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Structure and properties of a series of 2-cinnamoyl-1,3indandiones and their metal complexes

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Abstract A series of seven 2-cinnamoyl-1,3-indandiones and their metal(II) complexes were synthesized and characterized by means of spectroscopic (IR, NMR, electron absorption and emission spectroscopy) and/or single-crystal X-ray diffraction methods. The optical spectra of the organic compounds show very strong absorption in the visible region and weak fluorescence with moderate to strong Stokes shift. The effect of concentration, water addition and metal ion complexation on the optical properties was also studied. In search of potential practical application, the complexation of 2-cinnamoyl-1,3-indandiones with metal(II) ions was investigated. A series of

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non-charged complexes with Cu(II), Cd(II), Zn(II), Co(II) and Ni(II) was isolated and analyzed by elemental analyses and IR. Most of the complexes show presence of water molecules, most probably coordinated to the metal ion, thus forming octahedral geometry. For the paramagnetic Cu(II) complexes a distorted, flattened tetrahedral structure is proposed, basing on the EPR data. The optical properties of the metal complexes, however, do not differ appreciably from those of the free ligands.

Keywords Indan-1,3-dione · Crystal structure · Optical properties · Metal complexes

Introduction

The 2-substituted 1,3-indandiones show interesting photophysical properties and therefore were continuously the subjects of intense experimental and theoretical studies [1-5]. Intramolecular isomerization, electron and/or protontransfer processes are responsible for most of the observed optical properties and potential applications of these compounds [6-8]. The 1,3-indandione fragment is a very strong electron acceptor and coupling with electron donating substituents modulates the photophysical properties of the so-formed dipolar "push-pull" molecules. Excited state twisting was observed in N,N-dimethylaminobenzylidene-1,3-indandione [3, 5, 9] and its solid-state optical properties were studied in details [5, 10] with respect to the potential application of its derivatives in nonlinear optics [2]. On the other hand, derivatives possessing intramolecular hydrogen bond, such as 2-acyl-1,3-indandiones, were investigated for possible tautomeric equilibria in ground or excited states [11–13]. In most of the cases the fundamental findings on the structural and optical properties of these compounds led to their practical applications; the suggested fast and reversible tautomerization of 2-acetyl-1,3-indandione, 2AID [11] for example, gave the first indication that this compound should be photostable upon UV irradiation. Later this was experimentally proven and showed that 2AID has much higher photostability than the widely used sunscreens in practice such as benzophenone-3 and octylmethoxycinnamate [7]. Moreover, we also found that the Zn(II) and Cu(II) complexes of 2AID show even better photostability in the hydrogen-bond breaking solvent DMSO, which allowed us to propose them as promising sunscreen agents, too [7].

The strong chelation ability of 2-acyl-1,3-indandiones, in addition to the diversity of their optical properties, opened up a new door for searching potential application of their metal complexes. There are several suggestions for using 2-acyl-1,3-indandiones as extraction agents for metal ions [14–16] or their evaluation as optical sensors for metal ions [17–19]. Recently, we started a detailed study of the structural, optical, and complexation properties of 2AID [20–22] and its derivatives containing extended π -conjugated system [23–26].

In this study, we describe the structural and optical properties of a series of 2-cinnamoyl-1,3-indandiones with a common structure depicted in Fig. 1. The synthesis, spectroscopic and complexation properties of compounds 1 and 2 have been described elsewhere [23, 24]. The molecular and crystal structure of compound 7 is known since 1980 [27]. Presently, the crystal structure of compound 4 was solved from single-crystal X-ray diffraction data and will be compared with the available data for similar compounds. Metal complexes of compounds 3-7 with Cu(II), Zn(II), Co(II), Ni(II) and/or Cd(II) were also synthesized and investigated by means of various experimental methods. The main focus of this work is the optical (absorption and emission) properties of the studied



Fig. 1 Structure of the studied 2-cinnamoyl-1,3-indandiones

compounds and the way they are affected by the structure, solvent, concentration and metal ion complexation.

