

## 2-Amino-2-thiazoline and its 1:1 organic salt with 2-naphthoxyacetic acid

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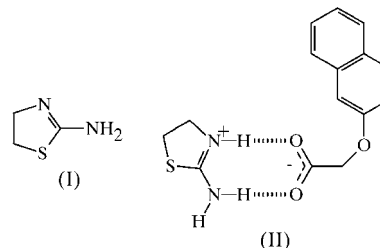
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The crystal structures of 2-amino-2-thiazoline,  $C_3H_6N_2S$ , and 2-amino-2-thiazolinium 2-naphthoxyacetate,  $C_3H_7N_2S^+ \cdot C_{12}H_9O_3^-$ , are reported. The structure of 2-amino-2-thiazoline consists of two unique molecules that construct a convoluted hydrogen-bonded ribbon involving  $R_2^2(8)$  graph-set association *via* both  $N-H \cdots N$  and  $N-H \cdots S$  interactions. The organic salt structure consists of the two molecules associated *via* an  $R_2^2(8)$  graph-set dimer through  $N-H \cdots O$  interactions, with the hydrogen-bonding network propagated *via* additional  $N-H \cdots O$  three-centre interactions from the second 2-amino H atom.

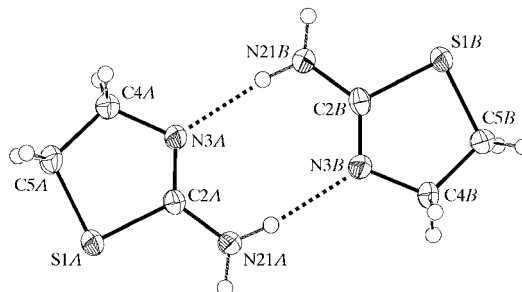
### Comment

2-Amino-2-thiazoline has been reported as a potential inducer of the reverse transformation of tumour cells, with the mechanism for anticancer action depending on strong metal-ligand binding *via* the N atoms (Brugarolas & Gosálvez, 1982). Alternatively, the placement of the N atoms in this molecule also makes it suitable for association with carboxylic acids, and four subsequent crystal structures have been reported (Lynch *et al.*, 1998; Lynch, Cooper *et al.*, 1999; Lynch, Nicholls *et al.*, 1999). Such structures are part of a broader study of complexes of carboxylic acids with 2-aminothiazole derivatives that has thus far resulted in the characterization of 19 published crystal structures, with three others published recently (Lynch *et al.*, 2004). Although the structure of 2-aminothiazole was published by Caranoni & Reboul (1982), the structure of 2-amino-2-thiazoline has not been reported; the structure of this compound, (I), is reported here. 2-Naphthoxyacetic acid is used as a plant hormone to promote growth of roots on clippings and to prevent fruit from falling prematurely, although stunted growth results if it is used in excess (The Merck Index, 2001). 2-Naphthoxyacetic acid is related in structure to phenoxyacetic acid, whose chloro derivatives have been used extensively by the author for complexing with carboxylic acids (Lynch, Cooper *et al.*, 1999) and should thus have comparable structural properties.

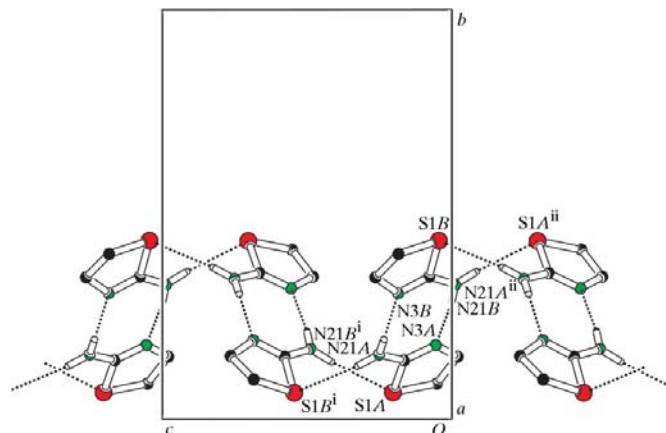
Furthermore, the Cambridge Structural Database (Allen, 2002) contains only four previously reported crystal structures containing the compound, of which two are the parent structure (Howie *et al.*, 2001), thus more structures containing 2-naphthoxyacetic acid are required. For these reasons, the structure of the 1:1 organic salt of (I) with 2-naphthoxyacetic acid is also reported here, *viz.* (II).



