organic compounds

An unusual acid: (±)-3-benzoyl-1,2-dimethyl-8a-phenyl-2-benzothieno[2,3-*b*]pyrrole-1,2-dicarboxylic anhydride

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The title compound, $C_{27}H_{21}NO_4S$, is a 2-benzothieno[2,3-*b*]pyrrole derivative with several substituents, present in the crystal as a racemate. The tetracyclic fused-ring system shows a 'U-shaped' molecular architecture, since the two rings flanking the central pyrrolidine ring both point in the same direction.

Comment

Several syntheses of shape-specific molecules through heteroaromatic annulations in a *cis–syn–cis* mode have been achieved (Mehta *et al.*, 1992). Often, 'U-shaped' structures are obtained and are driven by stereospecific syntheses (Albrecht *et al.*, 1992), and they are considered to be a new class of potential molecular hosts (Marchand *et al.*, 1990; Mehta *et al.*, 1989, 1998). 2-Benzothieno[2,3-*b*]pyrrole derivatives have been produced in a domino cascade reaction starting from mesoionic 1,3-oxazolin-5-olates and thiocoumarins having an electron-withdrawing group at the 3-position (Grassi *et al.*, 2005).
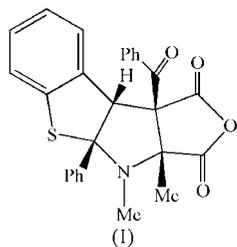
The crystal structure of the title compound, (I), contains molecules of (±)-3-benzoyl-1,2-dimethyl-8a-phenyl-2-benzothieno[2,3-*b*]pyrrole-1,2-dicarboxylic anhydride as a racemate.

The main body of (I) consists of four consecutive rings fused to each other by edge-sharing. The core pyrrolidine ring is flanked by a succinic anhydride group on one side and a benzothiophene group on the other. These condensed rings confer on the structure a 'U-shaped' configuration (*endo* form), with an angle between the mean benzothiophene and pyrrolidine planes of 68.5 (1)°, and an angle between pyrrolidine and succinic anhydride planes of 68.9 (1)° (Fig. 1). The succinic anhydride ring is close to being planar [maximum deviation from the mean plane for atom C23 of 0.037 (3) Å], but the other five-membered rings show significant deviations from planarity.

Puckering analysis (Cremer & Pople, 1975) of the thiophene ring (S1/C2/C3/C4/C9) shows an *E* (envelope) conformation, with $Q = 0.316$ (2) Å and $\varphi = 4.3$ (4)°. The same analysis of the pyrrolidine ring (C18/C3/C2/N16/C17) shows a $^3T_2$ (twist) conformation [$Q = 0.281$ (2) Å and $\varphi = -95.1$ (5)°], where the
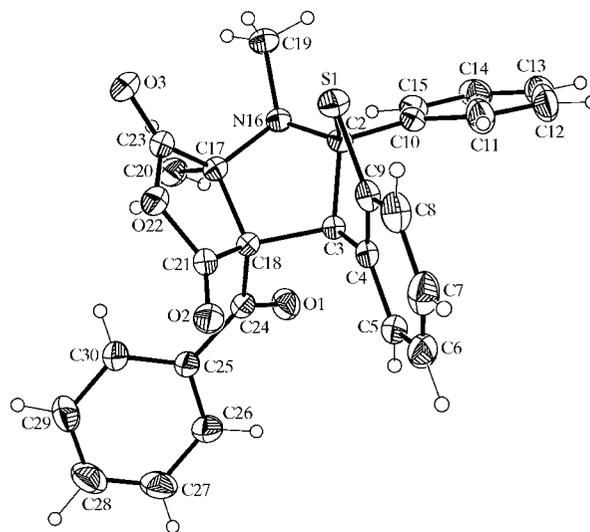
Figure 1
A view of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.
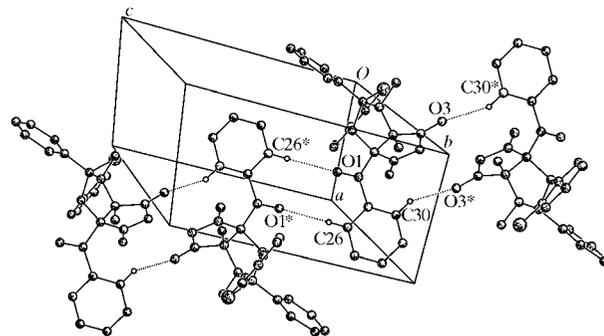
Figure 2
A view of the crystal packing of (I), showing a one-dimensional chain developing along the [101] direction. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($-x$, $2 - y$, $-z$) and ($1 - x$, $2 - y$, $1 - z$), respectively.

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pseudo-twofold symmetry axis passes through atom C18. The four atoms on the contact edges of this ring are stereogenic [C2(R), C3(R), C17(S) and C18(R)] and, since the space group is centrosymmetric, the molecule exists in the solid state as a racemic pair.