Experimental part

X-ray diffraction and spectroscopic experiments

The single-crystal X-ray and general data for structure **4** are reported in Table 1. The data collection was performed on an Oxford Xcalibur Nova with CCD detector with graphite-monochromated CuK_{α} radiation at ambient temperature using ω -scans. Programs CrysAlis CCD and CrysAlis RED (Version 1.171.32.29) [28] were employed

 Table 1 General and crystal data and summary of intensity data collection and structure refinement for compound 4

Compound	4
Formula	C ₁₉ H ₁₄ O ₃
M _r	290.30
Crystal system, color and habit	Monoclinic, orange, prism
Space group	$P 2_1/c$
Crystal dimensions (mm ³)	$0.24 \times 0.19 \times 0.11$
Unit cell parameters:	
<i>a</i> (Å)	6.9931 (1)
<i>b</i> (Å)	12.5465 (1)
<i>c</i> (Å)	17.0219 (2)
α/°	-
β/°	101.1202 (12)
γ / °	-
$V(\text{\AA}^3)$	1465.44 (3)
Ζ	4
$D_{\rm c} ~({\rm g}~{\rm cm}^{-3})$	1.316
<i>Т/</i> К	296
$\mu (mm^{-1})$	0.718
F (000)	608
θ range for data collection (°)	4.4-72.5
h, k, l range	-7 to 8, -14 to 15, -21 to 20
Scan type	ω
No. measured reflections	12,926
No. independent reflections (R_{int})	2,910 (0.023)
No. observed reflections, $I \ge 2\sigma(I)$	2,503
No. refined parameters/restraints	205/0
g_1, g_2 in w	0.0691, 0.1667
$R, wR [I \ge 2\sigma(I)]$	0.0402, 0.1178
R, wR [all data]	0.0455, 0.1217
Goodness of fit on F^2 , S	1.06
Extinction coefficient	0.0009 (6)
Max., min electron density (e $Å^{-3}$)	0.14, -0.13
Maximum Δ/σ	0.001

for data collection, cell refinement and data reduction. The Lorentz-polarization effect was corrected and the diffraction data have been scaled for absorption effects by the multi-scanning method.

The structure was solved by direct methods and refined on F^2 by weighted full-matrix least-squares. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically idealized positions $[Csp^3$ -H 0.96 Å, Csp^2 -H 0.93 Å with $U_{iso}(H) = 1.5$ or 1.2 U_{eq} (C)] and were constrained to ride on their parent atoms using the appropriate SHELXL97 HFIX instructions. The hydrogen atom which belongs to hydroxyl group in **4** is found in difference Fourier maps at distances 0.93(2) Å and was refined freely. Calculations were performed with programs SHELXS97 [29] and SHELXL97 [29] both integrated in the WinGX program package [30]. The molecular geometry calculations were done using PLA-TON [31] and the molecular graphics were done with ORTEP-3 [32], and Mercury [33].

The main geometrical features along with hydrogen bond geometry for compound 4 are given in Table 2.

The IR spectra were recorded on a Specord 75-IR (Carl-Zeiss, Jena, Germany) in Nujol mulls. Elemental analyses were performed on a Vario EU III instrument. The UV–vis absorption spectra were recorded on a JASCO V-570-UV/Vis/NIR. Fluorescence spectra were obtained using a Perkin-Elmer LS-5 and a Varian Eclipse fluorometers. All solvents were of spectroscopic grade and were used without further purification. Acetonitrile was dried over P_2O_5 and freshly distilled before use. The NMR spectra were recorded in CDCl₃ using a Bruker

DRX-250 spectrometer operating at 250.13 MHz for ¹H- and 62.90 MHz—for the ¹³C-nuclei. The chemical shifts are related to TMS used as reference. The EPR spectra were recorded on a Bruker B-ER 420 spectrometer at 293 K.

The photostability assessment of compounds 1 and 5 was performed with a medium-pressure mercury lamp, transmitting light between 250 and 450 nm. To remove IR rays, the light was filtered through a saturated solution of $CuSO_4$ in 5 cm long quartz cell. Irradiation was performed on ethanol solutions in fluorimetric quartz cells, well sealed to prevent evaporation at room temperature. The UV-vis absorption spectra were recorded during the irradiation at different time intervals.

Synthesis and characterization

Compounds 1–7 were obtained by refluxing 4.7 g (0.025 mol) 2-acetyl-1,3-indandione, 0.05 mol of the corresponding aldehyde (1, benzaldehyde; 2, *p*-fluoro-benzaldehyde; 3, *p*-chloro-benzaldehyde; 4, *p*-methyl-benzaldehyde; 5, *p*-cyano-benzaldehyde; 6, *p*-methoxy-benzaldehyde; 7, *p*-dimethylamino-benzaldehyde) in presence of 0.012 mol piperidine for 1 h. To the formed polycrystalline precipitate 50 cm³ ethanol was added and the reaction mixture was boiled for a half hour more. After cooling down the formed crystals were filtrated and repeatedly washed with ethanol. The filtrate was further diluted with water, acidified and the additionally formed amount of the products were recrystalized from ethanol.

