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2,5-Dibromo-3,6-dimethoxycyclohexa-2,5-diene-1,4-dione

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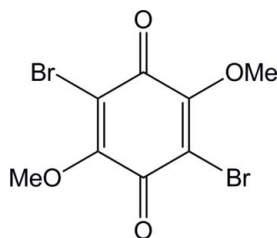
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.028; wR factor = 0.067; data-to-parameter ratio = 19.8.

In the structure of the title compound, $\text{C}_8\text{H}_6\text{Br}_2\text{O}_4$, the complete molecule is generated by the application of a centre of inversion. The molecule is planar (r.m.s. deviation for all non-H atoms but methyl C = 0.0358 Å), with only the methyl groups being deviated from the plane [by ± 0.321 (4) Å]. In the crystal packing, $\text{Br} \cdots \text{O}(\text{methoxy})$ halogen bonds [3.2407 (19) Å] connect molecules into supramolecular layers parallel to (101).

Related literature

For the synthesis of the title compound, see: Viault *et al.* (2011). For the structure of bromanilic acid, see: Robl (1987). For similar structures with a 2,5-cyclohexadiene-1,4-dione core, see: Nakatsuji *et al.* (2009). For an article dealing with the biological relevance of this type of compound, see: Viault *et al.* (2013). For papers using the title compound as a synthetic precursor, see: Khan & Driscoll (1976); Tatsuta *et al.* (2001); Kasahara & Kondo (2006); Gan *et al.* (2009). For metallassemblies obtained with analogous building blocks, see: Gupta *et al.* (2014); Therrien (2009).



Experimental

Crystal data

$\text{C}_8\text{H}_6\text{Br}_2\text{O}_4$	$V = 475.71$ (7) Å ³
$M_r = 325.95$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.4456$ (9) Å	$\mu = 8.50$ mm ⁻¹
$b = 5.4877$ (3) Å	$T = 173$ K
$c = 10.0341$ (9) Å	$0.23 \times 0.21 \times 0.20$ mm
$\beta = 113.846$ (7)°	

Data collection

Stoe IPDS diffractometer	8772 measured reflections
Absorption correction: part of the refinement model (ΔF) (<i>DIFABS</i> ; Walker & Stuart, 1983)	1284 independent reflections
$T_{\min} = 0.246$, $T_{\max} = 0.704$	1144 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	65 parameters
$wR(F^2) = 0.067$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.86$ e Å ⁻³
1284 reflections	$\Delta\rho_{\text{min}} = -0.98$ e Å ⁻³

Data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5317).

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supplementary materials

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2,5-Dibromo-3,6-dimethoxycyclohexa-2,5-diene-1,4-dione

Ersin Orhan, Amine Garci and Bruno Therrien

1. Chemical context**2. Structural commentary**

Embelin (2,5-dihydroxy-3-undecylcyclohexa-2,5-diene-1,4-dione) and its derivatives possess great biological potential (Viault *et al.*, 2013). Over the years, several synthetic strategies have been developed to prepare analogues of Embelin (Khan & Driscoll, 1976; Tatsuta *et al.*, 2001; Kasahara & Kondo, 2006; Gan *et al.*, 2009; Viault *et al.*, 2011), and among the precursors used to synthesize these Embelin derivatives, 2,5-dibromo-3,6-dimethoxycyclohexa-2,5-diene-1,4-dione (C₈H₆Br₂O₄) is often encountered. Moreover, such 2,5-dihydroxy-1,4-benzoquinones are commonly used as building blocks to generate metalla-assemblies (Therrien, 2009; Gupta *et al.*, 2014), which explains our interest in the title compound. The molecular structure is presented in Fig. 1.

In the solid-state, the molecule, which sits about an inversion centre, is planar with the methyl groups being only $\pm 0.321(4)$ Å out of this plane (the plane defined by the dibromobenzoquinone unit including the two O atoms of the methoxy groups has a r.m.s. deviation of 0.0358 Å). The electron delocalization within the cyclohexadiene core is reflected in the C—C bonds, which show intermediate values instead of the typical C—C and C=C bond distances. A similar pattern of C—C bond distances was observed in the analogous compound bromanilic acid (Robl, 1987) and other substituted 2,5-cyclohexadiene-1,4-dione derivatives (Nakatsuji *et al.*, 2009).

