Crystal structure, Hirshfeld surface and frontier molecular orbital analysis of 9-(3-bromo-4-hydroxy-5-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione

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In the fused ring system of the title compound, C24H27BrO5, the mean plane and maximum deviations of the central pyran ring are 0.0384 (2) and 0.0733 (2) Å, respectively. The cyclohexenone rings both adopt envelope conformations with the tetra-substituted C atoms as flap atoms, whereas the central pyran ring adopts a flattened boat conformation. The central pyran and phenyl substituent rings are almost perpendicular to each other, making a dihedral angle of 89.71 (2)°. In the crystal, pairs of molecules are linked via O—H⋯C1/C1/C1 hydrogen bonds, forming inversion dimers with an \( R_2^2(20) \) ring motif. A Hirshfeld surface analysis indicates that the most important contributions to the crystal packing are from H⋯H (50.6%), O⋯H/H⋯O (22.9%) and C⋯H/H⋯C (11.1%) contacts. Quantum chemical calculations for the frontier molecular orbitals were undertaken to determine the chemical reactivity of the title compound.

1. Chemical context

Xanthene is known as the parent compound of naturally occurring substances with various biological properties including antibacterial (Dimmock et al., 1988), antiviral (Naidu et al., 2012), antitumor (Al-Omran et al., 2014) and anti-inflammatory activities (Dimmock et al., 1988; Cottam et al., 1996). It is present in organic compounds that are widely used as synthetic dyes (Hilderbrand et al., 2007), in fluorescent materials used for visualization of biomolecules (Knight et al., 1989), and in laser technologies (Pohlers et al., 1997). Ehretianone, a quinonoid xanthene, was reported to possess anti-snake venom activity (Selvanayagam et al., 1996; Poupelin et al., 1978). Xanthenes whose structures resemble those of 1,4-dihydropyridines can function as calcium channel blockers (Reddy et al., 2010; Rathore et al., 2009).
2. Structural commentary

The title compound (I) (Fig. 1) crystallizes in the triclinic space group $P1$ with $Z = 2$. The central pyran ring $B$ (O1/C1/C8–C10/C17) is almost planar with a mean deviation from the mean plane of 0.0384 (2) Å and a maximum deviation of 0.0733 (3) Å for C9. Atoms C9 and O1 are displaced out of the mean plane in the same direction so the ring may also be described as having a highly flattened boat conformation.

Both cyclohexenone rings, $A$ (C10–C13/C16/C17) and $C$ (C1–C3/C6–C8), adopt envelope conformations with atoms C13 and C3 as the flaps being situated out of the plane of the ring with deviations of 0.3281 (2) and 0.325 (2) Å, respectively. Rings $A$, $B$ and $C$ show total puckering amplitudes $Q(T)$ of 0.4645 (2), 0.1070 (2) and 0.4607 (16) Å, respectively. The puckering parameters (Cremer & Pople, 1975) are $\psi = 179.52 (8)^\circ$ and $\theta = 57.55 (2)^\circ$ for $A$, $\psi = 178.99 (2)^\circ$ and $\theta = 68.92 (2)^\circ$ for $B$, $\psi = 304.73 (12)^\circ$ and $\theta = 125.47 (2)^\circ$ for $C$. The planar phenyl substituent and the central pyran ring form a dihedral angle of 89.71 (2)$^\circ$. In the pyran ring, C1–C8 and C10–C17 are double bonds, as indicated by the bond lengths \[ C1–C8 = 1.344 (3) \text{ Å} \] and \[ C10–C17 = 1.336 (3) \text{ Å} \]. The angles and bond lengths (Allen et al., 1987; Li et al., 2019) are within normal ranges. The observed carbonyl bond lengths \[ C11–O3 = 1.216 (3) \text{ Å} \] and \[ C7–O2 = 1.227 (2) \text{ Å} \] are also normal.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecules are linked by pairs of O4–H4⋯O2 hydrogen bonds (Table 1), forming inversion dimers with an $R_2^2(20)$ ring motif, parallel to the (001) plane (Fig. 2). The molecules are further linked by C6–H6B⋯O2, C16–H16A⋯Br1 and O4–H4⋯O5 hydrogen bonds, forming ribbons (Fig. 3). Overall, the O–H⋯O and C–H⋯O interactions yield a three-dimensional supramolecular network.

![Figure 1](image1.png)

**Figure 1**
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

![Figure 2](image2.png)

**Figure 2**
A view of the structure of (I) showing the O–H⋯O hydrogen bonds, forming a centrosymmetric dimer with an $R_2^2(20)$ ring motif.

