}BrClN_2O_3$, (I), and $C_{17}H_{19}ClN_2O_3$, (II), are stabilized by intramolecular C—H···O and C—H···π interactions. The stability of the molecular packing in (I) and (II) arises from a diverse set of weak intermolecular C—H···O, C—H···π and C—halogen···π interactions. In the crystal structure of (I), molecules aggregate in dimeric subunits *via* C—Br···π interactions. The dimers are interlinked by C—H···O hydrogen bonds. The halogens cluster together and form a channel along the *b* axis. In (II), the packing is mainly governed by intermolecular C—H···O and C—H···π interactions.

Comment

The molecular assembly in a crystal is predominantly governed by intermolecular forces, conventionally described by strong and directional N—H···O, O—H···O and O—H···N hydrogen bonds (Desiraju, 2002). In molecules having an imbalance of hydrogen-bond donors and acceptors, the deficiency in either donor or acceptor is fulfilled by other types of weak and less-directional forces. Interactions involving the π cloud in aromatic compounds also belong to this category. The presence of several types of aromatic, X—H···π, X—Hal···π (Hal is halogen) and π–π interactions has been established and characterized in many different molecular systems (Desiraju & Steiner, 1999; Desiraju, 2002). The motivation for understanding these interactions arises from their potential importance in generating supramolecular architectures for the design of molecular solids with novel properties. Organic molecules with such characteristics provide an excellent means of exploring the roles of non-conventional intermolecular forces in crystal engineering and supramolecular chemistry. In the present work, we report the syntheses and structures of two imidazole derivatives, and discuss the relevance of weak intermolecular interactions in molecular packing. The title compounds, (I) and (II), are intermediates in the syntheses of biologically active isoxazoles and isoxazolines (Pruitt *et al.*, 2000).



(I)



(II)

In the crystal structure, planar moieties are formed by groups of atoms attached to the aromatic imidazole (Imd) ring, namely atoms C1–C4, C8, C9, Cl1, N1 and N2 in both (I) and (II), and to the phenyl (Ph) ring, *i.e.* atoms C9–C17, O2 and O3 in (II) and atoms C9–C17, O2, O3 and Br1 in (I). The dihedral angles between these planar groups are 82.8 (1) and 85.5 (1)° in (I) and (II), respectively. The overall structures of (I) and (II) can be inferred from the ellipsoid plots shown in Fig. 1. The molecular conformation is essentially described by torsion angles about the N2—C9 and C9—C10 bonds. The C1—N2—C9—C10 torsion angle is 105.2 (4)° in (I) and 93.9 (2)° in (II), and the N2—C9—C10—C11 angles are 164.5 (3) and 172.3 (2)° in (I) and (II), respectively. The sign of the torsion angle, which otherwise has no meaning for centrosymmetric crystals, corresponds to the reported coordinates of the structure. The non-planar part of both molecules, *i.e.* the butyl chain attached to the imidazole ring, is characterized by the N1—C1—C4—C5, C1—C4—C5—C6 and C4—C5—C6—C7 torsion angles. These angles are −15.6 (10), −176.9 (7) and 97.6 (10)° in (I), and −4.2 (3), 174.3 (2) and −176.4 (3)° in (II), indicating that the conformation of the butyl chain is bent in (I) and fully extended in (II). The geometric parameters for the inter- and intramolecular interactions are given in Tables 1 and 2. The molecular structures are primarily stabilized by intramolecular C15—H15···π(Imd) and C9—H9*B*···O1 interactions. The C9—H9*B*···O1 contact forms an S_6 hydrogen-bonded pattern (Bernstein *et al.*, 1995) in both molecules. As observed in a similar compound (Gaonkar *et al.*, 2004), and the very few related structures found in the Cambridge Structural Database (Allen, 2002), these two interactions appear to play a predominant role in shaping the molecular structure.

