Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

1,5-Bis(3,4,5-trimethoxyphenyl)penta-1,4-dien-3-one 1.333-hydrate–1,5-bis(3-bromo-4,5-dimethoxyphenyl)penta-1,4-dien-3-one 1.333-hydrate 0.919 (3):0.081 (3) cocrystal

H. J. Ravindra,[a] S. M. Dharmaprakash[a] and William T. A. Harrison[b]*

[a]Department of Physics, Mangalore University, Mangalagangotri 574 199, India, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
H-atom completeness 91%
Disorder in main residue
R factor = 0.064
wR factor = 0.158
Data-to-parameter ratio = 15.3

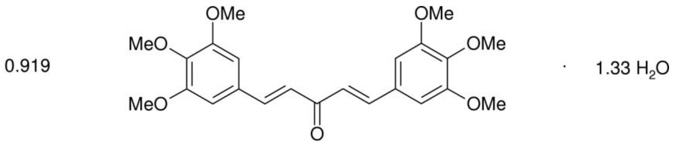
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 March 2007
Accepted 1 May 2007

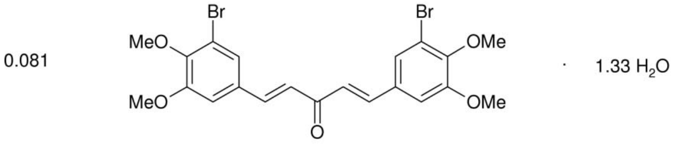
The title cocrystal, 0.919 (3)($C_{23}H_{26}O_7 \cdot 1.333H_2O$)·0.081 (3)($C_{22}H_{20}Br_2O_5 \cdot 1.333H_2O$), arose due to the presence of an impurity in one of the starting materials. In both cases, the complete organic molecule has twofold rotation symmetry, with the central C═O group lying on the rotation axis.

Comment

The title cocrystal, (I)+(II), was prepared as part of our ongoing studies (Fun *et al.*, 2007) of the structures and optical properties of chalcone derivatives. The unexpected presence of the bromine-containing molecule (II) arose due to an impurity in one of the starting materials. A similar situation in a related cocrystal was recently described by Ng *et al.* (2006). No second-harmonic generation (SHG) response in (I)+(II) is observed, because it crystallizes in a centrosymmetric space group. However, it exhibits a good third-order non-linear optical response (non-linear absorption and refraction).



(I)



(II)

The two organic constituents occur in a 0.919 (3):0.081 (3) ratio in the cocrystal studied here. Both complete molecules have twofold rotation symmetry, with C1 and O1 lying on the rotation axis. All atoms except O4/C12/H12*a*/H12*b*/H12*c* [for (I)] and Br1 [for (II)] are common to the two components (Fig. 1).

Because the complete molecules of (I) and (II) are generated by twofold symmetry, the real situation could be even more complex, with the possibility of a 'mixed' molecule containing a Br atom attached to one of the C8 atoms and a methoxy group attached to its symmetry-related partner. Lower-symmetry models of the structure were tried to assess this possibility, but were inconclusive.

Compound (I)+(II) largely possesses normal geometrical parameters (Allen *et al.*, 1987). The dihedral angle between

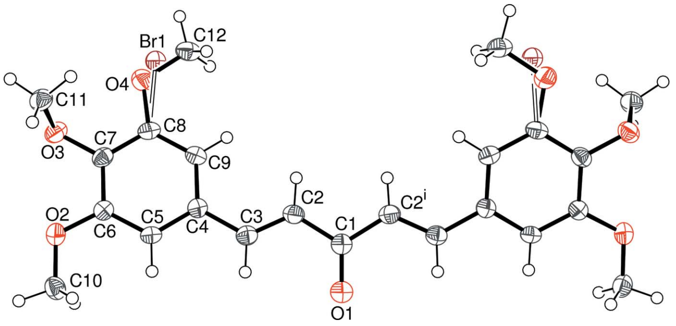


Figure 1
The molecular structure in the cocrystal of (I)+(II), showing the disorder of O4/C12 and Br1 atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. Water molecules have been omitted. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

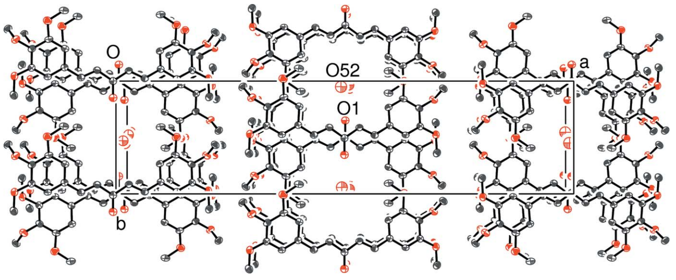


Figure 2
View down [001] of the packing. All H atoms are omitted for clarity, as is the Br atom of (II).

the two aromatic rings in the molecule is 25.15 (7)°. Atoms C10, C11 and C12 deviate from the mean plane of the C4–C9 ring by −0.169 (5), 1.293 (5) and 0.099 (5) Å, respectively. The central C3/C2/C1/C2^i/C3^i/O1 [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$] fragment is close to planar (r.m.s. deviation from the mean plane = 0.032 Å) but there is a significant twisting about the C3—C4 bond; the dihedral angle between C3/C2/C1/C2^i/C3^i/O1 and C4–C9 is 14.07 (8)°.

