

## Short Note

# *tert*-Butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate

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**Abstract:** Non-fullerene acceptors have recently attracted much attention as components of organic solar cells. 1*H*-indene-1,3(2*H*)-dione is a key compound for the synthesis of the end-capping component of non-fullerene acceptors. In this communication, an intermediate for the synthesis of this compound, *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate, was prepared by the reaction between phthalic anhydride and *tert*-butyl acetoacetate. Further treatment with sodium methoxide in methanol led to the formation of 1*H*-indene-1,3(2*H*)-dione in a high yield. The structure of the newly synthesized compound was established by means of elemental analysis, high-resolution mass spectrometry, <sup>1</sup>H, <sup>13</sup>C NMR, IR spectroscopy, mass spectrometry and X-ray analysis.

**Keywords:** non-fullerene acceptors; end-capping component; 1*H*-indene-1,3(2*H*)-dione; *tert*-butyl acetoacetate; Knoevenagel reaction; X-ray analysis



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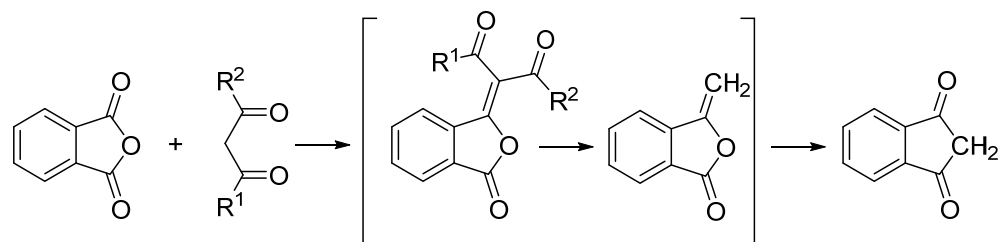


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## 1. Introduction

Organic solar cells (OSCs) have made significant progress over the past decades due to the urgent need to replace exhaustible energy sources with renewable and clean solar energy. Among them, bulk heterojunction solar cells are of particular interest because of their remarkable flexibility, semi-transparency, and high potential for large-scale production and achieved power-conversion efficiency of more than 17% [1,2]. One of the key parts of organic solar cells are acceptors, including the rapidly developing non-fullerene ones (NFAs) [3–5]. The most frequently studied NFA structure is the A-D-A, where 1*H*-indene-1,3(2*H*)-dione derivatives play the role of end-capping acceptors with activated methylene group [6–8]. However, despite its simplicity, the synthesis of 1*H*-indene-1,3(2*H*)-dione acceptors often proceeds with low yields (20–30%) [9–12], and the procedure for preparing these compounds needs to be improved. Typically, this protocol involves the reaction of phthalic anhydride and its derivatives with a compound containing an activated CH<sub>2</sub> group in acetic anhydride and triethylamine. The mechanism of this multi-step transformation has not been studied in detail, but it seems to involve Knoevenagel condensation, elimination of the acetyl and ester groups to form isobenzofuranone, and rearrangement to indanedione (Scheme 1). The most commonly used CH<sub>2</sub> component is *tert*-butyl acetoacetate [9,11–15].

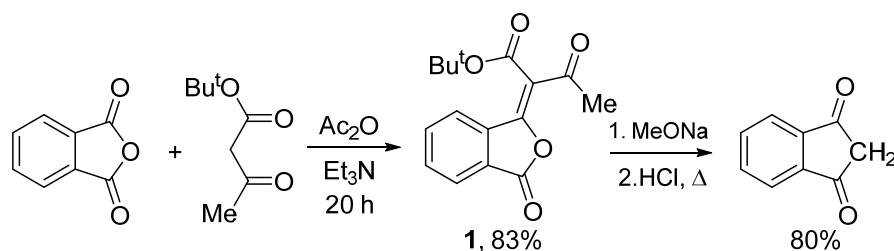
Herein, we report the synthesis of *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate **1** and its conversion to 1*H*-indene-1,3(2*H*)-dione.



**Scheme 1.** The mechanism of the formation of 1H-indene-1,3(2H)-dione via *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3H)-ylidene)butanoate.