Table 2 Selected interatomic distances (Å) and valence angles (°) as well as hydrogen bond geometry (Å, °) for the compound 4

Bond distances				Bond angles		
O1–C9	1.217 (2)			C2C1C6	117.7 (1)	
O2–C7	1.232 (2)			C1-C2-C3	121.3 (1)	
O3–C10	1.326 (2)			C2-C3-C4	121.3 (1)	
C7–C8	1.450 (2)			C3-C4-C5	117.6 (1)	
C8–C9	1.468 (2)			C4-C5-C6	121.2 (1)	
C8-C10	1.377 (2)	.377 (2)		C1-C6-C5	120.9 (1)	
C10-C11	1.439 (2)					
C11-C12	1.337 (2)					
C12–C13	1.457 (2)					
Hydrogen bond geor	netry					
D–H…A	D–H	Н…А	D…A	∠D–H…A	Symmetry code	
O3–H1O3…O2	0.93 (2)	1.80 (2)	2.625 (1)	147 (2)	_	
C3–H3…O2	0.93	2.610	3.302 (2)	132	-x + 1, y + 1/2, -z + 1/2 + 1	
C15-H15…O1	0.93	2.556	3.296 (2)	137	-x, y-1/2, -z+1/2	
C17–H17…O1	0.93	2.560	3.296 (2)	137	-x, -1/2 + y, 1/2 - z	

Compound 1; 2-[1-hydroxy-3-phenyl-allylidene]-indan-1,3-dione, Yield 70%, M.p. 186 °C (Ref. [26] 186–187 °C); the IR and NMR spectral data were also found to be identical with the one described in Ref. [26].

Compound 2; 2-[1-hydroxy-3-(4-fluoro-phenyl)-allylidene]-indan-1,3-dione, Yield 79%, M.p. 205 °C. (Ref. [23] 205–206 °C); all the spectral data are identical with the one described in Ref. [23].

Compound 3; 2-[1-hydroxy-3-(4-chloro-phenyl)-allylidene]-indan-1,3-dione, Yield 79%, M.p. 200–201 °C. Anal. Found, %: C, 69.05; H, 3.55; Calc. for $C_{18}H_{11}CIO_3$, %: C, 69.58; H, 3.57. **IR** (Nujol) v, cm⁻¹: broad 3,450 (v_{O-H}), 1,700 ($v_{C=O}$), 1,650 ($v_{C=O}$, $v_{C=C}$), 1,630 ($v_{C=O}$, $v_{C=C, (Ph)}$), 1,590 ($v_{C=O}$, $v_{C=C, (Ph)}$), 1,560 ($v_{C=O}$, $v_{C=C, (Ph)}$), 985 (γ_{eC-H}), 810 (γ_{Ar-H}).

Compound 4; 2-[1-hydroxy-3-(4-methyl-phenyl)-allylidene]-indan-1,3-dione, Yield 96%; M.p. 181–182 °C. Anal. Found, %: C, 79.04; H, 4.96; Calc. for C₁₉H₁₄O₃%: C, 78.60, H, 4.86. IR (Nujol) ν , cm⁻¹: 3,500 ($\nu_{\text{O-H}}$), 1,700 ($\nu_{\text{C=O}}$), 1,650 ($\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$), 1,630 ($\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$), 1,595 ($\nu_{\text{C=O}}$, $\nu_{\text{C=C}, (Ph)}$), 1,580 ($\nu_{\text{C=O}}$, $\nu_{\text{C=C}, (Ph)}$), 1,545 ($\nu_{\text{C=O}}$, $\nu_{\text{C=C}, (Ph)}$), 990 ($\gamma_{\text{C-H}}$), 835 ($\gamma_{\text{Ar-H}}$).

