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The crucial role of C—H···O and C=O···π interactions in the building of three-dimensional structures of dicarboxylic acid–biimidazole compounds

Xiao-Li Gao, Li-Ping Lu* and Miao-Li Zhu*

Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China
Correspondence e-mail: luliping@sxu.edu.cn, miaoli@sxu.edu.cn

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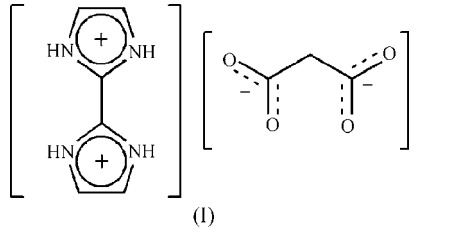
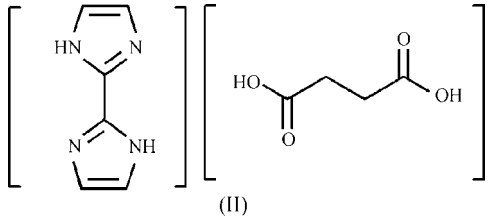
The supramolecular architectures of three dicarboxylic acid–biimidazole compounds, namely, 2,2′-biimidazolium malonate, $C_6H_8N_4^{2+}\cdot C_3H_2O_4^{2-}$, (I), 2,2′-bi(1*H*-imidazole) succinic acid, $C_6H_6N_4\cdot C_4H_6O_4$, (II), and 2,2′-biimidazolium 2,2′-iminiodiacetate chloride, $C_6H_8N_4^{2+}\cdot C_4H_6NO_4^{-}\cdot Cl^{-}$, (III), are reported. The crystal structures are assembled by the same process, namely double conventional N—H···O or O—H···N hydrogen bonds link the dicarboxylates and biimidazoles to form tapes, which are stacked in parallel through lone-pair–aromatic interactions between carbonyl O atoms and biimidazole groups and are further linked *via* weak C—H···O interactions. The C=O···π interactions involved in stacking the tapes in (II) and the C—H···O interactions involved in linking the tapes in (II) and (III) demonstrate the crucial role of these interactions in the crystal packing. There is crystallographically imposed symmetry in all three structures. In (I), two independent malonate anions have their central C atoms on twofold axes and two biimidazolium dications each lie about independent inversion centres; in (II), the components lie about inversion centres, while in (III), the unique cation lies about an inversion centre and the iminiodiacetate and chloride anions lie across and on a mirror plane, respectively.

Comment

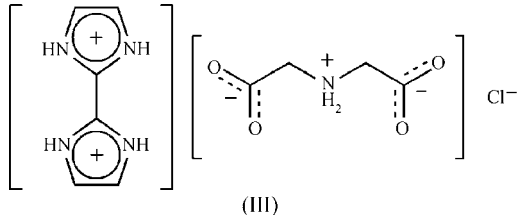
Noncovalent weak interactions, such as C—H···O and C=O···π, have attracted much interest. These weak interactions have been widely discussed in relation to the crystal packing of organic molecules and the determination of the folded structures of biological molecules (Derewenda *et al.*, 1995; Desiraju, 1996, 2005; Khurram *et al.*, 2006; Jain *et al.*, 2007; Lu *et al.*, 2007; Wan *et al.*, 2008). However, self-assembled supramolecular architectures are often stabilized as a result of the synergy of a variety of weak interactions (Khurram *et al.*, 2006; Shukla *et al.*, 2007; Wan *et al.*, 2008). It is difficult to distinguish the effect of an individual weak interaction. Desiraju (2005) suggested that weak interactions can be classified as innocuous, supportive or intrusive. We describe here the decisive role of carbonyl–π and C—H···O interactions in the assembly of the supramolecular architectures of three dicarboxylic acid–biimidazole compounds, (I)–(III).



