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The 2-aminobenzothiazole–*N*-benzyl-2-oxo-2*H*-1-benzopyran-3-carboxamide (1/1) donor–acceptor complex

Francisco J. Martínez-Martínez,[a] Efrén V. García-Báez,[a] Herbert Höpfl[b] and Itzia I. Padilla-Martínez[a]*

[a]Unidad Profesional Interdisciplinaria de Biotecnología, Instituto Politécnico Nacional, Avenida Acueducto s/n, Barrio La Laguna Ticomán, México DF 07340, México, and [b]Centro de Investigaciones Químicas, Universidad Autónoma de Morelos, Cuernavaca Morelos, México

Correspondence e-mail: ipadilla@acei.upibi.ipn.mx

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.051
wR factor = 0.150
Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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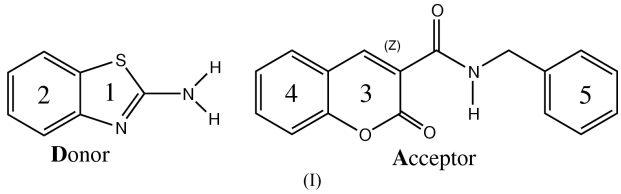
The title complex, $C_7H_6N_2S{\cdot}C_{17}H_{13}NO_3$, consists of donor and acceptor π-stacks in the alternating A–D–D'–A' pattern, through parallel displaced interactions, with a mean interplanar distance of 3.50 (3) Å. The complete three-dimensional supramolecular arrangement is achieved by both N—H···O and C—H···X (X = O, aryl) hydrogen-bonding interactions, which define an $A{\cdots}D{\cdots}D'{\cdots}A'$ hydrogen-bonded tetramer, among other supramolecular structures.

Comment

The donor–acceptor (D–A) nature of the complex, (I), formed between 2-aminobenzothiazole, as donor, and *N*-benzyl-2-oxo-2*H*-1-benzopyran-3-carboxamide, as acceptor, was confirmed by the charge-transfer band measured at 399 nm in the solid phase. This was obtained by digital subtraction (Bosch *et al.*, 1998) from the electronic spectra of the individual components ($\lambda_{max}D$ = 361 nm, $\lambda_{max}A$ = 368 nm). The molecular structure is depicted in Fig. 1*a*. Bond distances and angles are close to the reported values for the individual acceptor molecule (García-Báez *et al.*, 2003) and other donor complexes (Armstrong *et al.*, 1992).



(I)

The carboxamide group and the double bond of the lactone ring of the acceptor molecule are synperiplanar, with a C4—C3—C11—O11 torsion angle of 4.5 (3)°. This conformation may be influenced by the formation of N12*A*—H12*A*···O2 and C13—H13*A*···O11 intermolecular hydrogen bonds (Table 1). Their topological motifs correspond to S(6) and S(5) rings, respectively (Bernstein *et al.*, 1995). Donor and acceptor molecules are hydrogen bonded (D···A) through N22—H22*B*···O11 (*DA* motif in Fig. 1a; Table 1). In addition, two molecules are connected pairwise (D···D') through the self-complementary hydrogen bonds N22—H···N23^{i} [N22···N23^{i} = 2.902 (3) Å and N22—H···N23^{i} = 176°; symmetry code: (i) $1-x, 1-y, 1-z$] to form an $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995). This is similar to the arrangement found in the free donor molecule (Goubitz *et al.*, 2001). Thus, a hydrogen-bonded pseudo-tetramer $A{\cdots}D{\cdots}D'{\cdots}A'$ is generated by symmetry in the plane (110) (Fig. 2).

These pseudo-tetramers pack along the [012] direction, giving rise to the donor–acceptor D–A pair shown in Fig. 1*b*. The mean interplanar distance of 3.50 (3) Å is in agreement

