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Refinement of crystal structure of 2-(2,3-dihydro-3-oxo-1*H*-inden-1-ylidene)-1*H*-indene-1,3(2*H*)-dione $C_{18}H_{10}O_3$

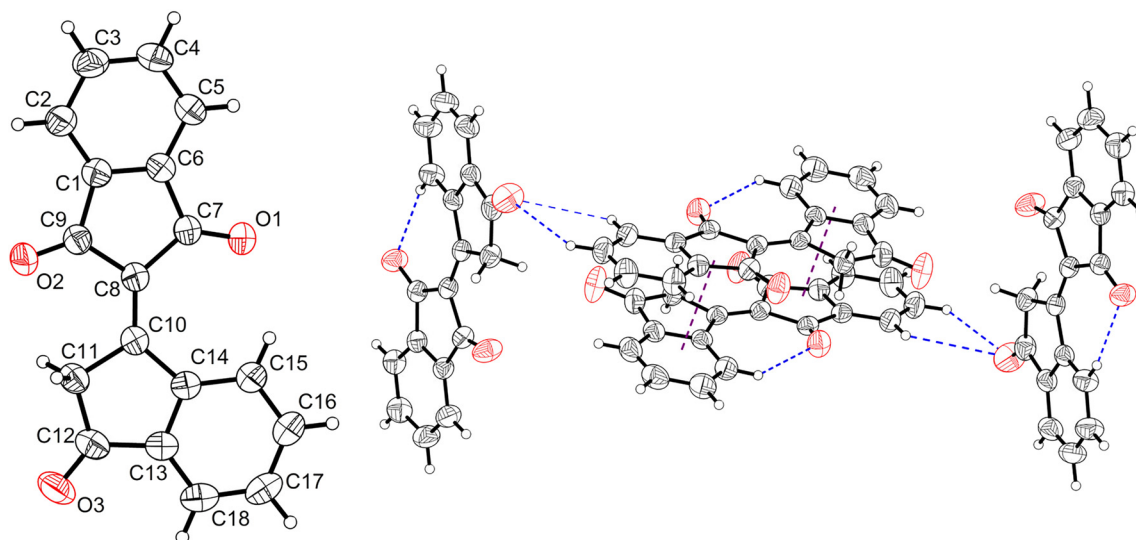


Figure 1: A view of the molecule. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radii.

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Abstract

$C_{18}H_{10}O_3$, monoclinic, $P2_1/n$ (no. 14), $a = 9.9981(2)$ Å, $b = 9.3873(2)$ Å, $c = 13.7621(3)$ Å, $\beta = 102.841(2)^\circ$, $V = 1,259.34(5)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0463$, $wR_{ref}(F^2) = 0.1235$, $T = 293$ K.

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The molecular structure is shown in the Figure 1. Table 1 contains the crystallographic data.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.28 \times 0.16 \times 0.14$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	0.81 mm^{-1}
Diffractometer, scan mode:	Rigaku, ω scans
θ_{max} , completeness:	71.5° , 100 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5382, 2407, 0.023
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2,044
$N(\text{param})_{\text{refined}}$:	191
Programs:	Rigaku ¹ , SHELX ^{2–4} , Olex2 ⁵ , Diamond ⁶

1 Source of material

The title compound, 2-(2,3-dihydro-3-oxo-1*H*-inden-1-ylidene)-1*H*-indene-1,3(2*H*)-dione, also known as bindone. It was synthesized according to the literature method with a slight modification.⁷ 1,3-Indanedione (1.2 g, 7 mmol) was charged in 100 mL two-neck round bottle and mixed with 35 mL anhydrous ethanol. After 10 min stirring, anhydrous sodium acetate (760 mg, 9.3 mmol) was added to the solution. Immediately, the solution color was turned to be violet. Then the solution was heated to reflux (about 80 °C) for about 5 h. And

