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Absorption and fluorescence of arylmethylidenoxindoles and isoindigo

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ABSTRACT

A series of arylmethylidenoxindoles was synthesized by acid or base catalysed condensation of substituted aldehydes with oxindole. The products were formed as mixtures of *Z*- and *E*-isomers that were separated using column chromatography and identified by ¹H and ¹³C NMR. The effect of substituents on absorption maxima was investigated both experimentally and theoretically, based on time dependent density functional theory. Low temperature absorption spectroscopy in a solvent glass enabled identification of the position of the 0-0 vibronic bands. The spectral features of the parent *Z*-benzylidenoxindole were compared to those of *trans*-isoindigo and *trans*-stilbene. Fluorescence of arylmethylidenoxindoles in solution was not observed, as *E*–*Z* isomerization represents a dominant deactivation channel after irradiation; when this geometrical isomerization was sterically hindered at low temperature solvent glass or in solid, fluorescence of planar *Z*-isomers was observed.

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PIGMENTS

1. Introduction

Z-Benzylidenoxindole (I) is a π -isoelectronic N-analogue of isoaurone, a parent chromophore of naturally occurring yellow pigments [1]. The compound I was prepared in both *Z*- and *E*-isomeric forms [2] and the X-ray structural data are available for them [3,4] (file LOHZAJ in Cambridge structural database (CSD) for *Z*-isomer). The compound I can be also formally considered as a hemistilbene/hemiisoindigo hybrid (Fig. 1).

There were several reasons for our interest on this class of compounds. We are generally interested in the dyes arising from a relatively simple condensation of aldehydes with heterocycles containing an activated methylene group [5]. N-acylated I was reported to show solid state fluorescence [4], which is also of our interest, because of its potential use in OLED devices [6]. While the spectral properties and excited state processes occurring in *trans*-stilbene were widely studied, there is a limited knowledge of the effect of its cyclization into one (I) or two (isoindigo) pyrrolinone rings on the absorption spectra and excited state behaviour. A recent theoretical study of the indigo isomers has found a significant discrepancy between theoretical excitation energy and a position of long wavelength absorption maximum of *trans*-isoindigo [7]. An explanation based on underestimation of excitation energies of charge-transfer transitions by time dependent density functional

theory (TD DFT) is not supported by our experience with related molecular structures [8], so we decided to reinvestigate this feature.

The aim of this paper is to study in detail the relation between structure and absorption spectra of arylmethylidenoxindoles and isoindigo and to look for their so far unknown fluorescence properties in various environments, i.e. in room temperature dimethyl sulfoxide (DMSO) and 2-methyltetrahydrofuran (MTHF) solutions. low temperature MTHF glass and polycrystalline solid state. We have synthesized a set of model compounds shown in Fig. 1. The biphenylyl compound (II) was synthesized for the first time in order to investigate an effect of a conjugated chain elongation on the spectral properties. The derivative with strong electrondonating group in *para* position of pendant phenyl (III) is known in both its isomeric forms [3]. There are several studies on the antitumour activity of III, that we will not review here. The compound III also appeared as an example of a dye for mass colouration of plastics [9], but it is not clear whether the Z- or E-isomer or their mixture was used.

Structural calculations of arylideneoxindoles were reported [4]. No quantum-chemical study of spectral properties of these chromophores was found. That is why DFT was used to geometry calculations and TD DFT to calculate the vertical excitation energies, with the same hybrid B3LYP exchange – correlation functional. The solvent effect was involved through polarized continuum model (PCM). No experimental absorption spectra of the compounds under study have been reported other than in solution and fluorescence has not been investigated up until now.



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Fig. 1. Chemical structure of synthesized compounds (drawn as of *Z*-isomers) together with *trans*-isoindigo and *trans*-stilbene formulas.

2. Results and discussion

2.1. Syntheses

trans-Isoindigo was synthesized by a condensation of oxindole and isatin [10]. Compounds I and II were synthesized by *p*-toluenesulfonic acid catalysed condensation of benzaldehyde (4-biphenylcarboxaldehyde) with oxindole. Compound III was synthesized by base (piperidine) catalysed condensation of p-dimethylaminobenzaldehyde and oxindole. The reaction mixture always contained both the *E*- and *Z*-isomers. Compounds I and III crystallized as *E*-isomers and were converted to *Z*-isomers by an exposure of their solutions to daylight. Pure *Z*-II crystallized from a hot reaction mixture, while *E*-II was obtained from cooled filtrates. Final products were obtained by flash column chromatography on silica (acetone – hexane 2:3). The identity of both isomers of I and III was checked by a comparison of their melting points with the published data [3] and the purity was monitored by elemental analysis and mass spectrometry.

