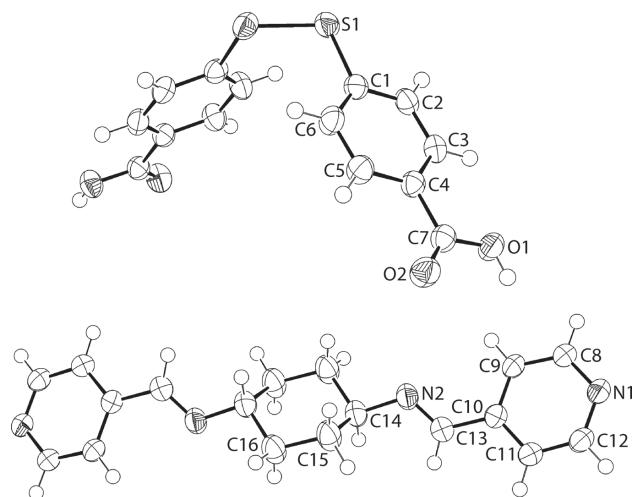


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Crystal structure of the co-crystal 4-[(4-carboxyphenyl)disulfanyl]benzoic acid–(1*E*,4*E*)-1-*N*,4-*N*-bis(pyridin-4-ylmethylidene)cyclohexane-1,4-diamine (1/1), C₁₄H₁₀O₄S₂·C₁₈H₂₀N₄



<https://doi.org/10.1515/ncrs-2019-0488>

Received July 11, 2019; accepted August 5, 2019; available online August 17, 2019

Abstract

C₃₂H₃₀N₄O₄S₂, monoclinic, *I*2/*a* (no. 15), *a* = 21.2034(7) Å, *b* = 5.0614(2) Å, *c* = 27.5987(12) Å, β = 105.991(4)°, *V* = 2847.3(2) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0431, *wR*_{ref}(*F*²) = 0.1246, *T* = 100(2) K.

CCDC no.: 1945351

The molecular structures are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title co-crystal was prepared through physical mixing of 4-mercaptobenzoic acid (Acros, Geel, Antwerp, Belgium) (0.154 g, 1 mmol) and *N,N'*-bis((pyridine-4-yl)methylene)cyclohexane-1,4-diamine [5] (0.292 g, 1 mmol) in a 1:1 molar

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.16 × 0.10 × 0.06 mm
Wavelength:	Cu <i>K</i> α radiation (1.54184 Å)
μ:	2.07 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ _{max} , completeness:	76.9°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	34319, 2996, 0.063
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 2795
<i>N</i> (<i>param</i>) _{refined} :	193
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

ratio. Colourless crystals were obtained three days after crystallization by the layering of benzene (2 mL) onto an equivalent volume of DMSO containing the dissolved mixture. **M.pt**: 438–439 K. **IR** (ATR, cm⁻¹): 3060(*w*) ν(N–H), 2940–2826(*m*) ν(C–H), 1675(*m*) ν(C=O), 1556(*m*) ν(C=N), 1321(*m*) ν(C–N), 815(*s*) δ(C=C).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with *U*_{iso}(H) = 1.2*U*_{eq}(C). The O-bound H atoms were located in difference Fourier maps but were refined with a distance restraint of O–H = 0.84 ± 0.01 Å, and with *U*_{iso}(H) set to 1.5*U*_{eq}(O).

Comment

The isolation and crystallographic characterization of the title co-crystal is a rare example formed by one of the isomeric Schiff bases, *N,N'*-bis((pyridine-*n*-yl)methylene)cyclohexane-1,4-diamine, for *n* = 2, 3 and 4 [5]. The co-crystal co-former is disulfide 4-[(4-carboxyphenyl)disulfanyl]benzoic acid (4-DTBA), whose crystal structure has been reported in the literature [6]. The observation of *n*-DTBA, or its derived di-anion, arises from the oxidation of the *n*-mercaptobenzene, for *n* = 2, 3 and 4, starting material, as has been commented upon previously [7–9]; the species with a single sulfur bridge has also been found [10]. Up to the present time, a characteristic of the aforementioned Schiff bases is their breakdown during co-crystallization [11–14]. Often, this results in isolation