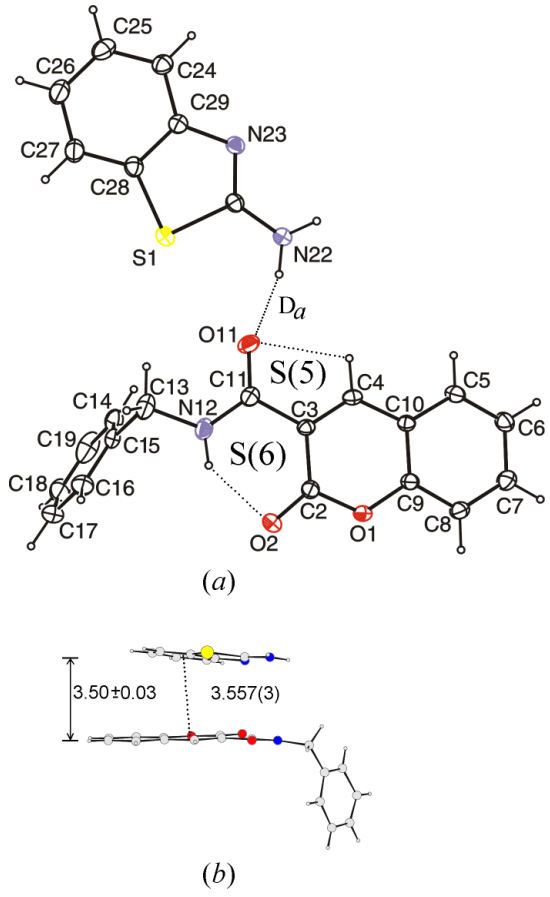


Figure 1
(*a*) The molecular structure of the title complex in which the hydrogen-bonded *S*(6) and *S*(5) motifs are shown. Displacement ellipsoids are drawn at the 20% probability level. (*b*) A lateral view, showing the mean interplanar and the shortest *Cg*2···*Cg*3 intercentroid distances in Å.

with the values reported for other donor–acceptor complexes (Rathore *et al.*, 1997). The shortest intercentroid distance between the aromatic donor ring *Cg*2 and the lactone acceptor ring *Cg*3 is 3.565 (2) Å (symmetry code: *x, y, z*), which is very close to the interplanar distance of 3.479 Å (see chemical scheme for ring numbering). This resembles an almost face-to-face approach between these rings, whereas the intercentroid distance and the interplanar angle γ between the other donor and acceptor rings [3.819 (2) Å and 23.6°, and 4.121 (2) Å and 23.6° for *Cg*1···*Cg*3 and *Cg*2···*Cg*4 interactions, respectively (symmetry code: *x, y, z*)] lie in the range corresponding to parallel displaced (pd) π-stacking interactions (Sinnokrot *et al.*, 2002).

The donor and acceptor molecules are rotated by 52° with respect to their long axes (C22–C26 and C2–C6, respectively). This conformation generates a tilt between the donor and acceptor molecular planes of approximately 11°. In this way, the steric crowding caused by the larger-sized S atom is avoided. Two acceptor molecules are also associated (*Cg*3···*Cg*4) through parallel displaced (pd) π-stacking interactions of the *AA*′ type [3.783 (2) Å, 3.512 Å, 21.8° and $(1-x, 1-y, -z)$ for the intercentroid and interplanar distances, angle γ and symmetry code, respectively]. Hence,

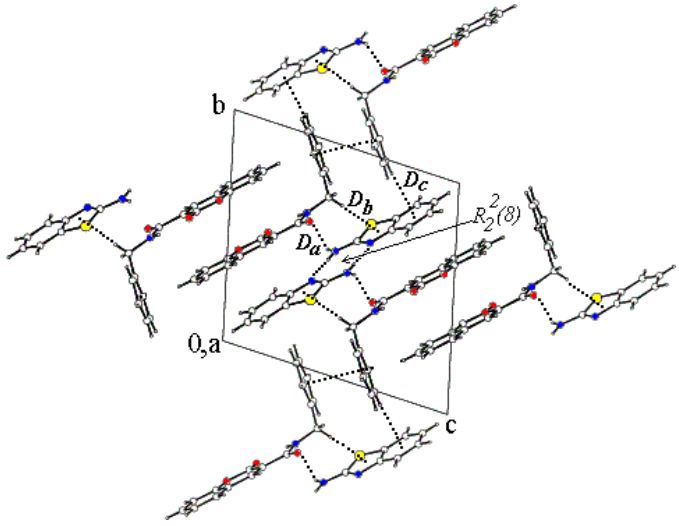


Figure 2
The molecular arrangement of the *D*–*A*–*A*′–*D*′ alternating π-stacking and the complete hydrogen-bonding scheme in the [110] direction. The *A*···*D*···*D*′···*A*′ hydrogen-bonded tetramer in the (110) direction should be noted.

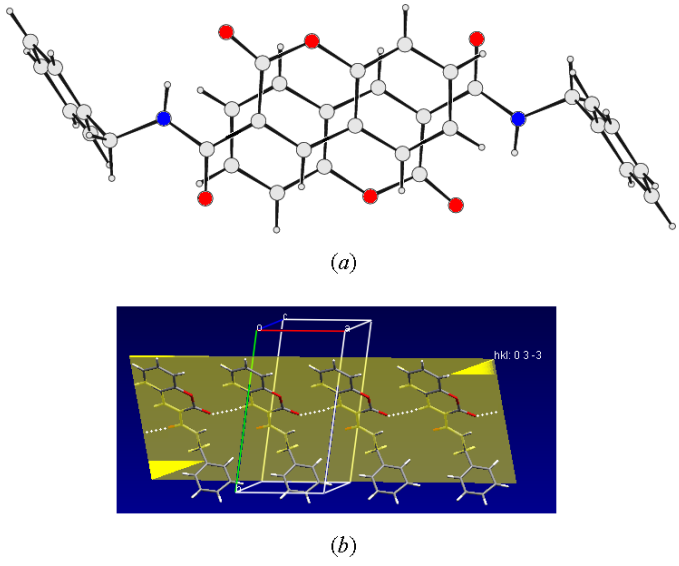


Figure 3
(*a*) Top view of the *A*–*A*′ homodimer stacked in an anti-tail-to-tail orientation. (*b*) The *C*(5) chain motif of the coumarin acceptor extending along the *a* axis.