The syntheses of both isomers of a new compound II are described in detail in Experimental. The isomers were preliminary assigned according to the shifts of their absorption spectral maxima after irradiation ($Z \rightarrow E$ hypsochromic and hypochromic, $E \rightarrow Z$ bathochromic and hyperchromic) and checked by recently verified methodology based on J(¹³C, ¹H) coupling constants [5]. We utilised a method proposed by Cho et al. [11], based on a stereochemical dependence of ${}^{3}J({}^{13}C, {}^{1}H)$ coupling constants on a C=C double bond. Cho et al. found that coupling constant of carbon trans to the olefinic proton is considerably larger to that of carbon cis to the same proton utilising single crystal X-ray data in the solid state and heteronuclear Overhauser effect in solution in suitable model compounds. Stereochemical dependence of the ³J(¹³C, ¹H) coupling constants were studied in the fragment HN-C(=O)-C(=CH-)having measured proton-coupled ¹³C NMR spectra of chromatographically separated isomers of compound II at digital resolution better than 0.5 Hz/point. The NH-C=O resonances gave a dd in the proton-coupled ¹³C NMR spectra. The small coupling constant in the dd in both cases corresponds to the interaction of carbonyl carbon with NH proton $({}^{2}J({}^{13}C(O)N^{1}H) = 2.5$ Hz). The coupling constant ${}^{3}J({}^{13}C(0)C=C{}^{1}H) = 12.1$ Hz belongs to Z form on double bond (compound Z-II) while ${}^{3}J({}^{13}C(0)C=C^{1}H) = 6.9$ Hz belongs to *E* form on double bond (compound *E*-**II**).

2.2. DFT ground state geometry and energy

Restricted B3LYP/6-311++G(d,p) DFT calculations in vacuum resulted in a strictly planar geometry for *Z*-isomers of all three arylmethylidenoxindoles (except for the phenyl–phenyl torsion in *Z*-II) and *trans*-stilbene. On the other hand, all three *E*-isomers were computed to be non-planar with pendant phenyl ring rotated out of oxindole plane. The experimental [3] dihedral angles for both *Z*-I (8.0°) and *E*-I (49.7°) are rather higher than the theoretical ones (0°, resp. 37.0°), that can be ascribed to packing effects in the crystal, not being taken into account in these calculations. The corresponding dihedral angles of *E*-II and *E*-III were computed to be 35.2° and 28.6°, respectively. The dihedral angle between both phenyls rings was 38.1° for *Z*-II and 38.9° for *E*-II.

Z-isomers are generally only a bit more stable than *E*-isomers by calculation. The energy differences are 0.32 kcal mol⁻¹ (**I**), 0.60 kcal mol⁻¹ (**II**) and 1.35 kcal mol⁻¹ (**III**). The thermodynamic stability of both isomers is thus very similar, that can be one of the reasons of their simultaneous rise in a reaction mixture.

The central ethylenic bond is significantly elongated when going from *trans*-stilbene (theor. 1.346 Å, exp. [12] 1.326 Å) to *trans*-isoindigo (theor. 1.377 Å, exp. [13] 1.369 Å), which agrees with a significant decrease of the frequency of the corresponding C=C stretching mode [10]. Thus *Z*-**I** is their true hybrid, as the corresponding bond length lies between those ones of its two symmetrical parent compounds both theoretically (1.359 Å) and experimentally [3] (1.350 Å).

There is a known discrepancy between the calculated nonplanarity [7,10] and experimental planarity [13] of *trans*-isoindigo. So we have focused on this problem in a more detailed manner. The dependence of the total energy of *trans*-isoindigo on the central double bond torsion, as computed in vacuum and DMSO solution involved by PCM, is shown in Fig. 2. The energy minimum shifts from 10.0° in vacuum to 14.6° in DMSO, as the polar environment more efficiently stabilizes the non-planar and thus polar structure through solute—solvent interaction. The minimum is shallow and the energy of a transition state (180°) and the structure with a dihedral angle 150° is almost the same in DMSO.

