



Synthesis, optical and electrochemical properties of substituted 2-cinnamoyl-1, 3-indandione O-methyl ethers



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ABSTRACT

Seven new 2-cinnamoyl-1,3-indandione (2CID) O-methyl ethers with different substituents (R = –H, –CH₃, –OCH₃, –N(C₆H₅)₂, –N(CH₂CH₂CN)₂, julolidyl, –N(CH₃)₂) in 4-position of the cinnamoyl moiety were synthesized. The methylation with dimethylsulfate occurred at the oxygen atom of the exocyclic enol group with high selectivity.

The synthesized compounds were characterized by ¹H, ¹³C NMR, IR, UV–Vis and luminescence spectroscopy, their electrochemical properties were investigated by cyclic voltammetry. The obtained results indicates that introducing an electron donating substituents in the 4-position of cinnamoyl moiety facilitates electrochemical oxidation, remarkably shifts absorption and emission bands to longer wavelengths, simultaneously increases extinction coefficient (ϵ). O-methyl ethers with strong electron donating groups (R = –N(C₆H₅)₂, –N(CH₂CH₂CN)₂, julolidyl, –N(CH₃)₂) in molecule are characterized by luminescence with maximum in range from 547 to 647 nm and absolute photoluminescence quantum yields from 0.02 to 0.32. Quantum yield (QY) of chromophore containing julolidyl fragment is solvent dependent. It was 0.32 in chloroform and decreased in other polar (ethanol, acetone) solvents.

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1. Introduction

1,3-Indandione and its derivatives have been intensively studied over years due to their wide range of potential applications. First studies were devoted to investigate biological activity for derivatives of 1,3-indandione. Rat-extermination [1], anti-inflammatory [2,3] and other properties were discovered for several 1,3-indandione compounds. But in the last few decades 1,3-indandione moiety has been used as structural element in synthesis of new chromophores and luminophores with non-linear optical (NLO) properties [4–10]. 1,3-Indandione is well known as strong electron acceptor moiety and, when it is bounded with electron donating substituents, the molecules with potential applications as photoactive organic materials can be obtained [5].

The most studied derivative of 1,3-indandione is 4-*N,N*-dimethylaminobenzylidene-1,3-indandione (DMABI) whose crystals and films are characterized with efficient photoconductivity [11] and non-linear luminescence [7].

In recent years particular interest has been focused to 2-acyl-

derivatives of 1,3-indandione. Due to the β,β' -triketone fragment, which has strong intramolecular hydrogen bond in the enol form, some compounds from this class are characterized with high stability upon UV-irradiation [12], large Stokes shift [13] and complexation ability with transition [14–16] and rare earth metal ions [17,18]. As a result compounds with excellent emission and thermal properties can be obtained, for example, 2-benzoyl-1,3-indandione complex with europium(III) ion has been proposed as potential molecular light converter material for new organic light emitting diodes (OLED) [18]. Whereas 2-acetyl-1,3-indandione complexes with transition metal ions such as silver(I) ion has shown proper thermal decomposition temperature and it can be used as precursor for silver films [16]. Only few studies have been devoted to 2-acyl derivatives of 1,3-indandione with prolonged π -conjugate system in molecule – 2-cinnamoyl-1,3-indandiones (2CID). 2CID similar as 2-acyl-1,3-indandiones exist in exocyclic enolic form, which is stabilized by intramolecular hydrogen bond. If the benzene ring of cinnamoyl part contains strong electron donating substituent in *para*-position, push–pull type molecules on the basis of 2CID can be obtained with excellent electronic and optical properties. Ahmedova et al. [19–22] have investigated optical and complexation properties of some 2CID and their

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analogues. The authors characterized obtained compounds as chromophores with high molar absorptivity, large Stokes shift, good photostability upon UV-irradiance, however due to low solubility in organic solvents transition metal ion complexes with 2CID ligands does not have practical application.

Due to relatively low number of the studies devoted to 2CID and their analogues, our work was directed towards investigation of new chromophores derived from 2CID – their O-methyl ethers. In some papers also O-methylation of β,β' -triketone fragment containing compounds were discussed [23–25], although the properties of O-methyl ethers up till now have not been reported. We are presenting here the synthesis of new chromophores, which contains 1,3-indandione moiety as electron acceptor and with different electron donating substituents derived methylated cinnamoyl fragment. These easily obtainable organic chromophores – 2CID O-methyl ethers consisting of π -conjugated system between electron donor and acceptor could possess pronounced emission characteristics and therefore could find an application in optoelectronic devices, for example in OLED. Newly synthesized 2CID O-methyl ethers are characterized by ^1H , ^{13}C NMR, FT-IR, UV–Vis and luminescence spectroscopy methods and electrochemical measurement. Furthermore, to investigate the structure modifying effects on the electrochemical and optical properties, 2-cinnamoyl-1,3-indandione O-methyl ether with $-\text{N}(\text{CH}_3)_2$ substituent is compared with the well investigated “push–pull” chromophore 4-*N,N*-dimethylaminobenzylidene-1,3-indandione (DMABI).

2. Experimental procedures

2.1. General

The FT-IR spectra in the range from 4000 to 650 cm^{-1} were recorded on a Perkin–Elmer Spectrum 100 FT-IR spectrometer using KBr pellets.

The ^1H and ^{13}C NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ solutions on a Bruker Avance 300 MHz spectrometer at 300 MHz for ^1H - and 75 MHz for ^{13}C - nuclei. Chemical shifts were expressed in parts per million (ppm) relative to solvent signal.

Diffraction data were collected on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structure was solved by direct methods [26,27] and refined by full-matrix least squares [28]. The crystal data, details of data collection and refinement are given in Table 1.