![Figure 3](image3.png)

**Figure 3**
Packing view for (I), showing the formation of O–H⋯O hydrogen bonds between molecules in the unit cell.

![Table 1](table1.png)

**Table 1**
Hydrogen-bond geometry (Å, $^\circ$).

| D—H⋯A       | D—H  | H⋯A  | D⋯A  | D—H⋯A  |
|--------------|------|------|------|--------|
| C6–H6B⋯O2   | 0.97 | 2.60 | 3.377 (3) | 137    |
| C16–H16A⋯Br1 | 0.97 | 2.94 | 3.736 (2) | 140    |
| O4–H4⋯O2    | 0.82 | 2.04 | 2.768 (2) | 148    |
| O4–H4⋯O5    | 0.82 | 2.28 | 2.701 (2) | 113    |

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+2$.

The crystal, molecules are linked by pairs of O4–H4⋯O2 hydrogen bonds (Table 1), forming inversion dimers with an $R_2^2(20)$ ring motif, parallel to the (001) plane (Fig. 2). The molecules are further linked by C6–H6B⋯O2, C16–H16A⋯Br1 and O4–H4⋯O5 hydrogen bonds, forming ribbons (Fig. 3). Overall, the O–H⋯O and C–H⋯O interactions yield a three-dimensional supramolecular network.
To quantify the intermolecular contacts in the crystal, Hirshfeld surfaces (Spackman & Jayatilaka, 2009) and two-dimensional fingerprint plots were generated using Crystal Explorer 17.5 (Turner et al., 2017). The Hirshfeld surfaces mapped over $d_{\text{norm}}$ in the range $0.5451$ to $1.6834$ a.u. (Fig. 4) show the intermolecular contacts as red-coloured spots, which indicate the closer contacts of C—H···O and O—H···O hydrogen bonds. The bright-red spots indicate their roles as donors and/or acceptors in hydrogen bonding; they also appear as red and blue regions corresponding to negative and positive potentials on the Hirshfeld surface mapped over electrostatic potential (Spackman et al., 2008) shown in Fig. 5. Here the red regions indicate negative electrostatic potential (hydrogen-bond acceptors), while the blue regions indicate positive electrostatic potential (hydrogen-bond donors). The 2D fingerprint plots are illustrated in Fig. 6. The H···H contacts comprise 50.6% of the total interactions. Besides these contacts, O···H/H···O (22.9%), C···H/H···C (11.1%)...
and Br· · · H/Br (11.6%) interactions make a significant contribution to the total Hirshfeld surface. The percentage contributions of the Br· · · O/O· · · Br, O· · · O and C· · · C contacts are 1.8, 0.7 and 0.1%, respectively.

4. Frontier molecular orbital analysis

The chemical reactivity of the title compound was studied by frontier molecular orbital analysis. For the calculation, the starting structural geometry was taken from the refined experimental structure obtained from X-ray diffraction data. The energy levels for the compound were computed using the DFT-B3LYP/6-311G++(d,p) level of theory as implemented in Gaussian09W (Frisch et al., 2013). The calculated frontier molecular orbitals, HOMO, HOMO—1, LUMO and LUMO+1, are shown in Fig. 7. The energies of HOMO, HOMO—1, LUMO and LUMO+1 were calculated to be −5.8915, −6.2499, −1.9353 and −1.0419 eV, respectively, and the energies required to excite one electron from HOMO to LUMO and from HOMO—1 to LUMO+1 are 3.9562 and 5.2080 eV, respectively. The chemical potential, chemical hardness, chemical softness and electrophilicity index of the title molecule are listed in Table 2. Parr et al. (1999) have proposed the electrophilicity index as a quantitative measure of the energy lowering due to the maximal electron flow between donor and acceptor orbitals. The electrophilicity index value of 3.8711 eV shows the global electrophilic nature of the molecule. Based on the wide band gap and its chemical hardness value of 1.9781 eV, the title molecule seems to be hard.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update May 2021; Groom et al., 2016) for the xanthen-1,8(2H)-dione unit resulted in 30 hits. They include the following analogues: 2,4-dinitrophenyl (LERZEP; Sureshbabu & Sughanya, 2013), 4-hydroxy-3,5-dimethoxyphenyl (YAVTAS; Sughanya & Sureshbabu, 2012), 2,4-difluorophenyl (VITWEC; Fun et al., 2011), pyridine-2-yl (YIDRIP; Purushothaman & Thiruvenkatam, 2018). In the title compound, the dihedral angle between the phenyl and pyran rings is 89.71 (2)°, similar to the values observed for LERZEP, the 2,4-dinitrophenyl analogue, YAVTAS, the 4-hydroxy-3,5-dimethoxyphenyl analogue, and VITWEC, the 2,4-difluorophenyl analogue, for which the dihedral angles are 85.88 (2), 86.32 (2) and 87.55 (4)°, respectively.