The phenyl and methyl substituents on C2 and C17 favour a flattening of the pyramid-like geometry around atom N16, resulting in the sum of the bond angles around N16 being 345.8 (6)°, compared with 335.31° measured for an analogous unsubstituted pyrrolidine moiety (Pedrosa *et al.*, 2002). Atom C8 bears a benzoyl group which, because of steric hindrance, cannot maintain a stable planar conformation. The O1—C24—C25—C26 torsion angle and the short C24—O1 and long C24—C25 bond distances (Table 1), compared with the corresponding geometric parameters of a similar structural moiety (O—C—C—C = 0.32°, C=O = 1.223 Å and C—C = 1.501 Å; Nagendrappa & Begum, 1999), indicate a hampered conjugation among the pure *p* orbitals belonging to each atom of this fragment. The peripheral rings flanking pyrrolidine occur on the same side and almost parallel to each other, thus causing a noteworthy steric hindrance; this is reflected in the C18—C3 bond distance, which is longer than expected (Table 2), as already shown in another 'boat-like' structure in which the equivalent bond length is 1.573 Å (Huang *et al.*, 2001).

The crystal packing of (I) features two weak cyclic hydrogen-bonding interactions both lying across crystallographic inversion centres (Table 2). The first interaction, *viz.* C30—H30···O3^{i} [C···O = 3.272 (3) Å; symmetry code: (i) −x, 2 − y, −z], involves one of the two anhydride O atoms as acceptor and an aromatic C—H group as donor, leading to a $R_2^2(16)$ graph-set pattern (Bernstein *et al.*, 1995). The second interaction, *viz.* C26—H26···O1^{ii} [C···O = 3.484 (3) Å; symmetry code: (ii) 1 − x, 2 − y, 1 − z], involves, uniquely, the benzoyl group of two enantiomeric units joined in an $R_2^2(10)$ graph-set pattern. These intermolecular connections combine to give a 'chain of rings' ribbon polymer $N_2 = C_2^2$ [$R_2^2(16)R_2^2(10)$] (Bernstein *et al.*, 1995) extending along the [101] crystallographic direction (Fig. 2). Other weak dipolar and hydrophobic interactions support the overall lattice.

Experimental

Thiocoumarin (1.0 equivalent) and *N*-benzoyl-*N*-methylalanine (1.2 equivalents) were reacted in dioxane (200 ml) after addition of acetic anhydride (5.0 equivalents), yielding (I), as described by Grassi *et al.* (2005). After purification, colourless crystals of (I) (m.p. 416–417 K) were obtained by slow evaporation from dioxane.

Crystal data

$C_{27}H_{21}NO_4S$	$Z = 2$
$M_r = 455.51$	$D_x = 1.300$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.6245$ (7) Å	Cell parameters from 4015
$b = 11.6423$ (10) Å	reflections
$c = 13.1778$ (11) Å	$\theta = 2.6$–25°
$\alpha = 97.658$ (3)°	$\mu = 0.17$ mm^{-1}
$\beta = 104.134$ (3)°	$T = 298$ (2) K
$\gamma = 110.821$ (3)°	Irregular, colourless
$V = 1163.44$ (17) Å^3	$0.58 \times 0.4 \times 0.32$ mm

Data collection

Bruker X8 CCD area-detector diffractometer	4015 independent reflections
	3329 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan	$\theta_{max} = 25°$
(*SADABS*; Sheldrick, 1996)	$h = -10 \rightarrow 10$
$T_{min} = 0.789$, $T_{max} = 0.95$	$k = -13 \rightarrow 13$
17961 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 0.5138P]$
$wR(F^2) = 0.162$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
4015 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
300 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C24	1.212 (3)	S1—C2	1.900 (2)
O2—C21	1.185 (3)	C3—C18	1.583 (3)
O3—C23	1.188 (3)	C24—C25	1.491 (3)
S1—C9	1.765 (2)		
C9—S1—C2	91.48 (10)	C2—N16—C19	117.0 (2)
C2—N16—C17	111.22 (17)	C17—N16—C19	117.56 (18)
S1—C2—N16—C17	−80.3 (2)	O1—C24—C25—C30	−147.8 (3)
C2—N16—C17—C23	86.5 (2)	O1—C24—C25—C26	30.0 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C30—H30···O3^{i}	0.93	2.48	3.272 (3)	143
C26—H26···O1^{ii}	0.93	2.60	3.484 (3)	159

Symmetry codes: (i) −x, −y + 2, −z; (ii) −x + 1, −y + 2, −z + 1.

All H atoms were positioned geometrically and refined using a riding model, with C—H distances in the range 0.93–0.98 Å and U_{iso}(H) values of 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *X8 APEX* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XPW* (Bruker, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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