

Two-component molecular crystals from *N*-heteroaromatics and nitrobenzoic acids

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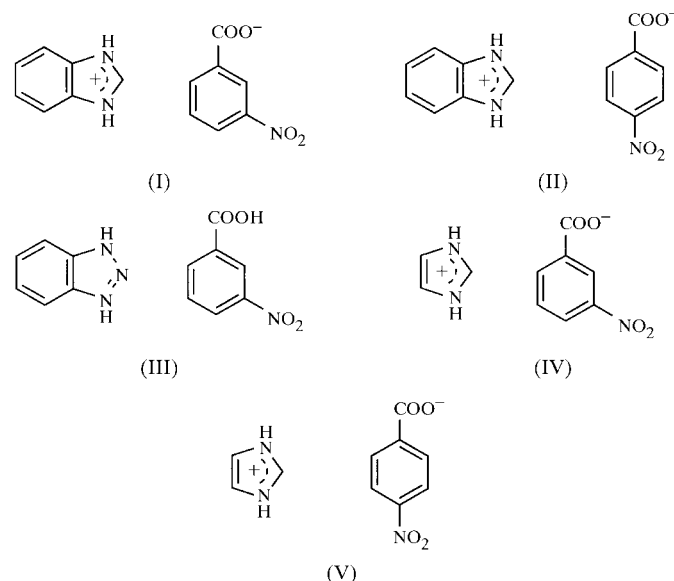
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Five two-component molecular crystals, benzimidazolium 3-nitrobenzoate, $C_7H_7N_2^+ \cdot C_7H_4NO_4^-$, (I), benzimidazolium 4-nitrobenzoate, $C_7H_7N_2^+ \cdot C_7H_4NO_4^-$, (II), 1*H*-benzotriazole–3-nitrobenzoic acid (1/1), $C_6H_5N_3 \cdot C_7H_5NO_4$, (III), imidazolium 3-nitrobenzoate, $C_3H_5N_2^+ \cdot C_7H_4NO_4^-$, (IV), and imidazolium 4-nitrobenzoate, $C_3H_5N_2^+ \cdot C_7H_4NO_4^-$, (V), were prepared with the aim of making chiral crystals. Only (I) crystallizes in a chiral space group. The molecules of (I) and (II) are linked by hydrogen bonds to form 2_1 spiral chains. In (III), (IV) and (V), macrocyclic structures are formed from two acid and two base components, by an alternate arrangement of the acid and base moieties.

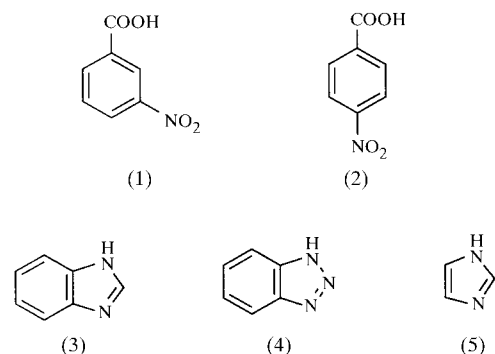
Comment

Chiral crystals composed of achiral molecules have attracted much scientific interest because of both the mystery of chiral generation and their various uses. Many studies aimed at forming chiral crystals have been summarized in the literature (Green *et al.*, 1979; Koshima & Matsuura, 1998*a,b*). It has been reported that mutually interacting bifunctional molecules tend to form chiral crystals by forming spiral structures. In order to obtain chiral crystals, the formation of two-component molecular crystals from organic acids and bases is one of the most promising methods (Koshima & Matsuura, 1998*c*; Koshima *et al.*, 1996, 1999). Chiral two-component molecular crystals are often obtained if, in addition to the formation of a spiral structure, one of the components crystallizes in a non-centrosymmetric space group. In this study, we have prepared chiral two-component molecular crystals using 3- and 4-nitrobenzoic acid, (1) and (2), benzimidazole, (3), benzotriazole, (4), and imidazole, (5), as hydrogen-bonding bifunctional acid and amine components, respectively, and we report herein the structures of the resultant crystals, (I)–(V).