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the solution color would be turned to deep violet. The reaction progress was monitored by thin-layer chromatography (TLC). When the starting 1,3-indanedione disappeared completely on the TLC, the reaction was diluted by adding water (20 mL). Subsequently, the reaction mixture was acidified by concentrated hydrochloric acid until large amount solid precipitate from the reaction solution appeared, which was collected by filtration and washed with distilled water. The crude product was purified by flash column chromatography on silica gel (200–300 mesh), using dichloromethane and hexane (50:1) as the eluent to give the title compound as a brownish solid with the yield of 65 %. ¹H NMR (400 MHz, CDCl₃): δ 9.67 (d, J = 8.0 Hz, 1 H), 8.04–7.93 (m, 3H), 7.88–7.85 (m, 3H), 7.74 (td, J = 7.2, 0.8 Hz, 1 H), 4.16 (s, 2H). The condensation is kinetically or thermodynamically controlled. Therefore, the 1,3-indanedione involved condensation always confused chemists whenever there exists other active methylene compounds (such as 3,5-difluorophenylacetonitrile). Actually, the product is bindone instead of the condensed product between bindone and 3,5-difluorophenylacetonitrile.⁸ The growth of a single crystal was carried out by dissolving bindone in ethanol and sealed in 10 mL vial with parafilm at room temperature. The holes in the parafilm were used to control a slow evaporation of solvent. Regular shaped crystals can be obtained.

2 Experimental details

Single-crystal X-ray diffraction measurements of the title compound were carried out on Rigaku SuperNova with mirror monochromatic Cu K α X-ray source (λ = 1.54184 Å) at room temperature. Data reduction was carried out using CrysAlis^{PRO} and empirical absorption corrections were made using SADABS.¹ The structure was solved by using the programs of SHELXT and refined by SHELXL through the Olex2 interface (Table 1).^{2–5} Hydrogen atoms were placed geometrically and refined using a riding model approximation, assigned isotropic thermal parameters with $d(\text{C–H})$ = 0.93 or 0.97 Å (–CH, –CH₂). $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH₂.² One outlier reflection (7, 1, 8) was omitted from the final cycles of refinement owing to the large deviation. The molecular graphics were drawn using DIAMOND software with 50 % probability ellipsoids (Figure 1).⁶ The structure was examined using the ADDSYM subroutine of PLATON 51222 to ensure that no additional symmetry could be applied to the models.⁹

3 Comment

The title compound, bindone, is a popular intermediate in cycloaddition to configure spiroconjugated cyclic ketones.

When a fluorescent molecular framework was incorporated in bindone, the reasonable designed cyclo rigidity of the molecule could be used to modulate the emission efficiency effectively. Therefore, many highly efficient fluorescent dyes were configured aiming for various applications in chemosensor, biological imaging, and dye-sensitized solar cells, etc.^{10–14} In the structure of bindone, there exist two sets of multiple aromatic systems and three carbonyl groups. The strong electron withdrawing character of carbonyl activates the hydrogen atoms of methylene, which is significant when bonding to various fluorophores. Owing to the reactive methylene, highly fluorescent dyes can be developed toward the application in optical device fabrication.

In the title crystal structure, the asymmetric unit contains only one molecule, which is different from that of literature published.⁷ Obviously, the bindone crystallized in monoclinic system with the space group $P2_1/n$ (no. 14). On the contrary, the literated bindone crystallized in orthorhombic system with the space group $Fdd2$ (no. 43). In the two 1,3-indanedione parts (C1/C2/C3/C4/C5/C6/C7/C8/C9/O1/O2 and C11/C12/C13 /C14/C15/C16/C17/C18/O3), the double ring structure of indanedione is coplanar with the root mean square error (RMSD) in distance estimated to be 0.026 and 0.039 Å, respectively. The two indanedione cyclic parts are bonded by a typical double bond, which is estimated to be 1.354 Å. In addition, the bond of C10–C11 and C12–C11 has the typical single C–C bond character with the bond length of 1.520 and 1.503 Å, which is slightly shorter than the typical single bond length 1.54 Å due to the adjacent electron-withdrawing carbon (C12–O3). Conversely, the bond length of C7–C8/C8–C9 is 1.497/1.493 Å and also shorter than that of C10–C11/C12–C11, indicating the conjugation between C8–C10 (1.354 Å) and C7–O1 (1.220 Å)/C9–O2 (1.218 Å). Therefore, the two 1,3-indanedione parts (C1/C2/C3/C4/C5/C6/C7/C8/C9/O1/O2, and C11/C12/C13/C14/C15/C16/C17/C18/O3) should be coplanar theoretically. However, the two planes are twisted with the angle of 8.27°. At the same time, the twist between the two planes was also inhibited and fixed by an intramolecular hydrogen bond C15–H15...O1ⁱ (i : x, y, z). The distance between electron donor (C15) and acceptor (O1) was estimated to be 2.953 Å and the C–H...O angle was 137.9°, which is well inside the interval of 3.0–4.0 Å and quoted by Desiraju.¹⁵ And C–H...O angles are also in agreement with the above mentioned survey. Totally, the comprehensive repelling and locking derived from C15–H15...O1 generates a slightly twist between the two indanedione. In contrast to that of bindone in literature, the twisted angle is similar to values from the literature (8.5 and 10.0°). And the only left reactive methylene can be applied in construction the controllable molecule rigidity, specifically optical photophysical properties can be effectively developed.^{16–19} The adjacent parallel molecules