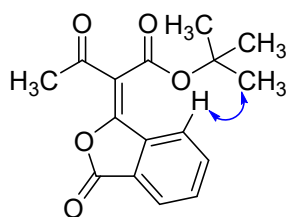
## 2. Results and Discussion

*tert*-Butyl-(*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3H)-ylidene)butanoate **1** was obtained using a simple and convenient procedure, which included the reaction of phthalic anhydride and *tert*-butyl acetoacetate in acetic anhydride in the presence of triethylamine at room temperature for 20 h (Scheme 2). The reaction proceeded with high yield (83%) and regioselectivity. It is interesting to note that in the reaction between phthalic anhydride and silylenol ether, obtained from *tert*-butyl acetoacetate, product **1** was not isolated [16]. To confirm the possibility of using product **1** as an intermediate in the synthesis of 1H-indene-1,3(2H)-dione, it was shown that the reaction of ester **1** with sodium methoxide in methanol at room temperature for 20 h, followed by treatment with hydrochloric acid, produced 1H-indene-1,3(2H)-dione in a high yield (80%).

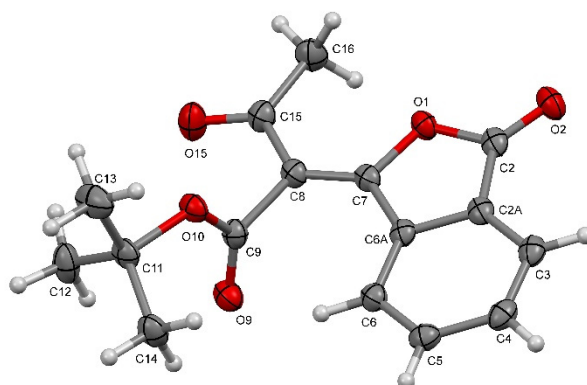


**Scheme 2.** Synthesis of 1H-indene-1,3(2H)-dione via *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3H)-ylidene)butanoate **1**.

The structure of *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3H)-ylidene)butanoate **1** was confirmed by means of elemental analysis, high-resolution mass spectrometry, <sup>1</sup>H, <sup>13</sup>C NMR, IR spectroscopy as well as mass spectrometry. The configuration of the double bond of ether **1** was established on the basis of NOESY experiments (Figure 1). The singlet corresponding to the hydrogen atoms of *tert*-butyl (1.18 ppm) correlates with aromatic protons (8.26 ppm), while the methyl singlet (3.14 ppm) does not correlate with aromatic protons of the system, which proves the existence of a single isomer **1** of the proposed compound. The structure of compound **1** was also unambiguously confirmed using an X-ray diffraction analysis (Figure 2). X-ray diffraction analysis in combination with NOESY NMR spectra showed the presence of only one *E*-regiomer in the structure, in which the bulky *tert*-butyloxycarbonyl group is closer to the aromatic ring.



**Figure 1.** A key NOE interatomic interaction in *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3H)-ylidene)butanoate **1**.



**Figure 2.** X-Ray structure (ORTEP at 50% level) of *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate **1**.

In conclusion, it was shown that the reaction of phthalic anhydride with *tert*-butyl acetoacetate is regioselective and led to *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate **1**, which is an intermediate in the synthesis of 1*H*-indene-1,3(2*H*)-dione from phthalic anhydride.

### 3. Materials and Methods

The solvents and reagents were purchased from commercial sources and used as received. Elemental analysis was performed on a 2400 Elemental Analyzer (Perkin Elmer Inc., Waltham, MA, USA).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken with a Bruker AM-300 machine (Bruker AXS Handheld Inc., Kennewick, WA, USA) (at frequencies of 300 and 75 MHz) in  $\text{CDCl}_3$  solution, with TMS as the standard. *J* values are given in Hz. MS spectrum (EI, 70 eV) was obtained with a Finnigan MAT INCOS 50 instrument (Hazlet, NJ, USA). High-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). IR spectrum was measured with a Bruker “Alpha-T” instrument in KBr pellet.

X-ray diffraction data were collected at 100 K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless  $\omega$ -scan technique), using graphite monochromatized  $\text{Cu K}\alpha$ -radiation. The intensity data were integrated and corrected for absorption and decay using the CrysAlisPro program [17]. The structure was solved with direct methods using SHELXT [18] and refined on  $F^2$  using SHELXL-2018 [19] in the OLEX2 program [20]. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideally calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite [21] was used for molecular graphics. Cambridge Crystallographic Data Centre contains the supplementary crystallographic data for this paper No. CCDC 2247414. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (accessed on 7 March 2023) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate **1** (Supplementary Materials).