(I)



(II)



(III)

The asymmetric unit of (I) contains two independent malonate anions, with their central C atoms on twofold axes, and two biimidazolium cations, each lying about independent inversion centres (Fig. 1). Strong N—H···O hydrogen bonds

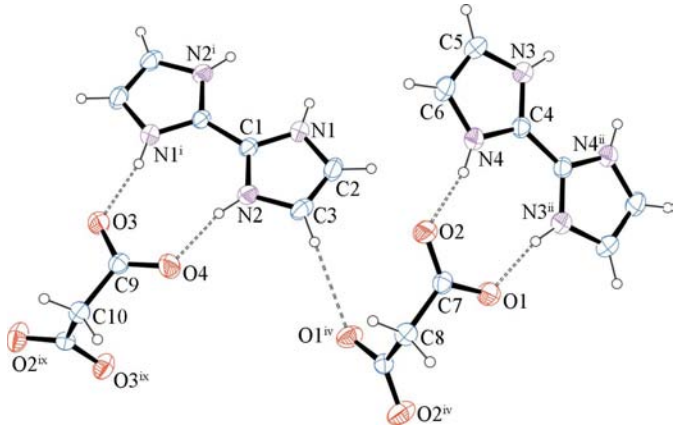


Figure 1
A view of the structure of (I), with displacement ellipsoids drawn at the 30% probability level. Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y, -z+1$; (iv) $-x, y, -z+\frac{1}{2}$; (ix) $-x+1, y, -z+\frac{1}{2}$.]

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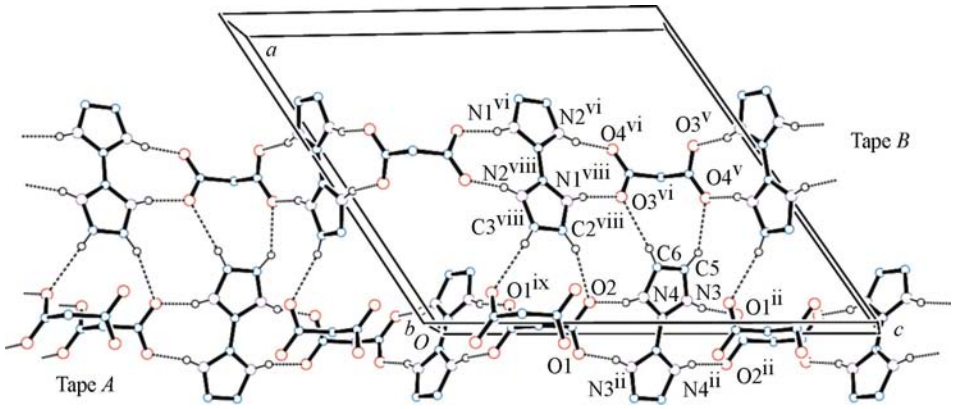

Figure 2
The structure built from N—H···O hydrogen bonds and C—H···O interactions in (I). Dashed lines represent hydrogen bonds. [Symmetry codes: (ii) $-x, -y, -z+1$; (v) $x, -y+1, z+\frac{1}{2}$; (vi) $-x+1, -y+1, -z+1$; (viii) $x, y+1, z$; (ix) $-x+1, y+1, -z+\frac{3}{2}$.]

