

Short Note

2-((4-(2-Ethylhexyl)-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indol-7-yl)methylene)malononitrile

Nikita S. Gudim, Ekaterina A. Knyazeva *, Konstantin P. Trainov and Oleg A. Rakitin 

N. D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences, 47 Leninsky Prospekt, Moscow 119991, Russia

* Correspondence: katerina_knyazev@ioc.ac.ru; Tel.: +7-499-1355327

Abstract: New small acceptor–donor (A–D) molecules have been recently investigated as a component of organic solar cells. In this research, 2-((4-(2-ethylhexyl)-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indol-7-yl)methylene)malononitrile was prepared from 4-(2-ethylhexyl)-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indole in a two-step process via Vilsmeier–Haack formylation and Knoevenagel reaction with malononitrile. The structures of newly synthesized compounds were established by means of elemental analysis, high-resolution mass spectrometry, ¹H, ¹³C NMR, IR and UV–Vis spectroscopy, as well as mass spectrometry.

Keywords: small acceptor–donor (A–D) molecules; 1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indole; Vilsmeier–Haack formylation; Knoevenagel reaction; luminescent properties



Citation: Gudim, N.S.; Knyazeva, E.A.; Trainov, K.P.; Rakitin, O.A. 2-((4-(2-Ethylhexyl)-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indol-7-yl)methylene)malononitrile. *Molbank* **2022**, *2022*, M1490. <https://doi.org/10.3390/M1490>

Academic Editor: R. Alan Aitken

Received: 7 October 2022

Accepted: 9 November 2022

Published: 11 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



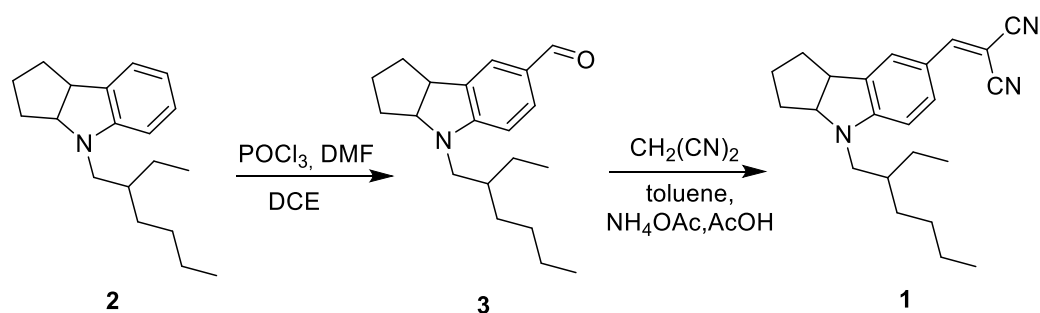
Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The development of the components of organic photovoltaic devices (solar cells (OSCs) and light-emitting diodes (OLEDs)) has led to a significant increase in the structural complexities of organic compounds so that their physicochemical and special properties correspond to the necessary data [1,2]. Over the past decades, the small molecules used in these photovoltaic devices have evolved from the simplest ones with the structure D-A, D- π -A, D-A-D or A-D-A to more complex ones containing several different donor and acceptor moieties in various combinations (for example, D-A1- π -A2, A- π -D- π -A, etc.) [3]. The complication of the structure of organic compounds has led to difficulties in their synthesis, high costs of starting compounds, and, ultimately, the understanding that these compounds cannot be used in final devices [4]. This is all the more surprising because one of the advantages of using organic substances has always been their cheapness [5,6]. Recently, small molecules of the acceptor–donor type (A–D) have become more actively studied to create single-component organic solar cells with a homojunction (HOSC) based on small donor–acceptor molecules [7,8]. As a rule, triphenylamine [7,8] or phenothiazine [9] groups were studied as a donor component, while dicyanovinyl moiety was most often used as an acceptor [7–9]. Herein, we report the synthesis of 2-((4-(2-ethylhexyl)-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indol-7-yl)methylene)malononitrile as a new small molecule and study its photophysical properties.

2. Results and Discussion

The target 2-((4-(2-ethylhexyl)-1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indol-7-yl)methylene)malononitrile **1** was synthesized in two steps. The treatment of *N*-(2-ethylhexyl) 1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indole **2** with the Vilsmeier–Haack reagent prepared in situ from POCl₃ and DMF at 85 °C for 24 h resulted in the formation of 7-carbaldehyde derivative **3** (Scheme 1) as for other *N*-substituted 1,2,3,3*a*,4,8*b*-hexahydrocyclopenta[*b*]indoles [10,11]. The resulting aldehyde **3**, in turn, was introduced in the Knoevenagel condensation reaction with malononitrile by refluxing the reaction mixture in toluene for 4 h. The total yield of **1** for the two steps was 55%.