Triethylamine (0.7 mL, 4.7 mmol) was added dropwise with vigorous stirring to a solution of phthalic anhydride (200 mg, 1.35 mmol) and *tert*-butyl acetoacetate (490 mg, 2 mmol) in acetic anhydride (1.3 mL, 13.7 mmol). The mixture was stirred overnight at room temperature, poured into cold water (5 mL) and the crude product was collected using filtration and washed with water. Yield 324 mg (83%), white solid, mp 150–152 °C.  $R_f$  = 0.8 ( $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 8.26 (d, *J* = 6.3, 1H), 8.02 (d, *J* = 5.1, 1H), 7.81 (td, *J* = 5.7, *J* = 0.9, 1H), 7.74 (td, *J* = 5.4, *J* = 0.6, 1H), 2.64 (s, 3H), 1.62 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 195.6, 164.4, 163.4, 152.0, 136.7, 135.3, 132.7, 126.0, 125.9, 125.4, 117.8, 83.7, 31.8, 28.0 (3  $\text{CH}_3$ ). MS (EI, 70 eV), *m/z* (I, %): 288 (7), 232 (8), 217 (20), 190 (15), 173 (100), 57 (33), 43 (36). HRMS-ESI (*m/z*): calcd. for ( $\text{C}_{16}\text{H}_{17}\text{O}_5$ ) 289.1071, found *m/z* 289.1074. IR,

$\nu$ ,  $\text{cm}^{-1}$ : 3433, 3092, 2986, 1814, 1726, 1640, 1472, 1372, 1254, 1160, 1056, 997, 837, 691. Anal. calcd. For  $\text{C}_{16}\text{H}_{16}\text{O}_5$  (288.2952): C, 66.66; H, 5.59. Found: C, 66.84; H, 5.72%.

Synthesis of 1*H*-indene-1,3(2*H*)-dione from *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate **1** (Supplementary Materials).

A 5.4 M solution of sodium methoxide in MeOH (0.04 mL, 1.1 mmol) was added to a solution of *tert*-butyl (*E*)-3-oxo-2-(3-oxoisobenzofuran-1(3*H*)-ylidene)butanoate **1** (200 mg, 0.7 mmol) in dry methanol (7 mL), and the mixture was stirred overnight at room temperature. The solvent was evaporated under reduced pressure and the residue was treated with a mixture of hydrochloric acid (3 mL) and ice-water (4 mL). The resulting mixture was refluxed for 1 h, cooled to room temperature, diluted with water (3 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic extracts were dried over  $\text{MgSO}_4$  and evaporated under reduced pressure. The residue was purified using column chromatography on silica gel (Silica gel Merck 60, eluent dichloromethane). Yield 82 mg (80%), pale yellow solid, mp 128–131 °C (lit. mp 130–132 °C [22]).  $R_f$  = 0.5 (dichloromethane). The data on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra correspond to data in the literature [23].

Crystallographic data of the compound **1** are given in Table 1.

**Table 1.** Crystal data and structure refinement for compound **1**.

Empirical Formula	$\text{C}_{16}\text{H}_{16}\text{O}_5$
Formula weight	288.29
Temperature	99.9(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P 2_1/c$
Unit cell dimensions	$a = 6.68587(5)$ Å $a = 90^\circ$ $b = 10.54420(10)$ Å $b = 94.2747(7)^\circ$ $c = 20.48957(18)$ Å $c = 90^\circ$
Volume	$1440.44(2)$ Å <sup>3</sup>
Z	4
Density (calculated)	$1.329$ g/cm <sup>3</sup>
Absorption coefficient	$0.824$ mm <sup>−1</sup>
$F(000)$	608
Crystal size	$0.4 \times 0.16 \times 0.03$ mm <sup>3</sup>
Theta range for data collection	$4.328$ to $77.931^\circ$
Index ranges	$-7 \leq h \leq 8$ , $-13 \leq k \leq 13$ , $-25 \leq l \leq 25$
Reflections collected	16,388
Independent reflections	3062 [ $R(\text{int}) = 0.0234$ ]
Observed reflections	2878
Completeness to theta = $67.684^\circ$	100.0%
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.434
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3062/0/194
Goodness-of-fit on $F^2$	1.055
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0338$ , $wR2 = 0.0874$
R indices (all data)	$R1 = 0.0356$ , $wR2 = 0.0890$
Largest diff. peak and hole	$0.194$ and $-0.230$ e.Å <sup>−3</sup>

**Supplementary Materials:** The following are available online: copies of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, LR and HR mass-spectra for the compound **1**.