6. Synthesis and crystallization

Compound (I) was prepared in two stages (Vanag & Stankevich, 1960). A mixture of 5,5-dimethyl cyclohexane-1,3-dione (1.12 g, 8 mmol), 3-bromo-4-hydroxy-5-methoxybenzaldehyde (0.92 g, 4 mmol) and 20 ml of ethanol were heated to 343 K for about 10 minutes. The reaction mixture was allowed to cool to 298–301 K and the resulting intermediate compound, 2,2-[3-bromo-4-hydroxy-5-methoxyphenyl]methylene]bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) was filtered and dried (m.p. 491 K, 3.4 mmol, yield: 85%) (Sughanya & Sureshbabu, 2012). In the second stage, about 0.50 g (1.04 mmol) of this intermediate were dissolved in 20 ml of ethanol. The content was refluxed together with 5 drops of concentrated hydrochloric acid for 20 minutes with the reaction being monitored by TLC. After completion of the reaction, the reaction mixture was poured into 100 ml of ice-cold water and stirred well. The solid separated was filtered and dried. Yellow single crystals suitable for X-ray diffraction were obtained from 90% ethanol (m.p. 495 K, 0.455 g, 0.96 mmol, yield 92%). IR (KBr): cm⁻¹ 3360, 2953, 2865, 1667, 1622, 1584, 1497, 1278, 1234, 1046, 1003. ¹H NMR (500 MHz, CDCl₃): 1.04

| Frontier molecular orbitals | Energy |
|-----------------------------|--------|
| HOMO                        | −5.8915 eV |
| LUMO                        | −1.9353 eV |
| HOMO—1                      | −6.2499 eV |
| LUMO+1                      | −1.0419 eV |
| (E_HOMO − E_LUMO) gap       | 3.9562 eV |
| (E_HOMO—1 − E_LUMO+1) gap   | 5.2080 eV |
| Chemical potential (μ)      | 3.9134 eV |
| Chemical hardness (γ)       | 1.9781 eV |
| Chemical softness (S)       | 0.5055 eV |
| Electrophilicity index (ω)  | 3.8711 eV |
Table 3
Experimental details.

| Crystal data | Chemical formula | C_{24}H_{27}BrO_{5} |
|--------------|------------------|---------------------|
| M, (g/mol)   |                  | 475.36              |
| Crystal system, space group | Triclinic, PT |
| Temperature (K) | 296 |
| a, b, c (Å) | 9.851 (3), 10.763 (3), 12.313 (3) |
| α, β, γ (°) | 82.38 (1), 66.900 (9), 73.484 (10) |
| V (Å³) | 1150.9 (5) |
| Z | 2 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 1.82 |
| Crystal size (mm) | 0.30 × 0.25 × 0.20 |

Data collection

| Diffractometer | Bruker Kappa APEX3 CMOS |
|----------------|------------------------|
| Absorption correction | Multi-scan (SADABS; Bruker, 2016) |
| \(I_{min} - I_{max}\) | 0.550, 0.746 |
| No. of measured, independent and observed [\(|I| > 2\sigma(I)\)] reflections | 47600, 4052, 3694 |
| \(R_{int}\) | 0.029 |
| \(\sin(\theta)/\lambda\) max (Å⁻¹) | 0.950 |
| Refinement | H atoms treated by a mixture of independent and constrained refinement |
| \(R[F^2 > 2\sigma(F^2)], wR(F^2), S\) | 0.027, 0.072, 1.08 |
| No. of reflections | 4052 |
| No. of parameters | 276 |
| Crystal size (mm) | 0.30 × 0.25 × 0.20 |

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Computing details
Data collection: APEX3 (Bruker, 2016); cell refinement: APEX3 and SAINT-Plus (Bruker, 2016); data reduction: SAINT-Plus and XPREP (Bruker, 2016); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae et al., 2020); software used to prepare material for publication: SHELXL2018 (Sheldrick, 2015a) and publCIF (Westrip, 2010).