Compound (I) packs with two unique thiazoline molecules associated in a hydrogen-bonded  $R_2^2(8)$  graph-set dimer (Etter, 1990) *via*  $N-H \cdots N$  interactions (Fig. 1). The hydrogen-bonding network is then extended by  $N-H \cdots S$  interactions, resulting in further  $R_2^2(8)$  graph-set arrangements. Hydrogen-bonding associations for this compound are listed in Table 1. Together, these interactions create a convoluted



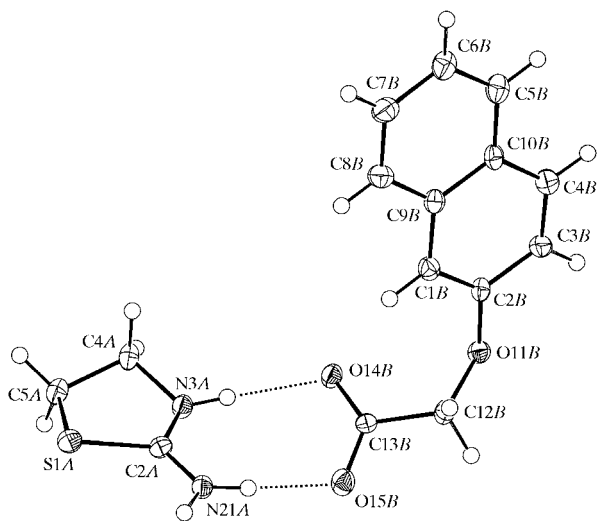
**Figure 1**  
A view of the asymmetric unit and atom-numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level. Broken lines indicate intramolecular hydrogen bonds.



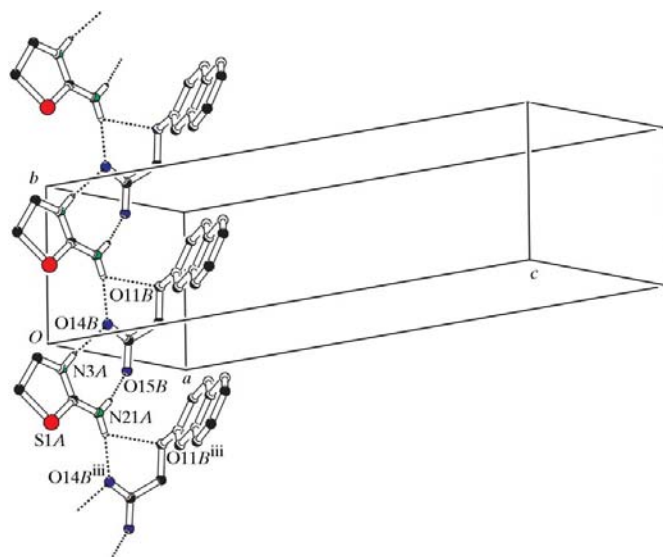
**Figure 2**  
A packing diagram for (I). [Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .]

hydrogen-bonded ribbon that runs in the direction of the *ac* axis diagonal (Fig. 2). The incorporation of the S atoms into the hydrogen-bonding network is not observed in the structure of 2-aminothiazole but is seen in the structure of a related 2-aminothiazole derivative, *viz.* 2-amino-4-(4-bisphenyl)-1,3-thiazole (Lynch *et al.*, 2002). In (I), there is a single S $\cdots$ S close contact [3.520 (5) Å] between atom S1B and the symmetry-equivalent atom at (2 - *x*, 1 - *y*, -*z*).

