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Crystal structure of the co-crystal 2-[(2-carboxyphenyl)disulfanyl]benzoic acid – 3-chlorobenzoic acid (2/1), C_{35}H_{25}ClO_{10}S_{4}

The molecular structure is shown in the figure. Tables 1 and 2, respectively, contain details on crystal characteristics and measurement conditions, and a list of the atoms including atomic coordinates and displacement parameters.

\[ \text{Table 1: Data collection and handling.} \]

| Crystal:                  | Colourless prism            |
|---------------------------|-----------------------------|
| Size:                     | 0.09 × 0.07 × 0.04 mm       |
| Wavelength:               | Cu K\(\alpha\) radiation (1.54178 Å) |
| \(\mu\):                  | 3.99 mm\(^{-1}\)           |
| Diffractometer, scan mode:| XtaLAB Synergy, \(\omega\)  |
| Completeness:             | 76.1\(^\circ\), >99\%      |

\[ \text{Table 2: Crystal characteristics.} \]

| Crystal system:          | Triclinic                   |
|--------------------------|-----------------------------|
| Space group:             | \(P\bar{1}\) (no. 2)        |
| \(a\):                   | 7.9798(2) Å                 |
| \(b\):                   | 10.2392(3) Å                |
| \(c\):                   | 20.6956(4) Å                |
| \(\alpha\):              | 103.632(2) \(^\circ\)      |
| \(\beta\):               | 96.082(2) \(^\circ\)       |
| \(\gamma\):              | 96.053(2) \(^\circ\)       |
| \(V\):                   | 1619.13(7) Å\(^3\)         |
| \(Z\):                   | 2                          |
| \(R_{gt}(F)\):           | 0.0493                     |
| \(wR_{ref}(F^2)\):       | 0.1413                     |
| Source of material:      | The title co-crystal was prepared through solvent drop grinding of 2-mercaptobenzoic acid (2-MBA; Merck) and 3-chlorobenzoic acid (CIBA; Merck) in a 1:1 molar ratio (0.001 mol, 0.154 g for 2-MBA and 0.157 g for CIBA). The mixture was ground for 15 min in the presence of few drops of methanol; the procedure was repeated three times. Colourless block crystals were obtained by carefully layering benzene (1.5 mL) on a dichloromethane (1.5 mL) solution of the ground co-crystal. M.p. (Hanon MP-450): 448.4–451.8 K. IR (Bruker Vertex 70v; cm\(^{-1}\)): 3074–2819\((w)\) \(\nu(C–H)\), 1675\((s)\) \(\nu(C=O)\), 1597\((s)\) and 1468\((m)\) \(\nu(C=C)\), 1414\((s)\) \(\delta(C–H)\), 740\((s)\) \(\delta(C–Cl)\). |

\[ \text{Experimental details} \]

The C-bound H atoms were geometrically placed (C–H = 0.95 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 \(U_{eq}(H)\) set to 1.5\(U_{eq}(O)\). Owing to poor agreement, three reflections, i.e. (1 6 3), (9 4 5) and (9 4 6), were omitted from the final cycles of refinement.

