2-Aminobenzimidazolium *O*-ethyl malonate: eight independent N—H···O hydrogen bonds generate sheets

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The title compound, $C_7H_8N_3{}^+ \cdot C_5H_7O_4{}^-$, crystallizes with $Z' = 2$ in space group $P2_1/c$; eight independent N—H···O hydrogen bonds [H···O = 1.75–1.88 Å, N···O = 2.699 (2)–2.829 (2) Å and N—H···O = 147–179°] link the four independent ions into sheets.

Comment

The title adduct, (I), was isolated as a direct intermediate in the synthesis of dihydropyrimido[1,2-*a*]benzimidazolones from a three-component reaction of 2-aminobenzimidazole with Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) and arylaldehydes. In fact, compound (I) is formed without participation of the arylaldehyde component and results simply from the reaction between 2-aminobenzimidazole and Meldrum's acid. It can also be obtained directly by reaction of 2-aminobenzothiazole with malonic acid monoethyl ester (see reaction scheme).

Compound (I) is a salt crystallizing with $Z' = 2$ in space group $P2_1/c$. The C—C and C—N distances in the two independent cations are very similar (Table 1) and both cations approximate to local C_{2v} ($mm2$) symmetry. The C—C distances in the cations span a rather narrow range, from 1.374 (3) to 1.400 (3) Å, consistent with classical aromatic delocalization. The C—N distances are indicative of guanidinium-type delocalization and this can be further explored in terms of the corresponding bond orders, calculated using the recent recalibration by Kotelevskii & Prezhdo (2001) of the original equation relating bond order to bond length (Gordy, 1947). If, for this purpose, the dimensions of the two cations

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are averaged under assumed local C_{2v} symmetry, the averaged C—NH$_2$ bond has a bond order of 1.77, the averaged endocyclic guanidinium bond has a bond order of 1.63, while the C—N bond exocyclic to the aromatic ring has a bond order of only 1.37. These values indicate strong guanidinium delocalization, isoelectronic with carbonate, with only modest interaction between the aromatic 6π system and the guanidinium


(I)
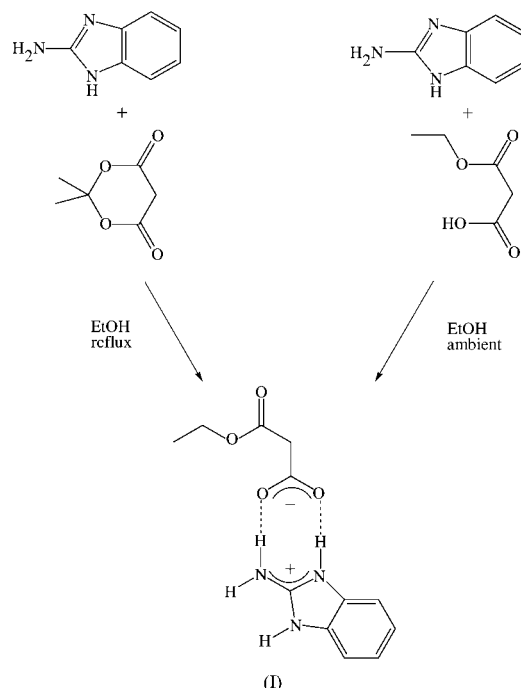
6π system. A similar pattern of C—N distances was found in 2-aminobenzimidazolium nitrate, where there are four independent cations in the asymmetric unit (Bats *et al.*, 1999). The bond distances within the two anions of (I) show no unusual values, but the conformations of the anions are different, particularly in respect of the *O*-ethyl groups, as demonstrated by the principal torsion angles (Table 1).

The four independent ions are linked by eight N—H···O hydrogen bonds (Table 2) into a two-dimensional structure of some complexity. With such a number of independent molecular components, there is considerable flexibility in the selection of the asymmetric unit. For simplicity of analysis and description of the supramolecular aggregation, it has been found convenient to specify the asymmetric unit in terms of the formation of two neutral ion-pair aggregates (Fig. 1), in each of which a cation is linked to an anion by means of two N—H···O hydrogen bonds, all four of which are nearly linear. Cation 1 (containing atom N11) and anion 1 (containing atom O31) form neutral aggregate 1 (Fig. 1*a*), while cation 2 (containing atom N21) and anion 2 (containing atom O41) form neutral aggregate 2 (Fig. 1*b*). There are then four N—H···O hydrogen bonds which link these aggregates into sheets and it is convenient to consider the action of each of these in turn.