3. Supramolecular features

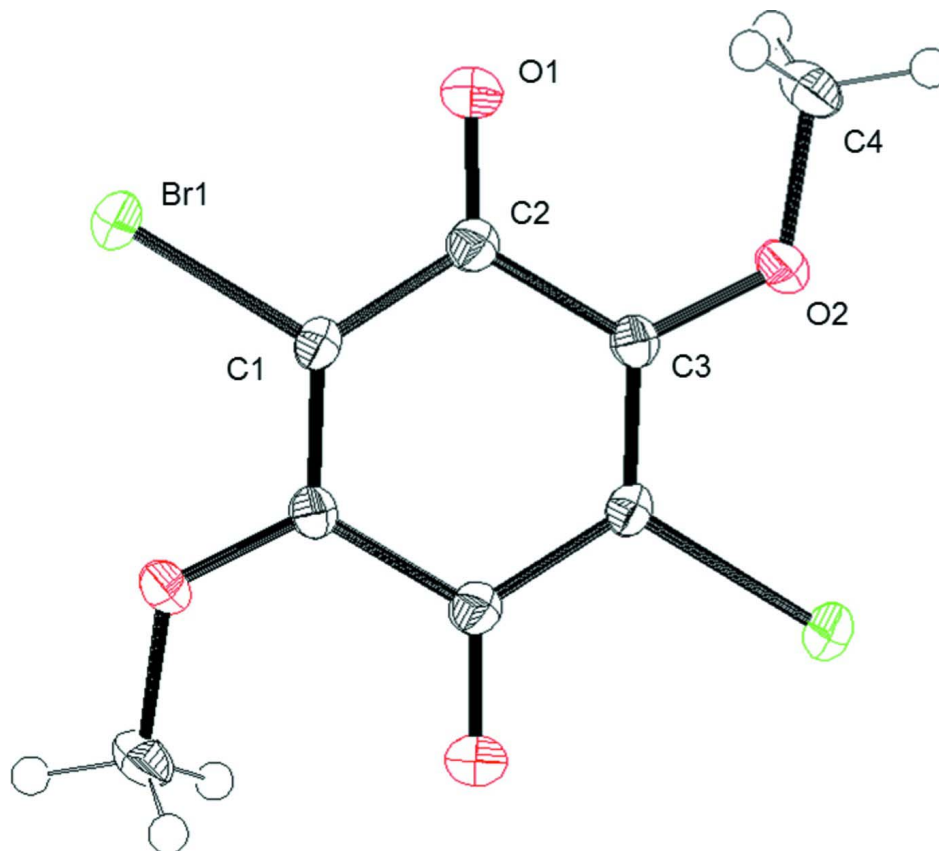
In the crystal packing Br \cdots O(methoxy) halogen bonds [3.2407(19) Å] connect molecules into supramolecular layers parallel to (101).

4. Database survey**5. Synthesis and crystallization**

2,5-Dibromo-3,6-dimethoxycyclohexa-2,5-diene-1,4-dione was prepared according to a published method (Viault *et al.*, 2011). Crystals were obtained by slow evaporation of an ethyl acetate solution containing the title compound.

6. Refinement

Hydrogen atoms were included in calculated positions and treated as riding atoms, with C—H = 0.96 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

**Figure 1**

The molecular structure of 2,5-dibromo-3,6-dimethoxy-2,5-cyclohexadiene-1,4-dione (symmetry operation $i = -x, 1 - y, 2 - z$). Displacement ellipsoids are drawn at the 50% probability level.

2,5-Dibromo-3,6-dimethoxycyclohexa-2,5-diene-1,4-dione

Crystal data

$C_8H_6Br_2O_4$

$M_r = 325.95$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2_1n$

$a = 9.4456 (9) \text{ \AA}$

$b = 5.4877 (3) \text{ \AA}$

$c = 10.0341 (9) \text{ \AA}$

$\beta = 113.846 (7)^\circ$

$V = 475.71 (7) \text{ \AA}^3$

$Z = 2$

$F(000) = 312$

$D_x = 2.276 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 7998 reflections

$\theta = 2.4\text{--}25.9^\circ$

$\mu = 8.50 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Block, red

$0.23 \times 0.21 \times 0.20 \text{ mm}$

Data collection

Stoe IPDS

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 0 pixels mm^{-1}

φ oscillation scans

Absorption correction: part of the refinement model (ΔF)

(*DIFABS*; Walker & Stuart, 1983)