Highly disordered water molecules accompany the organic species in the crystal. Because of close O⋯O contacts, the fractional site occupancies of O51 and O52 (general positions) cannot be greater than $\frac{1}{3}$, hence the unusual overall stoichiometry. There are probably O—H⋯O hydrogen bonds linking the water molecules together and also linking to O1, but the water H atoms could not be located in the present study.

The crystal packing for (I)+(II) results in the organic molecules delineating large [001] pseudo-channels occupied by the water molecules (Fig. 2). The view down [010] (Fig. 3) is very different, and shows the organic molecules all tilted in the same sense with respect to the *ab* plane.

Experimental

A Claisen–Schmidt condensation reaction was used. A solution of ethanol (20 ml) and 10% sodium hydroxide solution (5 ml) was placed in a conical flask. A previously prepared portion of 3,4,5-trimethoxybenzaldehyde (0.002 mol) and acetone (0.001 mol) dissolved in ethanol (15 ml) was added to the conical flask with stirring and the temperature of the solution was maintained between 293 and 298 K. A precipitate was obtained after stirring the solution for about five minutes. The remaining portion of the aldehyde and ketone mixture was added and the solution was stirred for about 60 minutes. The solid product was filtered, washed with excess water to remove the alkali, and dried. Single crystals of (I)+(II) were grown by slow evaporation of an acetone solution. The 3,4,5-trimethoxybenzaldehyde starting material was contaminated with some 3-bromo-4,5-dimethoxybenzaldehyde, resulting also in the formation of (II). The presence of bromine in the starting material as well as the product was confirmed by performing the halogen test.

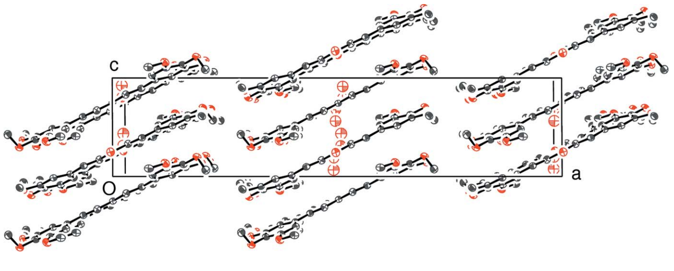


Figure 3
View down [010] of the packing. All H atoms are omitted for clarity, as is the Br atom of (II).

Crystal data

$0.919C_{23}H_{26}O_7\cdot0.081C_{21}H_{20}Br_2O_5\cdot1.333H_2O$
$M_r = 446.26$
Monoclinic, $C2/c$
$a = 34.035$ (3) Å
$b = 8.4017$ (9) Å
$c = 7.4385$ (5) Å
$\beta = 90.305$ (6)°
$V = 2127.0$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.40$ mm^{-1}
$T = 120$ (2) K
0.44 × 0.16 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.842$, $T_{\max} = 0.984$
8542 measured reflections
2346 independent reflections
1278 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.158$
$S = 1.06$
2346 reflections
153 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

After initial modelling as the expected compound (I), high residuals ($wR_2 > 0.20$) and a large difference peak in the vicinity of C12 and O4 resulted. The separation of the peak and C8 suggested the presence of a C—Br bond. Refinement as a cocrystal of (I)+(II) (occupancies of the –O4/C12 and –Br1 groups/atoms attached to C8 refined with their sum constrained to unity) converged to a physically plausible answer with low residuals. All the C-bound H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}$(methyl C). The water H atoms could not be located.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3*

o2878 Ravindra *et al.* • $0.919C_{23}H_{26}O_7\cdot0.081C_{21}H_{20}Br_2O_5\cdot1.333H_2O$ *Acta Cryst.* (2007). E**63**, o2877–o2879

(Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

We thank the EPSRC UK National Crystallography Service (University of Southampton) for the data collection.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fun, H.-K., Patil, P. S., Dharmaprakash, S. M. & Chantrapromma, S. (2007). *Acta Cryst.* E**63**, o561–o562.

Ng, S.-L., Razak, I. A., Fun, H.-K., Patil, P. S., Dharmaprakash, S. M. & Shettigar, V. (2006). *Acta Cryst.* E**62**, o2611–o2613.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Acta Cryst. (2007). E**63**, o2877–o2879 Ravindra *et al.* • $0.919C_{23}H_{26}O_7 \cdot 0.081C_{21}H_{20}Br_2O_5 \cdot 1.333H_2O$ **o2879**