Photoresponsive N,N'-disubstituted indigo derivatives

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A R T I C L E    I N F O

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A B S T R A C T

The synthesis and a comprehensive characterization of the excited state properties of five N,N'-substituted indigo (Ind) derivatives (acetyl-, benzoyl-, methoxybenzoyl-, nitrobenzoyl- and chlorobenzoyl-) was undertaken in various solvents and temperatures. In the excited state, rotation around the central double bond was found with N,N'-diacetilindigo (DAI) and N,N'-dibenzoylindigo (DBI) derivatives. Both DAI and DBI acyl derivatives show rotation in the excited state around the central C=C bond, leading to a conical intersection (CI). Steric hindrance prevents DBI from accomplishing full rotation (which consequently does not fully isomerize) with two conformers being experimentally found from both fi-transient absorption and time-resolved emission measurements. For DAI, the fluorescence decays are single exponential (varying from 2790 ps in 2MeTHF to 7520 ps in MCH), while fs-TA indicates the presence of two species, with lifetimes, in 2MeTHF, of 33 ps and 2790 ps. All the acyl derivatives show blue shifted absorption and emission from the parent indigo dye due to stabilization of the π HOMO orbital in the S1, n→π transition by delocalization to the acyl carbonyl. The extent of blue shift among the different acyl derivatives is found to depend on the geometric constraints imposed on the dihedral angle between indigo and the acyl group. With the DBI derivatives, interconversion between the two conformers in the excited state leads to rate constant values ranging from 1.3 10^10 s⁻¹ (in MeTHF) to 3.6 10^8 s⁻¹ for the nitrobenzoyl-DBI derivative (in dioxane).

1. Introduction

Indigo is one of the most light-stable organic dyes. Associated with its natural origin (it has been extracted from more than 700 Indigofera species) it is a molecule charged of mysticism, with its synthesis linked to the genesis of the modern chemical industry [1−3]. Besides its blue colour, associated to the particular configuration (in H) of N−H and C=O groups connected by a double bond [4], the nature of its high stability has led to a renewed interest in both indigo and also in some synthetic derivatives [5−7]. These include N-alkyl-indigo derivatives [6], imine derivatives [8], ruthenium complexes [9], donor-acceptor copolymers [10], tert-butoxy carbonyl (tBOC) derivatives [11−13] (where reversible trans-cis photoisomerizations have been reported) and thioindigo derivatives [14−18]. Indigo’s photostability is known to be imparted from an excited state proton transfer (ESPT) involving a single proton transfer from the N−H and C=O groups [2,6].

Photoisomerization (along the central C=C double bond) is a potential competitive pathway for the excited state deactivation, although there are contradictory views, from TDDFT calculations, of this potential deactivation channel in indigo [19,20]. Recent works on related compounds has showed evidence for photoisomerization in both thioidigo and indigo derivatives [13,17,21−23]. Trans-cis photoisomerization of indigo derivatives have led recently to the design of indigoid derivatives as potential photoswitches [5].

Trans-cis photoisomerization of N,N'-substituted indigo derivatives has been known since 1968 with the work of Giuliano et al. who reported its existence with N,N'-dimethylindigo and its tetrabrominated derivative, where the cis conformer shows an absorption wavelength maximum of 588 nm in benzene [24]. Pouliquen et al. [25] reported the absence of fluorescence for the cis form of DAI (and other derivatives), while the trans form in chloroform showed an emission maximum at 620 nm with a lifetime of 2.1 ns and a fluorescence quantum yield of

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0.022. Other groups showed that an increase in solvent viscosity decreases rotation/twisting of the molecule, leading to a decrease in the internal conversion process (i.e. the CI channel becomes less effective), a more efficient triplet state formation and, thus, less efficient cis formation [26]. Gowalski et al. [13] have shown that tert-butoxycarbonyl (t-Boc) indigo derivatives present very efficient trans-cis photoisomerization; moreover due to their better solubility than indigo and isoidigo, t-Boc derivatives have been used to build-in solution-processed conjugated polymers, with this group readily removed at high temperatures [10,11]. Recently DAI trans-cis photoisomerization has been studied with fs-TA techniques and shown to be solvent dependent (absent in DMP) [21]. Other N-alkyl and N-aryl indigo derivatives have also been investigated, showing the simultaneous presence of the Z and E isomers in the ground-state [22]. We report a comprehensive characterization of the excited state properties of five N, N'-substituted indigo derivatives as a function of solvent and temperature using fs-Transient Absorption (fs-TA), time resolved emission measurements and TD-DFT calculations.

