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2-Amino-1,3-benzothiazole–ethyl coumarin-3-carboxylate (1/1)

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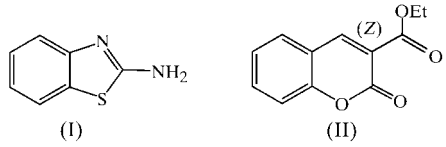
The title adduct, $C_7H_6N_2S{\cdot}C_{12}H_{10}O_4$, is formed *via* N—H···O and N—H···N hydrogen-bonding interactions, which generate a tetrameric unit with a pseudo-centre of symmetry. The tetramer further packs through parallel-displaced π–π stacking interactions along the *a* direction.

Comment

3-Carboxycoumarin derivatives have been reported as tautomerase (Orita *et al.*, 2001), elastase (Doucet *et al.*, 1999) and α-chymotrypsin inhibitors (Pochet *et al.*, 1996), although little is known about the forces that regulate the molecular recognition interactions involved. We report here the molecular structure of the hydrogen-bonded adduct formed between 2-aminobenzothiazole, (I), and ethyl coumarin-3-carboxylate, (II).



The title adduct forms yellow monoclinic crystals (space group *Pc*, $Z' = 2$) whose molecular structure is depicted in Fig. 1. The asymmetric unit is a hydrogen-bonded tetramer composed of two molecules of (I) and two molecules of (II) (see Fig. 1 for the labelling scheme). Bond distances and angles are close to reported values for an individual coumarin molecule (García-Báez *et al.*, 2003) and other 2-aminobenzothiazole adducts (Armstrong *et al.*, 1992). No comparison is made with the molecular structure of (I) since, to our knowledge, the only report of it as a single compound is from X-ray powder diffraction data where the *R* factor is 16.4% (Goubitz *et al.*, 2001).

Graph-set notation (Bernstein *et al.*, 1995) is used to describe the hydrogen-bonding patterns throughout this paper. Molecules of (I) and (II) are linked *via* the intermolecular three-centered hydrogen-bonding interaction O2···H22···O11 (Steiner, 2002), which involves the 2-amino group of molecule (I) and both coumarin carboxy groups

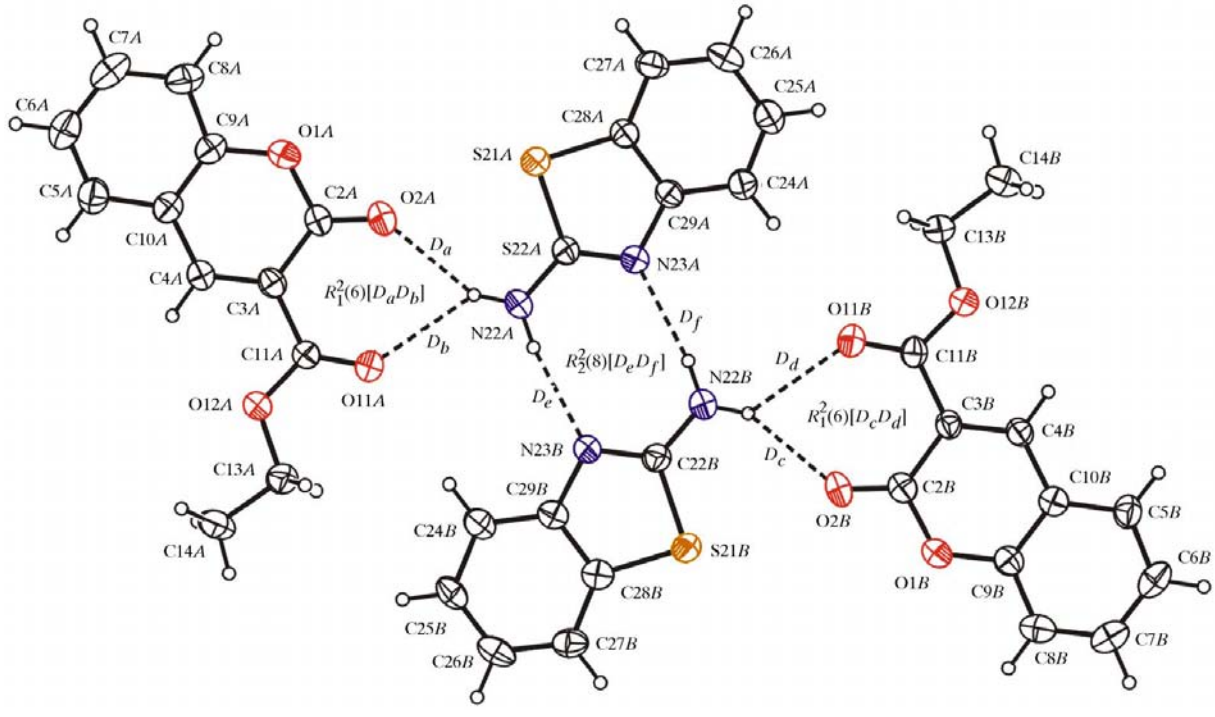


Figure 1
The molecular structure of the title adduct, showing displacement ellipsoids at the 30% probability level. Two independent adducts, labelled as *A* (left) and *B* (right), were found in the asymmetric unit, and these generate the tetrameric unit *via* hydrogen-bonding interactions.

