Luminescence Properties of Some 4- or 5-Aminosubstituted Indan-1,3-Diones

I. Timtcheva, P. Nikolov, St. Minchev [1], and N. Sofroniev [1]
Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

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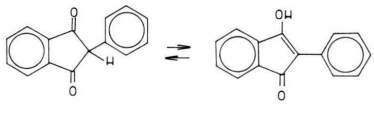
The photophysical characteristics of some 4(5)-amino-2-aryl- and 4(5)-amino-2-aryl-2-carboxymethyl-1,3-indandiones have been studied in solvents of different polarity at room temperature and at 77 °K. In contrast to the 2-arylindan-1,3-diones unsubstituted in the phthaloyl fragment, the compounds investigated are photostable and fluoresce in the region 25 000–18 000 cm^{-1} with fluorescence quantum yields between 0.1 and 0.5.

Key words: 4- and 5-amino indan-1,3-diones, absorption, fluorescence, phosphorescence.

I. Introduction

The 2-p-phenylsubstituted, as well as the 2-phenyl-2-substituted-1,3-indandiones do not fluoresce in solution [1, 2]. They photoisomerize to the corresponding 3-arylmethylene-1(3H)-isobenzofuranones (benzylydene phthalides) upon steady-state and pulse irradiation with UV light [1–3]. Depending on the polarity of the solvent, the 2-arylindan-1,3-diones can exist in two tautomeric forms [4], a diketo form (K) and an enol form (E):



K E

The diketo tautomeric form of the indandiones is responsible for their photoisomerization to benzylidenephthalides [5].

In the present paper, the results of the photophysical investigations of some 1,3-indandiones, substituted in the phthaloyl fragment are described.

The main structure investigated is that of 4(5)-amino-2-aryl-1,3-indandiones with the general formula I (Fig. 1); structures of the type II (Fig. 1), which cannot exist in the enol form, are also studied.

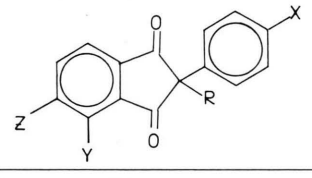
[1] Department of Chemistry, Higher Pedagogical Institute – Shoumen, Bulgaria.

Reprint requests to Dr. P. Nikolov, Institut für Organische Chemie, Bulgarische Akademie der Wissenschaften, Sofia 1113, Bulgarien.

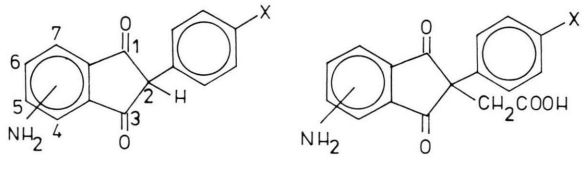
II. Experimental

Table 1 shows all compounds investigated (synthesised according to [6]) and the corresponding substituents.

Table 1. Compounds investigated (structures I and II in Fig. 1) and corresponding substituents.



No.	*X*	*Y*	*Z*	*R*
1	H	NH_2	H	H
2	CH_3	NH_2	H	H
3	OCH_3	NH_2	H	H
4	H	NH_2	H	CH_2COOH
5	CH_3	NH_2	H	CH_2COOH
6	OCH_3	NH_2	H	CH_2COOH
7	H	H	NH_2	H
8	H	H	NH_2	CH_2COOH
9	CH_3	H	NH_2	CH_2COOH
10	OCH_3	H	NH_2	CH_2COOH
11	Cl	H	NH_2	CH_2COOH



I II

Fig. 1. Structure of the compounds investigated. The *X*-substituents are given in Table 1.

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The absorption spectra are taken on a Specord M-40 (Carl-Zeiss, Jena, GDR). The fluorescence and phosphorescence spectra are recorded on a Perkin-Elmer MPF-44 Spectrofluorimeter. The fluorescence quantum yields Q_f are measured relative to 3-amino-phthalimid ($Q_f = 0.6$ in ethanol [7]). The fluorescence lifetimes are calculated from the decay curves, measured on a nanosecond spectrofluorimeter PRA – 2000 at 293 °K.

III. Results and Discussion

In contrast to the indandiones unsubstituted in the phthaloyl fragment, all 4- and 5-amino-indandiones are photostable upon steady-state and pulse irradiation with UV light and fluoresce intensively in the region 20000 – 23000 cm^{-1}. Table 2 shows the absorption and fluorescence characteristics of the compounds in ethanol, n-propanol, acetonitril and 1,4-dioxane.

Figure 2 shows the absorption spectra of compounds **1, 4** and 2-phenyl-2-carboxymethylindan-1,3-dione (the latter substance is similar in structure to the investigated ones).

The longest wavelength absorption Franck-Condon transition of the compounds with fixed keto-structure (general formula II, Fig. 1) is at 26000 cm^{-1} (Table 2, Figure 2). The longest wavelength absorption band of the 2-phenyl-2-carboxymethyl-1,3-

Table 2. Experimental spectral characteristics of the compounds investigated at 293 °K in solvents of different polarity. $\tilde{\nu}^A$, $\tilde{\nu}^F$ – energy of Franck-Condon absorption and fluorescence transition $[\tilde{\nu}] = cm^{-1}$; ε – molar absorptivity, $[\varepsilon] = 1 \cdot mol^{-1}\, cm^{-1}$; Q_f – fluorescence quantum yield.