2. Experimental section

2.1. Synthesis

Unless otherwise stated, all solvents and reagents were used as obtained from commercial sources without further purification. Dioxane, 2-MeTHF, and dimethyl sulfoxide solvents were all of spectroscopic grade and were purified and dried by conventional methods. Column chromatography was carried out using Silica gel 60, 230–400 mesh. HPLC analyses were performed on an Agilent 1100 instrument equipped with a Phenomenex LUNA® C-18 column (150 mm 4.6 mm i. d., 2 µm, Torrance, CA, USA), using acetonitrile or THF (HPLC grade) as the mobile phase. 1H and 13C NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz operating at 400 MHz, and 100.6 MHz, respectively. IR spectra in the range of 400–4000 cm−1 were performed using KBr pellets on a Bruker Tensor 27 FT-IR Spectrometer with a resolution of 4 cm−1. Details of the synthetic procedures for diacetyl- and dibenzoindigo indigo derivatives, as well as NMR (1H and 13C) and FT-IR spectra are given as supporting material.

2.2. Material and methods

Absorption spectra were recorded on a Cary 5000 UV–Vis–NIR. Fluorescence spectra were recorded in a Horiba-Jobin-Yvon Spex Fluorolog 3–2.2. spectrophotometer and all spectra were corrected for the instrumental response of the system. The fluorescence quantum yields of the compounds were determined using indigo as standard (ΦF 0.0023 in DMP) [27]. The molar absorption coefficients (εsol) Table 1 were obtained from the plot of the absorption vs. concentration obtained with solutions with concentrations ranging from 8 × 10−5 to 3 × 10−5 mol dm−3. In all cases R2 values 0.99 were obtained. For the low temperature measurements (fluorescence quantum yields and emission maxima) these were made with an Horiba-Jobin-Yvon Spex Fluorolog 3–2.2. spectrophotometer and collected in a Dewar with liquid nitrogen. A sample in a quartz EPR-like tube was cooled down with liquid nitrogen (forming a clear glass) and the emission spectra were obtained at this temperature.

Fluorescence decays were measured using a home-built time-correlated single photon counting (TCSPC) apparatus described in detail elsewhere [28]. Briefly, it consists of a PicoQuant Picosecond Laser Diode (with excitation at 451 nm) as excitation source light, a double subtractive Oriel Cornerstone 260 monochromator and an Hamamatsu microchannel plate photomultiplier (R3809U-50). The signal acquisition and data processing is performed with a Becker & Hickl SPC-630 TCSPC module. The fluorescence decays and the instrumental response function (IRF) were collected using 1024 channels in time scales varying from 3.26 to 6.4 ps/channel scale, until 2000–5000 counts at maximum were reached. The full width at half-maximum (fwhm) of the IRF was 0.95–1.10 ns. Deconvolution of the fluorescence decay curves was performed using the modulating function method as implemented by Striker et al. in the SAND program [29] which allows a value of ca. 10% of the fwhm (9 ps) as the time resolution of the equipment with this excitation source.

Femtosecond Transient Absorption Spectroscopy (fs-TA) were performed with a Helios spectrometer (Ultrafast Systems) with an instrumental response function of ~250 fs in an apparatus described elsewhere [6]. The instrumental response function of the system was assumed to be equal to that of the pump probe cross correlation determined from the measurement of the instantaneous stimulated Raman signal from the pure solvent (in a 2 mm cuvette). To avoid photodegradation, the solutions were stirred during the experiments or

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral data (including wavelength absorption, λabs (nm), and emission λem (nm), maxima, molar extinction coefficient, ε, and Stokes Shift, Δνss) for Indigo (Ind), N,N’-diacetyldiindigo (DAI), N,N’-Dibenzoindigo (DBI), N,N’-Dibenzoyldiindigo in methycyclohexane (MCH), Dioxane, DMSO and 2-methyltetrahydrofuran (2MeTHF) at room (293K) and low (77K) temperature.</td>
</tr>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Ind</td>
</tr>
<tr>
<td>2-MeTHF</td>
</tr>
<tr>
<td>Dioxane</td>
</tr>
<tr>
<td>DAI</td>
</tr>
<tr>
<td>2-MeTHF</td>
</tr>
<tr>
<td>Dioxane</td>
</tr>
<tr>
<td>DBI</td>
</tr>
<tr>
<td>2-MeTHF</td>
</tr>
<tr>
<td>Dioxane</td>
</tr>
<tr>
<td>DBIOMe</td>
</tr>
<tr>
<td>Dioxane</td>
</tr>
<tr>
<td>DBICl</td>
</tr>
<tr>
<td>Dioxane</td>
</tr>
<tr>
<td>DBINO2</td>
</tr>
</tbody>
</table>

* Data from Refs. [27,36].
in movement using a motorized translating sample holder. The spectral chirp of the data was corrected using Surface Xplorer PRO program from Ultrafast Systems [30].

Photoisomerization studies (in the case of DBI) were obtained through irradiation with a high energy laser at 570 nm during 3 min and monitored with an Ocean Optics spectrophotometer with absorption spectra collected each 10 s.