2.3. Absorption and fluorescence of arylmethylidenoxindoles

All three arylmethylidenoxindoles easily undergo a photochemical Z-E isomerization in both directions in solution. The absorption spectra of non-planar *E*-isomers show hypsochromic and hypochromic shift relative to the *Z*-isomers (Table 1) caused by an imperfect conjugation.

No fluorescence of any arylmethylidenoxindole was observed in DMSO or MTHF solution at room temperature. On the other hand, all three *Z*-isomers of **I**, **II** and **III** show fluorescence both in rigid



Fig. 2. The dependence of a total energy of *trans*-isoindigo on a central dihedral angle in vacuum (\bullet) and DMSO (\blacksquare).

Table	1
IdDie	: 1

Theoretical excitation energies of the first two $\pi\pi^*$ transitions (converted to λ_{00}) and experimental absolute absorption maximum λ_{max} in DMSO (room temperature) and a position of 0–0 vibronic band in MTHF (low temperature).

	PCM (DMSO) TD-DFT						Exp. λ_{max} DMSO (λ_{00} MTHF)			
	S ₀ -S ₁			S ₀ -S ₂		S ₀ -S ₁		S ₀ -S ₂		
	λ ₀₀	f _{osc}	coeff.	λ ₀₀	f _{osc}	coeff.	$\lambda_{\max} (\lambda_{00})$	٤ _{max}	$\lambda_{\max}(\lambda_{00})$	٤ _{max}
Z-I	421	0.179	0.63 (1-1') 0.22 (2-1')	352	0.663	0.18 (1-1') 0.64 (2-1')	~400	~4000	341 (355)	19200
E-I	403	0.164	0.64 (1-1') 0.18 (2-1')	339	0.422	0.15 (1-1') 0.65 (2-1')	~388	~2100	321	8600
Z-II	434	0.441	0.63 (1-1') 0.21 (2-1')	378	0.869	0.18 (1-1') 0.65 (2-1')			359 (380)	32500
E-II	415	0.381	0.64 (1-1') 0.18 (2-1')	366	0.509	0.16 (1-1') 0.66 (2-1')			345	18150
Z-III	434	0.973	0.63 (1-1') 0.12 (2-1')	377	0.206	0.10 (1-1') 0.67 (2-1')	444 (478)	37500		
E-III	431	0.803	0.65 (1-1′)	375	0.044	0.10 (1-1') 0.67 (2-1')	436	15100		

 λ_{max} [nm] – measured absolute absorption maxima, ε_{max} [l mol⁻¹ cm⁻¹] – measured molar absorptivity, λ_{00} [nm] – computed or measured absorption maximum of 0–0 vibronic band, f_{osc} – computed oscillator strength of 0–0 vibronic band, coeff. – expansion coefficient of the monoexcited configurations in TD DFT.

MTHF glass and in the solid state. The fluorescence of *Z*-**III** is strong, observable by naked eye under UV irradiation of the solid sample. The fluorescence of *Z*-**II** is measurable without problems, while for *Z*-**I** it is only detectable with low signal/noise ratio. *E*-arylmethylidenoxindoles do not fluoresce under these conditions, as is usual for less planar isomers [14].

The absorption spectra of Z-I and Z-II in DMSO are qualitatively similar, only the latter is bathochromically shifted as a consequence of enlarged conjugated system. They show two main spectral features: structureless long wavelength band (usually observed as a shoulder) in a visible region, tailing up to about 500 nm, and more intense band in UV region (Fig. 3). PCM TD DFT results (Table 1) qualitatively agree with all these spectral characteristics of *E*- and *Z*-isomers of I and II. The long wavelength shoulder represents $S_0 \rightarrow S_1 \pi \pi^*$ transitions of 1-1' (HOMO \rightarrow LUMO) character, while the UV band corresponds to $S_0 \rightarrow S_2 \pi \pi^*$ transitions of 2-1' (HOMO-1 \rightarrow LUMO) character. Both transitions are generally allowed, but weak, especially for I. The spectral positions of 0–0 vibronic subbands of both transitions, necessary for a quantitative correlation of theoretical and experimental values, were not generally available from room temperature spectra.



Fig. 3. Absorption spectra of Z-I (black line) and E-I (grey line) in DMSO at room temperature.