are packed by strong $\pi \cdots \pi$ interactions. The distance between the two indanedione planes (C1/C2/C3/C4/C5/C6/C7/C8/C9/O1 / O2ⁱ¹, and C11/C12/C13/C14/C15/C16/C17/C18/O3ⁱ²; 1-x, -y, 1-z) is determined to be 3.602 Å and the parallel shift is 1.024 Å, corresponding to the parallel-displaced geometry (Figure 1). It is interesting that another indanedione plane does not involve the $\pi \cdots \pi$ interaction. The cohesion of adjacent non-parallel molecules is totally contributed by intramolecular hydrogen bonds. Four hydrogen bonds are found (C2-H2...O1ⁱ³, C3-H3...O2ⁱ⁴, C11-H11A...O3ⁱ⁴, C15-H15...O2ⁱ⁴, i3: 1/2 + x, 3/2 - y, 1/2 + z; i4: x, 1 + y, z) with the C...O contacts ranging from 3.289 to 3.828 Å, C-H...O angles ranging from 122.3 to 161.5° (Figure 1, right). Furthermore, the adjacent non-parallel molecules are almost perpendicular to each other due to the hydrogen bond interaction, yielding to its unique packing model. It also indicates that there exist significant intramolecular interactions between the monoclinic (this work) and orthorhombic (literature: CCDC 1456538) crystal system. Among various intermolecular interactions, the hydrogen bond established in the crystal is also significant to the optical properties of fluorescent dyes.^{20–23} Therefore, reasonable introduction of inter- and/or intra-molecular hydrogen bonds into the crystal lattice is an effective methodology to inhibit the ration of nonradiative channels.^{24,25} Weaker intramolecular interactions benefit to maintain the highly emissive character of crystals. The contrary had been proved true: stronger interactions could inactivate the excited state of dye molecule and quench the fluorescence.^{26–28}

In the crystal, the molecules are regularly packed by various intermolecular forces, including hydrogen bonds and $\pi \cdots \pi$ interactions. The driving forces that pack the dye molecules parallel to each other along the axis *a* is based on the stronger $\pi \cdots \pi$ interaction. While the hydrogen bonds join the parallel molecules to form the network. The weaker hydrogen bonds are the determining factor to optical properties of the compound in crystal state.^{29–31} The perpendicular conformation of adjacent non-parallel molecules inhibit a tight regular packing model in some degree, and thus avoiding significant fluorescence quenching.^{32–36} The ratio of radiative and nonradiative channels is significantly influenced by the external environment (various interactions).^{37,38} In case of bindone, it is an useful intermediate to design the dye with unique fluorescent properties in solid and crystal state.^{39,40} It indicates that reasonable configuration of inter- and intra-molecular interactions by introducing heteroatoms and/or aromatic system is the effective strategy in dye designing.^{41–43} In conclusion, weak intra- and inter-molecular non-covalent interactions were identified in the crystal structure, including hydrogen bonds and T-type intermolecular $\pi \cdots \pi$ stacking.

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