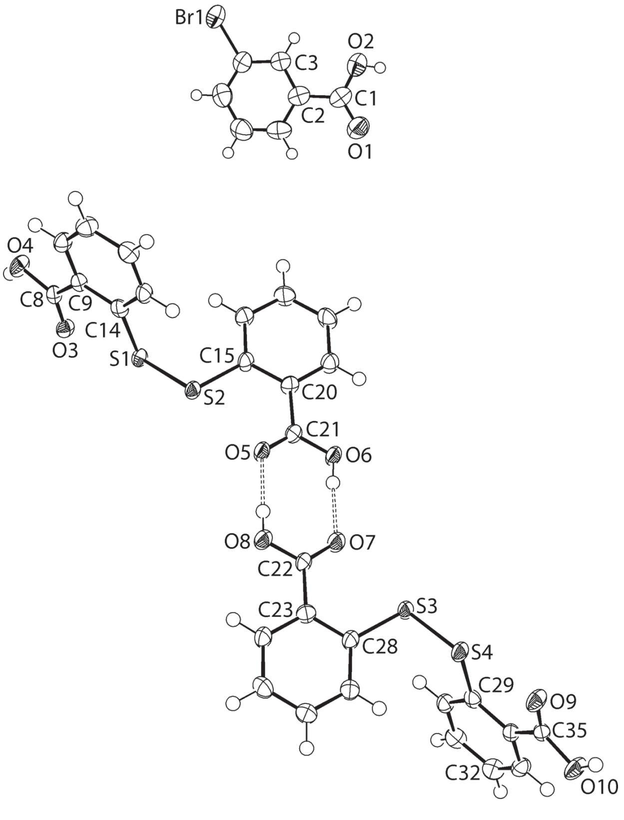
DE GRUYTER Z. Kristallogr. NCS 2019; 234(6): 1305–1308

Sang Loon Tan and Edward R.T. Tiekink*

Crystal structure of the 2:1 co-crystal 2-[(2-carboxyphenyl)disulfanyl]benzoic acid – 3-bromobenzoic acid, $2(C_{14}H_{10}O_4S_2)\cdot C_7H_5BrO_2$



https://doi.org/10.1515/ncrs-2019-0489
Received July 11, 2019; accepted September 12, 2019; available online September 21, 2019

Abstract

$C_{35}H_{25}BrO_{10}S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9533(2)$ Å, $b = 10.27180(10)$ Å, $c = 20.6598(4)$ Å, $\alpha = 103.462(1)°$, $\beta = 95.933(2)°$, $\gamma = 96.008(1)°$, $V = 1618.11(5)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0624$, $wR_{ref}(F^2) = 0.1759$, $T = 100(2)$ K.

CCDC no.: 1953253

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

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.09 \times 0.06 \times 0.05$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	4.68 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	76.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	41307, 6729, 0.041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6431
$N(param)_{refined}$:	466
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The title 2:1 co-crystal was prepared through solvent drop grinding of 2-mercaptobenzoic acid (Merck, Darmstadt, Germany) (0.154 g, 1 mmol) and 3-bromobenzoic acid (Alfa Aesar, Heysham, Lancashire, United Kingdom) (0.201 g, 1 mmol) in a 1:1 molar ratio. The mixture was ground for 15 mins in the presence of a few drops of methanol and the process was repeated three times. Upon dissolving the mixture in dimethylformamide (1 mL), the solution was then carefully layered with benzene (1.5 mL). Colourless crystals formed after two weeks. **M.pt:** 491–493 K. **IR** (ATR, cm^{-1}): 3066–2829(w) ν(C—H), 1683(s) ν(C=O), 1560(m) ν(C=C), 1415(m) δ(C—H), 739(s) δ(C=C), 669(m) ν(C—Br), 493(w) ν(S—S).

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 a difference Fourier map but were refined with a distance restraint O—H = 0.84 ± 0.01 Å, and with $U_{iso}(H)$ set to $1.5U_{eq}(O)$. Owing to poor agreement, one reflection, i.e. (0 −1 1), was omitted from the final cycles of refinement.