Scheme 1. Synthesis of 2-((4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)methylene)malononitrile **1**.

The structures of 4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde **3** and 2-((4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)methylene)malononitrile **1** were confirmed by means of elemental analysis, high-resolution mass spectrometry, ^1H , ^{13}C NMR, IR and UV-Vis spectroscopy, as well as mass spectrometry. Based on the ^{13}C NMR data, compounds **1** and **3** were found to exist as mixtures of two diastereomers due to the stereocenter in the 2-ethylhexyl group (see Materials and Methods and Supplementary Materials).

We measured the optical absorption spectra for compound **1** in DMSO and compared it with the spectra of compounds containing the dicyanomethylene group [12], a similar donor framework and a rhodanine acceptor fragment (Figure 1) [13]. It was found that chromophore **1** intensely absorbs visible light, with a maximum intensity at a wavelength of 430 nm ($\epsilon = 97,028 \text{ M}^{-1} \cdot \text{cm}^{-1}$). For this chromophore, an emission spectrum was also recorded; the emission band turned out to be a mirror absorption band, and its maximum was 510 nm (Stokes shift = 2038 cm^{-1}).

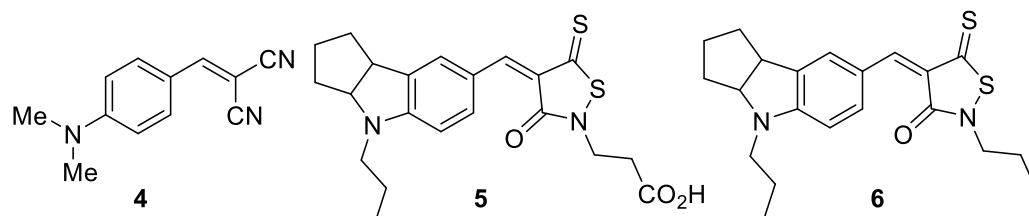


Figure 1. Chromophores with a structure close to that of compound **1**.

Compared to the most studied analogue, 2-(4-(dimethylamino)benzylidene)malononitrile **4**, chromophore **1** has a longer wavelength absorption maximum with a slightly higher extinction coefficient and, at the same time, a shorter wavelength emission band and, consequently, a smaller Stokes shift. This can be explained by the greater rigidity of the amino group and the absence of rotational degrees of freedom of this fragment in compound **1**, in comparison with analogue **4**. If we compare compound **1** with compounds containing a similar donor framework and a rhodanine acceptor fragment (**5,6**), compound **1** exhibits a shift, in the absorption band, to the blue region due to the lower electron-withdrawing ability of the dicyanomethylidene fragment, and the Stokes shift is slightly smaller but, at the same time, it is comparable (Table 1).

Table 1. Photophysical parameters obtained for 2-((4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)methylene)malononitrile **1** and similar chromophores **4–6**: absorption maximum wavelength λ_{abs} , maximum molar extinction coefficient ϵ , emission maximum wavelength λ_{em} and Stokes shift $\Delta\nu$.

Compound	λ_{abs} nm	ϵ_{max} $\text{mol} \times 10^{-1} \times \text{cm}^{-1}$	λ_{em} nm	Stokes Shift $\Delta\nu$ cm^{-1}
1	462	97,028	510	2038
4	447	81,008	557	4418
5	519	–	592	2376
6	517	–	590	2393

3. Materials and Methods

4-(2-Ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole **2** was prepared according to the published method [14]. 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). ^1H and ^{13}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 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). IR spectrum was measured with a Bruker “Alpha-T” instrument in KBr pellet. High-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). Solution UV–visible absorption spectra were recorded using an Agilent Cary 60 UV–Vis spectrophotometer (Agilent Technologies, Inc. Headquarters, Santa Clara, CA, USA) in standard 10 mm photometric quartz cells in HPLC-grade DMSO at a concentration of 5×10^{-6} M. Luminescence spectra were recorded using an Agilent Cary Eclipse (Agilent Technologies, Inc. Headquarters, Santa Clara, CA, USA) in HPLC-grade DMSO at a concentration of 10^{-6} M.

Synthesis of 4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde **3** (Supplementary Materials).