9-(3-Bromo-4-hydroxy-5-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione

Crystal data
C_{24}H_{27}BrO_{5}  \quad F(000) = 492
Mr = 475.36  \quad D_{\text{c}} = 1.372 \text{ Mg m}^{-3}
Triclinic, \ P\overline{1}  \quad \text{Melting point: 495 K}
a = 9.851 (3) Å  \quad \text{Mo } K\alpha \text{ radiation, } \lambda = 0.71073 \text{ Å}
b = 10.763 (3) Å  \quad \text{Cell parameters from 9325 reflections}
c = 12.313 (3) Å  \quad \theta = 2.6–30.0°
a = 82.38 (1)°  \quad \mu = 1.82 \text{ mm}^{-1}
b = 66.900 (9)°  \quad T = 296 \text{ K}
c = 73.484 (10)°  \quad \text{BLOCK, yellow}
V = 1150.9 (5) Å³  \quad 0.30 \times 0.25 \times 0.20 \text{ mm}
Z = 2

Data collection
Bruker Kappa APEX3 CMOS diffractometer  \quad 47600 measured reflections
Radiation source: fine-focus sealed tube  \quad 4052 independent reflections
Graphite monochromator  \quad 3694 reflections with \( I > 2\sigma(I) \)
\( \omega \) and \( \varphi \) scan  \quad R_{\text{int}} = 0.029
Absorption correction: multi-scan  \quad \theta_{\text{max}} = 25.0°, \theta_{\text{min}} = 3.4°
(SADABS; Bruker, 2016)  \quad h = -11→11
\( T_{\text{min}} = 0.550, T_{\text{max}} = 0.746 \quad k = -12→12\)
\( l = -14→14\)

