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Powder study of *N*-[2-(4-hydroxy-2-oxo-2,3-dihydro-1,3-benzothiazol-7-yl)ethyl]-3-[2-(2-naphthalen-1-ylethoxy)ethylsulfonyl]propylaminium benzoate

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Key indicators

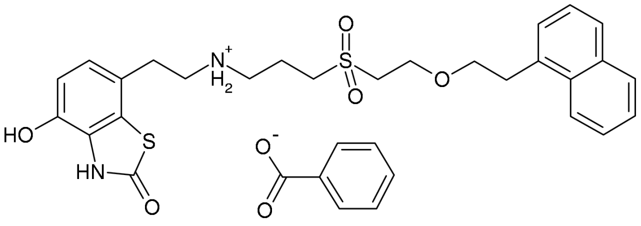
Powder X-ray study
T = 295 K
Mean σ(C–C) = 0.089 Å
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.038
Data-to-parameter ratio = 6.3

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

The crystal structure of the title compound, $C_{26}H_{31}N_2O_5S_2^+\cdot C_7O_2H_5^-$, also known as AR-C69457CC, was solved by simulated annealing from laboratory X-ray powder diffraction data collected at room temperature to 2.1 Å resolution. Subsequent Rietveld refinement yielded an R_{wp} of 0.038 and site-occupancy factors for the disordered anion components of 0.5.

Comment

The title compound, (I), was synthesized by AstraZeneca during the development of a potential treatment for chronic obstructive pulmonary disease. The crystal structure of (I) was solved as part of a wider investigation into the application of simulated annealing to the problem of solving pharmaceutical crystal structures from laboratory X-ray powder diffraction data (Docherty, 2004). The hydrogen bonding and ring interactions in (I) are summarized in Fig. 3. Hydrogen bond '*a*' [O1···N2 = 2.82 (6) Å] links two cations to form a centrosymmetric dimer, within which the heterocyclic rings make face-to-face contact ($R1\cdots R1'$ in Fig. 3) and the carbonyl O atom makes a close approach to the centroid of benzene ring $R2'$ [O1···centroid = 3.54 (3) Å and C1—O1···centroid = 95 (3)°]. The heterocyclic ring also engages in face-to-face contact with the C2–C7 benzene ring (Fig. 3, top right, $R1\cdots R2a$ and $R2\cdots R1a$). The donor–acceptor distances for the three cation–anion hydrogen bonds '*b*' to '*d*' fall in the range 2.38 (12)–2.51 (13) Å and the hydrogen-bonding scheme is preserved on switching between the two half-occupancy anion sites. The naphthalene rings engage with each other in offset face-to-face interactions (Fig. 3, bottom right) and pack, along with the benzoate phenyl ring, to form a hydrophobic layer in the *ab* plane.



(I)

Experimental

A polycrystalline sample of the title compound was recrystallized from acetonitrile solution by slow evaporation at room temperature. Data were collected from a sample in a rotating 0.7 mm borosilicate glass capillary using a variable count time scheme (Hill & Madsen, 2002).

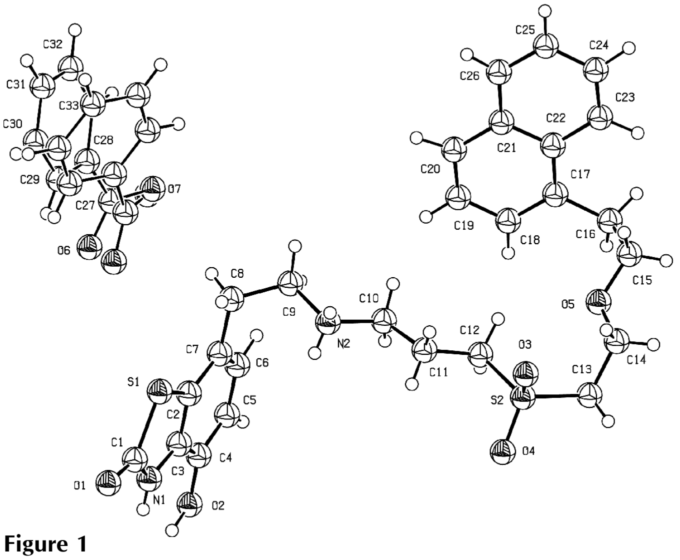


Figure 1

The atomic arrangement in (I), showing the anion disordered over two half-occupancy sites. Isotropic displacement spheres are shown at the 50% probability level.

Crystal data

$C_{26}H_{31}N_2O_5S_2^+\cdot C_7H_5O_2^-$
$M_r = 636.77$
Triclinic, $P\bar{1}$
$a = 7.63122$ (17) Å
$b = 13.66728$ (32) Å
$c = 15.8058$ (5) Å
$\alpha = 84.3849$ (21)°
$\beta = 87.4653$ (19)°
$\gamma = 75.7135$ (13)°
$V = 1589.52$ (7) Å^3
$Z = 2$
$D_x = 1.328$ Mg m^{-3}

Cu $K\alpha_1$ radiation
Cell parameters from 1347 reflections
$\theta = 2.5$–34.5°
$\mu = 1.94$ mm^{-1}
$T = 295$ K
White
Specimen shape: cylinder
12 × 0.7 × 0.7 mm
Specimen prepared at 295 K
Particle morphology: needle

Data collection

Bruker AXS *D*8 Advance diffractometer
Specimen mounting: 0.7 mm borosilicate capillary
Specimen mounted in transmission mode

1347 measured reflections
$h = 0 \rightarrow 5$
$k = -9 \rightarrow 10$
$l = -11 \rightarrow 11$
$2\theta_{\min} = 5$, $2\theta_{\max} = 69.$°
Increment in $2\theta = 0.014$°

