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Weak and strong hydrogen-bonding patterns in the structure of 2,4-bis-(2-hydroxybenzoyl)-2,3-dihydro-1*H*-pyrido[2,1-*b*][1,3]benzothiazole

Jairo Quiroga,[a] Braulio Insuasty,[a] Rodrigo Abonia,[a] Pedro Hernández,[a] Justo Cobo,[b] Manuel Nogueras,[b] Adolfo Sánchez[b] and John Nicolson Low[c]*†

[a]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360, Cali, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland
Correspondence e-mail: j.n.low@dundee.ac.uk

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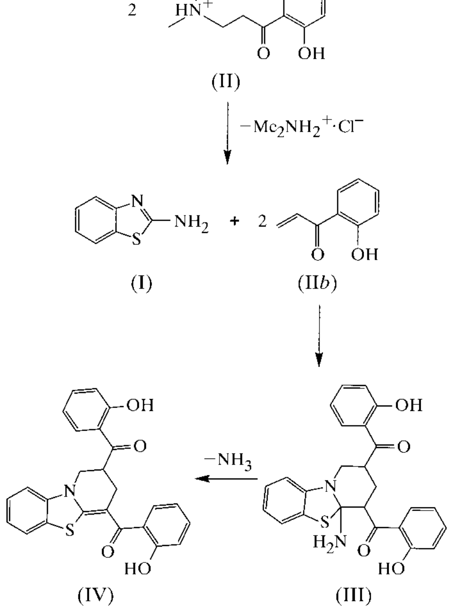
The title compound, $C_{25}H_{19}NO_4S$, (IV), was produced by a cyclocondensation reaction similar to that which had previously produced an unexpected product, thus giving a novel route for such reactions. The structure of (IV) contains two $S(6)$ motifs formed by strong intramolecular O—H···O hydrogen bonds. Weak C—H···O hydrogen bonds form primary $C(11)$, $R^1_2(7)$ and $R^2_2(8)$ motifs which combine to form a complex three-dimensional network.

Comment

Recently, we reported the formation of an unexpected product, 1,3,4-thiadiazolo[3,2-*a*]pyridine, produced by cyclocondensation of 2-amino-1,3,4-thiadiazole with two molecules of dimethylaminopropiophenone and elimination of ammonia (Quiroga *et al.*, 1998). The title compound, (IV), was obtained by a similar cyclocondensation reaction from 2-aminobenzothiazole, the reaction mechanism is shown in the schematic diagram below.

Two strong intramolecular hydrogen bonds are formed at the two 2-hydroxyphenylcarbonyl residues, one with O15 as the donor atom and O13 as the acceptor, 2.5527 (18) Å, and the other with O23 as the donor and O22 as the acceptor, 2.4919 (18) Å. Both of these have a primary $S(6)$ motif. The latter shorter interaction occurs because of the higher nucleophilic character of oxygen, O22, resulting from the delocalization of the lone pair on N1 of the thiazole ring with the carbonyl group at C21; the observed bond distances N1—C2 1.359 (2), C2—C11 1.405 (2), C11—C21 1.419 (2) and C21—O22 1.2817 (18) Å support this view.

The benzene ring in the benzothiazole moiety has the bonds and angles expected for an isolated aromatic ring, with all its bonds distances varying between 1.378 (2) and 1.394 (2) Å. These π systems are inclined at 1.48 (5)° to one another. The angle between the mean plane of the phenyl group defined by atoms C22 through C27 to that of the benzothiazole moiety is 16.77 (2)°. Selected bond lengths are given in Table 1.



The conformation of the N1—C2—C11—C10—C9—C8 ring is an envelope with a slight skew boat contribution [puckering parameters: amplitude, Q = 0.509 (2) Å, θ = 124.3 (2)° and φ = 70.0 (2)°; Boeyens, 1978], with C9 above the mean plane formed by the other atoms. The phenyl ring attached to C9 through C12 makes a nearly orthogonal angle to the mean plane of the molecule; the angle between the latter ring and benzothiazole mean planes is around 81.01 (5)°,

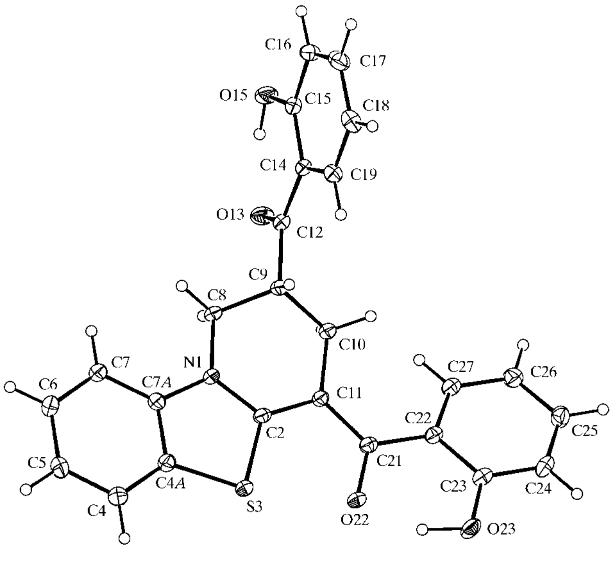


Figure 1
A view of (IV) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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† Postal address: Department of Electronic Engineering & Physics, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland.

giving the molecule a shape similar to that of a scorpion with the latter phenyl ring being the tail.