The purity of prepared organic compounds was established on Waters 2695 HPLC using Waters 2996 Photodiode array UV–Vis detector. The chromatographic analyses were performed using XTerra[®] MS C18 (5 μm 2.1 \times 100 mm) column, 50% Acetonitrile/0.1% formic acid solution as mobile phase and flow rate 0.2 ml/min. MS spectra were acquired on a Waters EMD 1000MS mass detector. Mass spectra were obtained in ESI + mode, voltage 30 V.

The UV–Vis absorption spectra in CHCl_3 solutions were acquired using Perkin–Elmer 35 UV/Vis spectrometer with a 1 cm path length quartz cell.

Emission spectra in CHCl_3 solutions were measured on Quanta Master 40 steady state spectrofluorometer (Photon Technology International, Inc.) using 1 cm path length quartz cuvettes. Absolute photoluminescence quantum yields in CHCl_3 solutions were determined using QuantaMaster 40 steady state spectrofluorometer (Photon Technology International, Inc.) equipped with 6 inch integrating sphere by LabSphere.

The cyclic voltammograms were recorded using a computer controlled electrochemical system PARSAT 2273. The measurements were carried out using a three-electrode cell configuration. Stationary glassy carbon disk (\varnothing 0.5 cm) was used as a working electrode, Pt wire – as an auxiliary electrode. Potentials were

Table 1
Crystal data and refinement parameters for compound **3f**.

Compound	3f
Molecular formula	$\text{C}_{24}\text{H}_{21}\text{NO}_3$
Molecular weight	371.42
Crystal system	Monoclinic
Space group	$P 2_1/n$
a (\AA)	8.5990 (4)
b (\AA)	21.7570 (5)
c (\AA)	10.5800 (14)
β ($^\circ$)	108.692 (3)
V (\AA^3)	1875.0 (3)
Z	4
D_c ($\text{Mg}\cdot\text{m}^{-3}$)	1.316
T (K)	293
μ (mm^{-1})	0.09
$F(000)$	784
$2\theta_{\text{max}}$ ($^\circ$)	54.2
h, k, l range	–10 to 10, –27 to 26, –12 to 13
No. measured reflections	11204
No. independent reflections (R_{int})	4089 (0.139)
No. observed reflections ($I > 2\sigma(I)$)	1399
No. refined parameters/restraints	257/0
$R, wR [I > 2\sigma(I)]$	0.0936, 0.2348
R, wR [all data]	0.2702, 0.3341
Goodness of Fit on F^2, S	0.902
Max., Min electron density ($\text{e}\text{\AA}^{-3}$)	0.23, –0.21
Maximum Δ/σ	0.021

measured vs saturated calomel electrode (SCE) and recalculated vs normal hydrogen electrode (NHE). The potential scan rate was 100 mV/s. Electrochemical redox reactions were studied in 0.1 M tetrabutyl-ammonium tetrafluorophosphate (TBAPF₆) acetonitrile solution under Ar atmosphere. Acetonitrile (Merck, puriss. grade) was distilled over phosphorus pentoxide, stored over calcium hydride and distilled just before use.

Melting points were determined using Stuart SMP101 apparatus and are uncorrected. TLC analyses were performed on MERCK silica gel plates and were detected with EURO-BST-203LS UV detector.

All solvents were purchased from Acros Organics with purity of $\geq 99\%$. Dimethylsulphate was purchased from Sigma–Aldrich with purity of $\geq 99\%$. Acetone was dried and distilled over K_2CO_3 . Piperidine was purified by distillation before use. 2-Acetyl-1,3-indandione was synthesized as described in the literature [17] and 4-*N,N*-dimethylaminobenzylidene-1,3-indandione as in the study [29]. The synthetic route of compounds **3a-g** and **4a-g** are shown in Scheme 1.

2.2. Synthesis of compounds 3a-g

2-Acetyl-1,3-indandione **1** (0.010 mol), derivative of benzaldehyde **2a-g** (0.010 mol) and piperidine (0.005 mol) was refluxed at 110 $^\circ\text{C}$ for 2 h. Then reaction mixture was cooled to 80 $^\circ\text{C}$ and 8 ml of ethanol was added. Solution was boiled for 30 min, and after cooling, the formed crystals were filtered off and washed with ethanol. Products were recrystallized from CH_2Cl_2 and EtOH mixture.

(*E*)-2-(1-hydroxy-3-phenylallylidene)-2H-indene-1,3-dione (**3a**), Yield 32%, M.P. = 186–187 $^\circ\text{C}$. ^1H NMR (CDCl_3), δ , [ppm]: 13.20 (s, 1H), 8.04 (d, $J = 15.0$ Hz, 1H), 7.92 (d, $J = 15.0$ Hz, 1H), 7.89 (m, 2H), 7.74 (m, 4H), 7.46 (m, 3H). ^{13}C NMR (CDCl_3), δ , [ppm]: 197.59, 188.60, 173.25, 145.04, 138.65, 134.25, 134.25, 134.00, 133.50, 131.00, 129.03, 122.94, 122.50, 118.14, 108.02. IR, (KBr), ν , [cm^{-1}]: 3400–3200 (ν_{OH}), 3027 (ν_{CH}), 1704 ($\nu_{\text{C=O}}$), 1620 ($\nu_{\text{C=O}}$, C=C), 1579, 1564 ($\nu_{\text{C=C(Ph)}}$). MS (ES+) m/z : 277.00 (M^+ requires 277.08), (ES-) m/z : 275.20 (M^- requires 275.08).

(*E*)-2-(1-hydroxy-3-(*p*-tolyl)allylidene)-2H-indene-1,3-dione (**3b**),

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