POCl_3 (2.53 mL, 27.42 mmol) was introduced dropwise into dry DMF (15 mL) at 5°C , and the reaction mixture was stirred at room temperature for 30 min. Then, a solution of 4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole **2** (630 mg, 2.32 mmol) in dichloroethane (15 mL) (preliminarily distilled over P_2O_5) was added, and the reaction mixture was kept for 24 h at 85°C in an argon atmosphere, and then cooled, poured into cold water (50 mL) and extracted with chloroform (3×35 mL). The combined organic extracts were washed with brine, dried over MgSO_4 and evaporated. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane/ethyl acetate, 10:1, v/v). Yield 414 mg (60%), pale-yellow oil. $R_f = 0.26$ (Hexane:ethyl acetate, 10:1, v/v). ^1H NMR (300 MHz, CDCl_3): 9.54 (s, 1H), 7.54–7.41 (m, 2H), 6.21 (d, $J = 8.6$, 1H), 4.36–4.24 (m, 1H), 3.78–3.63 (m, 1H), 3.24–3.12 (m, 1H), 3.08–2.96 (m, 1H), 2.08–1.57 (m, 9H), 0.97–0.78 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , signals of the second diastereomer are given in brackets): 189.4, 157.6, 134.8, 134.1, 126.0, 124.4, 103.4, 69.3 (68.9), 49.0 (48.8), 44.7, 37.7 (37.6), 35.3, 32.6 (32.4), 31.1 (30.9), 28.9 (28.8), 24.4, 24.3 (24.1), 23.2, 14.1, 10.9 (10.8). HRMS-ESI (m/z): calcd for ($\text{C}_{20}\text{H}_{29}\text{NO}$) 300.2321, found m/z 300.2322. MS (EI, 70 eV), m/z (I, %): 299 (27), 200 (100), 172 (4), 158 (12), 143 (4), 130 (8), 57 (3), 41 (8), 29 (9), 18 (25). IR, ν , cm^{-1} : 2957, 2929, 2860, 2729, 1672, 1602, 1511, 1455, 1327, 1229, 1163, 1100, 801, 734. UV–Vis spectrum, λ_{max} : 358 nm ($\epsilon = 18,323 \text{ M}^{-1}\text{cm}^{-1}$). Anal. calcd for $\text{C}_{20}\text{H}_{29}\text{NO}$ (300.2321): C, 80.22; H, 9.76; N, 4.68. Found: C, 80.24; H, 9.73; N, 4.72%.

Synthesis of 2-((4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)methylene)malononitrile **1** (Supplementary Materials).

A mixture of aldehyde **3** (142 mg, 0.48 mmol), malononitrile (47 mg, 0.712 mmol), NH_4OAc (55 mg, 0.712 mmol) and AcOH (1 mL) in toluene (40 mL) was refluxed with

molecular sieves 4 Å (3 g) for 4 h. The reaction mixture was diluted with water (50 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with a 1% sodium carbonate solution (3 × 50 mL), dried over MgSO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent dichloromethane/methanol, 10:1, *v/v*). Yield 92 mg, (55%), dark-red oil. *R_f* = 0.53 (CHCl₃). ¹H NMR (300 MHz, CDCl₃): 7.67 (1H, s), 7.43 (d, *J* = 8.6, 1H), 7.29 (s, 1H), 6.22 (d, *J* = 8.6, 1H), 4.42–4.31 (m, 1H), 3.78–3.66 (m, 1H), 3.27–3.16 (m, 1H), 3.12–3.01 (m, 1H), 2.06–1.60 (m, 6H), 1.43–1.18 (m, 9H), 0.94–0.79 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, signals of the second diastereomer are given in brackets): 157.7, 157.39, 157.36, 136.8, 135.1, 126.1, 120.2, 116.8, 115.8, 104.4, 69.4 (69.0), 48.6 (48.4), 44.5, 37.7 (37.5), 35.4, 32.1 (32.3), 31.0 (30.8), 28.9 (28.8), 24.3, 24.13 (24.07), 23.1, 14.1, 10.8 (10.7). HRMS-ESI (*m/z*): calcd for (C₂₃H₂₉N₃) 348.2434, found *m/z* 348.2434. MS (EI, 70eV), *m/z* (I, %): 347 (17), 248 (100), 232 (11), 220 (15), 206 (67), 192 (8), 182 (11), 165 (7), 152 (10), 140 (12), 127 (4), 115 (3), 57 (8), 41 (17), 29 (17). IR, ν , cm⁻¹: 2957, 2925, 2857, 2389, 2214, 1727, 1616, 1499, 1328, 1178, 1104, 805, 604. UV-Vis spectrum, λ_{max} : 462 nm (ϵ = 97,028 M⁻¹cm⁻¹). Emission spectrum, λ_{max} : 510 nm. Anal. calcd for C₂₃H₂₉N₃: C, 79.50; H, 8.41; N, 12.09. Found: C, 79.54; H, 8.37; N, 12.11%.

Supplementary Materials: The following are available online: copies of ¹H, ¹³C NMR, IR, UV-Vis, LR and HR mass spectra for compounds **1** and **3**, as well as luminescence spectrum for compound **1**.