***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. https://orcid.org/0000-0003-1401-1520
Sang Loon Tan: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	1.00883(7)	0.79638(5)	0.31164(3)	0.03747(17)
S1	0.78070(11)	0.40858(9)	0.26241(4)	0.01657(19)
S2	0.81477(12)	0.50631(8)	0.36235(4)	0.0170(2)
S3	0.53249(12)	0.89453(8)	0.74523(4)	0.0186(2)
S4	0.56038(12)	1.00647(9)	0.84254(4)	0.0184(2)
O1	0.7024(5)	0.5139(4)	0.00345(18)	0.0443(9)
O2	0.5582(5)	0.5877(4)	0.08759(19)	0.0389(8)
H2O	0.477(10)	0.554(7)	0.060(4)	0.058*
O3	0.7131(3)	0.3124(3)	0.12900(13)	0.0182(5)
O4	0.9000(4)	0.2621(3)	0.05612(13)	0.0223(6)
H4O	0.810(4)	0.229(5)	0.030(2)	0.033*
O5	0.7635(4)	0.6292(3)	0.48742(13)	0.0197(5)
O6	0.6687(4)	0.5222(3)	0.56240(13)	0.0204(5)
H6O	0.646(7)	0.600(2)	0.579(3)	0.031*
O7	0.5956(4)	0.7640(3)	0.62061(13)	0.0218(6)
O8	0.6849(4)	0.8689(3)	0.54466(14)	0.0242(6)
H8O	0.711(7)	0.793(3)	0.527(3)	0.036*
O9	0.6224(3)	1.1430(3)	0.97132(13)	0.0221(6)
O10	0.4344(4)	1.2113(3)	1.04050(14)	0.0250(6)
H10O	0.520(5)	1.236(6)	1.070(2)	0.038*
C1	0.6985(6)	0.5727(4)	0.0625(2)	0.0311(9)
C2	0.8582(6)	0.6280(4)	0.1091(2)	0.0284(9)
C3	0.8523(6)	0.6768(4)	0.1773(2)	0.0266(8)
H3	0.7471	0.6762	0.1953	0.032*
C4	1.0049(6)	0.7261(4)	0.2178(2)	0.0289(9)
C5	1.1596(6)	0.7260(5)	0.1935(3)	0.0371(11)
H5	1.2634	0.7583	0.2227	0.045*
C6	1.1593(7)	0.6770(5)	0.1244(3)	0.0408(11)
H6	1.2646	0.6771	0.1064	0.049*
C7	1.0125(7)	0.6296(5)	0.0827(3)	0.0349(10)
H7	1.0142	0.5976	0.0358	0.042*
C8	0.8611(5)	0.3092(3)	0.11679(17)	0.0150(7)
C9	1.0095(5)	0.3574(3)	0.16954(17)	0.0149(7)
C10	1.1742(5)	0.3543(4)	0.15098(19)	0.0188(7)
H10	1.1875	0.3249	0.1049	0.023*
C11	1.3176(5)	0.3933(4)	0.1986(2)	0.0221(8)
H11	1.4285	0.3909	0.1855	0.027*
C12	1.2966(5)	0.4360(4)	0.2659(2)	0.0208(7)
H12	1.3941	0.4613	0.2991	0.025*
C13	1.1350(5)	0.4420(4)	0.28533(18)	0.0193(7)
H13	1.1234	0.4726	0.3315	0.023*
C14	0.9891(5)	0.4038(3)	0.23784(18)	0.0170(7)
C15	0.8289(5)	0.3753(4)	0.40607(18)	0.0170(7)
C16	0.8785(5)	0.2520(4)	0.37535(19)	0.0196(7)
H16	0.9071	0.2375	0.3309	0.023*
C17	0.8864(5)	0.1499(4)	0.4093(2)	0.0236(8)
H17	0.9183	0.0658	0.3874	0.028*
C18	0.8485(5)	0.1695(4)	0.4743(2)	0.0236(8)
H18	0.8550	0.0998	0.4973	0.028*
C19	0.8005(5)	0.2931(4)	0.50569(19)	0.0208(7)
H19	0.7744	0.3072	0.5504	0.025*
C20	0.7904(5)	0.3960(3)	0.47256(18)	0.0162(7)
C21	0.7398(5)	0.5266(4)	0.50773(17)	0.0170(7)
C22	0.6129(5)	0.8653(4)	0.59878(17)	0.0170(7)
C23	0.5550(5)	0.9938(4)	0.63122(19)	0.0186(7)
C24	0.5407(5)	1.0916(4)	0.59543(19)	0.0229(8)
H24	0.5715	1.0756	0.5513	0.027*
C25	0.4821(6)	1.2127(4)	0.6229(2)	0.0270(9)
H25	0.4758	1.2800	0.5984	0.032*
C26	0.4336(6)	1.2337(4)	0.6860(2)	0.0285(9)
H26	0.3905	1.3150	0.7047	0.034*
C27	0.4469(6)	1.1369(4)	0.7228(2)	0.0257(8)
H27	0.4129	1.1534	0.7664	0.031*
C28	0.5088(5)	1.0165(4)	0.69696(18)	0.0193(7)
C29	0.3508(5)	1.0177(3)	0.86487(18)	0.0172(7)
C30	0.2067(5)	0.9649(4)	0.81789(19)	0.0191(7)
H30	0.2201	0.9236	0.7729	0.023*
C31	0.0434(5)	0.9719(4)	0.8360(2)	0.0219(8)
H31	−0.0531	0.9357	0.8032	0.026*
C32	0.0205(5)	1.0311(4)	0.9012(2)	0.0233(8)
H32	−0.0911	1.0336	0.9136	0.028*
C33	0.1622(5)	1.0868(4)	0.94836(19)	0.0197(7)
H33	0.1470	1.1286	0.9931	0.024*
C34	0.3271(5)	1.0823(3)	0.93098(18)	0.0153(7)
C35	0.4743(5)	1.1469(3)	0.98236(18)	0.0159(7)