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
S1	0.70397(2)	1.25411(8)	0.47699(2)	0.02786(16)
O1	0.61712(6)	0.3255(3)	0.30000(5)	0.0291(3)
H1O	0.6164(12)	0.211(4)	0.2777(7)	0.044*
O2	0.72569(6)	0.2874(3)	0.31164(5)	0.0329(3)
N1	0.60383(7)	−0.4412(3)	0.73461(5)	0.0272(3)
N2	0.52646(7)	0.1957(3)	0.59005(6)	0.0306(3)
C1	0.70173(8)	0.9950(3)	0.43315(6)	0.0242(3)
C2	0.63918(8)	0.9125(3)	0.40682(6)	0.0259(3)
H2	0.601792	0.989443	0.413862	0.031*
C3	0.63136(8)	0.7185(3)	0.37037(7)	0.0263(4)
H3	0.588525	0.663798	0.352179	0.032*
C4	0.68600(8)	0.6026(3)	0.36015(6)	0.0237(3)
C5	0.74839(8)	0.6844(4)	0.38727(7)	0.0284(4)
H5	0.785844	0.604956	0.380784	0.034*
C6	0.75666(8)	0.8798(4)	0.42354(7)	0.0291(4)
H6	0.799465	0.934929	0.441734	0.035*
C7	0.67887(8)	0.3894(3)	0.32177(6)	0.0250(3)
C8	0.54347(8)	−0.3588(4)	0.70955(7)	0.0278(4)
H8	0.506677	−0.441202	0.716538	0.033*
C9	0.53257(8)	−0.1595(4)	0.67407(7)	0.0277(4)
H9	0.489132	−0.109413	0.656416	0.033*
C10	0.58639(8)	−0.0326(3)	0.66453(6)	0.0263(4)
C11	0.64912(8)	−0.1116(4)	0.69167(7)	0.0296(4)
H11	0.686848	−0.024814	0.687188	0.035*
C12	0.65532(8)	−0.3200(4)	0.72544(7)	0.0301(4)
H12	0.698118	−0.379035	0.742789	0.036*
C13	0.57796(9)	0.1793(4)	0.62631(7)	0.0297(4)
H13	0.611930	0.305537	0.629081	0.036*
C14	0.52312(9)	0.4082(4)	0.55304(7)	0.0319(4)
H14	0.546158	0.568047	0.570713	0.038*
C15	0.55623(10)	0.3195(4)	0.51338(8)	0.0380(5)
H15A	0.536724	0.150136	0.498537	0.046*
H15B	0.603466	0.289115	0.529606	0.046*
C16	0.54863(9)	0.5243(4)	0.47160(8)	0.0370(4)
H16A	0.568568	0.455127	0.445665	0.044*
H16B	0.572529	0.687005	0.485848	0.044*

of cyclohexane-1,4-diammonium di-cation [11–13]. Intriguingly, the original 2-pyridyl isomer of the Schiff base has also been converted to a 2-(4-ammoniocyclohexyl)-3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-2-ylium di-cation [14]. Herein, as a continuation of studies in this area and employing the same general procedure as previously, perhaps unexpectedly, the anticipated 1:1 co-crystal was formed from 4-mercaptobenzoic acid and the *n* = 4 isomer of the Schiff base.