Refinement
Refinement on \( F^2 \)  \quad wR(F^2) = 0.072
Least-squares matrix: full  \quad S = 1.08
\( R[F^2 > 2\sigma(F^2)] = 0.027 \quad 4052 \text{ reflections} \)
276 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x      | y      | z      | Uiso*/U_eq |
|---|--------|--------|--------|------------|
| Br1 | 0.49132 (3) | 0.69406 (2) | 0.62363 (2) | 0.05292 (10) |
| C1  | 0.5946 (2)  | 0.11911 (17) | 0.64639 (15) | 0.0319 (4)    |
| C2  | 0.4569 (2)  | 0.0735 (2)  | 0.66746 (17) | 0.0412 (5)    |
| H2A | 0.484623 | −0.020439 | 0.666673 | 0.049*        |
| H2B | 0.420396 | 0.105743 | 0.603872 | 0.049*        |
| C3  | 0.3280 (2)  | 0.1192 (2)  | 0.78588 (18) | 0.0423 (5)    |
| C4  | 0.2057 (3)  | 0.0452 (3)  | 0.8150 (2)  | 0.0676 (7)    |
| H4A | 0.250419 | −0.046032 | 0.819885 | 0.101*        |
| H4B | 0.125530 | 0.073181 | 0.889224 | 0.101*        |
| H4C | 0.164507 | 0.062167 | 0.754031 | 0.101*        |
| C5  | 0.2564 (3)  | 0.2644 (2)  | 0.7781 (3)  | 0.0617 (7)    |
| H5A | 0.332860 | 0.310996 | 0.759881 | 0.092*        |
| H5B | 0.215134 | 0.281231 | 0.717207 | 0.092*        |
| H5C | 0.176157 | 0.292245 | 0.852400 | 0.092*        |
| C6  | 0.3982 (3)  | 0.0887 (2)  | 0.88067 (18) | 0.0516 (6)    |
| H6A | 0.320679 | 0.124356 | 0.954643 | 0.062*        |
| H6B | 0.427417 | −0.004661 | 0.891856 | 0.062*        |
| C7  | 0.5345 (2)  | 0.13965 (17) | 0.85383 (16) | 0.0366 (4)    |
| C8  | 0.6339 (2)  | 0.15206 (16) | 0.72946 (15) | 0.0313 (4)    |
| C9  | 0.7704 (2)  | 0.20575 (17) | 0.70112 (16) | 0.0322 (4)    |
| C10 | 0.8672 (2)  | 0.19047 (17) | 0.57072 (16) | 0.0322 (4)    |
| C11 | 1.0196 (2)  | 0.2146 (2)  | 0.52605 (19) | 0.0439 (5)    |
| C12 | 1.1113 (2)  | 0.2068 (2)  | 0.3948 (2)  | 0.0495 (5)    |
| H12A | 1.180310 | 0.121046 | 0.378089 | 0.059*        |
| H12B | 1.127975 | 0.268803 | 0.372815 | 0.059*        |
| C13 | 1.0158 (2)  | 0.2333 (2)  | 0.31752 (18) | 0.0428 (5)    |
| C14 | 0.9298 (3)  | 0.3771 (2)  | 0.3217 (2)  | 0.0617 (7)    |
| H14A | 1.001793 | 0.429336 | 0.291989 | 0.093*        |
| H14B | 0.869236 | 0.392418 | 0.273983 | 0.093*        |
| H14C | 0.864478 | 0.399531 | 0.401812 | 0.093*        |
| C15 | 1.1185 (3)  | 0.1973 (3)  | 0.1891 (2)  | 0.0627 (7)    |
| H15A | 1.189481 | 0.250422 | 0.158058 | 0.094*        |
| H15B | 1.173617 | 0.107698 | 0.186491 | 0.094*        |
| H15C | 1.056780 | 0.211083 | 0.142489 | 0.094*        |
| Atomic displacement parameters ($\AA^2$) |
|----------------------------------------|
| $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
| Br1      | 0.06708 (17) | 0.03847 (13) | 0.05825 (15) | 0.00106 (10) | -0.03853 (12) | -0.00177 (9) |
| C1      | 0.0423 (10) | 0.0251 (9) | 0.0255 (9) | -0.0070 (8) | -0.0102 (8) | -0.0021 (7) |
| C2      | 0.0519 (12) | 0.0401 (11) | 0.0348 (10) | -0.0190 (9) | -0.0126 (9) | -0.0071 (8) |
| C3      | 0.0471 (12) | 0.0427 (11) | 0.0369 (10) | -0.0158 (9) | -0.0104 (9) | -0.0078 (9) |
| C4      | 0.0628 (16) | 0.0841 (19) | 0.0579 (15) | -0.0401 (15) | -0.0067 (13) | -0.0113 (14) |
| C5      | 0.0558 (14) | 0.0518 (14) | 0.0809 (18) | -0.0008 (11) | -0.0323 (13) | -0.0200 (13) |
| C6      | 0.0582 (14) | 0.0608 (14) | 0.0293 (10) | -0.0206 (11) | -0.0070 (10) | 0.0027 (10) |
| C7      | 0.0520 (12) | 0.0273 (9) | 0.0273 (9) | -0.0037 (8) | -0.0157 (9) | -0.0007 (7) |
| C8      | 0.0428 (10) | 0.0230 (8) | 0.0262 (9) | -0.0039 (7) | -0.0138 (8) | -0.0010 (7) |
| C9      | 0.0409 (10) | 0.0287 (9) | 0.0294 (9) | -0.0032 (8) | -0.0191 (8) | -0.0027 (7) |
| C10     | 0.0371 (10) | 0.0267 (9) | 0.0319 (9) | -0.0021 (7) | -0.0153 (8) | -0.0036 (7) |
| C11     | 0.0407 (11) | 0.0464 (12) | 0.0470 (12) | -0.0073 (9) | -0.0206 (10) | -0.0034 (9) |
| C12     | 0.0385 (11) | 0.0577 (14) | 0.0491 (12) | -0.0127 (10) | -0.0115 (10) | -0.0049 (10) |
| C13     | 0.0417 (11) | 0.0446 (11) | 0.0349 (10) | -0.0099 (9) | -0.0080 (9) | 0.0006 (9) |
| C14     | 0.0723 (17) | 0.0451 (13) | 0.0584 (15) | -0.0140 (12) | -0.0192 (13) | 0.0114 (11) |
| C15     | 0.0563 (14) | 0.0825 (18) | 0.0388 (12) | -0.0235 (13) | -0.0026 (11) | -0.0026 (12) |
| C16     | 0.0416 (11) | 0.0396 (10) | 0.0286 (9) | -0.0056 (8) | -0.0115 (8) | -0.0050 (8) |
| C17     | 0.0345 (10) | 0.0265 (9) | 0.0300 (9) | -0.0038 (7) | -0.0116 (8) | -0.0017 (7) |
| C18     | 0.0361 (10) | 0.0308 (9) | 0.0305 (9) | -0.0077 (8) | -0.0138 (8) | -0.0049 (7) |
| C19     | 0.0412 (10) | 0.0338 (10) | 0.0328 (9) | -0.0091 (8) | -0.0194 (8) | -0.0009 (8) |
| C20     | 0.0432 (11) | 0.0373 (10) | 0.0287 (9) | -0.0155 (8) | -0.0140 (8) | -0.0050 (8) |
sup-4

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C21 0.0862 (18) 0.0673 (16) 0.0484 (13) −0.0213 (14) −0.0426 (13) −0.0100 (11)
C22 0.0376 (10) 0.0295 (9) 0.0347 (10) −0.0097 (8) −0.0104 (8) −0.0060 (8)
C23 0.0361 (10) 0.0318 (9) 0.0346 (10) −0.0061 (8) −0.0175 (8) −0.0001 (8)
C24 0.0415 (10) 0.0345 (10) 0.0317 (9) −0.0076 (8) −0.0178 (8) −0.0062 (8)
O1 0.0420 (7) 0.0434 (7) 0.0240 (6) −0.0152 (6) −0.0112 (5) −0.0044 (5)
O2 0.0715 (10) 0.0505 (9) 0.0272 (7) −0.0142 (8) −0.0204 (7) −0.0024 (6)
O3 0.0588 (11) 0.1243 (17) 0.0587 (11) −0.0374 (11) −0.0297 (9) −0.0097 (11)
O4 0.0675 (10) 0.0325 (7) 0.0435 (8) −0.0032 (7) −0.0248 (8) −0.0116 (6)
O5 0.0739 (10) 0.0411 (8) 0.0421 (8) −0.0138 (7) −0.0303 (8) −0.0103 (6)