Amino atom N11 in the type 1 aggregate at (*x*, *y*, *z*) acts as hydrogen-bond donor, *via* H11*B*, to carboxylate atom O41 in the type 2 aggregate also at (*x*, *y*, *z*); N21 in aggregate 2 at
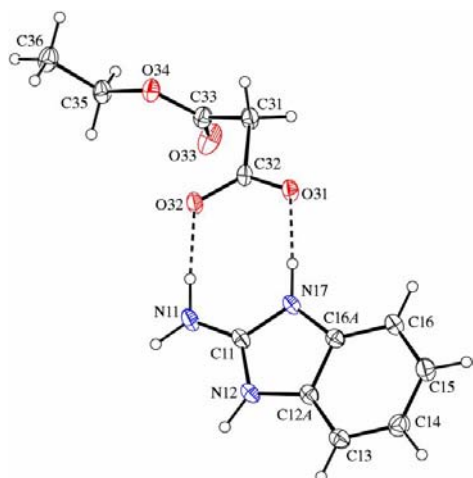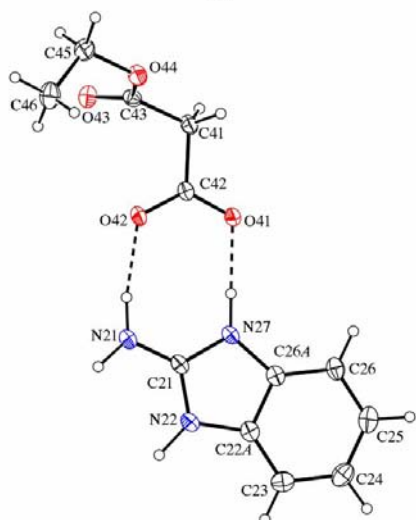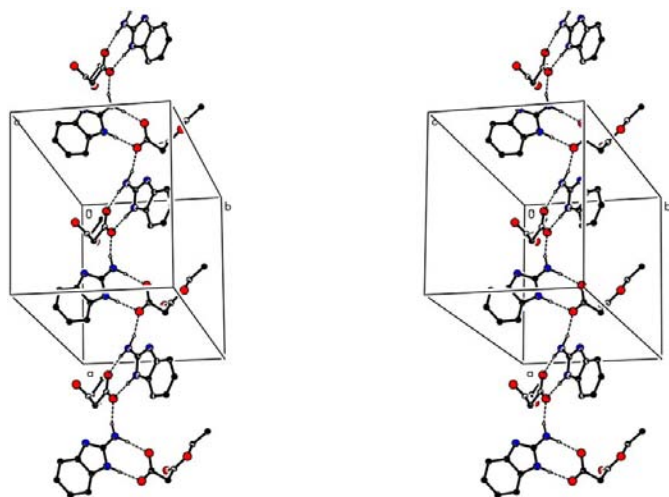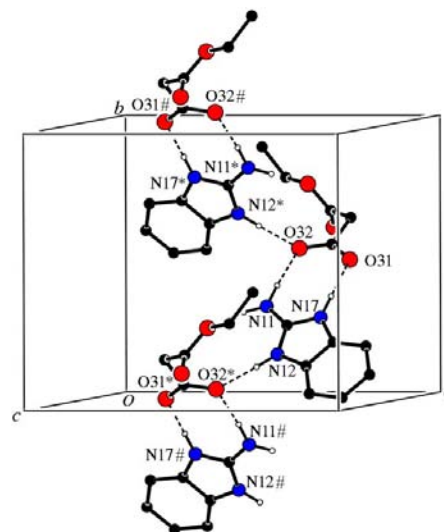
Figure 1
The independent components of compound (I), showing the atom-labelling schemes for (*a*) the neutral aggregate of type 1 and (*b*) the neutral aggregate of type 2. Displacement ellipsoids are drawn at the 30% probability level.
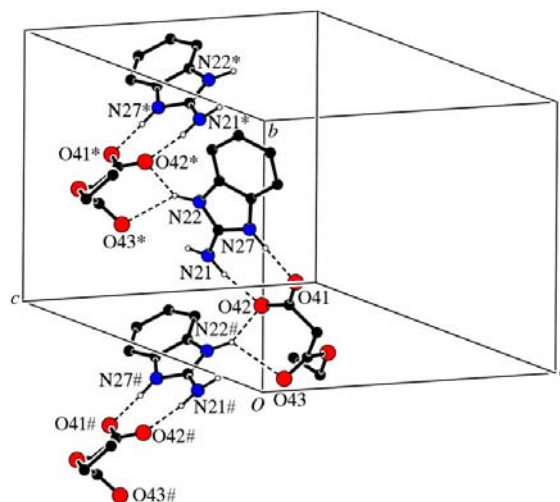

Figure 2
Stereoview of part of the crystal structure of (I), showing the formation of a chain of rings along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

(*x, y, z*) in turn acts as hydrogen-bond donor, *via* H21*B*, to carboxylate atom O31 in the type 1 aggregate at ($-1 + x, y, z$). Propagation of these two hydrogen bonds then generates by translation a $C_4^2(12)[R_2^2(8)][R_2^2(8)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to the [100] direction (Fig. 2).

There are two further N—H···O hydrogen bonds, one of which involves only the type 1 aggregates, while the other involves only type 2 aggregates. Atom N12 in the type 1 aggregate at (*x, y, z*) acts as hydrogen-bond donor to carboxylate atom O32 at ($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$), so producing a $C_2^1(6)[R_2^2(8)]$ chain of rings running parallel to the [010] direction and generated by the 2_1 screw axis along ($\frac{1}{2}, y, \frac{1}{4}$) (Fig. 3). In a similar way, atom N22 in the type 2 aggregate at

Figure 3
Part of the crystal structure of compound (I), showing the formation of a [010] chain of rings formed by the type 1 aggregates. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$) and ($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$), respectively.