The structure of (II) comprises the organic salt of a non-planar acetate molecule and a protonated thiazoline molecule arranged in a packing mode commonly observed for these types of molecules. In contrast to its planar parent structure, the acetate chain of the naphthoxyacetate molecule in (II) adopts an anticlinal (or hooked) arrangement, as classified for phenoxyacetic acids (Smith & Kennard, 1979) and defined by the C2B–O11B–C12B–C13B torsion angle [92.8 (2)°; Fig. 3]. Packing with the thiazoline molecule has an associated effect on (2,4,5-trichlorophenoxy)acetic acid, whose structure is planar in the parent compound but hooked in the salt complex (Lynch, Cooper *et al.*, 1999). The components of (II), like those of the vast majority of adducts/organic salts comprising a 2-amino-heterocycle and a carboxylic acid molecule, associate *via* an unsymmetrical  $R_2^2(8)$  graph-set dimer between the N=C–NH<sub>2</sub> site and the carboxylate group (Fig. 4). In general, this association is unsymmetrical in that the N3A $\cdots$ O14B distance, or equivalent, is (apart from a very few cases) shorter than the N21A $\cdots$ O15B distance, although the values listed in Table 2 indicate that the structure of (I) is one of the very few exceptions where the opposite has occurred. Another common feature of this association is the inconsistency of the C2A–N21A [1.302 (2) Å] and C2A–N3A [1.324 (2) Å] bond lengths, as previously highlighted (Lynch *et al.*, 2000). The propagation of the hydrogen-bonding network *via* the N21A–H22A $\cdots$ O14B(*x*, *y* - 1, *z*) interaction has also been observed previously for these types of systems



**Figure 3**  
A view of the asymmetric unit and atom-numbering scheme of (II). Displacement ellipsoids are drawn at the 50% probability level. Broken lines indicate intramolecular hydrogen bonds.



**Figure 4**  
A packing diagram for (II). [Symmetry code: (iii) *x*, *y* - 1, *z*.]

(Lynch, Nicholls *et al.*, 1999), although the additional interaction with atom O11B is not common amongst complexes of 2-aminothiazole derivatives and phenoxyacetic acids (Lynch, Cooper *et al.*, 1999).

The structure of (II) is actually the eighth known complex of a carboxylic acid with (I), with three others currently unpublished (Lynch *et al.*, 2004). Elucidation of the structure of (I) is important because, as highlighted above, when collecting data on the inconsistencies in the bond distances across the N=C–NH<sub>2</sub> site for any type of complexed 2-amino-heterocyclic compound, it is important to compare bond distances against those of the parent structure. For example, compare the C2A–N21A and C2A–N3A distances listed above with those for (I), *viz.* 1.348 (5)/1.267 (5) and 1.351 (5)/1.276 (5) Å for molecules *A* and *B*, respectively. The mean respective distances for the seven complex structures are 1.305 (5) and 1.314 (5) Å. Also of interest is the N3–C2–N21 (or equivalent) angle, which decreases upon association with a carboxylic acid. Compare, for (I), values of 124.8 (3) and 125.8 (3)° with that of 124.53 (17)° in (II) [the mean angle over the eight structures is 124.0 (5)°]. In one or two instances where N1A is a quaternary N atom, it might be suitable to suggest that the N1A–C2A double bond has moved to C2A–N21A, but this simple ‘pushing of the double bond around’ does not fit a significant portion of the available data. It is the intention of the author to publish such findings in a dedicated paper, but not without each of the parent structures and a supportive list of different complexes, which the structures in this paper add to.

## Experimental

Crystals of (I) were grown from an ethanol solution. For (II), equimolar amounts of (I) and 2-naphthoxyacetic acid were refluxed in ethanol for 20 min. Crystals of (II) were grown by slow evaporation of the reaction solution.