the C3═C4 double bond of the lactone coumarin ring is positioned approximately over the middle of the aromatic ring of the partner molecule (Fig. 3*a*). This arrangement is frequently observed for the self-association of 3-carboxycoumarins (García-Báez *et al.*, 2003). Furthermore, the pendant benzyl group of the acceptor is inclined by 98.3 (1)° to the coumarin mean plane, allowing close packing between the phenyl rings of neighbouring *AA*′ complexes, and through pd π-stacking interactions [3.813 (3) Å, 3.47 Å, 24.4° and $(1-x, 2-y, 1-z)$ for *Cg*5···*Cg*5 intercentroid and interplanar distances, angle γ and symmetry code, respectively]. The resulting ribbon grows along the [0$\bar{3}$2] direction and is cross-linked through the C4—H4*A*···O2^{ii} intermolecular hydrogen

bond [C4···O2^{ii} = 3.417 (3) Å and C4—H4*A*···O2^{ii} = 147°; symmetry code: (ii) 1 + *x*, *y*, *z*], which develops a *C*(5) chain motif along the *a* axis (Fig. 3*b*), finally leading to the formation of a coumarin bilayer.

The full network is achieved through T-shaped hydrogen-bonding interactions (Umezawa *et al.*, 1998); C13—H13*B*···*Cg*1 (D_b motif) and C16—H16*A*···*Cg*2 (D_c motif) [C13···*Cg*1 = 3.928 (3) Å, C13—H13*B*···*Cg*1 = 173.3° (symmetry code: 1 − *x*, 1 − *y*, 1 − *z*), and C16···*Cg*2 = 3.643 (5) Å, C16—H16*A*···*Cg*2 = 167.2° (symmetry code: *x*, 1 + *y*, *z*), respectively]. The complete hydrogen-bonding scheme can be seen in Fig. 2.

In conclusion, the title complex presents a *D*–*A*–*A*′–*D*′ π-stacking pattern that can be described as a guest composed of *AA*′ π-stacked homodimers intercalated between two layers of discrete hydrogen-bonded donor dimers as the host.

Experimental

N-Benzyl-2-oxo-2*H*-1-benzopyran-3-carboxamide was synthesized according to reported procedures (Espinosa *et al.*, 2001). ^{1}H and ^{13}C NMR data of the acceptor have been reported elsewhere (Martínez-Martínez *et al.*, 2001). 2-Aminobenzothiazole, other chemicals and solvents were of reagent grade and used as received (Aldrich). Equimolar quantities of 2-aminobenzothiazole (2 mmol) and *N*-benzyl-2-oxo-2*H*-1-benzopyran-3-carboxamide (2 mmol) were suspended in 15 ml of toluene; thereafter the resulting suspension was heated to boiling point on a hotplate until complete solubilization. The homogeneous solution was allowed to cool to room temperature, and after several days crystals suitable for X-ray diffraction separated in almost quantitative yield. Pale yellow crystals (m.p. 387–391 K).

Crystal data

$C_7H_6N_2S\cdot C_{17}H_{13}NO_3$	Z = 2
M_r = 429.49	D_x = 1.357 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 6.833 (2) Å	Cell parameters from 600 reflections
b = 12.526 (4) Å	θ = 20.0–25.0°
c = 12.786 (4) Å	μ = 0.19 mm^{-1}
α = 104.903 (5)°	T = 293 (2) K
β = 93.392 (5)°	Block, yellow
γ = 94.425 (5)°	0.38 × 0.20 × 0.17 mm
V = 1050.9 (6) Å^3	

Data collection

Bruker SMART area-detector diffractometer	4674 independent reflections
	2251 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.035
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 27.5°
	$h = -8 \rightarrow 8$
T_{min} = 0.946, T_{max} = 0.967	$k = -16 \rightarrow 16$
11581 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.051	$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.150	$(\Delta/\sigma)_{max}$ = 0.001
S = 0.99	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
4674 reflections	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
280 parameters	

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12*A*···O2	0.86	1.99	2.700 (3)	139
N22—H22*A*···N23^{i}	0.86	2.21	3.069 (3)	176
N22—H22*B*···O11	0.86	2.18	2.902 (3)	142
C4—H4*A*···O2^{ii}	0.93	2.60	3.417 (3)	147
C4—H4*A*···O11	0.93	2.43	2.764 (3)	101
C13—H13*A*···O11	0.97	2.45	2.823 (4)	103

Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*; (ii) 1 + *x*, *y*, *z*.

All H atoms were placed in calculated positions and refined using a riding model: C—H(aromatic) = 0.93 Å, CH_2 = 0.97 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(parent C or N atom). The disorder of atoms C14–C19 atoms remains unresolved.

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*-2003 (Farrugia, 1999).

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