Figure 4
Part of the crystal structure of compound (I), showing the formation of a [010] chain of rings formed by the type 2 aggregates. For the sake of clarity, H atoms bonded to C atoms have been omitted, but the long H···O contact (see *Comment*) is shown. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($-x, \frac{1}{2} + y, \frac{1}{2} - z$) and ($-x, -\frac{1}{2} + y, \frac{1}{2} - z$), respectively.

(x, y, z) acts as hydrogen-bond donor to carboxylate atom O42 at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, so generating a second $C_2^1(6)[R_2^2(8)]$ chain of rings around the 2_1 axis along $(0, y, \frac{1}{4})$ (Fig. 4). This last hydrogen bond is accompanied by, and possibly weakly augmented by, a long contact between H22 at (x, y, z) and O43 at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ [H···O = 2.50 Å, N···O = 3.150 (2) Å and N—H···O = 121°], although it is doubtful if this can be regarded as a hydrogen bond.

The combination of [100] and [010] chains generates a (001) sheet. Two such sheets, related to one another by inversion, pass through each unit cell in the domains $-0.03 < z < 0.53$ and $0.47 < z < 1.03$, but there are no direction-specific interactions between adjacent sheets. The two-dimensional supramolecular structure of (I) may be contrasted with the ribbon-type structure formed by 2-aminobenzimidazolium nitrate (Bats *et al.*, 1999).

Experimental

A mixture of 2-aminobenzimidazole (0.20 g, 1.50 mmol), Meldrum's acid (0.22 g, 1.52 mmol) and ethanol (10 ml) was heated under reflux for 1 h. Compound (I) was formed as a white solid which was collected by filtration and washed with ethanol (84% yield; m.p. 430 K). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by crystallization from ethanol. Compound (I) was also obtained by crystallization from an ethanol solution containing equimolar amounts of 2-aminobenzimidazole and malonic acid monoethyl ester.

Crystal data

$C_7H_8N_3^+ \cdot C_5H_7O_4^-$	$D_x = 1.341$ Mg m^{-3}
$M_r = 265.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5983
$a = 12.0121$ (2) Å	reflections
$b = 10.5379$ (2) Å	$\theta = 3.2$–27.5°
$c = 20.8249$ (6) Å	$\mu = 0.10$ mm^{-1}
$\beta = 94.7550$ (8)°	$T = 120$ (2) K
$V = 2626.99$ (10) Å^3	Plate, colourless
$Z = 8$	$0.22 \times 0.16 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer	5983 independent reflections
φ scans, and ω scans with κ offsets	4204 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.115$
(*DENZO–SMN*; Otwinowski &	$\theta_{max} = 27.5°$
Minor, 1997)	$h = -15 \rightarrow 15$
$T_{min} = 0.974$, $T_{max} = 0.998$	$k = -13 \rightarrow 13$
33 691 measured reflections	$l = -27 \rightarrow 27$

Table 1
Selected geometric parameters (Å, °).

O31—C32	1.253 (2)	O41—C42	1.262 (2)
O32—C32	1.255 (2)	O42—C42	1.253 (2)
C11—N11	1.317 (3)	C21—N21	1.325 (3)
C11—N12	1.341 (3)	C21—N22	1.342 (3)
C11—N17	1.350 (2)	C21—N27	1.347 (3)
N12—C12A	1.401 (3)	N22—C22A	1.395 (3)
N17—C16A	1.390 (3)	N27—C26A	1.391 (3)
O31—C32—C31—C33	160.1 (2)	O41—C42—C41—C43	−178.5 (2)
C32—C31—C33—O34	89.9 (2)	C42—C41—C43—O44	10.5 (2)
C32—C31—C33—O33	−88.7 (3)	C42—C41—C43—O43	−69.5 (3)
C31—C33—O34—C35	−176.0 (2)	C41—C43—O44—C45	−178.2 (2)
C33—O34—C35—C36	−179.5 (2)	C43—O44—C45—C46	89.1 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···O32	0.97	1.83	2.797 (2)	175
N11—H11B···O41	0.93	1.87	2.781 (2)	164
N12—H12···O32^i	0.93	1.81	2.724 (2)	168
N17—H17···O31	0.94	1.83	2.759 (2)	168
N21—H21A···O42	0.96	1.88	2.829 (2)	170
N21—H21B···O31^{ii}	1.01	1.81	2.794 (2)	166
N22—H22···O42^{iii}	1.03	1.81	2.739 (2)	147
N27—H27···O41	0.95	1.75	2.699 (2)	179

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.061$	$+ 0.7506P]$
$wR(F^2) = 0.171$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
5983 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
346 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0125 (18)

All H atoms were located in difference maps. H atoms bonded to C atoms were subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH$_3$) and 0.99 Å (CH$_2$). H atoms bonded to N atoms were allowed to ride at the positions identified from the difference maps (N—H = 0.93–1.03 Å).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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