organic compounds

2-Amino-5-chloro-1,3-benzoxazol-3-ium 2-(3,4-dichlorophenoxy)acetate

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The 1:1 organic salt of the title compound, $C_7H_6ClN_2O^+ \cdot C_8H_5Cl_2O_3^-$ or [(2-ABOX)(3,4-D)], comprises the two constituent molecules associated by an $R_2^2(8)$ graph-set interaction through the carboxylate group of 3,4-D across the protonated N/N sites of 2-ABOX [N···O 2.546 (3) and 2.795 (3) Å]. Cation/anion pairs associate across an inversion centre forming discrete tetramers via an additional three-centre hydrogen-bonding association from the latter N amino proton to a phenoxy O atom [N···O 3.176 (3) Å] and a carboxylate O atom [N···O 2.841 (3) Å]. This formation differs from the polymeric hydrogen-bonded chains previously observed for adduct structures of 2-ABOX with carboxylic acids.

Comment

2-Amino-5-chloro-1,3-benzoxazole (2-ABOX), first prepared in 1953 (Nagana et al., 1953), was formerly used as a skeletal muscle relaxant and is a uricosuric agent in gout. It is commonly known as Zoxazolamine; other names include Deflexol, Flexilon, Flexin, Zoxamin, Zoxine and McN-485 (Stecher, 1968). 2-ABOX is the only commercially available 2-amino-1,3-oxazole which we have investigated in tandem with the more readily available 2-amino-1,3-thiazole derivatives. Studies on the carboxylic acid adducts of 2-amino-1,3-thiazole derivatives (Lynch et al., 1998; Lynch, Nicholls et al., 1999; Lynch, Cooper et al., 1999) have shown that there is a significant difference in the two distances between the non-H atoms involved in the dominant $R_2^2(8)$ graph-set association

(I)
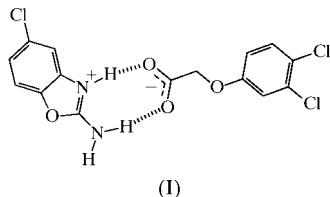
(Etter, 1990). For the 2-amino-1,3-thiazole series, the average distance difference [i.e. N21A—O(acid) minus N3A—O(acid)] from 13 examples is 0.109 Å, whereas for three

2-ABOX complexes, the equivalent average difference is 0.213 Å (Lynch et al., 2000). Thus, to increase the data set of 2-amino-1,3-oxazole complexes, we report here the 2-ABOX complex with 2-[(3,4-dichlorophenyl)oxy]acetic acid (3,4-D), as [(2-ABOX)(3,4-D)], (I), which itself is an active member of the herbicidal phenoxyacetic acid series (Crafts, 1957).

Phenoxyacetic acids primarily exist in the solid state in either one of two conformations, synplanar (i.e. hooked) or antiperiplanar (i.e. flat). Depending on the adducting molecule, examples of 2-[(2,4-dichlorophenyl)oxy]acetic acid and 2-[(2,4,5-trichlorophenyl)oxy]acetic acid in both conformations are known (Lynch, Nicholls et al., 1999). The two previously reported adducts of 3,4-D, those with triphenylphosphine oxide (Lynch et al., 1993) and 2-aminopyrimidine (Lynch et al., 1994), as well as the parent structure of 3,4-D (Smith et al., 1981), only show 3,4-D in the antiperiplanar conformation. This is also the case in the 3,4-D molecule reported here; the three important torsion angles are listed in Table 1 and the dihedral angle between the plane of the carboxylate group and the phenyl ring is 15.67 (6)°. The carboxylate group of 3,4-D associates with the protonated N3A/N21A site of 2-ABOX; details are listed in Table 2.

The solid-state packing of the two associated molecules in (I) deviates from that observed for both previously reported 2-ABOX and 2-amino-1,3-thiazole complexes because in these structures, the second amino proton hydrogen bonds to an adjacent carboxylate O atom, thus propagating a one-dimensional hydrogen-bonded chain. However, the two coplanar molecules in (I) lie near an inversion centre which in
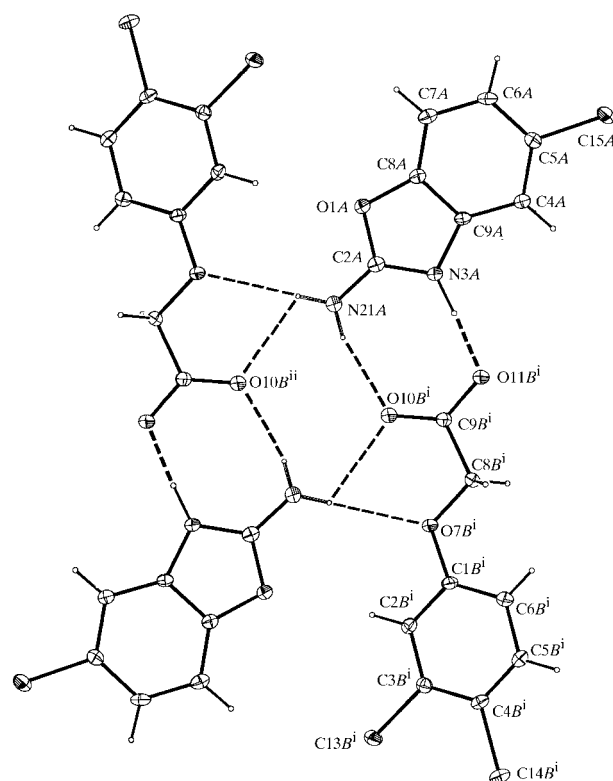