Components (3) and (4) crystallize in the non-centrosymmetric space groups $Pna2_1$ and $P2_1$, respectively (Escande & Galigne, 1974; Escande *et al.*, 1974).



Among the five two-component molecular crystals described here, only (I) belongs to a chiral space group, *viz.* $P2_1$. The H atom of the carboxyl group of (1) in (I) is transferred to atom N3*B* of (3) (Fig. 1), as indicated by the bond distances in the carboxyl and imidazole moieties, and by the IR spectra of (I). The molecules of (1) and (3) are arranged alternately and are linked by hydrogen bonds to form a 2_1 spiral structure (Fig. 2). Neighbouring spirals are connected by C–H...O hydrogen bonds along the *a* and *c* axes.



In (II), the H atom of the carboxyl group is also transferred to the basic N atom, N3*B*, of (4) (Fig. 3) and a 2_1 spiral

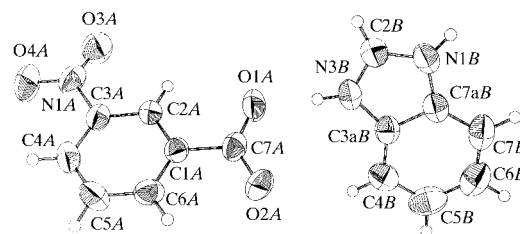


Figure 1

The molecular components of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

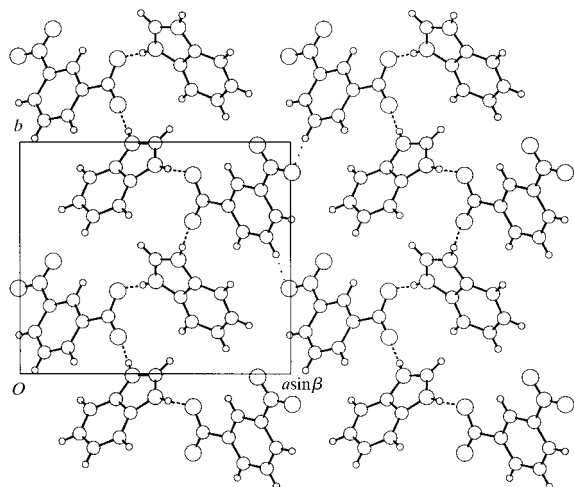


Figure 2
The crystal structure of (I) viewed along the c axis. N—H...O and C—H...O hydrogen bonds are indicated by broken and dotted lines, respectively.

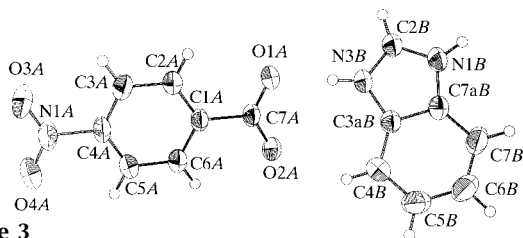


Figure 3
The molecular components of (II) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

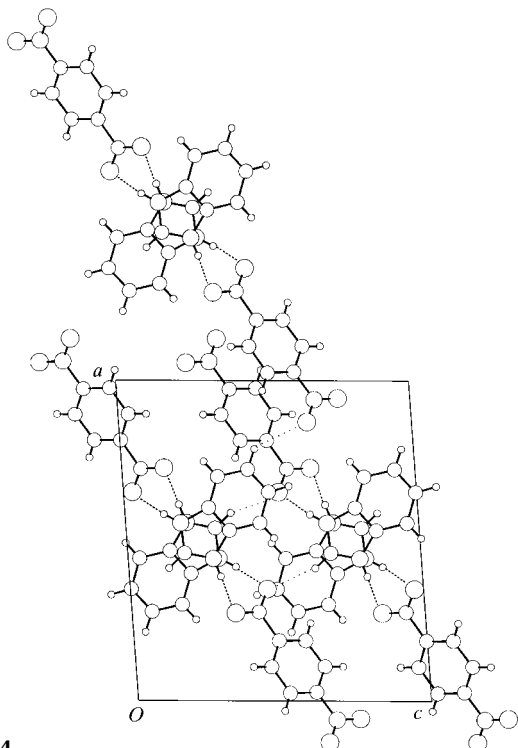


Figure 4
The crystal structure of (II) viewed along the b axis. N—H...O and C—H...O hydrogen bonds are indicated by broken and dotted lines, respectively.