While no vibronic progressions can be observed for the shoulder in the visible region in MTHF glass, the stilbene-like [15] vibronic structure of the UV band is significantly sharper, showing that the absolute absorption maximum corresponds to 0-1 vibronic transition (Fig. 4). It is not surprising [16], that the low temperature MTHF glass behaves as an even more polar environment than DMSO at room temperature: the absolute absorption maxima in DMSO (341 nm for Z-I and 359 nm for Z-II) are slightly (1 nm for Z-I and 3 nm for Z-II) hypsochromically shifted with respect to the 0-1maximum in MTHF glass (342 nm for Z-I and 362 nm for Z-II). Thus, it is reasonable to compare the theoretical excitation energies. computed in DMSO by PCM model, with well resolved 0-0 vibronic sub-bands in MTHF glass rather than with hardly detectable shoulders in DMSO spectra. The agreement is excellent – the difference is 3 nm for Z-I and 2 nm for Z-II (Table 1). The absorption spectra of E-I (Fig. 3) and E-II are qualitatively similar, but no significant vibronic progressions of either the visible shoulder or the UV band can be observed in MTHF glass, so the exact quantitative comparison with the theoretical values is impossible.

The position of 0-0 vibronic sub-band of a long wavelength shoulder of *Z*-**I** and *Z*-**II** is not clear even from the low temperature absorption. Rather better insight on a position of 0-0 vibronic sub-band can be indirectly derived from a shape of low temperature fluorescence spectra. The fluorescence emission spectrum of *Z*-**II** clearly shows, that its maximum corresponds to 0-2 vibronic sub-band (Fig. 5). This effect is usually connected with a significant difference between equilibrium geometries in S₀ and S₁ states. Thus, although the fluorescence excitation spectrum of a long wavelength transition is not resolved into the vibronic sub-bands, we can reasonably suppose, that the 0-0 vibronic band is hidden at the long



Fig. 4. Room (DMSO – grey line) and low (MTHF – black line) temperature absorption spectra of Z-II.



Fig. 5. Fluorescence excitation and emission spectra of Z-II in MTHF at low temperature.

wavelength spectral tail. This is the reason, why the computed absorption maxima are generally red shifted with respect to the observed maxima (or inflections) of I and II corresponding to their $S_0 \rightarrow S_1$ transition.

The absorption and fluorescence spectra of electron donor substituted Z-III show significant differences from parent Z-I. The intensities of both spectral transitions are inverted by theory (Table 1) and the stronger long wavelength band shows well resolved vibronic structure at low temperature (Fig. 6). Both absorption and emission maxima correspond to 0-1 vibronic transition, so the difference between equilibrium geometries of S_0 and S_1 is probably not so pronounced. The second $S_0 \rightarrow S_2$ absorption band is not observable, as it is overlapped by stronger $S_0 \rightarrow S_1$ band. Z-III (4.04 D) is more polar than parent Z-I (2.04 D) by computations, so it is more sensitive to environment polarity. So the 0-1 vibronic band in MTHF is significantly (20 nm) bathochromically shifted with respect to room temperature maximum in DMSO and the wavelength of 0-0 subband in MTHF at 77 K is thus dramatically higher than the computed one in DMSO at 20 °C. The computed excitation energy is overestimated by PCM TD DFT in this case. Hypsochromic shift of E-III with respect to Z-III is less pronounced both by theory and experiment, as $S_0 \rightarrow S_1$ transition is of charge transfer (CT) character and E-III is even more polar (6.00 D) than Z-III. The non-planarity of E-III



Fig. 6. Fluorescence excitation and emission spectra of Z-III in MTHF at low temperature (black line), together with absorption in DMSO at room temperature (grey line).



Fig. 7. Normalized solid state fluorescence emission spectra of *Z*-**II** (grey line) and *Z*-**III** (black line) at room temperature.

manifests itself mainly by hypochromic shift — relative decrease of ε_{max} with respect to *Z*-III is comparable with that of the parent *E*- and *Z*-I pair (Table 1).

The solid state fluorescence emission spectra of *Z*-isomers of **II** and **III** are shown in Fig. 7. The emission of *Z*-**III** shows a maximum in the red region (665 nm). Such a strong solid state luminescence is remarkable, as it is not a common phenomenon in the area of organic dyes and pigments [17–19]. The absence of solid state fluorescence of all three *E*-isomers is a consequence of their non-ability to fluoresce as isolated molecules, that is always the necessary condition of solid state emission [17,18].