Compound 5; 2-[1-hydroxy-3-(4-cyano-phenyl)-allylidene]-indan-1,3-dione, Yield 65%; M.p. 193–194 °C. Anal. Found, %: C, 75.90; H, 3.68; N, 4.52. C₁₉H₁₁O₃N. Calc., %: C, 75.74; H, 3.68; N, 4.65. IR (Nujol) v, cm⁻¹: 3,400 broad (v_{O-H}), 2,220, 1,700 (v_{C=O}), 1,650 (v_{C=O}, v_{C=C}), 1,620 (v_{C=O}, v_{C=C}), 1,580 (v_{C=O}, v_{C=C, (Ph)}), 1,570 (v_{C=O}, v_{C=C, (Ph)}), 1,550 (v_{C=O}, v_{C=C, (Ph)}), 1,320 (v_{N-Ar}), 1,285 (δ_{OH}), 1,150 (δ_{CH}), 985 ($\gamma_{=C-H}$), 820 (γ_{Ar-H}), 780 (γ_{Ar-H}).

Compound 6; 2-[1-hydroxy-3-(4-methoxy-phenyl)-allylidene]-indan-1,3-dione, Yield 98%; M.p. 192–193 °C. Anal. Found, %: C, 74.36; H, 4.84. Calc. for $C_{19}H_{14}O_4$, %: C, 74.49; H, 4.61. IR (Nujol) v, cm⁻¹: 3,500 (v_{O-H}), 1,700 ($v_{C=O}$), 1,640 ($v_{C=O}$, $v_{C=C}$), 1,610 ($v_{C=O}$, $v_{C=C}$), 1,595 ($v_{C=O}$, $v_{C=C, (Ph)}$), 1,570 ($v_{C=O}$, $v_{C=C, (Ph)}$), 1,540 ($v_{C=O}$, $v_{C=C, (Ph)}$), 1,250 ($v_{C=O-C}^{as}$), 980 ($\gamma_{=C-H}$), 810 (γ_{Ar-H}).

Compound 7; 2-[1-hydroxy-3-(4-dimethylamino-phenyl)-allylidene]-indan-1,3-dione, Yield 60%; M.p. 214-215 °C. Anal. Found, %: C, 75.11; H, 5.30; N, 4.68. Calc. for C₂₀H₁₇NO₃; %: C, 75.22; H, 5.37; N, 4.39. IR (Nujol) $v, \text{ cm}^{-1}$: 3,400–3,500 ($v_{\text{O-H}}, v_{\text{NH}}$), 1,700 ($v_{\text{C=O}}$), 1,635 $(v_{C=O}, v_{C=C}), 1,630 (v_{C=O}, v_{C=C}), 1,590 (v_{C=O}, v_{C=C, (Ph)}),$ 1,570 ($v_{C=O}$, $v_{C=C, (Ph)}$), 1,560 ($v_{C=O}$, $v_{C=C, (Ph)}$), 1,550 $(v_{C=O}, v_{C=C, (Ph)}), 1,515 (\delta_{CH_3}), 1,300 (v_{N-Ar}), 1,280 (\delta_{OH}),$ 1,230 ($v_{\rm N-C}$), 1,150 ($\delta_{\rm CH}$), 985 ($\gamma_{\rm =C-H}$), 850 ($\gamma_{\rm Ar-H}$), 800 (γ_{Ar-H}) . ¹H-NMR (CDCl₃), δ [ppm]: 11.7 (s, 1H), 7.8–7.9 (m, 2H), 7.7-7.8 (m, 4H), 7.5-7.7 (m, 4H), 2.8-3.2 (m, 6H). ¹³C-NMR (CDCl₃), δ [ppm]: 197.36 (C7), 188.99 (C9), 174.28 (C10), 152.50 (C16), 146.36 (C11), 140.79 (C6), 138.71 (C5), 134.28 (C3), 133.48 (C2), 131.51 (C12), 122.58 (C13), 122.12 (C1), 121.76 (C4), 111.79 (C14, C18), 111.71 (C15, C17), 106.38 (C8), 40.10 (CH₃).

Synthesis of the metal complexes of compounds 3–7

All metal complexes were obtained after mixing methanol solutions of the corresponding metal acetates and the corresponding ligands, compounds **3–7**, dissolved in dioxane, in metal-to-ligand ratio 1:2. Non-charged complexes were formed as precipitates, which were further filtrated, repeatedly washed with ethanol, and dried over P_4O_{10} for 2 weeks. Elemental analyses data were found to be in good agreement (±0.5%) with the calculated values and are provided in the Supplementary material along with the IR data for the complexes.