structure is formed along b (Fig. 4). By contrast with (I), neighbouring spirals are mirror images and are engaged and connected by a C—H...O hydrogen bond. Each spiral is also connected to a neighbouring spiral, related by a translation along the a axis, through a C—H...O contact.

The molecular structures of the components of (III) are shown in Fig. 5. Contrary to the other crystals reported here, the H atom of the carboxyl group of (1) is not transferred to atom N3B of (4), as is indicated by the asymmetric C—O and N—N bond distances in the carboxyl and triazole moieties, respectively, and by the IR spectra. The neutral molecular component is due to the lower basicity of (4) compared with that of (3). *PM3* calculations (Stewart, 2000) for (3) and (4) provided the difference between the net charges on the basic N atoms: the Mulliken charges on atom N3B are -0.12 and -0.02 e for (3) and (4), respectively. The crystal structure of (III) is shown in Fig. 6. No spiral structure is found in the crystal, despite the similarity between the molecular structures of (3) and (4). Instead of the spiral structure, a macrocyclic ring is formed from two molecules of (1) and two molecules of (4), around a centre of symmetry. This structure can be regarded as analogous to the well known centrosymmetric dimer structure of carboxylic acids. In the present case, (4) acts

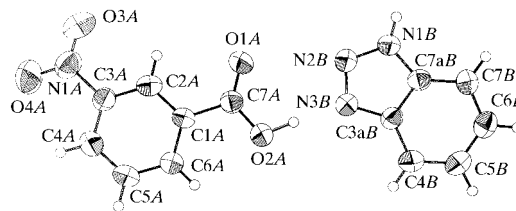


Figure 5
The molecular components of (III) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

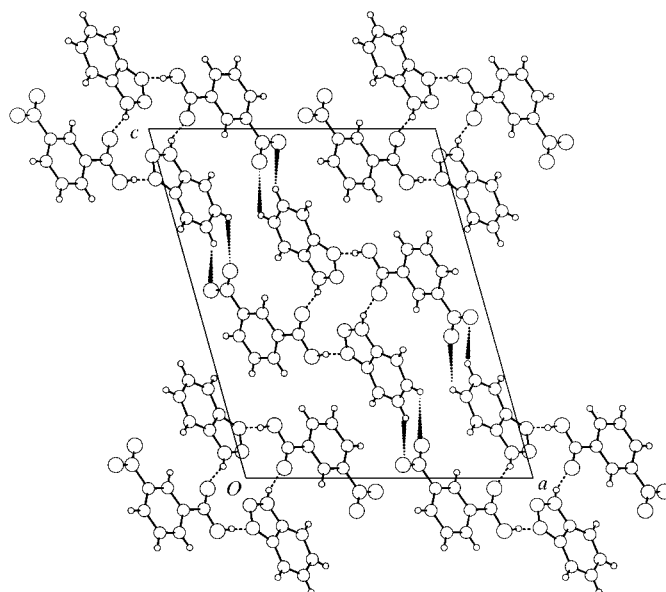


Figure 6
The crystal structure of (III) viewed along the b axis. N—H...O and C—H...O hydrogen bonds are indicated by broken and dotted lines, respectively.