In addition, the molecules in (IV) are linked together into a three-dimensional framework by means of C—H···O weak hydrogen bonds. Atom C4 acts as a donor and atom O15($x, y, -1 + z$) acts as an acceptor, 3.345 (2) Å, forming a $C(11)$ motif which forms, by translation, an infinite chain which runs parallel to [001]. A second motif involves O22($1 - x, 1 - y, z$) as an acceptor atom with both C9, 3.498 (2) Å, and C19, 3.415 (2) Å, as donor atoms, thus giving rise to an $R_2^1(7)$ ring. This motif is repeated by the centre at ($\frac{1}{2}, \frac{1}{2}, 0$), so forming a variety of further ring motifs which can be seen in Fig. 2. Finally, atom C24 acts as a donor to atom O23($1 - x, 2 - y, z$), 3.474 (2) Å, so forming an $R_2^2(8)$ motif centred at ($\frac{1}{2}, 1, 0$). Full details of the hydrogen bonding are given in Table 2. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

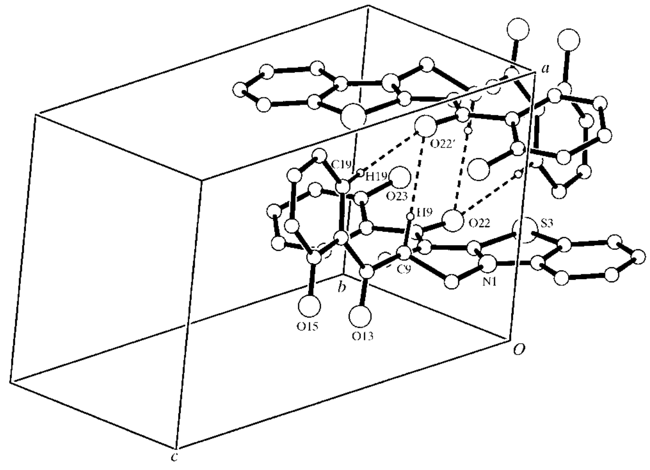

Figure 2
A view of the $R_2^1(7)$ ring. This motif is repeated by the centre at ($\frac{1}{2}, \frac{1}{2}, 0$), so forming a variety of further ring motifs.

Experimental

A mixture of 2-aminobenzothiazole (2 mmol) and 3-(dimethylamino)-1-(2-hydroxyphenyl)propan-1-one hydrochloride (2 mmol) in ethanol (5 ml) was heated to reflux for 10 min. Yellow crystals appeared in hot solution and were filtered off without cooling, washed with fresh ethanol and dried to give the title compound. Crystals suitable for X-ray diffraction were obtained after recrystallization from ethanol (yield 45%, m.p. 252 K). Analysis, calculated for $C_{25}H_{19}NO_4S$: C 69.9, H 4.46, N 3.26%; found: C 70.17, H 4.27, N 3.14%.

Crystal data

$C_{25}H_{19}NO_4S$
$M_r = 429.47$
Triclinic, $P\overline{1}$
$a = 7.4978$ (15) Å
$b = 11.265$ (2) Å
$c = 12.322$ (3) Å
$\alpha = 108.12$ (3)°
$\beta = 99.38$ (3)°
$\gamma = 94.75$ (3)°
$V = 966.0$ (3) Å^3
$Z = 2$
$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4393 reflections
$\theta = 2.99$–27.45°
$\mu = 0.203$ mm^{-1}
$T = 150$ (2) K
Block, yellow
0.22 × 0.15 × 0.15 mm

Table 1
Selected bond lengths (Å).

N1—C2	1.359 (2)	S3—C4*A*	1.7551 (17)
C2—C11	1.405 (2)	C11—C21	1.419 (2)
C2—S3	1.7485 (15)	C21—O22	1.2817 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
O15—H151···O13	0.93	1.74	2.5527 (18)	144
O23—H231···O22	1.03	1.54	2.4919 (18)	152
C4—H4···O15^{i}	0.95	2.46	3.345 (2)	154
C9—H9···O22^{ii}	1.00	2.53	3.498 (2)	162
C19—H19···O22^{ii}	0.95	2.51	3.415 (2)	159
C24—H24···O23^{iii}	0.95	2.53	3.474 (2)	171

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, 2 - y, -z$.

Data collection

KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.956$, $T_{\max} = 0.970$
14805 measured reflections
4393 independent reflections
3506 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 27.45°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.111$
$S = 1.049$
4393 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.2149P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

$P\overline{1}$ was asssumed and confirmed by the analysis. H atoms were treated as riding with C—H 0.95–1.00 Å and O—H 0.93–1.03 Å. The hydroxyl H-atom positions were determined from a difference map.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *WordPerfect macro PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC, X-ray Crystallographic Service, University of Southampton. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1110). Services for accessing these data are described at the back of the journal.

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