Results and discussion

Synthesis and structures

Compounds 1–7 were obtained in good yields according to a previously described procedure [34], namely by condensation of 2AID with the corresponding benzaldehyde in presence of piperidine. All compounds were characterized with M.p., FT-IR and elemental analyses. NMR spectroscopy (¹H and ¹³C) was used for the compounds well soluble in DMSO. The synthesis and characterization of compounds **1** and **2** have been reported elsewhere [23, 26]. The 2-acyl-1,3-indandiones are known to exist in their exocyclic enolic form, as depicted in Fig. 1, stabilized by the presence of intramolecular hydrogen bond. Such enolic group is seen in the ¹H NMR spectra, showing a resonance peak in the range of 11.2–13.2 ppm, and a broad band in the IR spectra of the studied compounds, at ca. 3,200 cm⁻¹.

Good quality single crystals were obtained from compound 4 by slow evaporation of a saturated ethanol solution. The crystal structure of 4 was solved from singlecrystal X-ray diffraction data and is depicted in Fig. 2a. It confirms that the compound exists in the exocyclic enolic form. Selected geometrical parameters are listed in Table 2. The structure has *trans* configuration regarding spatial orientation of substituents at the central C11=C12 double bond of allylidene moiety. The molecule is not planar; the dihedral angle between the 1,3-indandione fragment and the phenyl plane is 11.34(7)°. Planarity of the 1,3-indandione moiety is confirmed by the dihedral angle of $1.21(7)^{\circ}$ between benzene and cyclopentane ring planes in 4. Keto oxygen atoms O(1) and O(2) deviate insignificantly from the cyclopentane ring plane in opposite directions by 0.005(1) and -0.027(1) Å, respectively.

The enol form is stabilized by the resonance-assisted intramolecular hydrogen bond (RAHB) [35, 36] of the O-H…O type with expected geometry (O…O distance is 2.625(1) Å and O-H…O angle is $147(2)^{\circ}$; Table 2). The







pseudoaromatic six-membered ring is formed. The RAHB forms well-recognized supramolecular synthon described by the graph-set analysis as the S(6) type. The geometry of RAHB is comparable with those found in 2-(1-hydroxy-3-thiophen-3-yl-allylidene)-1,3-indandione [26] and 2-(3-furan-2-yl-1-hydroxy-allylidene)-1,3-indandione [26], i.e., the geometry of RAHB is not influenced by the type of the substituent.

The participation of the keto O(2)–C(7) group in RAHB formation has reflection on O(2)–C(7) bond distance value (elongation) in relation to the keto O(1)–C(9) bond distance [O(1)–C(9) equal to 1.217(2) Å and O(2)–C(7) of 1.232

(2) Å]. On the contrary, the O(3)–C(10) bond (1.326(2) Å; Table 2), has a character of σ Car–OH bond such as that found in phenols [37]. Such molecular geometry of the β -diketone fragment in **4** is in agreement with that found in similar 1,3-indandione and indan-1-one derivatives such as 2-pivaloyl-1,3-indandione [38], 2-acetyl-1,3-indandione [39], 2-(hydroxy(amino)methylidene)-1,3-indandione [12], 2-(1-hydroxy-3-thiophen-3-yl-allylidene)-1,3-indandione [26] and 2-(3-furan-2-yl-1-hydroxy-allylidene)-1,3-indandione [26] and 2-acylindan-1-one [40].

Flattening of the β -diketone fragment is accompanied by the conjugation within the 1,3-indandione moiety and with

the allylidene part of the molecule. Therefore, shortening of the single C–C bonds and elongation of the double C=C bonds in the conjugated chain of the allylidene moiety in **4** is observed; C(8)–C(10) and C(11)–C(12) bond distances amount to 1.376(2) and 1.337(2) Å, while C(10)–C(11) and C(12)–C(13) bond distances are 1.439(2) and 1.456(2) Å; respectively (Table 2).

The five-membered indane ring deformation reveals general shortening of endocyclic C–C ring bonds in relation to those in cyclopentane ring itself (C–C 1.543 Å) [37] and are close to the $C(sp^2)$ – $C(sp^2)$ bond length (1.474 Å) [37] with the pronounced conjugation of shorter and longer C–C bonds; C(7)–C(8) equal to 1.450(2) Å and C(8)–C(9)–1.468(2) Å; Table 2.

The crystal packing in **4** and intermolecular interactions are presented in Fig. 2b. The molecules are linked by C– H…O hydrogen bonds (Table 2) with phenyl CH groups acting as proton donors and the keto O(1) and O(2) atoms—as proton acceptors, thus producing zigzag chains of R(32) rings running parallel to the *b* axis. Both atoms O(1) and O(2) participate in intramolecular O–H…O type of hydrogen bond and intermolecular C–H…O type of hydrogen bond. There are no contacts and π … π stackings between the chains except van der Waals' interactions.