The crystal packing is governed by a diverse set of weak intermolecular interactions (Tables 1 and 2). The molecules of (I) and (II) contain no amine donor atoms. This deficiency is partially compensated by interactions involving halogen atoms and the aromatic rings. Short intermolecular C—Hal$\cdots\pi$ contacts stabilize the dimeric subunits in (I) (Fig. 2). A dimer is formed by a C11—Br1$\cdots\pi$(Imd)($-x+1$, $-y$, $-z+1$) contact. The Br1$\cdots$*Cg*1 distance (*Cg*1 is the centroid of the Imd ring) and C11—Br1$\cdots$*Cg*1 angle are 3.857 (4) Å and 123.6 (2)°, respectively, whereas the minimum atomic distance, in Br1$\cdots\pi$, is 3.51 Å. The Br$\cdots\pi$ interaction is less well documented, among both small and macromolecules, than the F$\cdots\pi$ and Cl$\cdots\pi$ interactions (Prasanna & Guru Row, 2000; Saraogi *et al.*, 2003). The average value reported for the minimum atomic distance in intermolecular C—Br$\cdots\pi$

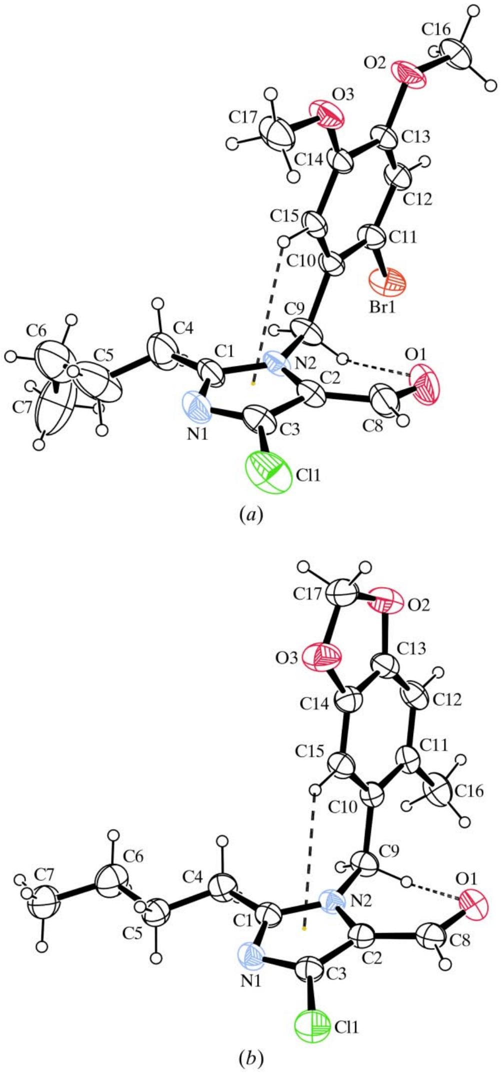


Figure 1
ORTEP-3 plots (Farrugia, 1997) of (*a*) (I) and (*b*) (II), in comparable orientations, with the atom-numbering schemes. Displacement ellipsoids are shown at the 30% probability level. H atoms are shown as small spheres of arbitrary radii and the dashed lines represent intramolecular C—H$\cdots$O and C—H$\cdots\pi$ interactions.

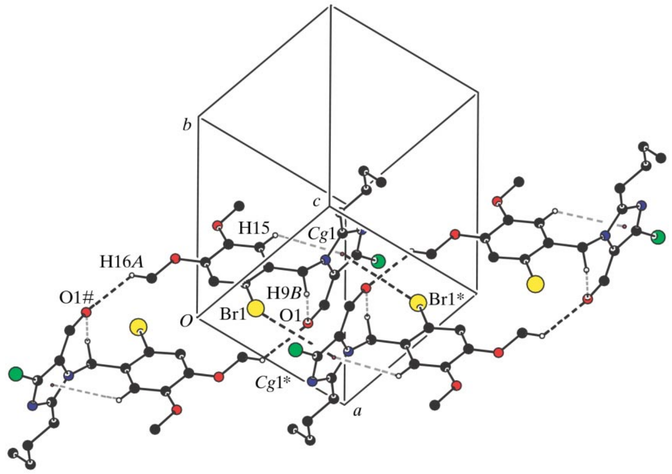


Figure 2
The crystal packing in (I), showing a chain of molecules along the [101] direction. For clarity, intermolecular interactions are represented by dark dashed lines, whereas intramolecular interactions are shown as light dashed lines. Atoms marked with an asterisk (*) or hash (#) are related by the symmetry codes ($-x+1$, $-y$, $-z+1$) and ($-x$, $-y$, $-z$), respectively.