Refinement

$R_p = 0.037$
$R_{wp} = 0.038$
$R_{exp} = 0.015$
$S = 1.60$
213 parameters

Only coordinates of H atoms refined
$(\Delta/\sigma)_{\max} = 0.049$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}

The diffraction pattern indexed to a triclinic cell [*F*(20) = 124.5, *M*(20) = 33.5; *DICVOL*91 (Boultif & Louer, 1991)] and space group $P\bar{1}$ was assigned from volume considerations and a lack of systematic absences. The data set was background subtracted and truncated to 42° 2θ for Pawley fitting (Pawley, 1981; $\chi^2_{\rm Pawley} = 2.7$) and the structure solved using the simulated annealing (SA) global optimization procedure, described previously (David *et al.*, 1998), that is now implemented in the *DASH* computer program (David *et al.*, 2001). The SA structure solution involved the optimization of two fragments (the cation with 13 torsion angles plus the anion) totaling 26 degrees of freedom. The best SA solution had a favourable $\chi^2_{\rm SA}/\chi^2_{\rm Pawley}$ ratio of 5.7 and a chemically sensible packing arrangement, but suffered from a significant misfit to the data, even at modest 2θ angles. Rerunning the SA with the cation fixed in its previously determined position and optimizing the positions and orientations of two 50% occupancy anions halved the $\chi^2_{\rm SA}/\chi^2_{\rm Pawley}$ ratio to 2.9 and significantly improved the fit at lower 2θ angles. The solved structure was then refined against the full data set (5–69° 2θ) using a restrained Rietveld method (Rietveld, 1969) as implemented in *TOPAS* (Coelho, 2003), with the R_{wp} falling from 0.064 to 0.038 during the refinement. All cation atomic positions (including H atoms) were refined, subject to a series of restraints on bond lengths, angles and, where appropriate, planarity. The distance and angle restraints were based on a geometric analysis of five cations in four crystal structures (Docherty, 2004) closely related to the title compound, namely (*a*) 2-(4-hydroxy-2-oxo-2,3-dihydro-1,3-benzothiazol-7-yl)ethylammonium chloride, (*b*) the monohydrate of (*a*), (*c*) *N*-[2-(4-hydroxy-2-oxo-2,3-dihydro-1,3-benzothiazol-7-yl)ethyl]-3-[2-(2-(4-methylphenyl)ethoxy)ethylsulfamoyl]propylaminium besilate besilate and (*d*) the tosilate analogue of (*c*). This was supplemented by a geometric analysis of naphthalene rings using the knowledge base, *MOGUL* (Bruno *et al.*, 2004). The half-occupancy anions could not be refined reliably using the strategy just described and were therefore refined as rigid bodies. A March–Dollase correction of intensities for preferred orientation (Dollase, 1986) was applied and

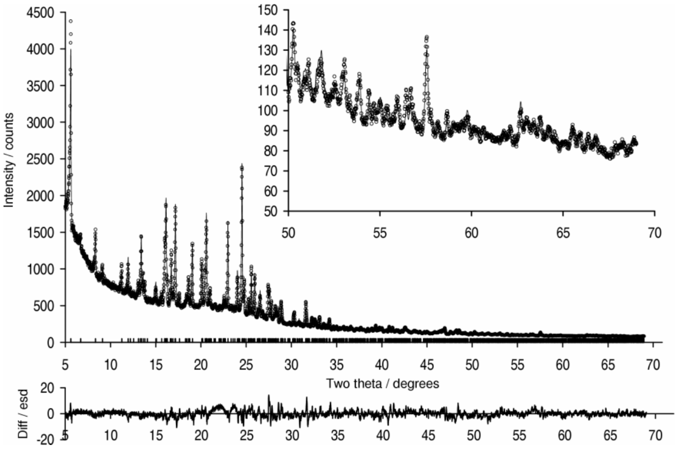


Figure 2

Final observed (points), calculated (line) and difference [$(y_{\rm obs} - y_{\rm calc})$/s.u.] profiles for the Rietveld refinement of (I). The reflection positions are shown by vertical bars.

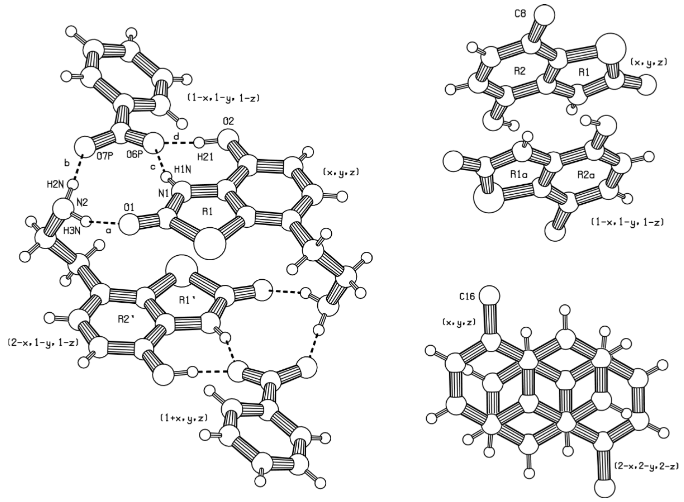


Figure 3

The hydrogen-bonding and ring interactions in (I), calculated and illustrated using *PLATON* (Spek, 2003; program version 280604).

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the refined value of the preferred orientation coefficient along the [001] direction was 1.13 (1).

Data collection: *DIFFRAC Plus XRD Commander* (Kienle & Jacob, 2003); cell refinement: *TOPAS* (Coelho, 2003); data reduction: *DASH* (David *et al.*, 2001); program(s) used to solve structure: *DASH*; program(s) used to refine structure: *TOPAS*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Cambridge Crystallographic Data Centre, 2004).

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