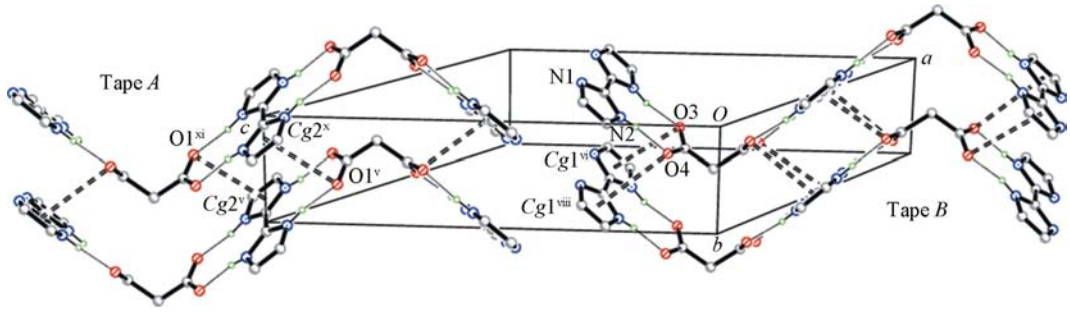

Figure 3
The C═O···π interaction (double dashed lines) between neighbouring *A* tapes and *B* tapes in (I). Dotted lines represent hydrogen bonds. [Symmetry codes: (v) $x, -y+1, z+\frac{1}{2}$; (vi) $-x+1, -y+1, -z+1$; (viii) $x, y+1, z$; (x) $-x, y+1, -z+\frac{3}{2}$; (xi) $-x, y, -z+\frac{3}{2}$.]

(Fig. 1 and Table 1) link the malonate and biimidazolium moieties to form two distinct units, which further assemble into two different zigzag tapes designated as *A* and *B*, as shown as Fig. 2. Four C—H···O interactions (Fig. 2 and Table 1) link the two tapes into a three-dimensional network, and concomitantly there are three possible C═O···π(imidazole ring) interactions, one of which takes part in the stacking of tapes *A* while the other two link tapes *B*, as described in Table 1 and shown in Fig. 3.

In (II), there is crystallographically imposed inversion symmetry with the succinic acid and neutral biimidazole molecules lying about inversion centres. The succinic acid and biimidazole molecules are linked by pairs of O—H···N and N—H···O hydrogen bonds (Fig. 4 and Table 2), leading to linear tapes which are further linked to form sheets in the $(10\bar{2})$ plane by the C3—H3···O2($x+1, -y+\frac{1}{2}, z+\frac{1}{2}$) interaction (Fig. 5 and Table 2). The sheets assemble into a three-dimensional structure by the C4═O1···π(imidazole ring) ($-x+1, -y+1, -z+1$) interaction (Fig. 6 and Table 2).

In (III) (Fig. 7), the biimidazolium dication lies about an inversion centre, the iminiodiacetate ion lies across a mirror

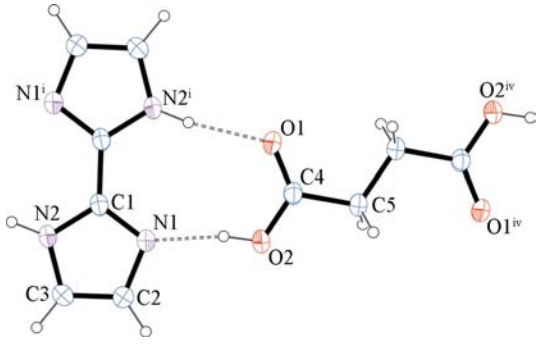

Figure 4
A view of the structure of (II), with displacement ellipsoids drawn at the 30% probability level. Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x+2, -y+1, -z+1$; (iv) $-x, -y+1, -z$.]

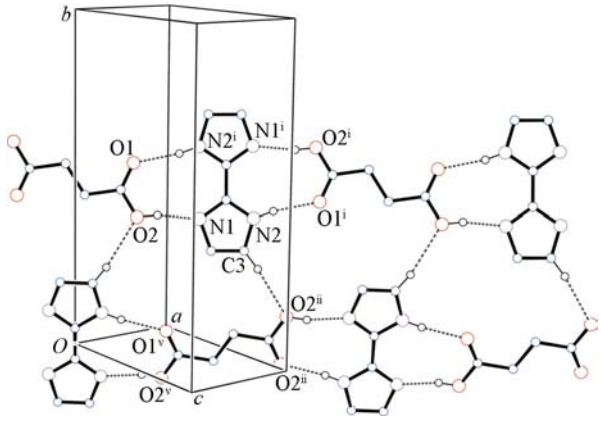

Figure 5
Part of the two-dimensional sheet assembled from O—H···N, N—H···O and C—H···O interactions in (II). Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.]