No.	Ethanol				1,4-dioxane		n-propanol			Acetonitrile	
	$\tilde{\nu}^A$	ε	$\tilde{\nu}^F$	Q_f	$\tilde{\nu}^A$	$\tilde{\nu}^F$	$\tilde{\nu}^A$	$\tilde{\nu}^F$	Q_f	$\tilde{\nu}^A$	$\tilde{\nu}^F$
1	25 800	5 480	21 320	0.14	26 316	22 730	25 680	21 230	0.22	26 320	22 080
2	25 910	3 590	21 410	0.02	25 970	22 220	25 780	20 880	0.02	26 300	22 220
3	25 910	6 550	21 230	0.03	25 970	21 980	25 770	20 860	0.03	26 300	22 620
4	25 880	7 560	21 250	0.40	26 316	22 470	25 880	21 440	0.50	26 360	22 170
5	26 040	7 850	21 500	0.35	26 450	22 470	25 800	21 350	0.40	26 320	22 220
6	26 040	6 060	21 280	0.14	26 380	22 470	25 880	21 300	0.19	26 360	22 220
7	31 120	20 320	20 320	0.10	32 050	–	30 770	20 410	0.12	32 050	–
8	33 100	18 470	20 140	0.10	31 250	22 470	30 300	20 200	0.11	31 340	21 830
9	31 120	17 920	20 240	0.17	31 746	22 720	30 750	19 960	0.20	32 000	21 920
10	31 150	22 070	20 120	0.06	31 746	22 730	31 030	20 330	0.10	31 940	22 272
11	30 980	15 460	20 200	0.20	31 827	22 830	30 630	20 060	0.25	31 620	22 470

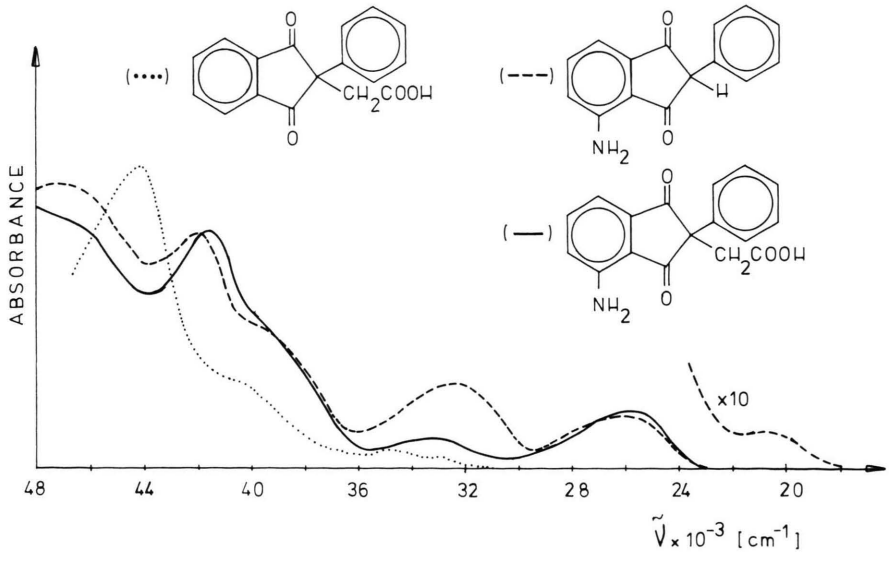

Fig. 2.
Absorption spectra of 2-phenyl-2-carboxymethyl-1,3-indandione (...), 4-amino-2-phenyl-1,3-indandione (---) and 4-amino-2-phenyl-2-carboxymethyl-1,3-indandione (—) in C_2H_5OH at 20 °C.

indandione is at 33000 cm^{-1} (Fig. 2) and the absorption in this region can be unambiguously attributed to the $S_0 - S_1$ ($n\pi^*$) transition [4]. A series of absorption bands is observed at shorter wavelengths; the most intensive one is at 44000 cm^{-1}, it is characteristic for all indandiones and results from a singlet $\pi\pi^*$ transition [4, 5]. The longest wavelength absorption band (21000 cm^{-1}) of the 4(5)-amino-2-arylindan-1,3-diones is due to absorption of the enol form [4]. The amino group at position 4 or 5 of the phthaloyl fragment leads to a red shift of the band at 44000 cm^{-1} with about 2000 cm^{-1} relative to the 2-aryl-1,3-indandiones unsubstituted in the phthaloyl fragment, accompanied with the appearance of a new absorption band at 26000 cm^{-1} for the 4-amino-derivatives and at 31000 cm^{-1} for the 5-amino ones; upon excitation in this new band fluorescence is observed.

The analysis of the spectral characteristics of the investigated 4- and 5-amino-2-arylindan-1,3-diones shows that their diketo-form is responsible for the fluorescence observed. This conclusion is based on the following experimental results:

1. The 4- and 5-amino-2-aryl-2-carboxymethylindan-1,3-diones, which have a fixed diketo structure fluorescence; their excitation spectra coincide with the absorption ones.