Author Contributions: Conceptualization, E.A.K.; methodology, O.A.R.; software, E.A.K.; validation, O.A.R.; formal analysis, investigation, N.S.G. and K.P.T.; resources, O.A.R.; data curation, N.S.G.; writing—original draft preparation, N.S.G.; writing—review and editing, E.A.K.; visualization, N.S.G.; 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.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

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

References

1. Zampetti, A.; Minotto, A.; Cacialli, F. Near-Infrared (NIR) Organic Light-Emitting Diodes (OLEDs): Challenges and Opportunities. *Adv. Funct. Mater.* **2019**, *29*, 1807623. [[CrossRef](#)]
2. Lee, C.-P.; Li, C.-T.; Ho, K.-C. Use of organic materials in dye-sensitized solar cells. *Mater. Today* **2017**, *20*, 267–283. [[CrossRef](#)]
3. Knyazeva, E.A.; Rakitin, O.A. Influence of structural factors on the photovoltaic properties of dye-sensitized solar cells. *Russ. Chem. Rev.* **2016**, *85*, 1146–1183. [[CrossRef](#)]
4. Zhang, Y.; Song, J.; Qu, J.; Qian, P.-C.; Wong, W.-Y. Recent progress of electronic materials based on 2,1,3-benzothiadiazole and its derivatives: Synthesis and their application in organic light-emitting diodes. *Sci. China Chem.* **2021**, *64*, 341–357. [[CrossRef](#)]
5. van der Staaij, F.M.; van Keulen, I.M.; von Hauff, E. Organic Photovoltaics: Where Are We Headed? *Sol. RRL* **2021**, *5*, 2100167. [[CrossRef](#)]
6. Carella, A.; Borbone, F.; Centore, R. Research Progress on Photosensitizers for DSSC. *Front. Chem.* **2018**, *6*, 481. [[CrossRef](#)] [[PubMed](#)]
7. Nakayama, K.; Okura, T.; Okuda, Y.; Matsui, J.; Masuhara, A.; Yoshida, T.; White, M.S.; Yumusak, C.; Stadler, P.; Scharber, M.; et al. Single-Component Organic Solar Cells Based on Intramolecular Charge Transfer Photoabsorption. *Materials* **2021**, *14*, 1200. [[CrossRef](#)] [[PubMed](#)]
8. Terenti, N.; Giurgi, G.-I.; Crişan, A.P.; Anghel, C.; Bogdan, A.; Pop, A.; Stroia, I.; Terec, A.; Szolga, L.; Grosu, I.; et al. Structure-properties of small donor-acceptor molecules for homojunction single-material organic solar cells. *J. Mater. Chem. C* **2022**, *10*, 5716–5726. [[CrossRef](#)]
9. Slodek, A.; Zych, D.; Kotowicz, S.; Szafraniec-Gorol, G.; Zimosz, S.; Schab-Balcerzak, E.; Siwy, M.; Grzelak, J.; Maćkowski, S. “Small in size but mighty in force”—The first principle study of the impact of A/D units in A/D-phenyl- π -phenothiazine- π -dicyanovinyl systems on photophysical and optoelectronic properties. *Dye. Pigment.* **2021**, *189*, 109248. [[CrossRef](#)]
10. Matsui, M.; Fujita, T.; Kubota, Y.; Funabiki, K.; Jin, J.; Yoshida, T.; Miura, H. Substituent effects in a double rhodanine indoline dye on performance of zinc oxide dye-sensitized solar cell. *Dye. Pigment.* **2010**, *86*, 143–148. [[CrossRef](#)]
11. Matsui, M.; Shiota, T.; Kubota, Y.; Funabiki, K.; Jin, J.; Yoshida, T.; Higashijima, S.; Miura, H. N-(2-Alkoxyphenyl)-substituted double rhodanine indoline dyes for zinc oxide dye-sensitized solar cell. *Tetrahedron* **2012**, *68*, 4286–4291. [[CrossRef](#)]

12. Gupta, V.K.; Singh, R.A. An investigation on single crystal growth, structural, thermal and optical properties of a series of organic D- π -A push-pull materials. *RSC Adv.* **2015**, *5*, 38591–38600. [[CrossRef](#)]
13. Tanaka, T.; Watanabe, K.; Nomoto, T.; Okano, M.; Shintou, T.; Miyazaki, T.; Nishimura, Y.; Shimada, Y. Evaluation Probe for Central Nervous System Permeability, Evaluation Method for Central Nervous System Permeability, and Screening Method Using an Evaluation Probe for Central Nervous System Permeability. U.S. Patent 10,227,337, 12 March 2019.
14. Tanaka, E.; Mikhailov, M.S.; Gudim, N.S.; Knyazeva, E.A.; Mikhalchenko, L.V.; Robertson, N.; Rakitin, O.A. Structural features of indoline donors in D-A- π -A type organic sensitizers for dye-sensitized solar cells. *Mol. Syst. Des. Engl.* **2021**, *6*, 730–738. [[CrossRef](#)]