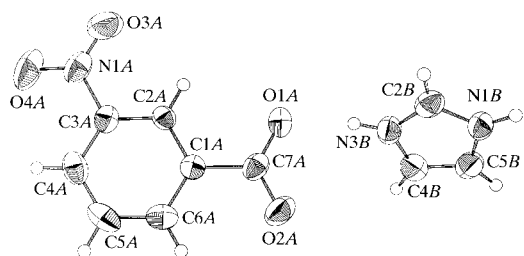


Figure 7

The molecular components of (IV) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

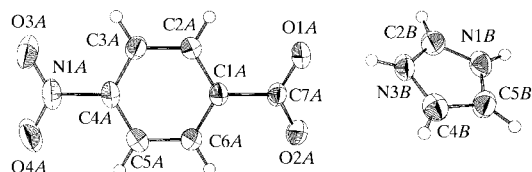


Figure 8

The molecular components of (V) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

as a coupler of the carboxyl groups. The macrocyclic rings are planar to within 0.26 Å and are stacked with an interplanar distance of 3.32 Å. The stacked rings are bridged by the nitro group of (1) from neighbouring macrocyclic rings, related by 2_1 symmetry through C—H...O contacts.

The molecular structures of (IV) and (V) are shown in Figs. 7 and 8, respectively. The H atoms of the carboxyl groups

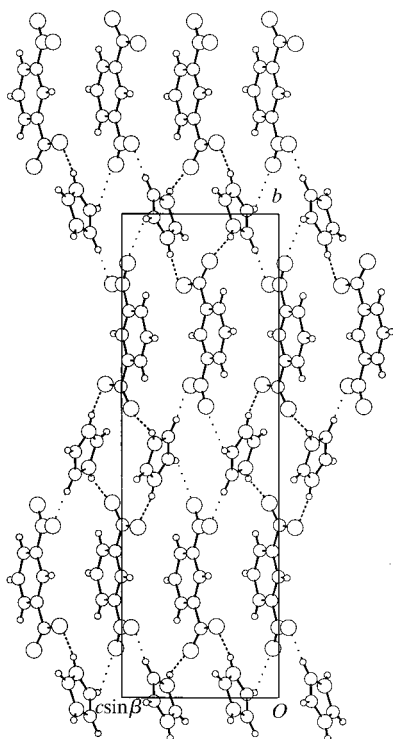


Figure 9

The crystal structure of (IV) viewed along the *a* axis. N—H...O and C—H...O hydrogen bonds are indicated by broken and dotted lines, respectively.

are transferred to the basic N atoms. The crystal structures of (IV) and (V) are shown in Figs. 9 and 10, respectively. No formation of spiral structures is observed in either (IV) or (V). Although the positions of the substituents on the acid components are different, the packing motifs of these crystals are very similar. Each component is arranged alternately along the *b* axis. Centrosymmetric hydrogen-bonding dimer structures are formed, as in (III), and the dimers are linked by

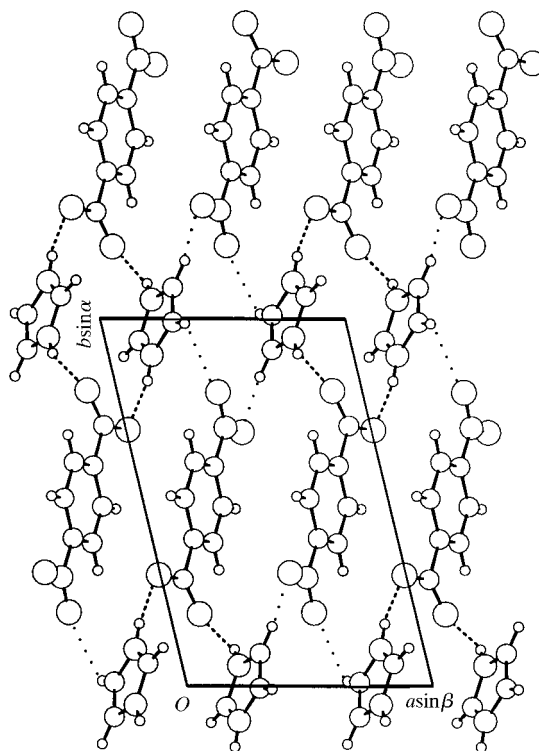


Figure 10

The crystal structure of (V) viewed along the *c* axis. N—H...O and C—H...O hydrogen bonds are indicated by broken and dotted lines, respectively.