Comment

In continuation of a long-held interest in co-crystals of 2-[(2-carboxyphenyl)disulfanyl]benzoic acid (2,2′-dithiodibenzoic acid; DTBA) [5, 6], recent attention has been directed to co-crystal formation of this conformationally flexible di-acid [7] with benzoic acid derivatives. Thus, it has been possible to isolate the anticipated 1:2 co-crystal, DTBA.2 (benzoic acid) whereby each carboxylic acid group of DTBA associated with benzoic acid *via* a non-symmetric, eight-membered $\{\cdots HOCO\}_2$ synthon [8]. However, analogous experiments with 3-chlorobenzoic acid (3-ClBA) gave rise to an unexpected 1:1:1 multi-component crystal comprising DTBA, 3-ClBA and dimethylformamide (DMF) [9]. Here, one carboxylic acid associated with 3-ClBA *via* the $\{\cdots HOCO\}_2$ synthon but the second residue formed a seven-membered $\{\cdots HOCO\cdots HCO\}$ heterosynthon with the DMF molecule [9]. This species was isolated from the recrystallisation of a thoroughly ground powder (solvent drop method with methanol) comprising a 1:1 mixture of 2-mercaptobenzoic acid and 3-ClBA in toluene which was layered with DMF; co-crystallisation experiments with 2-mercaptobenzoic acid are well-known to produce DTBA [5, 6, 10] and, indeed, other side-products [11]. A similar experiment in which the powder was crystallised from dichloromethane layered with benzene gave the 2:1 co-crystal 2DTBA.3-ClBA [12]. In the present report, analogous experiments were conducted but with 3-bromobenzoic acid (3-BrBA) as the co-former. After recrystallisation from dimethylformamide layered with benzene, the non-solvated 2:1 co-crystal 2DTBA.3-BrBA was isolated, the crystal and molecular structures of which are reported herein.