$T_{\min} = 0.246, T_{\max} = 0.704$

8772 measured reflections

1284 independent reflections

1144 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$
 $\theta_{\text{max}} = 29.2^\circ$, $\theta_{\text{min}} = 2.5^\circ$
 $h = -12 \rightarrow 12$

$k = -7 \rightarrow 7$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.067$
 $S = 1.04$
 1284 reflections
 65 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.86 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.98 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. A crystal was mounted at 173 K on a Stoe Image Plate Diffraction System (Stoe & Cie, 2000) using Mo $K\alpha$ graphite monochromated radiation. Image plate distance 100 mm, φ oscillation scans 0 - 180°, step $\Delta\varphi = 1.2^\circ$, 3 minutes per frame.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.14128 (3)	0.21073 (5)	0.79296 (3)	0.02303 (10)
C2	-0.0827 (3)	0.2940 (4)	0.9112 (3)	0.0197 (4)
C4	-0.3943 (3)	0.2112 (5)	0.9080 (3)	0.0253 (5)
H4A	-0.4045	0.2467	0.8109	0.038*
H4B	-0.4925	0.2333	0.9138	0.038*
H4C	-0.3608	0.0457	0.9320	0.038*
O2	-0.2815 (2)	0.3740 (4)	1.00971 (19)	0.0262 (4)
O1	-0.1483 (2)	0.1143 (4)	0.8426 (2)	0.0332 (4)
C1	0.0654 (3)	0.3806 (4)	0.9134 (2)	0.0176 (4)
C3	-0.1485 (2)	0.4344 (4)	1.0024 (2)	0.0174 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02309 (14)	0.02542 (15)	0.02416 (15)	0.00012 (9)	0.01326 (10)	-0.00545 (8)
C2	0.0212 (11)	0.0197 (10)	0.0193 (11)	-0.0009 (8)	0.0093 (9)	-0.0011 (8)
C4	0.0178 (10)	0.0290 (12)	0.0266 (12)	-0.0072 (9)	0.0064 (9)	-0.0016 (9)
O2	0.0216 (8)	0.0326 (9)	0.0283 (9)	-0.0113 (7)	0.0143 (7)	-0.0098 (8)
O1	0.0311 (10)	0.0297 (10)	0.0443 (11)	-0.0119 (8)	0.0209 (9)	-0.0171 (9)
C1	0.0185 (10)	0.0190 (10)	0.0169 (9)	0.0013 (8)	0.0090 (8)	-0.0011 (8)

C3 0.0176 (9) 0.0184 (10) 0.0177 (9) -0.0004 (8) 0.0086 (8) 0.0012 (7)

Geometric parameters (Å, °)

Br1—C1	1.882 (2)	C4—H4B	0.9600
C2—O1	1.219 (3)	C4—H4C	0.9600
C2—C1	1.469 (3)	O2—C3	1.330 (3)
C2—C3	1.509 (3)	C1—C3 ⁱ	1.351 (3)
C4—O2	1.448 (3)	C3—C1 ⁱ	1.351 (3)
C4—H4A	0.9600		
O1—C2—C1	122.3 (2)	H4B—C4—H4C	109.5
O1—C2—C3	121.0 (2)	C3—O2—C4	123.90 (19)
C1—C2—C3	116.68 (19)	C3 ⁱ —C1—C2	124.14 (19)
O2—C4—H4A	109.5	C3 ⁱ —C1—Br1	119.87 (16)
O2—C4—H4B	109.5	C2—C1—Br1	115.96 (16)
H4A—C4—H4B	109.5	O2—C3—C1 ⁱ	118.4 (2)
O2—C4—H4C	109.5	O2—C3—C2	122.4 (2)
H4A—C4—H4C	109.5	C1 ⁱ —C3—C2	119.05 (19)
O1—C2—C1—C3 ⁱ	-174.0 (2)	C4—O2—C3—C2	-15.5 (4)
C3—C2—C1—C3 ⁱ	4.2 (4)	O1—C2—C3—O2	-1.7 (4)
O1—C2—C1—Br1	4.2 (3)	C1—C2—C3—O2	-179.9 (2)
C3—C2—C1—Br1	-177.59 (16)	O1—C2—C3—C1 ⁱ	174.3 (2)
C4—O2—C3—C1 ⁱ	168.5 (2)	C1—C2—C3—C1 ⁱ	-4.0 (4)

Symmetry code: (i) $-x, -y+1, -z+2$.