Geometric parameters (Å, °)

| Bond/Value | Value   |
|------------|---------|
| C1—O1      | 1.378 (2) |
| C1—C2      | 1.489 (3) |
| C2—C3      | 1.537 (3) |
| C2—H2A     | 0.9700   |
| C2—H2B     | 0.9700   |
| C3—C4      | 1.530 (3) |
| C3—C6      | 1.534 (3) |
| C4—H4A     | 0.9600   |
| C4—H4B     | 0.9600   |
| C5—H5A     | 0.9600   |
| C5—H5B     | 0.9600   |
| C6—H6A     | 0.9700   |
| C6—H6B     | 0.9700   |
| C7—O2      | 1.227 (2) |
| C7—C8      | 1.471 (3) |
| C8—C9      | 1.511 (3) |
| C9—C10     | 1.515 (3) |
| C9—C18     | 1.530 (2) |
| C9—H9      | 0.98 (2)  |
| C10—C17    | 1.336 (3) |
| C10—C11    | 1.470 (3) |
| C11—O3     | 1.216 (3) |
| C11—C12    | 1.510 (3) |
| C12—C13    | 1.533 (3) |
| C8—C1—O1   | 122.25 (17) |
| C8—C1—C2   | 126.24 (17) |
| O1—C1—C2   | 111.51 (15) |
| C1—C2—C3   | 112.21 (16) |
| C1—C2—H2A  | 109.2    |

Br1—C23 1.8954 (19) C12—H12A 0.9700
C1—C8 1.344 (3) C12—H12B 0.9700
C1—O1 1.378 (2) C13—C16 1.530 (3)
C1—C2 1.489 (3) C13—C14 1.535 (3)
C2—C3 1.537 (3) C13—C15 1.536 (3)
C2—H2A 0.9700 C14—H14A 0.9600
C2—H2B 0.9700 C14—H14B 0.9600
C3—C5 1.529 (3) C14—H14C 0.9600
C3—C4 1.530 (3) C15—H15A 0.9600
C3—C6 1.534 (3) C15—H15B 0.9600
C4—H4A 0.9600 C15—H15C 0.9600
C4—H4B 0.9600 C16—C17 1.489 (3)
C4—H4C 0.9600 C16—H16A 0.9700
C5—H5A 0.9600 C16—H16B 0.9700
C5—H5B 0.9600 C17—O1 1.378 (2)
C5—H5C 0.9600 C18—C24 1.380 (3)
C6—C7 1.494 (3) C18—C24 1.380 (3)
C6—H6A 0.9700 C19—C20 1.383 (3)
C6—H6B 0.9700 C19—H19 0.9300
C7—O2 1.227 (2) C20—O5 1.378 (2)
C7—C8 1.471 (3) C20—C22 1.400 (3)
C8—C9 1.511 (3) C21—O5 1.403 (3)
C9—C10 1.515 (3) C21—H21A 0.9600
C9—C18 1.530 (2) C21—H21B 0.9600
C9—H9 0.98 (2) C21—H21C 0.9600
C10—C17 1.336 (3) C22—O4 1.362 (2)
C10—C11 1.470 (3) C22—C23 1.384 (3)
C11—O3 1.216 (3) C23—C24 1.387 (3)
C11—C12 1.510 (3) C24—H24 0.9300
C12—C13 1.533 (3) O4—H4 0.8200