According to our experience with the structural properties of 2-acyl-1,3-indandiones conjugated with an aromatic ring via allylidene bridge, the molecular geometry remains virtually the same changing the type of the aromatic or heterocyclic substituent [26]. What is affected is the way of crystal packing and the intermolecular hydrogen bondings. This can also be seen comparing the available crystallographic data with the molecular structure of compound 4, currently described. The enol form of compound 4 is revealed in the crystalline state, similarly to other 2-acyl derivatives, such as 2-pivaloyl-1,3-indandione structure [38], 2-acetyl-1,3-indandione [39], 2-(hydroxy (amino)methylidene)-1,3-indandione [12], 2-(1-hydroxy-3thiophen-3-yl-allylidene)-1,3-indandione [26], 2-(3-furan-2-yl-1-hydroxy-allylidene)-1,3-indandione [26] and 2-(4dimethylamino-cinnamoyl)-1,3-indandione [27]. The substituent in the benzene ring of compound 4 is a methyl group and has no proton donor or acceptor and therefore it is not surprising that there are no intermolecular interactions in the crystal packing. As far as the molecular structure is concerned, we expect that all other compounds from the series have similar structure as compound 4, since their spectroscopic characteristics are very similar. For all compounds exocyclic enolic form is proposed with trans configuration of the C(11)-C(12) double bond and s-trans configuration of C(10)–C(11) bond, as depicted in Fig. 1.

The presence of intramolecular hydrogen bond and β -diketone fragment in the structure of the compounds implies a possibility for intramolecular proton transfer

either in ground or excited state, on one hand, and strong coordination ability with metal ions-on the other. Therefore, we studied thoroughly the optical properties of the compounds as well as their metal complexes. The complexation properties of compounds 1 and 2 were described earlier [23, 24], so we focused on compounds 3-7 and their complexes with metal(II) ions. The purpose was to obtain initial information about the composition and structure of the formed metal complexes prior searching for potential practical applications. All complexes were isolated as amorphous precipitates and have rather poor solubility in the most common organic solvents, except for strongly coordinating solvents such as DMSO and DMF. Therefore, the complexes were characterized mainly with IR spectra in solid and qualitative absorption spectra in DMSO.

The elemental analyses data show composition of the complexes with 1:2 metal-to-ligand ratio. Coordination of the 2-cinnamoyl-1,3-indandiones after deprotonation of the enolic OH group is supposed after comparing the IR spectra of the metal complexes with that of the free ligand. The vibrational frequencies for the OH group are absent in the spectra of the complexes. Thereby, the compounds 3-7coordinate as bidentate monoanion ligands forming 6-membered chelate ring with the metal ion. More complicated are the analyses of the IR spectra of the complexes where water molecules are present in the composition of the complexes. However, based on our previous studies on the structure of metal complexes of 2-acetyl-1,3-indandione [20, 22], it is supposed that the Zn(II), Cd(II), Co(II) and Ni(II) complexes contain at least two water molecules, axially coordinated to the metal center, and octahedral structure of these complexes is suggested. This is not the case for the Cu(II) complexes showing no presence of water molecules in their IR spectra and confirmed by the elemental analyses data. Additional information for the Cu(II) complexes is obtained from their EPR spectra recorded for powder samples at room temperature. The estimated values of the g-factors are listed in Table 3. All EPR spectra are characterized by axial anisotropy, except

 Table 3 EPR parameters for the Cu(II) complexes of 1–7 obtained for powder samples at ambient temperature

Complex	g⊥	g	g _{iso}
1-Cu(II)	2.076	2.295	2.149
2–Cu(II)	2.068	2.279	2.138
3-Cu(II)	2.071	2.286	2.143
4-Cu(II)	2.062	2.285	2.136
5–Cu(II)	2.079	2.310	2.156
6-Cu(II)			2.081
7–Cu(II)			2.068
5–Cu(II) 6–Cu(II) 7–Cu(II)	2.079	2.310	2.156 2.081 2.068