C—H...O hydrogen bonds to form dimer structures, in the same manner as those of the N—H...O hydrogen-bonding dimers. The reason why spiral structures are not formed in (IV) and (V) is considered to be due to the difference between the lengths of the longest molecular axes of each component. The importance of molecular lengths for the formation of spiral structures has been discussed for the diastereomeric salts of carboxylic acids with 1-arylethylamine and its derivatives (Kinbara *et al.*, 1996).

Experimental

Crystals of the five compounds were obtained from solutions of equimolar mixtures of the components in acetonitrile–methanol (4:1), methanol, acetonitrile, acetonitrile–methanol (8:1) and acetonitrile–ethanol (5:4) for (I), (II), (III), (IV) and (V), respectively. Cocrystals of (2) and (4) suitable for structure analysis were unfortunately not obtained, in spite of many attempts. IR spectra and elemental analyses were carried out with a Bio-Rad FTS 135 spectrometer and a Yanaco CHN CORDER MT-3 analyser, respectively.

IR spectroscopic data for (I), cm^{-1} : 3423 (*br*), 3136, 3067, 2962, 2896, 2831, 1615, 1525, 1345, 1067, 790, 753, 600; analysis, calculated for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_4$: C 58.94, H 3.89, N 14.73%; found: C 59.23, H 3.97, N 14.91%. IR spectroscopic data for (II), cm^{-1} : 3447 (*br*), 3089, 2990, 1626, 1547, 1516, 1239, 1101, 1005, 800, 750, 721, 612, 517; analysis, calculated for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_4$: C 58.94, H 3.89, N 14.73%; found: C 59.21, H 3.77, N 14.70%. IR spectroscopic data for (III), cm^{-1} : 3470 (*br*), 3213, 1881, 1698, 1616, 1529, 1445, 1351, 1310, 1269, 1220, 1147, 1021, 820, 718, 695; analysis, calculated for $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4$: C 54.55, H 3.52, N 19.58%; found: C 54.23, H 3.56, N 19.61%. IR spectroscopic data for (IV), cm^{-1} : 3450 (*br*), 3160, 3099, 3031, 1593, 1564, 1523, 1376, 1069, 838, 816, 709, 635, 515; analysis, calculated for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_4$: C 51.06, H 3.86, N 17.87%; found: C 51.07, H 4.01, N 17.44%. IR spectroscopic data for (V), cm^{-1} : 3450 (*br*), 3160, 3098, 3010, 1555, 1516, 1392, 1342, 763, 722, 513; analysis, calculated for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_4$: C 51.06, H 3.86, N 17.87%; found: C 51.20, H 3.99, N 17.85%.

Compound (I)

Crystal data

$\text{C}_7\text{H}_7\text{N}_2^+ \cdot \text{C}_7\text{H}_4\text{NO}_4^-$
 $M_r = 285.26$
 Monoclinic, $P2_1$
 $a = 12.522$ (2) Å
 $b = 10.7827$ (12) Å
 $c = 4.8838$ (6) Å
 $\beta = 93.230$ (4)°
 $V = 658.35$ (15) Å³
 $Z = 2$

$D_x = 1.439$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8583 reflections
 $\theta = 2.5\text{--}27.5^\circ$
 $\mu = 0.11$ mm⁻¹
 $T = 297$ K
 Plate, colourless
 $0.45 \times 0.25 \times 0.05$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 Oscillation scans
 10 657 measured reflections
 1568 independent reflections
 1152 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -16 \rightarrow 16$
 $k = -13 \rightarrow 13$
 $l = -6 \rightarrow 6$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.113$
 $S = 1.10$
 1568 reflections
 192 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.0577P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.15$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.037 (7)

Table 1

Selected bond lengths (Å) for (I).