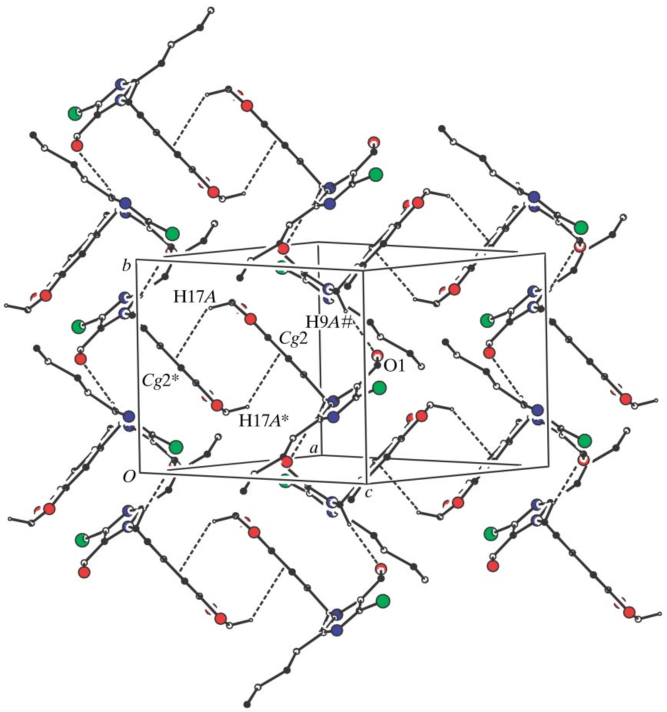


Figure 3
The crystal packing in (II), showing a sheet structure formed by molecules about the (20$\overline{2}$) plane. The intermolecular contacts are represented by dashed lines. Atoms marked with an asterisk (*) or hash (#) are related by the symmetry codes ($-x+1$, $-y+1$, $-z$) and ($-x+\frac{3}{2}$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$), respectively.

contacts is 3.625 (9) Å (Prasanna & Guru Row, 2000). The C—Hal$\cdots\pi$ dimer interactions, which have also been referred to as PHD (π–halogen-dimer) interactions, have recently been shown to play an important role in host–guest chemistry (Noman *et al.*, 2004). The dimeric subunits are interlinked by an intermolecular C16—H16*A*$\cdots$O1 contact, contributing further to the stability of the crystal packing. In the crystal structure, the halogen atoms cluster together and form a channel along the *b* axis. The closest Hal$\cdots$Hal contacts are Cl1$\cdots$Cl1($-x+2$, $-y+1$, $-z+1$) [3.503 (2) Å] and Cl1$\cdots$Br1($-x+1$, $-y$, $-z+1$) [3.555 (6) Å]. However, the halogen atoms fail to form a network similar to that reported for tetrakis(4-iodophenyl)methane (Thaimattam *et al.*, 1998). It is not clear if such clustering is the result of characteristic intermolecular forces among halogens (Price *et al.*, 1994). The packing in (II) is mainly governed by intermolecular C—H$\cdots$O and C—H$\cdots\pi$ interactions other than van der Waals forces [C9—H9*A*$\cdots$O1 and C17—H17*A*$\cdots\pi$(Ph); Table 2]. The crystal packing of (II) is shown in Fig. 3.

In summary, the role of weak intermolecular interactions in the stability of the crystal packing in the two examples, which lack strong amine and O donor atoms, have been highlighted. C—H$\cdots$O, C—Hal$\cdots\pi$ and C—H$\cdots\pi$ interactions govern the packing in (I) and (II). The identification of such motifs signifies the importance of non-conventional weak intermolecular interactions in ordering the crystal packing. It will be of particular interest to examine the occurrences and roles of C—Hal$\cdots\pi$ dimer interactions in organic compounds.