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

| Atom | x     | y     | z     | Uiso*/Ueq |
|------|-------|-------|-------|-----------|
| C1   | 0.99576(11) | 0.78924(9) | 0.30664(4) | 0.0374(2) |
| O1   | 0.7090(3) | 0.5151(3) | 0.00324(12) | 0.0370(6) |
| O2   | 0.5573(3) | 0.5863(3) | 0.08599(13) | 0.0342(5) |
| H2O  | 0.480(8) | 0.551(8) | 0.054(3) | 0.16(4)* |
| C1   | 0.6993(4) | 0.5270(3) | 0.06257(16) | 0.0258(6) |
| C2   | 0.8567(4) | 0.6284(3) | 0.11016(16) | 0.0244(6) |
| C3   | 0.8490(4) | 0.6768(3) | 0.17820(16) | 0.0259(6) |
| H3   | 0.7429 | 0.6755 | 0.1951 | 0.031* |
| C4   | 0.9988(4) | 0.7269(3) | 0.2206(9) | 0.0285(7) |
| C5   | 1.1553(4) | 0.7277(3) | 0.19732(18) | 0.0312(7) |
| H5   | 1.2571 | 0.7611 | 0.2276 | 0.037* |
| C6   | 1.1614(4) | 0.6795(3) | 0.12970(18) | 0.0310(7) |
| H6   | 1.2680 | 0.6804 | 0.1132 | 0.037* |
| C7   | 1.0129(4) | 0.6296(3) | 0.08563(17) | 0.0285(6) |
| H7   | 1.0175 | 0.5965 | 0.0390 | 0.034* |
| S1   | 0.78621(9) | 0.40830(7) | 0.26149(3) | 0.02272(17) |
| S2   | 0.81972(9) | 0.50572(7) | 0.36157(3) | 0.02302(17) |
| O3   | 0.7184(3) | 0.3119(2) | 0.12761(10) | 0.0232(4) |
| O4   | 0.9046(3) | 0.2609(3) | 0.05497(10) | 0.0246(4) |
| H40  | 0.818(4) | 0.2335(3) | 0.0272(8) | 0.056(1)* |
| C35  | 0.4784(4) | 1.1473(3) | 0.98131(13) | 0.0194(5) |
| C33  | 0.1658(4) | 1.0873(3) | 0.9138(2) | 0.0222(6) |
| C32  | 0.0246(4) | 1.0321(3) | 0.9138(2) | 0.0222(6) |
| H31  | 0.0457(4) | 0.9726(3) | 0.83558(15) | 0.0245(6) |
| C31  | 0.1514 | 1.1295 | 0.9926 | 0.027* |
| C34  | 0.3309(4) | 1.0821(3) | 0.93034(13) | 0.0188(5) |
| C35  | 0.4784(4) | 1.1473(3) | 0.98131(13) | 0.0194(5) |

Table 2 (continued)

| Atom | x     | y     | z     | Uiso*/Ueq |
|------|-------|-------|-------|-----------|
| C24  | 0.543(4) | 1.0907(3) | 0.5950(15) | 0.0247(6) |
| C25  | 0.5872 | 1.0759 | 0.5516 | 0.030* |
| C26  | 0.4830(4) | 1.2109(3) | 0.62180(15) | 0.0265(6) |
| H26  | 0.4757 | 1.2781 | 0.5972 | 0.032* |
| C27  | 0.4331(4) | 1.2313(3) | 0.68499(16) | 0.0272(6) |
| H27  | 0.3905 | 1.3128 | 0.7038 | 0.033* |
| C28  | 0.4444(4) | 1.1336(3) | 0.72139(15) | 0.0240(6) |
| H28  | 0.4080 | 1.1491 | 0.7645 | 0.029* |
| C29  | 0.5084(4) | 1.0133(3) | 0.69551(14) | 0.0203(6) |
| C30  | 0.3519(4) | 1.0168(3) | 0.86387(14) | 0.0197(5) |
| C31  | 0.2075(4) | 0.9642(3) | 0.81723(14) | 0.0223(6) |
| H30  | 0.2198 | 0.9220 | 0.7722 | 0.027* |
| C32  | 0.0457(4) | 0.9726(3) | 0.83558(15) | 0.0245(6) |
| C33  | -0.0513 | 0.9372 | 0.8029 | 0.029* |
| C34  | 0.0246(4) | 1.0321(3) | 0.90117(16) | 0.0251(6) |
| H32  | -0.0863 | 1.0349 | 0.9138 | 0.030* |
| C35  | 0.1658(4) | 1.0873(3) | 0.94788(15) | 0.0229(6) |
| H33  | 0.1514 | 1.1295 | 0.9926 | 0.027* |
| C36  | 0.3309(4) | 1.0821(3) | 0.93034(13) | 0.0188(5) |
| C37  | 0.4784(4) | 1.1473(3) | 0.98131(13) | 0.0194(5) |

Comment

Owing to the presence of a central disulphide bond, 2-(2-carboxyphenyl)disulfanyl]benzoic acid (2,2'-dithiobenzoic acid; DTBA), is a flexible dicarboxylic acid. This conformational flexibility is emphasized in a recent report of a tri-polymorphic inclusion compound formed between DTBA and trimethylamine [5]. Indeed, most studies of DTBA are motivated by co-crystal formation and it is of interest that sometimes DTBA found in co-crystals is a product of co-crystallisation experiments starting with 2-mercaptobenzoic acid (2-MBA) [6, 7] whereby 2-MBA is oxidised to DTBA. As a continuation of studies in this area [6, 8, 9], the title co-crystal was isolated from the attempted 1:1 co-crystallisation experiments between 2-MBA and a second carboxylic acid, namely 3-chlorobenzoic acid (3-CIBA).

