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

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In the structure of the title compound, $C_8H_6Br_2O_4$, 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, $Br\cdots O$(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 metalla-assemblies obtained with analogous building blocks, see: Gupta *et al.* (2014); Therrien (2009).
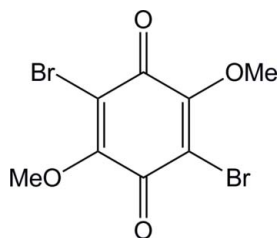


## Experimental

### Crystal data

| | |
|---|---|
| $C_8H_6Br_2O_4$ | $V$ = 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 × 0.21 × 0.20 mm |
| $\beta$ = 113.846 (7)° | |

### Data collection

| | |
|---|---|
| Stoe IPDS diffractometer | 8772 measured reflections |
| Absorption correction: part of the refinement model ($\Delta F$) (*DIFABS*; Walker & Stuart, 1983) | 1284 independent reflections |
| | 1144 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.246, $T_{max}$ = 0.704 | $R_{int}$ = 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 | $\Delta\rho_{max}$ = 0.86 e Å$^{-3}$ |
| 1284 reflections | $\Delta\rho_{min}$ = −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

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

**Ersin Orhan, Amine Garci and Bruno Therrien**

### S1. 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 ($C_8H_6Br_2O_4$) 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 ±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).

### S2. Supramolecular features

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

### S3. 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.

### S4. Refinement

Hydrogen atoms were included in calculated positions and treated as riding atoms, with C—H = 0.96 Å, and with $U_{iso}$(H) = 1.5$U_{eq}$(C).
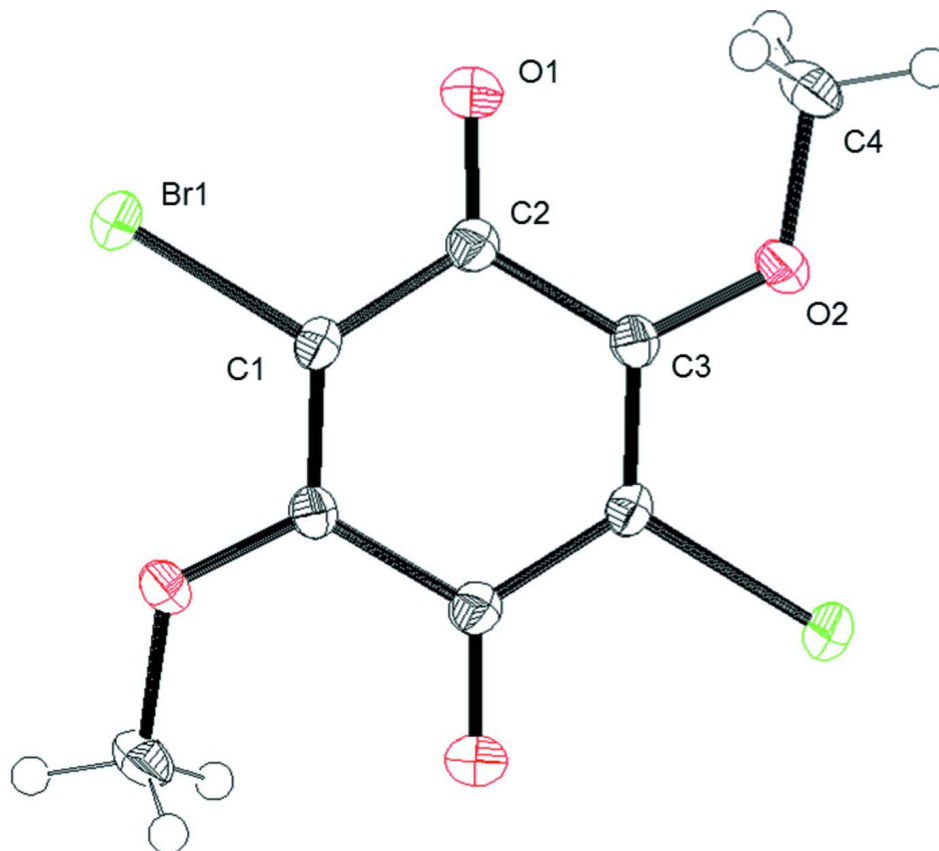
**Figure 1**

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*

| | |
|---|---|
| $C_8H_6Br_2O_4$ | $F(000) = 312$ |
| $M_r = 325.95$ | $D_x = 2.276$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2yn | Cell parameters from 7998 reflections |
| $a = 9.4456$ (9) Å | $\theta = 2.4$–$25.9°$ |
| $b = 5.4877$ (3) Å | $\mu = 8.50$ mm$^{-1}$ |
| $c = 10.0341$ (9) Å | $T = 173$ K |
| $\beta = 113.846$ (7)° | Block, red |
| $V = 475.71$ (7) Å$^3$ | $0.23 \times 0.21 \times 0.20$ mm |
| $Z = 2$ | |

*Data collection*

| | |
|---|---|
| Stoe IPDS diffractometer | Absorption correction: part of the refinement model ($\Delta F$) |
| Radiation source: fine-focus sealed tube | (*DIFABS*; Walker & Stuart, 1983) |
| Graphite monochromator | $T_{min} = 0.246$, $T_{max} = 0.704$ |
| Detector resolution: 0 pixels mm$^{-1}$ | 8772 measured reflections |
| $\varphi$ oscillation scans | 1284 independent reflections |
| | 1144 reflections with $I > 2\sigma(I)$ |

$R_{int} = 0.071$

$\theta_{max} = 29.2°$, $\theta_{min} = 2.5°$

$h = -12\rightarrow12$

$k = -7\rightarrow7$

$l = -13\rightarrow13$

## Refinement

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.028$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.067$ | |
| $S = 1.04$ | H-atom parameters constrained |
| 1284 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ |
| 65 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 0.86$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.98$ e Å$^{-3}$ |

## 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, $\varphi$ oscillation scans 0 - 180°, step $\Delta\varphi = 1.2°$, 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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—C3i | 1.351 (3) |
| C4—O2 | 1.448 (3) | C3—C1i | 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) | C3i—C1—C2 | 124.14 (19) |
| O2—C4—H4A | 109.5 | C3i—C1—Br1 | 119.87 (16) |
| O2—C4—H4B | 109.5 | C2—C1—Br1 | 115.96 (16) |
| H4A—C4—H4B | 109.5 | O2—C3—C1i | 118.4 (2) |
| O2—C4—H4C | 109.5 | O2—C3—C2 | 122.4 (2) |
| H4A—C4—H4C | 109.5 | C1i—C3—C2 | 119.05 (19) |
| | | | |
| O1—C2—C1—C3i | −174.0 (2) | C4—O2—C3—C2 | −15.5 (4) |
| C3—C2—C1—C3i | 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—C1i | 174.3 (2) |
| C4—O2—C3—C1i | 168.5 (2) | C1—C2—C3—C1i | −4.0 (4) |

Symmetry code: (i) −*x*, −*y*+1, −*z*+2.