2.4. Absorption of trans-isoindigo

No spectral changes upon irradiation were observed for *trans*isoindigo, thus there is no evidence for the formation of the *cis* isomer. *trans*-Isoindigo does not fluoresce at all. The room and low temperature absorption spectra of *trans*-isoindigo (Fig. 8) show a remarkable similarity with those of *Z*-**I** (and *Z*-**II**). Its long wavelength band (490 nm/3900 l mol⁻¹ cm⁻¹ in DMSO, 498 nm in MTHF glass) is of lower intensity and unresolved even at low temperature, while the more intense UV band shows resolved vibronic progressions. The absolute absorption maximum in DMSO (367 nm/10 600 l mol⁻¹ cm⁻¹) is slightly hypsochromically shifted with respect to the maximum in MTHF glass (370 nm), so the parallel with *Z*-**I** is evident. Nevertheless, it is not clear, whether this maximum corresponds to 0–1 or 0–2 vibronic transition. It is not obvious, whether the vibronic sub-band in MTHF glass at 393 nm is of 0–0 character,



Fig. 8. Room (DMSO – grey line) and low (MTHF – black line) temperature absorption spectra of *trans*-isoindigo.

as in *Z*-I, or 0-1, as the there is a remarkable shoulder at about 415 nm, which is not observable neither in *Z*-I, nor in *Z*-II.

PCM TD DFT calculations of *trans*-isoindigo in DMSO resulted in three transitions covering the investigated spectral region. Their positions depend significantly on a central torsion angle being: $S_0 \rightarrow S_1$ (518 nm, $f_{osc} = 0.139$), $S_0 \rightarrow S_2$ (493 nm, $f_{osc} = 0.000$) and $S_0 \rightarrow S_3$ (395 nm, $f_{osc} = 0.565$) for planar structure and $S_0 \rightarrow S_1$ (537 nm, $f_{osc} = 0.175$), $S_0 \rightarrow S_2$ (505 nm, $f_{osc} = 0.000$) and $S_0 \rightarrow S_3$ (420 nm, $f_{osc} = 0.293$) for the equilibrium minimum at 165°. Qualitatively the situation is clear: $S_0 \rightarrow S_1$ is responsible for a long wavelength band and $S_0 \rightarrow S_3$ for a more intense band near 400 nm. $S_0 \rightarrow S_2$ is symmetry forbidden, thus not observable in absorption. Its eventual role in a deactivation processes after excitation, leading to the absence of both fluorescence and Z-E isomerization, is out of the scope of this paper.

The quantitative comparison of the theoretical excitation energies and experimental spectral features is complicated, because the uncertainty lies both on experimental (position of 0-0 vibronic bands) and theoretical (geometry in DMSO solution) aspects. We tend to the following explanation: the shoulder at about 415 nm in MTHF glass really corresponds to 0-0 vibronic sub-band, that quite well relates with the value 420 nm computed for non-planar geometry in DMSO. Thus, trans-isoindigo is, because of relatively long central double bond, unable to retain a planar geometry as in crystal. The position of a 0-0 vibronic sub-band of a long wavelength band is not clear from the absorption spectra. It is evident from a broad spectral shape, that its maximum does not correspond to 0-0, but probably to 0-2 vibronic transition, the same way as for more intense band near 400 nm. In this case the computed value 537 nm is not overestimated [7], but may be even underestimated, as this band is tailing up to 600 nm. The usual energy difference between vibronic sub-bands, corresponding to carbon–carbon stretching, is about 1500 cm⁻¹. If a double of this value is subtracted from the spectral maximum relating to 0-2 vibronic sub-band (490 nm = 20 408 cm⁻¹), the position of 0-0 vibronic sub-band reaches 574 nm (17 408 cm⁻¹), i.e. the value near to the spectral onset of this broad band (Fig. 8). At least, there is no reason to doubt the ability of the PCM TD DFT method to describe trans-indigo, that is only slightly polar (1.39 D by computation) for equilibrium C_2 non-planar geometry. The discrepancy between calculated and experimental values could mainly be ascribed to the difficulties associated with locating the correct spectral positions of 0–0 vibronic transitions.