The molecular structures of the two components of the title crystal are shown in the figure (70% probability displacement ellipsoids with unlabelled atoms for the 4-DTBA molecule being related by $3/2 - x, y, 1 - z$ and for the Schiff base, by $1 - x, 1 - y, 1 - z$). The 4-DTBA molecule exhibits crystallographic 2-fold asymmetry. The disparity in the C7–O1, O2 bond lengths [1.321(2) and 1.218(2) Å] confirm

the presence of the acid. The carboxyl group is co-planar with the phenyl ring to which it is attached, as seen in the dihedral angle between the two planes of 1.38(8)°. The characteristic orthogonal relationship between the phenyl rings is evidenced by the dihedral angle of 88.41(41)° between them, giving rise to a twisted, U-shaped molecule. The Schiff base is disposed about a center of inversion, as found in the free Schiff base [5]. However, a difference between the molecules is apparent in that in the free form [5], the C=C(H)C₅H₄N residue is almost orthogonal to the best plane through the cyclohexyl ring (which adopts a chair conformation in both structures) as seen in the dihedral angle of 86.01(5)°. This compares with the comparable angle in the title co-crystal of 38.93(3)° which arises from a twist about the C10–C13 bond, with the C9–C10–C13–N2 torsion angle being −24.0(3)°.

The key hydrogen bonding interactions in the crystal are of the type hydroxy-O–H···N(pyridyl) [O1–H10···N1ⁱ: H10···N1ⁱ = 1.78(2) Å, O1···N1ⁱ = 2.615(2) Å with angle at H10 = 170(2)° for symmetry operation (i) $x, -1/2 - y, -1/2 + z$]. The hydrogen bonding interactions lead to the formation of a supramolecular chain along the *c* axis direction, having a zigzag topology, being propagated by glide symmetry. The repeat distance of 35.1 Å is rather long as, owing to the kink in the 4-DTBA molecule, the edges are defined by a full Schiff base molecule and two half 4-DTBA molecules; the pitch is 53.4 Å. The 4-DTBA molecules stack along the *b* axis and are connected into a column by side-on C=O···π(phenyl) interactions [C7–O2···Cg(C1–C6)ⁱⁱ: O2···Cg(C1–C6)ⁱⁱ = 3.6026(16) Å, C7···Cg(C1–C6)ⁱⁱ = 3.6015(17) Å with angle at O2 = 80.22(10)° for (ii) $x, 1 + y, z$]. The layers thus formed are connected laterally to form a three-dimensional architecture by pyridyl-C–H···O(carbonyl) interactions [C11–H11···O2ⁱⁱⁱ: H11···O2ⁱⁱⁱ = 2.43 Å, C11···O2ⁱⁱⁱ = 3.357(2) Å with angle at H11 = 165° for (iii) $3/2 - x, y, 1 - z$].

Given the nature of weak interactions sustaining the supramolecular chains into a three-dimensional architecture, the Hirshfeld surfaces as well as the full and delineated two-dimensional fingerprint plots were calculated for the individual (symmetry expanded) co-crystal co-formers, using literature procedures [15] and Crystal Explorer 17 [16], in order to determine the most important contacts in the molecular packing.

Eleven different contacts were revealed in the analysis of the 4-DTBA molecule with the prominent contacts being H···H [39.4%] followed by O···H/H···O [14.4%], S···C/C···S [10.0%] and C···H/H···C [9.2%]. Significant contributions are also made by N···H/H···N [6.7%], S···H/H···S [6.6%], O···C/C···O [6.5%] and C···C [6.0%] contacts. Fractions of a percentage contributions are made by

$O \cdots N/N \cdots O$ [0.6%], $N \cdots C/C \cdots N$ [0.4%] and $O \cdots O$ [0.1%]. Some significant differences are noted in the contributors to the surface of the Schiff base. Reflecting the change in chemical composition, contributions from $H \cdots H$ [52.0%], $C \cdots H/H \cdots C$ [17.4%] and $N \cdots H/H \cdots N$ [12.3%] contacts have increased significantly. Complementing this observation are the decreases in the contributions from $O \cdots H/H \cdots O$ [9.6%], $S \cdots H/H \cdots S$ [3.1%], $O \cdots C/C \cdots O$ [1.0%] and $C \cdots C$ [2.5%]. Of the minor surface contacts, contributions from $O \cdots N/N \cdots O$ [0.6%] contacts remain the same, those from $N \cdots C/C \cdots N$ [1.6%] increase while there are no $O \cdots O$ contacts for the Schiff base molecule.

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001-2019.

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