As illustrated in the figure (50% probability displacement ellipsoids), the X-ray crystallographic analysis showed the asymmetric unit in the title 2:1 co-crystal to comprise two independent molecules of DTBA and one of 3-BrBA, consistent with oxidation of 2-MBA during co-crystal formation [5, 6, 10]. The 3-BrBA molecule exhibits a twist between the aromatic ring and the carboxylic acid residue with the dihedral angle between the planes being 8.38(3)°. The DTBA molecules are twisted as seen in the values of the C14—S1—S2—C15 and C28—S3—S4—C29 torsion angles of −90.73(19) and 86.79(19)°, respectively. This is also reflected in the dihedral angles between the (C9—C14) and (C15—C20) rings of 79.3(13)°, and between the (C23—C28) and (C29—C34) rings of 80.85(13)°. Variable twists between the O3-, O5-, O7- and O9-carboxylic acid groups and the phenyl rings to which they are attached are evident as seen in the sequence of C_6/CO_2 dihedral angles of 3.89(12), 15.6(4), 14.5(5) and 5.1(3)°, respectively. A least-squares fit calculation [13] comparing the independent DTBA molecules show the r.m.s. deviation of distances and angles to be 0.0051 Å and 0.483°, respectively, consistent with a high degree of concordance between the DTBA molecules.

In the molecular packing, and as shown in the figure, the DTBA molecules associate *via* hydroxy-O—H···O(carbonyl) hydrogen bonding and an eight-membered $\{\cdots HOCO\}_2$ synthon [O6—H6o···O7: H6o···O7 = 1.81(4) Å, O6···O7 = 2.648(4) Å with angle at H6o = 176(7)° and O8—H8o···O5: H8o···O5 = 1.80(4) Å, O8···O5 = 2.640(4) Å with angle at H8o = 179(7)°]. The remaining carboxylic acid residues of the DTBA molecules associate with symmetry-related DTBA molecules *via* hydroxy-O—H···O(carbonyl) hydrogen bonds [O4—H4o···O9$^{\mathrm{i}}$: H4o···O9$^{\mathrm{i}}$ = 1.82(4) Å, O4···O9$^{\mathrm{i}}$ = 2.660(4) Å with angle at H4o = 175(5)° and O10—H10o···O3$^{\mathrm{ii}}$: H10o···O3$^{\mathrm{ii}}$ = 1.84(4) Å, O10···O3$^{\mathrm{ii}}$ = 2.670(4) Å with angle at H10o = 171(5)° for symmetry operations (i) x, $-1+y$, $-1+z$ and (ii) x, $1+y$, $1+z$]. The result of the aforementioned mode of association is a linear supramolecular chain along [0 1 1]. The 3-BrBA molecules self-associate about a centre of inversion *via* hydroxy-O—H···O(carbonyl) hydrogen bonds to form a dimeric aggregate [O2—H2o···O1$^{\mathrm{iii}}$: H2o···O1$^{\mathrm{iii}}$ = 1.79(8) Å, O2···O1$^{\mathrm{iii}}$ = 2.598(5) Å with angle at 177(10)° for (iii) $1-x$, $1-y$, $-z$]. Neighbouring supramolecular chains are connected by dimeric aggregates formed by the 3-BrBA molecules *via* side-on C—Br···π interactions [C4—Br1···Cg(C23—C28)$^{\mathrm{iv}}$: Br1···Cg(C23—C28)$^{\mathrm{iv}}$ = 3.9117(19) Å, C4···Cg(C23—C28)$^{\mathrm{iv}}$ = 4.427(5) Å with angle at Br1 = 92.64(15)° for (iv) $2-x$, $2-y$, $1-z$]. In a similar fashion, centrosymmetrically-related supramolecular chains are connected directly *via* side-on C=O···π interactions [C21—O5···Cg(C15—C20)$^{\mathrm{v}}$: O5···Cg(C15—C20)$^{\mathrm{v}}$ = 3.300(3) Å, C21···Cg(C15—C20)$^{\mathrm{v}}$ = 3.662(4) Å with angle at O5 = 97.2(2)° for (v) $1-x$, $1-y$, $1-z$]. In addition, π—π stacking interactions link 3-BrBA and DTBA rings to consolidate the three-dimensional architecture [Cg(C9—C14)···Cg(C2—C7) = 3.706(3) Å and angle of inclination = 6.0(2)° and Cg(C29—C34)···Cg(C2—C7)$^{\mathrm{vi}}$ = 3.729(3) Å and angle of inclination = 7.0(2)° for (vi) $1-x$, $2-y$, $1-z$].