Figure 1
The molecular configuration and atom-numbering scheme of (I), showing 30% probability ellipsoids and hydrogen-bonding interactions as broken lines.

the unit cell produces a hydrogen-bonded cyclic tetramer, as shown in Fig. 1. The associations proceed *via* a three-centre interaction from the second N21 proton to both the phenoxy (O7*B*) and a carboxylate (O10*B*) O atom [$R_1^2(5)$ graph set]; details are listed in Table 2.

An interesting observation that has been made with the 2-amino-substituted heterocyclic bases used in these series of studies is that the C2*A*—N21*A* bond, which should be an sp^3 C—N bond, is consistently shorter than the adjacent C2*A*—N3*A* bond, which should be an sp^2 C=N bond; relevant bond distances for (I) are listed in Table 1. This has been observed in all carboxylic acid complexes of 2-aminopyridine, 2-aminopyrimidine, 3-amino-1,2,4-triazole, 2-amino-1,3-thiazole derivatives and 2-amino-5-chloro-1,3-benzoxazole, but not in their parent structures where the bonding distances are as expected with C—NH$_2$ > C=N. The occurrence of the shorter C—NH$_2$ bond cannot be explained in terms of whether the bases exist as cations. If this were so then the double bond could shift to form C=NH$_2^+$, with the heterocyclic N atom still retaining three bonds. However, the inconsistency in bond distances is observed irrespective of the acid proton location. We currently have no explanation for this interesting phenomenon, but before any meaningful molecular modelling results can be obtained, we need an extensive and diverse database of good quality cocrystal complexes from which to extract information.

Experimental

The synthesis of (I) was carried out by refluxing equimolar amounts (2 mmol) of 2-amino-5-chloro-1,3-benzoxazole (Aldrich) and 2-(3,4-dichlorophenyloxy)acetic acid (Lancaster) for 15 min at *ca* 350 K in 40 ml of 95% ethanol. Crystals were obtained by total evaporation of the solvent at room temperature (m.p. 438–439 K).

Crystal data

$C_7H_6ClN_2O^+\cdot C_8H_5Cl_2O_3^-$	$D_x = 1.669$ Mg m^{-3}
$M_r = 389.61$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 74
$a = 18.526$ (4) Å	reflections
$b = 6.9600$ (15) Å	$\theta = 20$–22°
$c = 12.759$ (3) Å	$\mu = 5.582$ mm^{-1}
$\beta = 109.512$ (16)°	$T = 150$ (2) K
$V = 1550.6$ (6) Å^3	Needle, colourless
$Z = 4$	$0.77 \times 0.14 \times 0.14$ mm

Data collection

Stoe Stadi-4 diffractometer	$R_{int} = 0.05$
ω–θ scans	$\theta_{max} = 70.35°$
Absorption correction: by integration (Stoe & Cie, 1995)	$h = -4 \rightarrow 22$
$T_{min} = 0.311$, $T_{max} = 0.615$	$k = -8 \rightarrow 7$
	$l = -15 \rightarrow 14$
3506 measured reflections	3 standard reflections
2827 independent reflections	frequency: 60 min
2430 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 1.4716P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2827 reflections	$\Delta\rho_{max} = 0.62$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C2*A*—N21*A*	1.301 (4)	C2*A*—N3*A*	1.322 (3)
C2*B*—C1*B*—O7*B*—C8*B*	175.0 (2)	O7*B*—C8*B*—C9*B*—O11*B*	170.3 (2)
C1*B*—O7*B*—C8*B*—C9*B*	−179.9 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N21*A*—H21*A*···O10*B*^{i}	0.88	1.95	2.795 (3)	161
N21*A*—H22*A*···O7*B*^{ii}	0.88	2.31	3.176 (3)	170
N21*A*—H22*A*···O10*B*^{ii}	0.88	2.46	2.841 (3)	106
N3*A*—H3*A*···O11*B*^{i}	0.88	1.68	2.546 (3)	168

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

After establishing that complex (I) was a salt by initially locating the acid proton in the difference syntheses, all H atoms were then included in the refinement at calculated positions as riding models, with C—H distances in the range 0.95 to 0.99 Å and N—H at 0.88 Å.

Data collection: *DIF*4 (Stoe & Cie, 1990); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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