X-ray diffraction showed the asymmetric unit in title co-crystal comprises two independent molecules of DTBA and one of 3-CIBA, indicating oxidation of 2-MBA had occurred during co-crystal formation. Confirmation that the molecule of 3-CIBA exists as a carboxylic acid is readily seen in the pattern of Cl—O1, O2 bond lengths, i.e. 1.243(4) Å and 1.288(4) Å. A small twist from planarity is noted in the molecule. The r.m.s. deviation from the least-squares plane through the ring-carbon and chloride atoms being 0.0036 Å, and the dihedral angle between this plane and that through the carboxylic acid residue is 7.55(16)°. The crystal structure of 3-CIBA was originally reported in 1975 with a low temperature (105 K) re-determination of this P21/c polymorph [11] subsequently complimented by the report of a C2/c polymorph [12].
The comparable dihedral angles between C6/O2 in these structures are 4.1(4)° [11] and 5.8(2)° [12].

The conformations of the two DTBA molecules comprising the asymmetric unit resemble each other as seen in the respective r.m.s. bond and angle fits of 0.0054 Å and 0.491° for the inverted-S1 and S3-molecules [13]; each lacks crystallographically imposed symmetry. The patterns in the C—O(hydroxy), O(carbonyl) bond lengths are consistent with the presence of carboxylic acid residues. The C6/O2 dihedral angles are 3.7(3)° [O3-residue], 14.2(2)° [O5], 14.0(2)° [O7] and 4.1(2)° [O9]. This effectively co-planar relationship coupled with the observation each carbonyl-O atom is orientated towards the adjacent disulphide-S atom is indicative of attractive, hypervalent S···O interactions [14]. The shortest such interaction in the present co-crystal structure is 2.675(2) Å for S4···O9 and the longest, 2.737(2) Å, for O3···O7. The twists in the molecules is best indicated by the C14—S1—S2—C15 and C28—S3—S4—C29 torsion angles of −91.06(15)° and 87.15(15)°, respectively, and the dihedral angles between the two phenyl rings in the S1- and S3-molecules, i.e. 79.54(11)° and 80.76(11)°, respectively. The crystal structure of the parent DTBA molecule has been determined and shows the asymmetric unit to comprise one and a half molecules, with the latter disposed about a 2-fold axis of symmetry [15]. The comparable C=S=S=C torsion and C6=O2 dihedral angles are 86.12(14)° and 87.90(13)° for the molecule in the general position, and 87.90(13)° and 77.55(8)° for the symmetry molecule.

In the molecular packing, two distinct aggregation patterns based on conventional hydroxy-O—H···O(carbonyl) hydrogen bonding are discerned, each resulting in an eight-membered (⋯-HOCO)2 synthon. In the first of these, centrosymmetrically-related two-molecule aggregates of 3-CIBA are formed [O2—H20···O1i=1.78(7) Å, O2···O1i=2.608(4) Å with angle at H20=170(7)° for symmetry operation i: 1−x, 1−y, −z]. The second aggregate is a twisted, supramolecular chain comprising alternating S1- and S3-molecules [O4—H4o···O9i=1.84(4) Å, O4···O9i=2.665(3) Å with the angle at H4o=170(5)°; O6—H6o···O7: 1.82(3) Å, 2.648(3) Å and 175(3)°; O8—H8o···O5: 1.80(3) Å, 2.633(3) Å and 171(4)°; O10—H10o···O3iii: 1.84(3) Å, 2.663(3) Å and 171(3)°, for ii: x, −1+y, −1+z and iii: x, 1+y, 1+z]. The chain is orientated along [0 1 1]. Connections between the aggregates mediated by hydrogen bonding include π-stacking interactions between (C2—C7)···(C9—C14) and (C2—C7)···(C29—C34)° phenyl rings with ring-centroid separations of 3.6865(18) and 3.7346(18) Å, respectively. These interactions indicate the 3-CIBA molecule effectively bridges two independent DTBA molecules. The packing also features several parallel C···O···π interactions [16, 17] with C21—O5···π(C15—C20) presenting the shortest O···ring-centroid contact of 3.299(3) Å; the angle at O5 is 96.85(19)°.

Co-crystals of 3-CIBA with other carboxylic acids have not been reported and the sole example of a carboxylic acid co-crystal of DTBA is its 1:1 co-crystal with 2-MBA [7]. In the structure of this co-crystal, two DTBA molecules associate via hydroxy-O—H···O(carbonyl) hydrogen bonds leaving each of the outer carboxylic acid groups free to form eight-membered synthons with a 2-MBA molecule to result in the formation of a four-molecule aggregate.

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