**Author Contributions:** Conceptualization, E.A.K.; methodology, O.A.R. and B.K.; software, E.A.K.; validation, O.A.R. and T.D.; formal analysis, investigation, A.S.C. and T.D.; resources, O.A.R.; data curation, E.A.K.; writing—original draft preparation, O.A.R.; writing—review and editing, B.K. and T.D.; visualization, O.A.R.; supervision, O.A.R.; project administration, O.A.R.; funding acquisition, O.A.R. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compound **1** are available from the authors.

## References

1. Lu, L.; Zheng, T.; Wu, Q.; Schneider, A.M.; Zhao, D.; Yu, L. Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem. Rev.* **2015**, *115*, 12666–12731. [[CrossRef](#)] [[PubMed](#)]
2. Luo, Z.; Ma, R.; Liu, T.; Yu, J.; Xiao, Y.; Sun, R.; Xie, G.; Yuan, J.; Chen, Y.; Chen, K.; et al. Fine-Tuning Energy Levels via Asymmetric End Groups Enables Polymer Solar Cells with Efficiencies over 17%. *Joule* **2020**, *4*, 1236–1247. [[CrossRef](#)]
3. Wang, J.; Ding, Y.; Li, C.; Zheng, N.; Xie, Z.; Ma, Z.; Lu, Y.; Wan, X.; Chen, Y. Effect of Nitro-Substituted Ending Groups on the Photovoltaic Properties of Nonfullerene Acceptors. *ACS Appl. Mater. Interfaces* **2020**, *12*, 41861–41868. [[CrossRef](#)] [[PubMed](#)]
4. Zhou, D.; Wang, J.; Xu, Z.; Xu, H.; Quan, J.; Deng, J.; Li, Y.; Tong, Y.; Hu, B.; Chen, L. Recent advances of nonfullerene acceptors in organic solar cells. *Nano Energy* **2022**, *103*, 107802. [[CrossRef](#)]
5. Luo, D.; Jang, W.; Babu, D.D.; Kim, M.S.; Wang, D.H.; Kyaw, A.K.K. Recent progress in organic solar cells based on non-fullerene acceptors: Materials to devices. *J. Mater. Chem. A* **2022**, *10*, 3255–3295. [[CrossRef](#)]
6. Wang, Y.; Zhang, Y.; Qiu, N.; Feng, H.; Gao, H.; Kan, B.; Ma, Y.; Li, C.; Wan, X.; Chen, Y. A Halogenation Strategy for over 12% Efficiency Nonfullerene Organic Solar Cells. *Adv. Energy Mater.* **2018**, *8*, 1702870. [[CrossRef](#)]
7. He, C.; Chen, Z.; Wang, T.; Shen, Z.; Li, Y.; Zhou, J.; Yu, J.; Fang, H.; Li, Y.; Li, S.; et al. Asymmetric electron acceptor enables highly luminescent organic solar cells with certified efficiency over 18%. *Nat. Commun.* **2022**, *13*, 2598. [[CrossRef](#)]
8. Fu, H.; Yao, J.; Zhang, M.; Xue, L.; Zhou, Q.; Li, S.; Lei, M.; Meng, L.; Zhang, Z.-G.; Li, Y. Low-cost synthesis of small molecule acceptors makes polymer solar cells commercially viable. *Nat. Commun.* **2022**, *13*, 3687. [[CrossRef](#)]
9. Planells, M.; Robertson, N. Naphthyl Derivatives Functionalised with Electron Acceptor Units—Synthesis, Electronic Characterisation and DFT Calculations. *Eur. J. Org. Chem.* **2012**, *2012*, 4947–4953. [[CrossRef](#)]
10. Liu, Z.; Zhang, R.; Meng, Q.; Zhang, X.; Sun, Y. Discovery of new protein kinase CK2 inhibitors with 1,3-dioxo-2,3-dihydro-1H-indene core. *Medchemcomm* **2016**, *7*, 1352–1355. [[CrossRef](#)]