Further insight into the supramolecular association in the title co-crystal and the isostructural 3-ClBA species [12] was gained through an analysis of the calculated Hirshfeld surfaces as well as the full and delineated two-dimensional fingerprint plots using literature procedures [14] and Crystal Explorer 17 [15]. The calculations were performed on the asymmetric unit illustrated in the figure, and for the entire asymmetric unit for the isostructural literature analogue [12]. This analysis reveals that a considerable number of different contacts impact upon the Hirshfeld surface with the most prominent contacts being H···H [30.8%], O···H/H···O [22.9%], C···H/H···C [12.8%] and S···H/H···S [10.0%]. Less prominent but significant contacts are of the type C···C [6.7%], O···C/C···O [6.4%] and Br···H/H···Br [5.0%]. The results of the analogous analysis of the molecular packing of the isostructural 3-ClBA species [12] mirror those of the title compound very closely. Thus, the greatest disparities are noted in the H···H [30.3%] and O···H/H···O [23.6%] percentage contibutions but, the differences are <1%; the differences in the other percentage contacts were 0.1% or less. These results emphasise the isostructural relationship in the two co-crystals.

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

References

1. Rigaku Oxford Diffraction: CrysAlis$^{\mathrm{PRO}}$. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Broker, G. A.; Tiekink, E. R. T.: Co-crystal formation between 2,2′-dithiodibenzoic acid and each of 4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethene and 1,2-bis(4-pyridyl)ethane. CrystEngComm **9** (2007) 1096–1109.
6. Broker, G. A.; Bettens, R. P. A.; Tiekink, E. R. T.: Co-crystallisation of 2,2′-dithiodibenzoic acid with the isomeric *n*-pyridinealdazines, $n = 2$, 3 and 4: supramolecular polymers and the influence of steric factors upon aggregation patterns. CrystEngComm **10** (2008) 879–887.

7. Yang, Y.; Li, L.; Zhang, L.; Dong, W.; Ding, K.: Three polymorphs of an inclusion compound of 2,2′-(disulfanediyl)dibenzoic acid and trimethyl-amine. Acta Crystallogr. **C72** (2016) 981–989.
8. Tan, S. L.; Tiekink, E. R. T.: A 1:2 co-crystal of 2,2′-dithiodibenzoic acid and benzoic acid: crystal structure, Hirshfeld surface analysis and computational study. Acta Crystallogr. **E75** (2019) 1–7.
9. Tan, S. L.; Tiekink, E. R. T.: A 1:1:1 co-crystal solvate comprising 2,2′-dithiodibenzoic acid, 2-chlorobenzoic acid and *N*,*N*-dimethylformamide: crystal structure, Hirshfeld surface analysis and computational study. Acta Crystallogr. **E75** (2019) 475–481.
10. Rowland, C. E.; Cantos, P. M.; Toby, B. H.; Frisch, M.; Deschamps, J. R.; Cahill, C. L.: Controlling disulfide bond formation and crystal growth from 2-mercaptobenzoic acid. Cryst. Growth Des. **11** (2011) 1370–1374.
11. Tan, S. L.; Tiekink, E. R. T.: A 1:2 co-crystal of 2,2′-thiodibenzoic acid and triphenylphosphane oxide: crystal structure, Hirshfeld surface analysis and computational study. Acta Crystallogr. **E74** (2018) 1764–1771.
12. Tan, S. L.; Tiekink, E. R. T.: Crystal structure of the co-crystal 2-[(2-carboxyphenyl)disulfanyl]benzoic acid – 3-chlorobenzoic acid (2/1), $C_{35}H_{25}ClO_{10}S_4$. Z. Kristallogr. NCS **234** (2019) 433–436.
13. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.
14. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. Acta Crystallogr. **E75** (2019) 308–318.
15. Turner, M. J.; Mckinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).