Experimental

Compound (I) was synthesized by condensing an equimolar mixture of 2-butyl-4-chloro-1*H*-imidazole-5-carbaldehyde and 2-bromo-4,5-dimethoxybenzyl bromide with potassium carbonate in a dimethylformamide medium with stirring at room temperature for 10 h (yield 90%, m.p. 360 K). Compound (II) was prepared by condensing an equimolar mixture of 2-butyl-4-chloro-1*H*-imidazole-5-carbaldehyde and 6-methyl-1,3-benzodioxol-5-ylmethyl chloride under the same conditions (yield 90%, m.p. 385 K). Both compounds were recrystallized from acetonitrile.

Compound (I)

Crystal data

$C_{17}H_{20}BrClN_2O_3$
$M_r = 415.72$
Triclinic, $P\bar{1}$
$a = 8.547$ (2) Å
$b = 10.308$ (2) Å
$c = 10.611$ (2) Å
$\alpha = 91.654$ (4)°
$\beta = 100.667$ (4)°
$\gamma = 93.623$ (3)°
$V = 916.2$ (4) Å^3

$Z = 2$
$D_x = 1.507$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1017 reflections
$\theta = 2.4$–25.6°
$\mu = 2.41$ mm^{-1}
$T = 193$ (2) K
Block, colorless
0.14 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.73$, $T_{max} = 0.79$
7830 measured reflections

4087 independent reflections
2655 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 28.0°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.170$
$S = 1.03$
4087 reflections
231 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0839P)^2 + 0.3943P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.013 (3)

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

*Cg*1 is the centroid of the Imd ring.

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C9—H9*B*$\cdots$O1	0.99	2.51	2.996 (6)	110
C15—H15$\cdots$*Cg*1	0.95	3.00	3.602 (3)	122
C16—H16*A*$\cdots$O1^{i}	0.98	2.59	3.142 (6)	115

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

Compound (II)

Crystal data

$C_{17}H_{19}ClN_2O_3$
$M_r = 334.79$
Monoclinic, $P2_1/n$
$a = 12.4899$ (5) Å
$b = 9.4887$ (3) Å
$c = 14.1018$ (5) Å
$\beta = 94.319$ (1)°
$V = 1666.5$ (1) Å^3
$Z = 4$
$D_x = 1.330$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1237 reflections
$\theta = 5.5$–23.6°
$\mu = 0.25$ mm^{-1}
$T = 130$ (2) K
Block, colorless
0.11 × 0.10 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
w scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 1996)
$T_{min} = 0.934$, $T_{max} = 0.982$
6694 measured reflections
2401 independent reflections

2090 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 23.3°$
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 5$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.106$
$S = 1.09$
2401 reflections
211 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.5705P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0166 (15)

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

*Cg*1 and *Cg*2 are the centroids of the Imd and Ph rings, respectively.

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C9—H9*B*$\cdots$O1	0.99	2.47	3.022 (3)	115
C9—H9*A*$\cdots$O1^{i}	0.99	2.57	3.528 (3)	167
C15—H15$\cdots$*Cg*1	0.95	2.97	3.585 (2)	124
C17—H17*A*$\cdots$*Cg*2^{ii}	0.99	2.89	3.654 (3)	135

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

The H atoms were refined with fixed geometry, riding on their carrier atoms with U_{iso}(H) values set at 1.2 (1.5 for methyl H atoms)

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times U_{eq} of the parent atom (C—H = 0.95–0.99 Å). In (I), the Br atom is statistically disordered over two adjacent sites; the partial occupancies refined to 0.54 (4) and 0.46 (4). Atoms Br1 and Br2, which occupy the former and latter positions, lie −0.16 and 0.11 Å, respectively, from the mean aromatic plane formed by atoms C10–C15. The C4—C5 bond length in (I) was restrained to 1.54 (1) Å because of thermal disorder.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; structure solution: *SHELXS86* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1810). Services for accessing these data are described at the back of the journal.

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