C8—C1—O1 122.25 (17) H12A—C12—H12B 107.6
C8—C1—C2 126.24 (17) C16—C13—C12 107.75 (17)
O1—C1—C2 111.51 (15) C16—C13—C14 110.89 (18)
C1—C2—C3 112.21 (16) C12—C13—C14 110.14 (19)
C1—C2—H2A 109.2 C16—C13—C15 108.20 (18)
C3—C2—H2A 109.2  C12—C13—C15 110.44 (19)  
C1—C2—H2B 109.2  C14—C13—C15 109.39 (19)  
C3—C2—H2B 109.2  C13—C14—H14A 109.5  
H2A—C2—H2B 107.9  C13—C14—H14B 109.5  
C5—C3—C4 109.3 (2)  H14A—C14—H14C 109.5  
C5—C3—C6 111.04 (18)  C13—C14—H14C 109.5  
C4—C3—C6 109.72 (19)  H14B—C14—H14C 109.5  
C5—C3—C2 109.94 (19)  C13—C15—H15A 109.5  
C4—C3—C2 109.43 (17)  C13—C15—H15B 109.5  
C6—C3—C2 107.36 (18)  C13—C15—H15C 109.5  
C3—C4—H4A 109.5  C15—C16—C13 112.68 (16)  
C3—C4—H4B 109.5  C15—C16—H16A 109.1  
H2A—C4—H4B 107.9  C15—C16—H16B 109.1  
C3—C4—H4C 109.5  C15—C16—H16C 109.8  
C3—C4—H4C 109.5  C10—C17—C16 123.42 (16)  
C3—C5—H5A 109.5  O1—C17—C16 111.41 (15)  
C3—C5—H5B 109.5  C24—C18—C19 124.98 (17)  
C3—C5—H5B 109.5  C24—C18—C9 122.64 (17)  
H5A—C5—H5B 109.5  C19—C18—C9 120.58 (16)  
C3—C5—H5C 109.5  C19—C18—C10 119.8 (17)  
H5A—C5—H5C 109.5  C20—C19—C10 111.38 (17)  
H5B—C5—H5C 109.5  C20—C19—H19 119.8 (12)  
C7—C6—C3 115.04 (17)  C1—O1—C17 118.39 (14)  
C7—C6—C3 118.04 (17)  O1—C17—C16 111.41 (15)  
C3—C6—C3 118.04 (17)  O5—C21—H21A 109.5  
C3—C6—H6A 108.5  O5—C21—H21B 109.5  
C7—C6—H6A 108.5  O5—C21—H21C 109.5  
C3—C6—H6B 108.5  C1—O1—C17 118.39 (14)  
C3—C6—H6B 108.5  O1—C17—C16 111.41 (15)  
H6A—C6—H6B 107.5  O4—C22—C23 119.68 (17)  
O2—C7—C8 119.91 (19)  O4—C22—C20 122.66 (17)  
O2—C7—C6 121.64 (18)  O5—C21—H21A 109.5  
C8—C7—C6 118.42 (17)  O5—C21—H21B 109.5  
C1—C8—C7 117.75 (18)  O5—C21—H21C 109.5  
C1—C8—C9 123.31 (16)  H21A—C21—H21C 109.5  
C7—C8—C9 118.90 (16)  H21B—C21—H21C 109.5  
C8—C9—C10 110.02 (15)  H21A—C21—H21B 109.5  
C8—C9—C18 111.38 (15)  H21B—C21—H21C 109.5  
C10—C9—C18 111.38 (15)  H21A—C21—H21B 109.5  
C8—C9—H9 107.8 (12)  H21B—C21—H21C 109.5  
C10—C9—H9 110.4 (11)  O4—C22—C23 119.68 (17)  
C18—C9—H9 108.0 (12)  O4—C22—C20 122.66 (17)  
C17—C10—C11 118.59 (17)  C23—C22—C20 117.67 (16)  
C17—C10—C9 122.45 (17)  C22—C23—C24 121.99 (17)  
C11—C10—C9 118.96 (16)  C22—C23—Br1 119.16 (14)  
O3—C11—C10 120.3 (2)  C24—C23—Br1 118.84 (14)  
O3—C11—C12 121.2 (2)  C18—C24—C23 119.71 (16)  
C10—C11—C12 118.47 (18)  C18—C24—H24 120.1  
C11—C12—C13 114.73 (18)  C23—C24—H24 120.1  
C11—C12—H12A 108.6  C1—O1—C17 118.39 (14)
C13—C12—H12A 108.6  C22—O4—H4  109.5
C11—C12—H12B 108.6  C20—O5—C21 117.51 (16)
C13—C12—H12B 108.6