O1A—C7A	1.269 (5)	N1B—C2B	1.326 (5)
O2A—C7A	1.234 (5)	N3B—C2B	1.316 (5)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1B—H1B ⁱ ···O2A ⁱ	0.86	1.86	2.717 (4)	177
N3B—H3B ⁱ ···O1A	0.86	1.69	2.550 (3)	178
C5B—H5B ⁱ ···O3A ⁱⁱ	0.93	2.70	3.553 (6)	153
C5A—H5A ⁱ ···O4A ⁱⁱⁱ	0.93	2.71	3.340 (5)	126

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

Compound (II)

Crystal data

$\text{C}_7\text{H}_7\text{N}_2^+ \cdot \text{C}_7\text{H}_4\text{NO}_4^-$
 $M_r = 285.26$
 Monoclinic, $P2_1/c$
 $a = 13.8524$ (5) Å
 $b = 7.6666$ (4) Å
 $c = 12.5193$ (7) Å
 $\beta = 94.1400$ (17)°
 $V = 1326.09$ (11) Å³
 $Z = 4$

$D_x = 1.429$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 22 373 reflections
 $\theta = 3.0\text{--}30.0^\circ$
 $\mu = 0.11$ mm⁻¹
 $T = 297$ K
 Block, colourless
 $0.60 \times 0.38 \times 0.33$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 Oscillation scans
 23 459 measured reflections
 3869 independent reflections
 2856 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 30^\circ$
 $h = -19 \rightarrow 19$
 $k = -10 \rightarrow 10$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.153$
 $S = 1.07$
 3869 reflections
 191 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 0.2721P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.017 (3)

Table 3

Selected bond lengths (Å) for (II).

O1A—C7A	1.2494 (19)	N1B—C2B	1.3265 (18)
O2A—C7A	1.2632 (18)	N3B—C2B	1.3231 (19)

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1B—H1B ⁱ ···O2A ⁱ	0.86	1.81	2.6600 (15)	171
N3B—H3B ⁱ ···O1A	0.86	1.79	2.6469 (15)	177
C2B—H2B ⁱ ···O2A ⁱⁱ	0.93	2.26	3.125 (2)	155
C6B—H6B ⁱ ···O3A ⁱⁱⁱ	0.93	2.83	3.478 (3)	128

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

Compound (III)

Crystal data

$\text{C}_8\text{H}_5\text{N}_3 \cdot \text{C}_7\text{H}_5\text{NO}_4$
 $M_r = 286.25$
 Monoclinic, $P2_1/n$
 $a = 14.342$ (3) Å
 $b = 5.218$ (1) Å
 $c = 18.161$ (4) Å
 $\beta = 105.40$ (1)°
 $V = 1310.3$ (5) Å³
 $Z = 4$

$D_x = 1.451$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1254 reflections
 $\theta = 1.6\text{--}27.5^\circ$
 $\mu = 0.11$ mm⁻¹
 $T = 297$ K
 Needle, colourless
 $0.35 \times 0.15 \times 0.10$ mm

Data collection

MacScience DIP3000 diffractometer
 Weissenberg scans
 12 254 measured reflections
 2465 independent reflections
 1486 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 26.5^\circ$
 $h = -18 \rightarrow 18$
 $k = -6 \rightarrow 6$
 $l = -22 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.184$
 $S = 1.08$
 2465 reflections
 194 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 1.2302P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.015 (2)

Table 5

Selected bond lengths (Å) for (III).

O1A—C7A	1.211 (4)	N1B—N2B	1.338 (4)
O2A—C7A	1.323 (4)	N2B—N3B	1.311 (4)

Table 6

Hydrogen-bonding geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
O2A—H22A...N3B	1.02 (4)	1.65 (4)	2.669 (4)	173 (3)
N1B—H1B...O1A ⁱ	0.86	2.01	2.826 (4)	157
C5B—H5B...O4A ⁱⁱ	0.93	2.68	3.490 (5)	146
C6B—H6B...O3A ⁱⁱⁱ	0.93	2.75	3.303 (5)	119

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

Compound (IV)