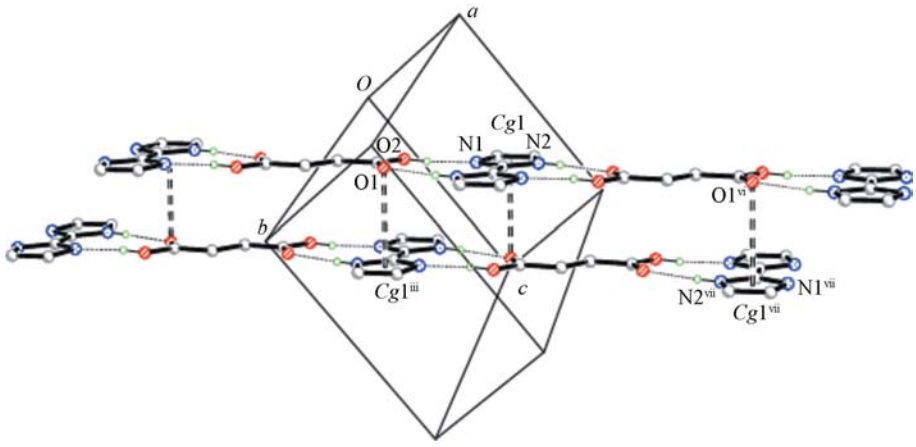

Figure 6
The C═O···π interaction (double dashed lines) between neighbouring sheets in (II). Dotted lines represent hydrogen bonds. [Symmetry codes: (iii) $-x+1, -y+1, -z+1$; (vi) $x+2, y, z+1$; (vii) $-x+3, -y+1, -z+2$.]

plane and the chloride ion lies on a mirror plane. Iminiodiacetate anions and biimidazolium dications are linked to form wave-like tapes by pairs of N—H···O hydrogen bonds (Fig. 8 and Table 3). These tapes are linked to form sheets by weak C3—H3···O1($-x+1, -y+1, -z$) interactions (Fig. 8 and Table 3). The sheets are packed to form a three-dimensional network *via* two N—H···Cl hydrogen bonds and two C5═O1···π interactions to imidazole rings at ($-x, -y+1, -z$) and ($-x+1, -y+1, -z+1$) (Fig. 9 and Table 3).

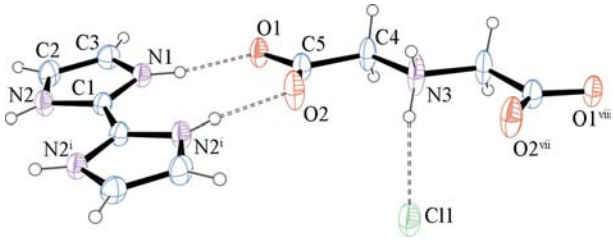

Figure 7
A view of the structure of (III), with displacement ellipsoids drawn at the 30% probability level. Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x, -y+1, -z+1$; (vii) $x, -y+\frac{3}{2}, z$.]

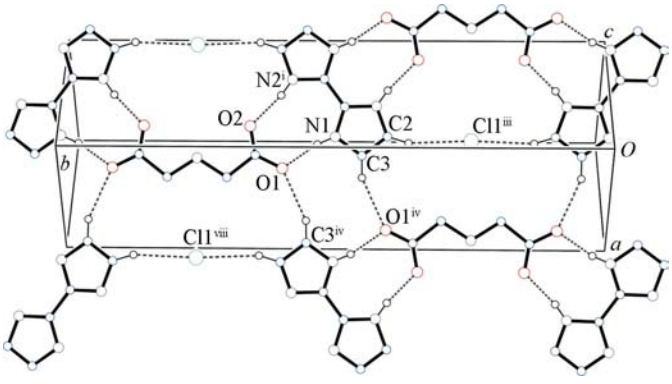

Figure 8
The two-dimensional sheet assembled from N—H···O and C—H···O interactions in (III). Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x, -y+1, -z+1$; (iii) $-x+1, y-\frac{1}{2}, -z+1$; (iv) $-x+1, -y+1, -z$; (viii) $x, y, z-1$.]