2. Two facts for the cases, when a keto-enol tautomerism is possible (compounds with general formula I) should be pointed out:

a) the excitation in the longest wavelength absorption maximum (21000 cm^{-1}), which results from absorption of the enol form, does not lead to fluorescence;

b) the excitation spectra of these compounds differ from the absorption spectra (which are, a superposition of the bands of the keto- and enol-forms) and coincide with the bands, which are due to absorption of the diketo-form only.

3. There is a mirror symmetry between the fluorescence spectrum and the longest-wavelength absorption band of the diketo-form.

4. The quantum yield of the compounds with a fixed diketo-form is greater than that of the compounds, for which a keto-enol tautomerism is possible. E.g., the fluorescence quantum yield of 4-amino-2-phenylindan-1,3-dione in ethanol is 0.14, while that of 4-amino-2-phenyl-2-carboxymethylindan-1,3-dione is 0.40.

The dipole moment change

$$\Delta\mu = \mu[S_1(\pi\pi^*)] - \mu[S_0]$$

can be evaluated, according to the model of Lippert [8] on the basis of the Stokes loss change $\Delta\tilde{\nu}(St)$ in solvents of different polarity.

Assuming an Onsager radius of 5 Å (approximately 1/2 of the geometric distance between the two most distant atoms in the indandiones investigated – Fig. 1), the following values of for some 4- and 5-substituted indandiones (Table 1) are obtained from linear correlation $\Delta\tilde{\nu}(St) \sim \Delta f$ [8]: **1:** $\Delta\mu = \pm 7.2$ D; **4:** $\Delta\mu = \pm 5.9$ D; **5:** $\Delta\mu = \pm 4.8$ D; **6:** $\Delta\mu = \pm 6.1$ D; **9:** $\Delta\mu = \pm 8.9$ D: (1,4-dioxane, diethyl ether, chloroform, dichloromethane, acetonitrile, n-propanol, ethanol and methanol were used).

In Table 3 are given the lifetimes τ of the $S_1(\pi\pi^*)$ state, computed from the fluorescence decay curve in ethanol and the corresponding constants of the radiative K_f and the non-radiative K_{nf} transitions, calculated from τ and Q_f.

As there are no data in the literature on the luminescence characteristics of 2-aryl-indandiones, a comparison can be made with their isomers – the benzylidenephthalides [9, 10]. These two groups of compounds have comparable fluorescence quantum yields and $\Delta\mu$, but their lifetimes are quite different: τ of the benzylidenephthalides is shorter than 2 ns, while that of some 5-NH_2-indandiones exceeds 10 ns (Table 3). The experimental data in Table 3 are not sufficient for more general conclusions about the influence of the different substituents in the indandiones on τ, but the tendency is, that 5-NH_2 indandiones have considerably longer lifetimes than the corresponding 4-NH_2 indandiones (compare e.g. **1** and **7**; **5** and **9**).

Table 3. Decay time τ and constants of the radiative K_f and the non-radiative K_{nf} transitions calculated from τ and Q_f in ethanol at 20 °C; τ is calculated from the fluorescence decay curve, fitted to a monoexponential linear function $I(t) = A \exp(-t/\tau)$; χ – mean error of fitting; λ^{ex} and λ^f – excitation and fluorescence wavelength. Dimensions: $[\lambda^{ex}], [\lambda^f]$ = nm; $[\tau]$ = ns; $[K_f], [K_{nf}] = ns^{-1}$.

No.	λ^{ex}	λ^f	τ	K_f	K_{nf}	χ
1	325	470	5.21	0.028	0.165	1.8
5	325	465	7.12	0.050	0.090	1.9
7	335	490	8.56	0.012	0.105	1.1
8	335	490	13.33	0.008	0.068	1.9
9	375	490	11.43	0.015	0.073	1.3

Upon freezing of the ethanolic solutions of the investigated NH_2-indandiones the fluorescence maxima move to the blue with about 10 nm and the fluorescence intensity slightly increases (2–5 times). Phosphorescence is observed only from the frozen solutions of compounds **5, 6** and **11**; the phosphorescence maximum is in the region 19500–20000 cm^{-1}. The S–T splitting, evaluated from the position of the fluorescence and phosphorescence Franck-Condon transitions, is about 4000 cm^{-1}.

The replacement of the amino group in the phthaloyl fragment with a hydroxy- or a nitro one leads practically to quenching of the fluorescence ($Q_f < 0.001$), while the 1,3-indandiones unsubstituted in the phthaloyl fragment do not fluoresce at all [1, 2]. Consequently it could be assumed that, besides the diketo form, the intense fluorescence of the investigated indandiones is unambiguously connected with the amino group in the phthaloyl fragment. This assumption is supported by the fact, that the acylation of the amino group leads to a significant diminishment of the fluorescence quantum yield (Q_f less than 0.001, like the compounds unsubstituted in the phthaloyl fragment). The indandiones which have an amino-group at position 2 or at p-position in the phenyl ring do not fluoresce either.

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