Crystal data

$\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{C}_7\text{H}_4\text{NO}_4^-$
 $M_r = 235.20$
 Monoclinic, $P2_1/c$
 $a = 5.826 (2) \text{ \AA}$
 $b = 23.411 (7) \text{ \AA}$
 $c = 7.556 (2) \text{ \AA}$
 $\beta = 90.53 (3)^\circ$
 $V = 1030.5 (6) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.516 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 297 \text{ K}$
 Plate, colourless
 $0.35 \times 0.23 \times 0.08 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω scans
 4708 measured reflections
 2361 independent reflections
 1081 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$
 $\theta_{\text{max}} = 27.5^\circ$

$h = -7 \rightarrow 7$
 $k = 0 \rightarrow 30$
 $l = -9 \rightarrow 9$
 3 standard reflections
 every 100 reflections
 intensity decay: 0.6%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.131$
 $S = 0.98$
 2361 reflections
 155 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.0063P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0090 (17)

Table 7

Selected bond lengths (Å) for (IV).

O1A—C7A	1.258 (3)	N1B—C2B	1.328 (3)
O2A—C7A	1.252 (3)	N3B—C2B	1.314 (3)

Table 8

Hydrogen-bonding geometry (Å, °) for (IV).

D—H...A	D—H	H...A	D...A	D—H...A
N1B—H1B...O2A ⁱ	0.86	1.93	2.745 (3)	157
N3B—H3B...O1A	0.86	1.80	2.644 (3)	166
C4B—H4B...O4A ⁱⁱ	0.93	2.69	3.372 (3)	130
C5B—H5B...O3A ⁱⁱⁱ	0.93	2.62	3.204 (3)	121

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

Compound (V)

Crystal data

$\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{C}_7\text{H}_4\text{NO}_4^-$
 $M_r = 235.20$
 Triclinic, $P\bar{1}$
 $a = 7.5395 (7) \text{ \AA}$
 $b = 11.8374 (15) \text{ \AA}$
 $c = 5.9689 (12) \text{ \AA}$
 $\alpha = 100.145 (14)^\circ$
 $\beta = 90.731 (13)^\circ$
 $\gamma = 102.998 (9)^\circ$
 $V = 510.19 (13) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.531 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 297 \text{ K}$
 Plate, colourless
 $0.43 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 6177 measured reflections
 2988 independent reflections
 1679 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 30^\circ$

$h = -10 \rightarrow 10$
 $k = -16 \rightarrow 16$
 $l = -8 \rightarrow 8$
 3 standard reflections
 every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.140$
 $S = 1.00$
 2988 reflections
 154 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 0.0303P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

Table 9

Selected bond lengths (Å) for (V).

O1A—C7A	1.256 (2)	N1B—C2B	1.329 (2)
O2A—C7A	1.2536 (19)	N3B—C2B	1.321 (2)

Table 10

Hydrogen-bonding geometry (Å, °) for (V).

D—H...A	D—H	H...A	D...A	D—H...A
N3B—H3B...O1A	0.86	1.80	2.6442 (18)	168
N1B—H1B...O2A ⁱ	0.86	1.94	2.7425 (19)	155
C4B—H4B...O3A ⁱⁱ	0.93	2.68	3.326 (2)	127
C5B—H5B...O4A ⁱⁱⁱ	0.93	2.63	3.236 (2)	123

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

In the data collection for (III), many overlapping Bragg spots were observed on the image plates. The rejection of such spots led to the low completeness of 0.90. All H atoms for compounds (I)–(V) were found on difference maps. The carboxylic acid H atom in (III) was refined freely, giving an O—H bond distance of 1.02 (4) Å and a C—O—H bond angle of 110 (2)°. The remaining H atoms of the five

compounds were refined as riding, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atom. In the refinement of (I), all reflections of Bijvoet pairs were merged, as well as equivalent reflections, because of small imaginary dispersion terms of the component atoms. Subsequently, the imaginary dispersion terms were set to zero.

For compounds (I) and (II), data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999). For compound (III), data collection: *DIP3000 Control Programs* (MacScience, 1992); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997). For compounds (IV) and (V), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN*. For all five compounds, program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1039). Services for accessing these data are described at the back of the journal.

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