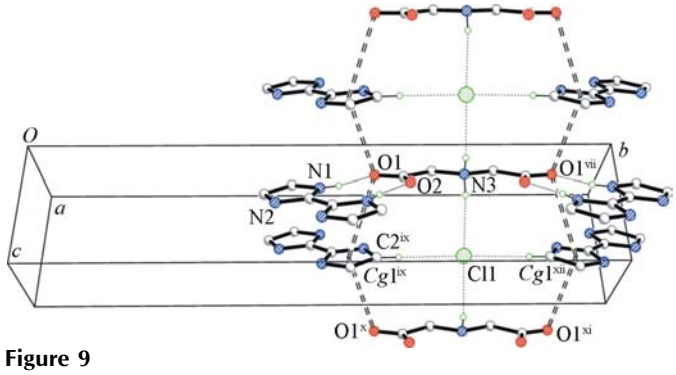

Figure 9
The C═O···π interactions (double dashed lines) between neighbouring sheets in (III). Dotted lines represent hydrogen bonds. [Symmetry codes: (vii) $x, -y+\frac{3}{2}, z$; (ix) $-x, y+\frac{3}{2}, -z+1$; (x) $x+1, y, z+1$; (xi) $x+1, -y+\frac{3}{2}, z+1$; (xii) $-x+1, -y, -z+1$.]

The supramolecular structures of (I), (II) and (III) reveal that they are assembled by the same process, namely that pairs of N—H···O or O—H···N hydrogen bonds link the dicarboxylate and biimidazole molecules to form tapes, which are stacked in parallel through lone-pair–aromatic interactions between carbonyl O atoms and biimidazole groups and are further linked *via* weak C—H···O interactions.

Experimental

Diimidazole (1 mmol) and malonic, succinic or iminodiacetic acid (1 mmol) were dissolved in water (10 ml) by adding 0.7–0.9 ml of 2 *M* HCl while stirring. The solutions were left to stand at room temperature and colourless crystals of (I) and (II) and yellow crystals of (III) were obtained after several days.

Compound (I)

Crystal data

$C_6H_8N_4^{2+}\cdot C_3H_2O_4^{2-}$
$M_r = 238.21$
Monoclinic, $P2_1/c$
$a = 15.663\ (5)$ Å
$b = 4.4319\ (14)$ Å
$c = 18.221\ (4)$ Å
$\beta = 124.517\ (18)^\circ$
$V = 1042.2\ (5)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 298$ K
$0.40 \times 0.40 \times 0.40$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer	4027 measured reflections 1841 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000) T_{min} = 0.845, T_{max} = 0.953	1519 reflections with $I > 2\sigma(I)$ R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041	155 parameters
$wR(F^2)$ = 0.122	H-atom parameters constrained
S = 1.07	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
1841 reflections	$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Compound (II)

Crystal data

$C_6H_6N_4{\cdot}C_4H_6O_4$	V = 574.9 (6) Å^3
M_r = 252.24	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 4.906 (3) Å	μ = 0.12 mm^{-1}
b = 13.887 (8) Å	T = 298 K
c = 8.468 (5) Å	0.30 × 0.30 × 0.27 mm
β = 94.839 (8)°	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	2390 measured reflections 1055 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000) T_{min} = 0.845, T_{max} = 0.970	868 reflections with $I > 2\sigma(I)$ R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046	82 parameters
$wR(F^2)$ = 0.117	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
1055 reflections	$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Compound (III)