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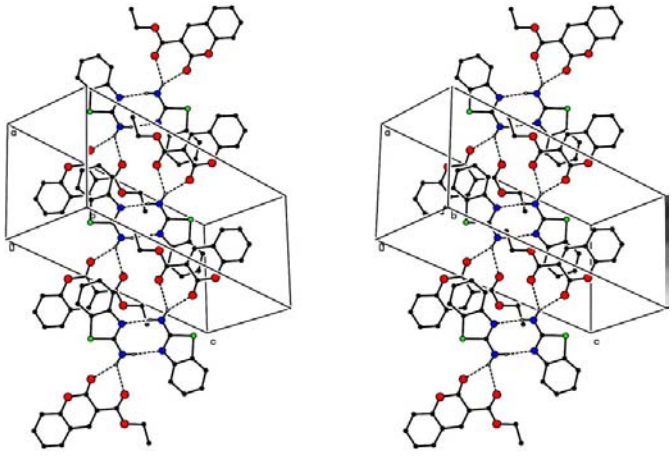

Figure 2
A stereoview of the title adduct, showing the π–π stacking interactions that propagate along the *a* direction.

[N22*A*—H22*B*···O2*A* (D_a) and N22*A*—H22*B*···O11*A* (D_b), and N22*B*—H22*D*···O2*B* (D_c) and N22*B*—H22*D*···O11*B* (D_d)], thus forming the six-membered ring motifs $R_1^2(6)[D_aD_b]$ and $R_1^2(6)[D_cD_d]$ for the $(I_A)\cdots(II_A)$ and $(I_B)\cdots(II_B)$ hydrogen-bonded aggregates, respectively (Table 1). Two molecules of (I) are linked by complementary hydrogen-bonding interactions *via* the free H atom of the amino group and the pyridine-like N atom into an eight-membered $R_2^2(8)[D_eD_f]$ ring (Fig. 1). It is noteworthy that this motif is also observed in the molecular structure of 2-aminobenzothiazole (Goubitz *et al.*, 2001). The overall hydrogen-bonding arrangement leads to an essentially coplanar $(II_A)\cdots(I_A)\cdots(I_B)\cdots(II_B)$ hydrogen-bonded pseudo-centrosymmetric tetramer [the angle between the $(I_A)\cdots(II_A)$ and $(I_B)\cdots(II_B)$ planes is 3.2 (3)°], as shown in Fig. 1.

The tetrameric unit packs along the *a* direction, giving rise to a π-stacked zigzag arrangement (Fig. 2). The shortest intermolecular distances are C24*A*···C11*A** and C28*A*···C4*A** of 3.267 (5) and 3.352 (5) Å, and C24*B*···C11*B*# and C28*B*···C4*B*# of 3.304 (6) and 3.348 (5) Å [atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(-1 + x, y, z)$, respectively], for $(I_A)\cdots(II_A)$ and $(I_B)\cdots(II_B)$ alternated π–π interactions, respectively (Fig. 3), which are considered to occur if the shortest C···C distance is less than 4.8 Å (Singh & Thornton, 1990). However, the mean interplanar and the mean inter-centroid distances between the (I)-aromatic and (II)-lactone rings are 3.38 (8) and 3.54 (3) Å, respectively, in agreement with strong parallel-displaced or offset face-to-face interactions (Sinnokrot *et al.*, 2002). A particular feature of this π–π interaction is that molecules of (I) and (II) are rotated by 110° in relation to their long axes (C22—C26 and C2—C6, respectively); this wide angle is probably related to the steric demand exerted by the hydrogen-bonded tetramer. Finally, the donor–acceptor nature of the title adduct was confirmed by the charge-transfer band measured at 423 nm in the solid phase, which was obtained by digital subtraction (Bosch *et al.*, 1998) from the electronic spectra of the individual components [λ_{max}(I) = 361 nm and λ_{max}(II) = 370 nm].

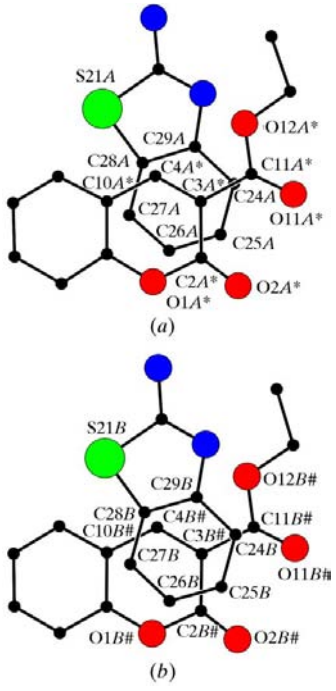

Figure 3
The individual overlap for complexes (*a*) $(I_A)\cdots(II_A)$ and (*b*) $(I_B)\cdots(II_B)$.

