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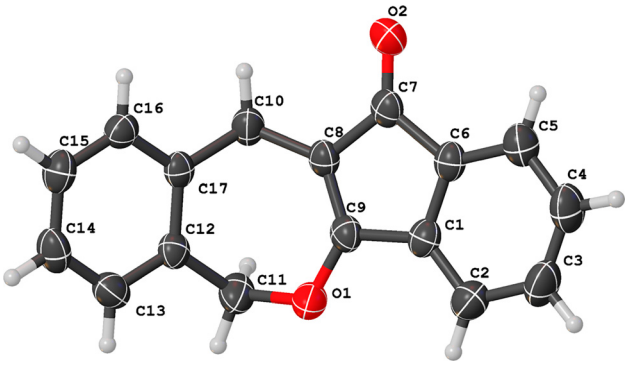
Crystal structure of 6,11-dihydro-12*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12-one, $C_{17}H_{12}O_2$



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Abstract

$C_{17}H_{12}O_2$, monoclinic, $P2_1/c$, a = 11.982(2) Å, b = 5.8563(11) Å, c = 17.894(3) Å, β = 99.892(4)°, V = 1237.0(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0506, $wR_{ref}(F^2)$ = 0.1221, T = 296.15 K.

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1 Source of materials

The synthesis of 6,11-dihydro-12*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12-one (DBIO) primarily referred to the literature of Jungang Wang and coworkers.[5] A reaction mixture containing 1,2-bis(bromomethyl)benzene (3.2 g, 12 mmol), 1*H*-indene-1,3(2*H*)-dione (1.5 g, 10 mmol), and Cs_2CO_3 (6.5 g, 20 mmol) was dissolved in DMSO (25 ml) and stirred at 80 °C for 12 h. Afterwards, the mixture was pouring into 250 ml of 1 *M* hydrochloric acid solution and subsequently extracted with ethyl acetate three times. The combined organic layers were dried using anhydrous sodium sulfate, filtered, and the solvent was evaporated to concentrate the mixture. The crude product was then purified *via* silica gel column chromatography using a petroleum ether/ethyl acetate eluent (40:1) to yield the final product as a yellow solid. To obtain the crystal of DBIO. A sample of DBIO (2.0 mmol) was transferred into a 20 ml glass tube containing a pre-mixed solvent composed of methanol and dichloromethane (10 ml, 1:1 *v*/*v*). The mixture was left for crystallization. After several days, well defined block crystals were isolated, washed with anhydrous methanol, and subsequently dried under air, yield 67 % (based on DBIO). The reagents and chemicals used in the synthesis were purchased from Anhui Zesheng Technology Co., Ltd.

2 Experimental details

The crystal data obtained from the X-ray single-crystal diffractometer show excellent quality parameters. The initial structural determination of the title compound was achieved through the application of the intrinsic phasing method with the SHELXT program. Subsequent refinement was executed utilizing the SHELXL program (Table 1).

3 Comment

As an organic compound used as a pharmaceutical intermediate, the crystal structure of 6,11-dihydro-12*H*-benzo[*e*]indeno[1,2-*b*]oxepin-12-one (DBIO) has been reported in the literature.[5] However, the exploration of its crystalline forms is far from exhausted. In this work, we have successfully synthesized a new crystalline form of DBIO by optimizing

Table 1: Data collection and handling.

Crystal:	Clear light colourless block
Size:	0.22 × 0.21 × 0.19 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX2, φ and ω scans
θ_{max}, completeness:	27.5°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7020, 2774, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1,649
$N(param)_{refined}$:	172
Programs:	Bruker,[1] Olex2,[2] SHELX[3,4]

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the crystallization conditions. The crystal structure of this new form of DBIO is completely different from the previously reported structure. This result not only enriches the crystalline structural diversity of the compound but may also exhibit unique physical and chemical properties. For example, the change in crystal form may have a significant impact on the solubility, safety and stability of medicine, thereby providing new possibilities for its applications in pharmaceuticals and other fields.[6–8] The new DBIO crystal was obtained by slow solvent evaporation at room temperature. X-ray single-crystal structure determination reveals that the compound crystallizes in the monoclinic crystal system and belonging to the $P2_1/c$ space group. The asymmetric unit comprises a complete DBIO molecule, with all atoms exhibiting full occupancy and no disorder observed. The C–C and C–O distances are of 1.340(2)–1.512(2) Å and 1.223(2)–1.340(2) Å, respectively. These bond lengths are similar to the reported isomeric DBIO crystal structure and crystals formed from structures analogous to DBIO.[9–13] The DBIO molecule can be regarded as consisting of two parts: a polycyclic structure (C1–C2–C3–C4–C5–C6–C7–C8–C9, including O1 and O2 connected to C7 and C9) and a benzene ring (C12–C13–C14–C15–C16–C17). These two parts are connected by C10 and C11, forming a certain angle, which ultimately results in the DBIO molecule not being a planar structure. Specifically, the angles of C8–C10–C17 and O1–C11–C12 are 111.295° and 112.937°, respectively. It is precisely this non-planar angular structure that enables the formation of isomers. Through calculations using the *PLATON* software and analysis with the Mercury software,[14,15] it is found that the aggregation of DBIO molecules in the DBIO crystal structure mainly relies on weak C–H···O interactions (C11–H11B···$O2^{x,\ 1+y,\ z}$ and C15–H15···$O2^{x,\ -1/2-y,\ 1/2+z}$) and p-p stacking interactions. It is worth noting that the effective overlap between the aromatic rings of adjacent DBIO molecules is minimal, preventing the formation of classical face-to-face sandwich or T-shaped stacking. Instead, a parallel-displaced stacking with significant slippage between the centroids is formed. This type of stacking results in relatively weak π-π interactions, with the perpendicular distance between the aromatic rings ranging from 3.6142 to 3.6206 Å, and the slippage ranging from 2.446 to 2.736 Å. In the end, the DBIO molecules form a final three-dimensional framework through the weak attractive interactions mentioned above.

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