## Compound (I)

## Crystal data

$C_3H_6N_2S$   
 $M_r = 102.17$   
 Monoclinic,  $P2_1/n$   
 $a = 5.8980$  (5) Å  
 $b = 14.8324$  (12) Å  
 $c = 10.7092$  (8) Å  
 $\beta = 101.974$  (4)°  
 $V = 916.47$  (13) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.481$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8580 reflections  
 $\theta = 2.9$ – $27.5$ °  
 $\mu = 0.53$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Prism, yellow  
 $0.20 \times 0.20 \times 0.10$  mm

## Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.826$ ,  $T_{\max} = 0.948$   
 10 396 measured reflections

2101 independent reflections  
 1149 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.112$   
 $\theta_{\text{max}} = 27.5$ °  
 $h = -7 \rightarrow 7$   
 $k = -19 \rightarrow 19$   
 $l = -13 \rightarrow 13$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.061$   
 $wR(F^2) = 0.160$   
 $S = 1.02$   
 2101 reflections  
 109 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0802P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.49$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.41$  e Å<sup>-3</sup>

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N21A-H21A\cdots N3B$	0.88	2.09	2.950 (5)	164
$N21A-H22A\cdots S1B^i$	0.88	2.75	3.575 (3)	156
$N21B-H21B\cdots N3A$	0.88	2.04	2.916 (5)	171
$N21B-H22B\cdots S1A^{ii}$	0.88	2.70	3.526 (3)	156

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

## Compound (II)

## Crystal data

$C_3H_7N_2S^+ \cdot C_{12}H_9O_3^-$   
 $M_r = 304.36$   
 Monoclinic,  $P2_1/c$   
 $a = 8.3669$  (2) Å  
 $b = 6.3707$  (1) Å  
 $c = 26.3457$  (6) Å  
 $\beta = 92.1992$  (9)°  
 $V = 1403.27$  (5) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.441$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 4067 reflections  
 $\theta = 2.9$ – $27.5$ °  
 $\mu = 0.24$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Plate, colourless  
 $0.32 \times 0.10 \times 0.04$  mm

## Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.710$ ,  $T_{\max} = 0.990$   
 15 534 measured reflections

3183 independent reflections  
 2546 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.091$   
 $\theta_{\text{max}} = 27.4$ °  
 $h = -10 \rightarrow 10$   
 $k = -7 \rightarrow 8$   
 $l = -34 \rightarrow 34$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.121$   
 $S = 1.02$   
 3183 reflections  
 194 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.8055P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N21A-H21A\cdots O15B$	0.88	1.88	2.754 (2)	171
$N21A-H22A\cdots O14B^{iii}$	0.88	1.93	2.787 (2)	166
$N21A-H22A\cdots O11B^{iii}$	0.88	2.56	2.965 (2)	109
$N3A-H3A\cdots O14B$	0.87 (2)	2.01 (2)	2.871 (2)	170 (2)

Symmetry code: (iii)  $x, y - 1, z$ .

All H atoms, except for the H atom on the  $N^+$  ion in (II), were included in the refinement at calculated positions in the riding-model approximation, with N–H distances of 0.88 Å, and C–H distances of 0.95 (aromatic H atoms) and 0.99 Å (CH<sub>2</sub> H atoms). The  $U_{\text{iso}}(\text{H})$  values were set at 1.25  $U_{\text{eq}}$  of the carrier atom. The H atom on the  $N^+$  ion was located in a difference synthesis and both the positional and displacement parameters were refined. A high  $R_{\text{int}}$  value for (I) was the result of weak high-angle data.

For both compounds, data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hoof, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO, SCALEPACK (Otwinowski & Minor, 1997) and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLUTON94 (Spek, 1994) and PLATON97 (Spek, 1997); software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1737). Services for accessing these data are described at the back of the journal.

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