Solvent comp.	Acetonitrile		Absolute ethanol	DMSO
	$\lambda_{ m abs}$	$\lambda_{ m emis}$	$\lambda_{ m abs}$	$\lambda_{ m abs}$
	371, 385	510 (385)	372, 385	378, 391, 410 sh
	370 sh, 387	513 (380)	370, 390 sh	376 sh, 391, 411 sh
	373, 390, 408 sh	512 (390)	373, 390, 408 sh	380, 392, 414 sh
	376, 392, 413 sh	500 (380)	375, 391, 414 sh	381 sh, 399, 419 sh
	371, 387, 409 sh	510 (385)	370, 386, 408 sh	378, 390, 417 sh
	410	494 (400)	415	415
	500	588 (500)	503	519
		Accountine λ_{abs} 371, 385 370 sh, 387 373, 390, 408 sh 376, 392, 413 sh 371, 387, 409 sh 410 500	Acctoinnine λ_{emis} λ_{abs} λ_{emis} 371, 385 510 (385) 370 sh, 387 513 (380) 373, 390, 408 sh 512 (390) 376, 392, 413 sh 500 (380) 371, 387, 409 sh 510 (385) 410 494 (400) 500 588 (500)	AcctonnineAcctonnineAbsolute cutator $\overline{\lambda_{abs}}$ $\overline{\lambda_{emis}}$ $\overline{\lambda_{abs}}$ 371, 385510 (385)372, 385370 sh, 387513 (380)370, 390 sh373, 390, 408 sh512 (390)373, 390, 408 sh376, 392, 413 sh500 (380)375, 391, 414 sh371, 387, 409 sh510 (385)370, 386, 408 sh410494 (400)415500588 (500)503

for the Cu(II) complexes of compounds **6** and **7**, which show broad isotropic signal. No hyperfine structure due to interaction with 63,65 Cu nuclei is observed. The EPR data are consistent with a d⁹ electronic structure of the metal center in distorted tetrahedral environment.

Optical properties

The data from the absorption spectra of compounds 1-7, in three different solvents, are summarized in Table 4. The molar absorptivity of the studied compounds is relatively high; 40,000–45,000 M⁻¹ cm⁻¹ and typical for $\pi - \pi^*$ transitions. Increasing solvent polarity causes slight bathochromic shift of the absorption maxima. The latter is located at ca. 385 nm for compounds 1-5 in acetonitrile. Increasing the electron donating strength of the substituent in the benzene ring is reflected in an expected bathochromic shift of the absorption maximum, as seen for compounds 6 and 7. The qualitative absorption spectra of the complexes were obtained in DMSO and show rather small hypsochromic shifts compared with that of the free ligands (ca. 20 nm, data not shown). The most intense absorption bands actually correspond to the ligand's transitions. Even for the green-colored Cu(II) complexes, the broad band at ca. 720 nm corresponding to the forbidden d-d-transitions could be only seen in very concentrated DMSO solutions. These data show that the intense ligands' $n-\pi^*$ and $\pi-\pi^*$ transitions dominate strongly in the absorption spectra of the complexes. Besides, the position of the absorption maxima are only slightly affected by the complexation with the metal ions and therefore the studied compounds are not appropriate for optical sensing of metal ions.

Steady-state fluorescence spectra of 1-7 in dry acetonitrile are characterized by a broad and structureless emission band. The observed Stokes shift is estimated to about 120 nm for compounds 1-5 (see Table 4), and less than 100 nm for compounds 6 and 7. These data imply possible intramolecular isomerizations accompanying the excitation of the molecule or strong electron redistribution in excited state.

Additional studies on the optical properties are performed for some of the compounds regarding the effect of concentration and water addition, as well as irradiation with UV light. The absorption spectrum of compound 7 in 96% ethanol consists of a broad band with a maximum at 503 nm and a shoulder at 404 nm. Interestingly, changing the concentration of the solution the relative intensity of these bands changes as depicted in Fig. 3a. Reducing the concentration 5 times the intensity of the band at 503 nm rapidly decreases whereas the band at 404 nm becomes more pronounced; so that at concentration 1.3×10^{-5} M both bands become of equal intensity. Such effect, but to a much lesser extent, is observed also in absolute ethanol. In this case, however, the shoulder at 404 nm is visible only in solutions of very low concentration; $C < 0.8 \times 10^{-5}$ M (see Fig. 4). Obviously the presence of the strong absorption band at 503 nm is sensitive not only to the concentration of the solution, but also to the presence of water. This effect is demonstrated through a series of spectra of 7 in 96% ethanol with addition of increasing amount of water and presented in Fig. 3b. Compound 7 is characterized with a strong electron delocalization between the conjugated strong electron acceptor (the 1,3-indandione) and the strong electron donor (the N,N-dimethylamino group) and high polarity of the molecule is expected. Most probably possible intermolecular interactions, such as dimerization and water adduction, are competing processes leading to the observed changes in the absorption spectra. Quantitative estimation of these processes, however, is obscured by the fact that the bands in the absorption spectrum are very broad and may have composite structure (see Figs. 3, 4). Obviously aggregation of neighboring molecules is highly possible and has contribution to the long-wavelength band in the spectrum. For accurate explanation of all these effects on the absorption spectra of compound 7 more sophisticated experimental studies would be required including thorough theoretical investigation with an explicit description of the solvent molecules. This is, however, beyond the scope of the present work.