The position of 0–0 vibronic sub-band of *trans*-stilbene in MTHF glass is 327 nm, rather lower with respect to the value computed in DMSO for equilibrium planar geometry (335 nm). This difference can be explained on the often discussed phenyl torsions in solution [20]. So the difference between experimental (theoretical) excitation wavenumbers of a UV transition with pronounced vibronic structure between *Z*-**I** and *trans*-stilbene is about 2400 cm⁻¹ (1450 cm⁻¹), while the same differences between *Z*-**I** and *trans*-isoindigo are considerably higher 4100 cm⁻¹ (4600 cm⁻¹). From this point of view *Z*-**I** can be considered to resemble a perturbed stilbene, rather than true hemistilbene/hemiisoindigo hybrid. The long wavelength CT transitions of *Z*-**I** and *trans*-isoindigo in a visible region have no counterpart in *trans*-stilbene spectrum and can be considered as a demonstration of their (coupled) merocyanine character [21].

3. Conclusions

All three *Z*-arylmethylidenoxindoles are batho- and hyperchromically shifted with respect to their *E*-isomers. The enlarged conjugated system of an aryl moiety causes a bathochromic shift without significant change of the mutual intensity of both main spectral features corresponding to $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, while a strong electron-donating substituent on the aryl ring inverts their mutual

intensity. Low temperature absorption spectroscopy in solvent glass enabled the identification of the position of the 0–0 vibronic bands in some cases. These 0–0 vibronic bands of $S_0 \rightarrow S_2$ transitions show excellent agreement with PCM TD DFT computed excitation energies. *Z*-benzylidenoxindole is a hemistilbene/hemiisoindigo hybrid from a structural point of view and its spectral features lie among those ones of *trans*-isoindigo and *trans*-stilbene. Fluorescence of arylmethylidenoxindoles in solution was not observed, as E-Z isomerization represents a dominant deactivation channel after irradiation. If this isomerization was sterically hindered in a low temperature solvent glass or in the solid state, fluorescence of the *Z*-isomer was observed.

4. Experimental

4.1. Syntheses and analyses

Oxindole, 4-biphenylcarboxaldehyde, dimethyl sulfoxide, 2methyltetrahydrofurane, piperidine and *trans* stilbene were purchased from Sigma–Aldrich. Benzaldehyde, *p*-toluenesulfonic acid and p-dimethylaminobenzaldehyde came from Lachema.

4.1.1. (3Z)-3-(1,1'-biphenyl-4-ylmethylen)-1,3-dihydro-2H-indol-2-on (Z-**II**)

Oxindole (2.7 g, 0.02 mol), 4-biphenylcarboxaldehyde (3.64 g, 0.02 mol), *p*-toluensulfonic acid (0.5 g) and toluene (50 ml), were placed in a 100 ml flask and the reaction mixture was stirred and heated under reflux. After three hours, the hot, orange suspension of *Z*-**II** was filtered off and washed with hot toluene. Yield 3.8 g (64%), m.p. 272–275 °C.

Calculated: C(84.82),H(5.08),N(4.71), Found: C(84.56),H(4.94),N (4.59)

GC/MS: M (297), RT (16.53 min), 100%

¹H NMR (500 MHz, DMSO-*d*6) δ 10.72 (1H, bs, NH), =CH-: 7.90 (1H, s), phenyl group: 8.56 (2H, d, J = 8.1 Hz) 7.56 (2H, t, J = 7.6 Hz), 7.45 (1H, tt, J = 7.6 and 1.3 Hz), 1,4-C₆H₄-: 7.84 (2H, m), 7.79 (2H, m), 1,2-C₆H₄-: 7.78 (1H, d, J = 7.5 Hz), 7.27 (1H, t, J = 7.6 Hz), 7.05 (1H, t, J = 7.5 Hz), 6.88 (1H, d, J = 7.5 Hz), ¹³C NMR (125 MHz, DMSO-*d*6) δ 167.3 (³J(¹³C(O)C=C¹H) = 12.1 Hz), 141.8, 140.8, 139.3, 136.3, 133.3, 132.8, 129.1, 129.0, 128.1, 126.9, 126.8, 126.4, 125.1, 121.2, 119.9 and 109.5.

4.1.2. (3E)-3-(1,1'-biphenyl-4-ylmethylen)-1,3-dihydro-

2H-indol-2-on (E-II)

The hot filtrate obtained from the preparation of *Z*-**II** was cooled to room temperature. Yellow crystals of *E*-**II** were filtered and dried. Yield 0.64 g (10.7%), m.p. 223–225 °C.