Experimental

Ethyl coumarin-3-carboxylate was synthesized according to the procedure reported by Bonsignore *et al.* (1995); the ^{1}H and ^{13}C NMR data for this compound are reported elsewhere (Martínez-Martínez *et al.*, 2001). 2-Aminobenzothiazole (of reagent grade) was purchased from Aldrich and used as received. Equimolar quantities of 2-aminobenzothiazole (2 mmol) and ethyl coumarin-3-carboxylate (2 mmol) were suspended in toluene (15 ml; Aldrich). The resulting suspension was heated to boiling point on a hotplate until the reagents dissolved completely. The homogeneous solution was allowed to cool to room temperature, and after several days, yellow crystals suitable for X-ray diffraction separated in almost quantitative yield (m.p. 379–380 K). IR (KBr, cm^{-1}): ν 1763 (C═O), 751 (C—S); ^{1}H NMR (p.p.m.): δ 8.74 (*s*, 1H, H4), 7.90 (*d*, 1H, H5), 7.72 (*dd*, 1H, H7), 7.62 (*d*, 1H, H24), 7.44 (*s*, 2H, NH_2), 7.42 (*d*, 1H, H8), 7.39 (*dd*, 1H, H6), 7.30 (*d*, 1H, H27), 7.17 (*dd*, 1H, H26), 6.97 (*dd*, 1H, H25), 4.27 (*q*, 2H, CH_2), 1.29 (*t*, 3H, CH_3); ^{13}C NMR (p.p.m.): δ 166.4 (C22), 162.6 (C11), 156.0 (C2), 154.5 (C9), 152.8 (C29), 148.7 (C4), 134.5 (C7), 130.9 (C28), 130.3 (C5), 125.4 (C25), 124.8 (C6), 120.8 (C24), 120.7 (C26), 117.7 (C27), 117.8 (C10), 117.6 (C3), 116.1 (C8), 61.2 (CH_2), 14.0 (CH_3). The melting point was measured on an electrothermal IA 9100 apparatus and is uncorrected. The IR spectrum was recorded using a Perkin–Elmer 16 F PC IR spectrophotometer. The UV–vis diffuse reflectance spectra were recorded on a CARY SE UV–vis–NIR spectrophotometer, with 0.1 *M* samples in KBr discs (IR spectroscopic grade). The NMR spectra were recorded with a Varian Mercury-300 MHz instrument.

Crystal data

$C_7H_6N_2S\cdot C_{12}H_{10}O_4$	D_x = 1.367 Mg m^{-3}
M_r = 368.40	Mo $K\alpha$ radiation
Monoclinic, *Pc*	Cell parameters from 600 reflections
a = 9.360 (2) Å	θ = 20–25°
b = 9.109 (2) Å	μ = 0.21 mm^{-1}
c = 21.242 (4) Å	T = 293 (2) K
β = 98.78 (3)°	Prism, yellow
V = 1789.9 (7) Å^3	0.38 × 0.20 × 0.09 mm
Z = 4	

Data collection

Bruker SMART area-detector diffractometer	5785 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.033
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	θ_{max} = 28.0°
T_{min} = 0.95, T_{max} = 0.97	$h = -12 \rightarrow 12$
20 092 measured reflections	$k = -11 \rightarrow 11$
8179 independent reflections	$l = -27 \rightarrow 27$
	100 standard reflections
	intensity decay: 5%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.050	$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$wR(F^2)$ = 0.131	$\Delta\rho_{min}$ = −0.18 e Å^{-3}
S = 1.00	Absolute structure: Flack (1983), 3880 Friedel pairs
8179 reflections	Flack parameter = 0.39 (7)
472 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N22*A*—H22*B*···O2*A*	0.86	2.23	3.019 (4)	152
N22*A*—H22*B*···O11*A*	0.86	2.39	3.047 (4)	133
N22*B*—H22*D*···O2*B*	0.86	2.22	2.998 (4)	150
N22*B*—H22*D*···O11*B*	0.86	2.39	3.034 (4)	133
N22*A*—H22*A*···N23*B*	0.86	2.19	3.024 (4)	163
N22*B*—H22*C*···N23*A*	0.86	2.18	3.021 (4)	166

The adduct crystallized in the monoclinic system and space groups *Pc* and *P*2/*c* were allowed from the systematic absences; however, structure solution was only possible in space group *Pc*. All H atoms were revealed clearly in difference maps and were treated as riding atoms, with C—H distances of 0.93 and 0.96 Å, and N—H distances of 0.86 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1703). Services for accessing these data are described at the back of the journal.

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