Fig. 3 Effect of concentration on the absorption spectra of compound **7** in 96% ethanol solution (**a**); effect of water addition on the absorption spectra of compound **7** in 96% ethanol solution (**b**)



Similarly to the parent compound, 2AID, which is characterized by very large Stokes shift in the fluorescence spectra and high photostability, we did photostability assessment of some of the compounds, namely 1 and 5. The irradiation was performed with a mercury lamp at room temperature. The absorption spectra were recorded at different time intervals, and 2AID is used as a reference compound with a proved high photostability [7]. The spectra after 1 and 2 h of irradiation of ethanol solution of compound 5 are presented in Fig. 5. For the sake of comparison, the spectra for 2AID are given in the inset of Fig. 5. The data show that after 1 h of irradiation with UV light the intensity of the most intensive band in the spectra of 1 and 5 is reduced by 10 and 16%, respectively. After 2 h of irradiation the intensity of 5 is further reduced with 7% more, while the spectrum of 1 remains unchanged. The same experiment for 2AID confirmed our previous observation that its absorption spectrum remains virtually unchanged; after 2 h of irradiation with UV light the intensity is reduced by less than 4%. These data show that

Fig. 4 Effect of concentration on the absorption spectra of compound 7 in absolute ethanol (concentrations and cell lengths given in the figure legend)





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compounds 1 and 5 are less photostable than 2AID. Similar result is expected for the other compounds from the studied series and their photostability was not studied.

All data for the optical and structural properties of compounds 1-7 indicate for the possibility for several photophysical phenomena. Firstly, the observed large Stokes shift in the fluorescence spectra of compounds 1-7 rises the question of any intramolecular rearrangements that could take place in excited state; such as ESIPT process shown for 2AID [11], or *cis-trans* isomerizations. Our earlier theoretical (quantum chemical) calculations of possible isomerizations of similar 2-acyl-1,3-indandiones in gas phase suggested that such processes would require much higher energy and could not take place upon UVirradiation [26]. Therefore, it was proposed that the observed large Stokes shift (ca. 100 nm) is caused most probably by strong charge redistribution during the electronic transitions. Such explanation seems appropriate for compounds 1-7, too. Moreover, the compounds having strong electron-donating substituent in the cinnamoyl fragment, such as *p*-methoxy and *p*-dimethylamino group in 6 and 7, respectively, show significant bathochromic shift in the absorption spectra as compared with compound 1 (see Table 4) and smaller Stokes shift in their fluorescence spectra. This is in accordance with the expected effect of degree of π -electron conjugation between the electron-acceptor part of the molecule (the 1,3-indandione fragment) and the electron donating part. The photostability data for compounds 1 and 5 show that they are less photostable than 2AID; the maximum loss of optical density for 5 is estimated to 23% after 2 h of irradiation. Although less photostable than 2AID, it is still comparable with the photostability data for an widely used sunscreen agent, i.e., octyl 4-methoxycinnamate (Parsol MCX) [7]. From structural point of view, the 2AID molecule possesses strong intramolecular hydrogen bond and a possibility for intramolecular proton transfer, whereas the octyl methoxycinnamate offers a possibility for cis-trans isomerization of the C=C double bond present in the molecule. Both intramolecular processes can be induced by UV irradiation and, if fast enough and reversible, they can give rise to a good photostability of the compound avoiding photodegradation. Our previous photostability studies [7] showed that fast and reversible proton transfer, as for 2AID and benzophenone-3, is much more efficient deactivation process leading to higher photostability than the cis-trans isomerization, which is the case for octyl methoxycinnamate showing 27% loss of optical density after 2 h of UVirradiation. The molecular structure of compounds 1-7 contain both intramolecular hydrogen bonding and flexible C-C bonds rendering possibility for intramolecular proton transfer and cis-trans isomerization. According to the photostability and the fluorescence data of compounds 1-7, the former process most probably does not occur.

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