Calculated: C(84.82), H(5.08), N(4.71) Found: C(84.77), H(5.25), N(4.96)

¹H NMR (500 MHz, DMSO-*d*6) δ 10.69 (1H, bs, NH), = CH-: 7.72 (1H, s), phenyl group: 7.82 (2H, d, *J* = 7.8 Hz), 7.56 (2H, t, *J* = 7.6 Hz), 7.46 (1H, t, *J* = 7.6 Hz), 1,4-C₆H₄-: 7.90 (2H, m), 7.86 (2H, m), 1,2-C₆H₄-: 7.70 (1H, d, *J* = 7.5 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 6.95 (1H, d, *J* = 7.7 Hz), 6.92 (1H, t, *J* = 7.6 Hz), ¹³C NMR (125 MHz, DMSO-*d*6) δ 168.8 (³*J*(¹³C (0)C=C¹H) = 6.9 Hz), 143.1, 141.3, 139.3, 135.5, 133.6, 130.3, 130.2, 129.2, 128.3, 127.6, 127.0, 126.8, 122.6, 121.3, 121.0, and 110.3.

4.2. Instrumental

4.2.1. Absorption and fluorescence spectra

Perkin Elmer Lambda 9 was used for the measurements of absorption spectra. Home made cryostat was used for low temperature measurements (103 K). Perkin Elmer LS 35 furnished with a commercial low temperature accessory was used for measurements of fluorescence emission and excitation spectra at low temperature (77 K). The room temperature solid state fluorescence emission spectra were measured with Perkin Elmer LS 35, too.

4.2.2. Mass spectrometry

The ion trap mass spectrometer MSD TRAP XCT Plus system (Agilent Technologies, USA) equipped with APCI probe was used. Positive-ion and negative-ion APCI mass spectra were measured in the mass range of 50–1000 Da in all the experiments. The ion trap analyzer was tuned to obtain the optimum response in the range of the expected m/z values (the target mass was set from m/z 289 to m/z 454). The other APCI ion source parameters: drying gas flow rate 7 L min⁻¹, nebulizer gas pressure 60 psi, drying gas temperature 350 °C, nebulizer gas temperature 350 °C. The samples were dissolved in a mixture of DMSO/acetonitrile and methanol in various ratios. All the samples were analyzed by means of direct infusion into LC/MS.

4.2.3. Elemental analysis

Perkin Elmer PE 2400 SERIES II CHNS/O and EA 1108 FISONS instruments were used for elemental analyses.

4.2.4. Nuclear magnetic resonance

The ¹H (500.13 MHz) and ¹³C (125.76 MHz) NMR spectra for compounds *Z*-**II** and *E*-**II** were recorded on a Bruker Avance 500 spectrometer. The samples were dissolved in hexadeuteriodimethyl sulfoxide-d₆. The ¹H and ¹³C chemical shifts were referenced to the central signal of the solvent (δ = 2.55 (¹H) and 39.6 (¹³C)).

4.3. Computational procedures

The geometry of *trans*-stilbene, *trans*-isoindigo and all three arylmethylidenoxindoles in both *E*- and *Z*-isomeric forms was optimised using quantum-chemical calculations based on DFT. The hybrid three-parameter B3LYP functional in combination with 6-311++G(d,p) basis was used. No constraints were employed. No imaginary frequencies were found after diagonalization of Hessian matrix, confirming that the computed geometries were the real minima on the ground state hypersurfaces.

The geometry of *trans*-isoindigo was also optimised on this level with an involvement of solvent effect (DMSO) by non-equilibrium PCM. The dependence of the total energy on a central bond torsion was computed on fully optimised geometry except the frozen central dihedral angle in a range $105-180^{\circ}$ with 15° step. C_2 symmetry constraint was used in these calculations.

TD DFT method was used for the computation of vertical excitation energies on the above-mentioned geometries in vacuum or DMSO for *trans*-isoindigo. The B3LYP/6-311++G(d,p) combination was employed, too. The solvent effect (DMSO) was also involved by means of the non-equilibrium PCM.

All the methods came from the Gaussian03W program suite [22] and the default values of computational parameters were used. The results were analyzed using GaussViewW from Gaussian Inc., too.

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