Crystal data

$C_6H_8N_4^{2+}{\cdot}C_4H_6NO_4^-{\cdot}Cl^-$	V = 660.8 (3) Å^3
M_r = 303.71	Z = 2
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation
a = 5.3095 (13) Å	μ = 0.31 mm^{-1}
b = 22.941 (6) Å	T = 298 K
c = 5.7023 (14) Å	0.40 × 0.40 × 0.40 mm
β = 107.930 (3)°	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	3079 measured reflections 1158 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000) T_{min} = 0.747, T_{max} = 0.886	1027 reflections with $I > 2\sigma(I)$ R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064	94 parameters
$wR(F^2)$ = 0.180	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 0.69 e Å^{-3}
1158 reflections	$\Delta\rho_{min}$ = −0.32 e Å^{-3}

For compound (III), the systematic absences permitted $P2_1$ or $P2_1/m$ as possible space groups; $P2_1/m$ was selected and confirmed by the structure analysis. H atoms attached to C atoms were placed in geometrically idealized positions and refined with U_{iso}(H) values of $1.2U_{eq}$(C). H atoms attached to N and O atoms were located from difference Fourier maps and refined using a riding model, with U_{iso}(H) values of $1.2U_{eq}$(N) or $1.5U_{eq}$(O) of their parent atoms.

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

*Cg*1 and *Cg*2 are the centroids of the N1/C1/N2/C3/C2 and N3/C4/N4/C6/C5 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{i}	0.86	1.78	2.612 (2)	163
N2—H2A···O4	0.86	1.80	2.646 (2)	166
N3—H3A···O1^{ii}	0.86	1.77	2.609 (2)	166
N4—H4···O2	0.86	1.79	2.626 (2)	164
C2—H2···O2^{iii}	0.93	2.58	3.401 (2)	148
C3—H3···O1^{iv}	0.93	2.41	3.292 (2)	158
C5—H5···O4^{v}	0.93	2.70	3.317 (2)	125
C6—H6···O3^{vi}	0.93	2.45	3.345 (2)	162
C7—O1···$Cg2^{vii}$	1.25 (1)	3.49 (1)	3.714 (3)	90
C9—O3···$Cg1^{vi}$	1.26 (1)	3.54 (1)	3.796 (2)	92
C9—O4···$Cg1^{viii}$	1.24 (1)	3.68 (1)	4.538 (3)	127

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y, -z+1$; (iii) $x, y-1, z$; (iv) $-x, y, -z+\frac{1}{2}$; (v) $x, -y+1, z+\frac{1}{2}$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x, -y+1, -z+1$; (viii) $x, y+1, z$.

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

*Cg*1 is the centroid of the N1/C1/N2/C3/C2 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N1	0.85	1.74	2.575 (2)	169
N2—H2B···O1^{i}	0.86	1.93	2.779 (2)	170
C3—H3···O2^{ii}	0.93	2.41	3.309 (3)	162
C4—O1···$Cg1^{iii}$	1.22 (1)	3.37 (1)	3.720 (3)	97

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

Table 3
Hydrogen-bond and contact geometry (Å, °) for (III).

*Cg*1 is the centroid of the N1/C1/N2/C2/C3 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.82	1.79	2.592 (3)	167
N2—H2A···O2^{i}	0.82	1.83	2.643 (3)	171
N3—H3A···Cl1	0.90	2.56	3.271 (7)	137
N3—H3B···Cl1^{ii}	0.90	2.50	3.244 (7)	141
C2—H2···Cl1^{iii}	0.93	2.63	3.520 (3)	161
C3—H3···O1^{iv}	0.93	2.38	3.253 (4)	156
C5—O1···$Cg1^{v}$	1.26 (1)	3.33 (1)	3.816 (4)	103
C5—O1···$Cg1^{vi}$	1.26 (1)	3.50 (1)	4.029 (4)	106

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

For all compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC* and *ORTEP-3* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3076). Services for accessing these data are described at the back of the journal.

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