C8—C1—C2—C3  24.0 (3)  C12—C13—C16—C17  49.6 (2)
O1—C1—C2—C3  −156.46 (16)  C14—C13—C16—C17 −71.0 (2)
C1—C2—C3—C5  72.5 (2)  C15—C13—C16—C17 169.04 (18)
C1—C2—C3—C4  −167.4 (2)  C11—C10—C17—O1  175.94 (16)
C1—C2—C3—C6  −48.4 (2)  C9—C10—C17—O1  −4.1 (3)
C5—C3—C6—C7  −67.4 (2)  C11—C10—C17—C16 −4.0 (3)
C4—C3—C6—C7  171.63 (19)  C9—C10—C17—C16 175.98 (17)
C2—C3—C6—C7  52.8 (2)  C13—C16—C17—C10 −24.5 (3)
C3—C6—C7—O2  151.79 (19)  C13—C16—C17—O1  155.55 (16)
C3—C6—C7—C8  −30.3 (3)  C8—C9—C18—C24 −68.8 (2)
O1—C1—C8—C7  −177.95 (16)  C10—C9—C18—C24 52.3 (2)
C2—C1—C8—C7  1.5 (3)  C8—C9—C18—C19 107.97 (19)
O1—C1—C8—C9  4.6 (3)  C10—C9—C18—C19 −130.94 (18)
C2—C1—C8—C9  −175.96 (17)  C10—C9—C18—C24 175.50 (17)
O2—C7—C8—C1  179.28 (17)  C9—C18—C19—C20 2.5 (3)
O2—C7—C8—C9  −3.1 (3)  C18—C19—C20—O5 −174.21 (17)
C6—C7—C8—C9  178.92 (17)  C18—C19—C20—C22 0.9 (3)
C1—C8—C9—C10 −10.9 (2)  O5—C20—C22—O4 −0.8 (3)
C7—C8—C9—C10  171.59 (15)  C19—C20—C22—O4 178.46 (18)
C1—C8—C9—C18  111.52 (19)  O5—C20—C22—O4 178.46 (18)
C1—C8—C9—C11  −65.9 (2)  C19—C20—C22—O4 −174.21 (17)
C8—C9—C10—C17  10.7 (2)  C20—C22—C23—C24 3.3 (3)
C18—C9—C10—C17  −111.0 (2)  C22—C23—C24—C18 −1.7 (3)
C8—C9—C10—C11  −169.39 (16)  Br1—C23—C24—C18 179.19 (14)
C18—C9—C10—C11  69.0 (2)  C20—C22—C23—Br1 −177.59 (14)
C17—C10—C11—O3  −174.2 (2)  C19—C18—C24—C23 175.50 (17)
C9—C10—C11—O3  5.9 (3)  C18—C19—C20—C22 2.0 (3)
C17—C10—C11—C12  3.5 (3)  C22—C23—C24—C18 179.19 (14)
C9—C10—C11—C12  −176.41 (18)  C8—C1—O1—C17  3.6 (2)
O3—C11—C12—C13  −156.7 (2)  C2—C1—O1—C17 −175.94 (15)
C10—C11—C12—C13  25.6 (3)  C10—C17—O1—C1 −3.8 (3)
C11—C12—C13—C16  −50.9 (2)  C16—C17—O1—C1 176.09 (15)
C11—C12—C13—C14  70.2 (2)  C19—C20—O5—C21 3.2 (3)
C11—C12—C13—C15  −168.9 (2)  C22—C20—O5—C21 −177.50 (19)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| C6—H6B···O2i | 0.97 | 2.60 | 3.377 (3) | 137 |
| C16—H16A···Br1ii | 0.97 | 2.94 | 3.736 (2) | 140 |
### Supporting Information

O4—H4···O2\(^{iii}\)  0.82  2.04  2.768 (2)  148
O4—H4···O5  0.82  2.28  2.701 (2)  113

Symmetry codes: (i) \(-x+1, -y, -z+2\); (ii) \(-x+1, -y+1, -z+1\); (iii) \(-x+1, -y+1, -z+2\).

**The frontier molecular orbital energies of the title compound**

| Orbital   | a.u.   | eV     |
|-----------|--------|--------|
| V\(_{130}\) | -0.00040 | -0.01088 |
| V\(_{129}\) | -0.00433 | -0.11782 |
| V\(_{128}\) | -0.00548 | -0.14911 |
| V\(_{127}\) | -0.00823 | -0.22394 |
| V\(_{126}\) | -0.01615 | -0.43945 |
| V\(_{125}\) | -0.03829 | -1.04190 |
| V\(_{124}\) | -0.07112 | 1.93524 |
| O\(_{123}\) | -0.21651 | -5.89145 |
| O\(_{122}\) | -0.22968 | -6.24982 |
| O\(_{121}\) | -0.24696 | -6.72002 |
| O\(_{120}\) | -0.25386 | -6.90778 |
| O\(_{119}\) | -0.25681 | -6.98805 |
| O\(_{118}\) | -0.28020 | -7.62452 |
| O\(_{117}\) | -0.28631 | -7.79078 |
| O\(_{116}\) | -0.29688 | -8.07840 |
| O\(_{115}\) | -0.33387 | -9.08493 |
| O\(_{114}\) | -0.33908 | -9.22670 |

* O- Occupied orbital V- Vacant orbital a.u-atomic unit eV-Electron Volt