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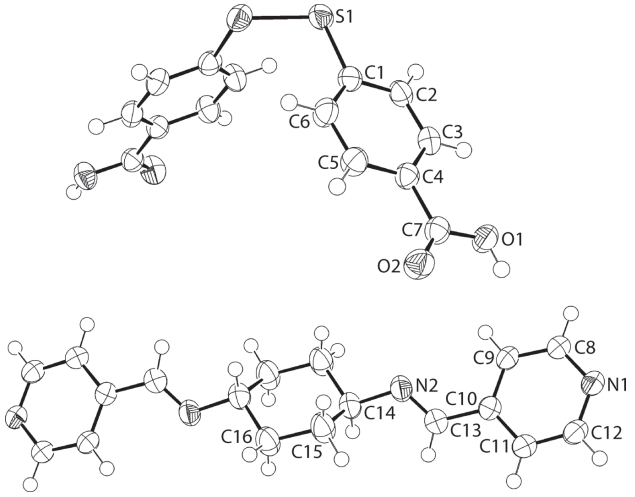
Crystal structure of the co-crystal 4-[(4-carboxyphenyl)disulfanyl]benzoic acid–(1*E*,4*E*)-1-*N*,4-*N*-bis(pyridin-4-ylmethylidene)cyclohexane-1,4-diamine (1/1), $C_{14}H_{10}O_4S_2 \cdot C_{18}H_{20}N_4$



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Abstract

$C_{32}H_{30}N_4O_4S_2$, monoclinic, *I*2/*a* (no. 15), $a = 21.2034(7)$ Å, $b = 5.0614(2)$ Å, $c = 27.5987(12)$ Å, $\beta = 105.991(4)°$, $V = 2847.3(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0431$, $wR_{ref}(F^2) = 0.1246$, $T = 100(2)$ K.

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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 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).

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.16 × 0.10 × 0.06 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	2.07 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	76.9°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	34319, 2996, 0.063
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2795
$N(param)_{refined}$:	193
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. 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 $1.5U_{eq}(O)$.

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

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

Atom	x	y	z	U_{iso}*/U_{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)C_5H_4N 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—H1o···N1^{i}: H1o···N1^{i} = 1.78(2) Å, O1···N1^{i} = 2.615(2) Å with angle at H1o = 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···O2^{iii}: H11···O2^{iii} = 2.43 Å, C11···O2^{iii} = 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···N/N···O [0.6%], N···C/C···N [0.4%] and O···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···H [52.0%], C···H/H···C [17.4%] and N···H/H···N [12.3%] contacts have increased significantly. Complementing this observation are the decreases in the contributions from O···H/H···O [9.6%] S···H/H···S [3.1%], O···C/C···O [1.0%] and C···C [2.5%]. Of the minor surface contacts, contributions from O···N/N···O [0.6%] contacts remain the same, those from N···C/C···N [1.6%] increase while there are no O···O contacts for the Schiff base molecule.

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