11. Aldrich, T.J.; Matta, M.; Zhu, W.; Swick, S.M.; Stern, C.L.; Schatz, G.C.; Facchetti, A.; Melkonyan, F.S.; Marks, T.J. Fluorination Effects on Indacenodithienothiophene Acceptor Packing and Electronic Structure, End-Group Redistribution, and Solar Cell Photovoltaic Response. *J. Am. Chem. Soc.* **2019**, *141*, 3274–3287. [[CrossRef](#)] [[PubMed](#)]
12. Jia, T.; Zhang, J.; Zhang, G.; Liu, C.; Tang, H.; Zhang, K.; Huang, F. Rationally regulating the terminal unit and copolymerization spacer of polymerized small-molecule acceptors for all-polymer solar cells with high open-circuit voltage over 1.10 V. *J. Mater. Chem. A* **2022**, *10*, 15932–15940. [[CrossRef](#)]
13. Li, M.; Xiong, Q.; Qu, B.; Xiao, Y.; Lan, Y.; Lu, L.; Xiao, W. Utilizing Vinylcyclopropane Reactivity: Palladium-Catalyzed Asymmetric [5+2] Dipolar Cycloadditions. *Angew. Chem. Int. Ed.* **2020**, *59*, 17429–17434. [[CrossRef](#)] [[PubMed](#)]
14. Liu, C.; Igci, C.; Yang, Y.; Syzgantseva, O.A.; Syzgantseva, M.A.; Rakstys, K.; Kanda, H.; Shibayama, N.; Ding, B.; Zhang, X.; et al. Dopant-Free Hole Transport Materials Afford Efficient and Stable Inorganic Perovskite Solar Cells and Modules. *Angew. Chem. Int. Ed.* **2021**, *60*, 20489–20497. [[CrossRef](#)]
15. Yu, H.; Luo, S.; Sun, R.; Angunawela, I.; Qi, Z.; Peng, Z.; Zhou, W.; Han, H.; Wei, R.; Pan, M.; et al. A Difluoro-Monobromo End Group Enables High-Performance Polymer Acceptor and Efficient All-Polymer Solar Cells Processable with Green Solvent under Ambient Condition. *Adv. Funct. Mater.* **2021**, *31*, 2100791. [[CrossRef](#)]
16. Mkrtchyan, S.; Chilingaryan, Z.; Ghazaryan, G.; Dede, R.; Rasool, N.; Rashid, M.; Villinger, A.; Görls, H.; Karapetyan, G.; Ghochikyan, T.; et al. E/Z-Selective Synthesis of Alkylidene-3-oxo-3H-isobenzofurans by Reaction of Silyl Enol Ethers with Phthaloyl Dichloride. *Synthesis* **2011**, *2011*, 2281–2290. [[CrossRef](#)]
17. CrysAlisPro. Version 1.171.41.106a. In *Rigaku Oxford Diffraction*; Rigaku Corporation: Oxford, UK, 2021.
18. Sheldrick, G.M. SHELXT-Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3–8. [[CrossRef](#)]
19. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8. [[CrossRef](#)]
20. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 229–341. [[CrossRef](#)]
21. Macrae, C.F.; Sovago, I.; Cottrell, S.J.; Galek, P.T.A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G.P.; Stevens, J.S.; Towler, M.; et al. Mercury 4.0: From visualization to analysis, design and prediction. *J. Appl. Crystallogr.* **2020**, *53*, 226–235. [[CrossRef](#)]
22. Kaliyaperumal Appayee, S.; Pandurang Nikumbh, S.; Reddy Govindapur, R.; Banerjee, S.; Bhalerao, D.S.; Syam Kumar, U.K. Ethenolate Transfer Reactions: A Facile Synthesis of Vinyl Esters. *Helv. Chim. Acta* **2014**, *97*, 1115–1122. [[CrossRef](#)]
23. He, G.; Wu, C.; Zhou, J.; Yang, Q.; Zhang, C.; Zhou, Y.; Zhang, H.; Liu, H. A Method for Synthesis of 3-Hydroxy-1-indanones via Cu-Catalyzed Intramolecular Annulation Reactions. *J. Org. Chem.* **2018**, *83*, 13356–13362. [[CrossRef](#)] [[PubMed](#)]

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