All theoretical calculations were of the DFT type, carried out using GAMESS-US version R3 [31]. A range corrected CAMB3LYP [32] functional, with 65% HF exact exchange at long range and 19% at short range, was used in both ground- and excited-state calculations. TDDFT calculations, with similar functionals, were used to probe the excited-state potential energy surface (PES). The LC-BPBE(ω 0.20 au-1) functional as implemented in GAMESS-US [31] was used to compute unscaled excitation energies in all the stationary points. The solvent was included using the polarizable continuum model with the solvation model density to add corrections for cavitation, dispersion, and solvent structure. In TDDFT calculation of FC (Franck-Condon) excitations the dielectric constant of the solvent was split into a “bulk” component and a fast component, which is essentially the square of the refractive index. In “adiabatic” conditions only the static dielectric constant is used. A 6-31G** basis set was used in both DFT or TDDFT calculations. CAMB3LYP slightly overestimates excitations with a scaling correction applied to the reported values (E_{\text{reported}} = E_{\text{DFT}} \times 0.92–0.1) [33]. Excitations were corrected for Zero Point Vibrational Energy by using, essentially, the frequency of the relaxing vibrational mode (0.05 eV). The results obtained with the LC-BPBE(20) functional are unscaled raw data from calculations.

3. Results and discussion

3.1. Absorption and fluorescence spectra

Scheme 1 shows the structures and acronyms of the five compounds studied.

Fig. 1 depicts the absorption and fluorescence emission spectra of the five compounds investigated (with indigo, Ind, included for comparison) in 2MeTHF and DMSO at room temperature (293 K). Fig. 2 presents the absorption and fluorescence spectra of DAI and DBI in methylcyclohexane at room (T 293 K) and low (T 77 K) temperatures. Spectral and photophysical data are given in Tables 1 and 3 to 5, respectively. From Figs. 1 and 2 and Table 1 it can be seen that, with the exception of indigo where the H-chromophore [34] seems to play a dominant role, the acetyl substitution leads to the shortest absorption (and emission) wavelength maxima, see Table 1. It is interesting to note that the Stokes Shifts follow the order DAI > DBI > IND. Analysis of Table 1 also suggests that the smaller value of the Stokes shift (ΔSS) for Ind is due to the similarity between the ground state and the S1 geometries [1,6,35,36]. The larger SS in DAI and DBI indicates the existence of differences in the potential energy curves, which are associated with different structures in the ground-state (GS) and excited state (ES) of these two compounds. However, the most interesting feature is the large Stokes shift (ΔSS) with the two compounds, in particular when compared with Ind, see Table 1. With Ind the small ΔSS indicates that in the ground state the hydrogen bonds connecting the N–H and C=O groups keep the molecule in a stable trans form and that both the excited state keto and enol forms are structurally similar to the GS structure. In contrast, with DAI and DBI there is a marked difference between the GS and ES geometries.

From Table 1 it can also be seen that the Stokes Shift (SS) is smaller in 2MeTHF than in the other two solvents for both DAI and DBI. Introduction of the methoxy (DBIOMe), chloro (DBICl), and nitro (DBINO2) substituents in the benzoyl group of DBI, leads to changes in the absorption and emission wavelength maxima and ΔSS. The ΔSS in DMSO for the DBINO2 derivative in comparison with DBI (2241 cm⁻¹ vs. 1533 cm⁻¹) is particularly worthy of note. DAI has the highest Stokes shift, which indicates the biggest difference between the S0 and S1 geometries. This was further supported by TDDFT calculations (see below).

Previous studies have shown that in solvents of low polarity, such as isooctane, CCl4, CHCl3 and benzene, the wavelength maxima is, for N, N’-dimethylindigo, found at ~559–560 nm [37]. The cis form of DAI in CCl4 has been associated with a broad band spanning from 360 to 570

Scheme 1. Structures and acronyms of the DAI and DBI derivatives investigated. The trans-to-cis photoisomerization scheme is also shown.
Fig. 77 293K derivatives (650). TDDFT.

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Fig. 1. Absorption (A, C) and fluorescence emission (B, D) spectra of Indigo (Ind), N,N'-diacetylindigo (DAI), N,N'-dibenzoylindigo (DBI) and N,N'-dibenzoyleindigo derivatives (DBIOMe, DBICI, DBINO2) in 2MeTHF (top hand panels A and B) and DMSO (bottom hand panels C and D) at T 293K, with concentrations in a range between 1.5 \times 10^{-5} \text{ M} and 2.3 \times 10^{-5} \text{ M} for all compounds and \lambda_{exc} 520 nm.

nm with maximum at \sim 440 nm [38]. Other groups have also reported the formation of cis derivatives of indigo diimines, although in these derivatives this form displays maxima at longer emission wavelengths (>650 nm) than the trans isomer [8].

3.2. TDDFT calculations

The difference between the emission spectra and maxima of DAI and DBI in Fig. 2 and Table 1 are worth noting. With the former, the fact that emission spectra and maxima at 293 and 77K are very similar indicates the possibility of free rotation leading to a single (and more stable) conformer in the excited state. In the case of DBI, the 20 nm shift of the emission maxima at 77K relative to 293 K indicates that the most stable form (conformer A in Fig. 3 and Table 2) is likely to be the only species present at low temperature, while at 293 K, two conformers are detectable (see Fig. 3 and Table 4).

This experimental data is supported by TDDFT calculations. Although it seems clear that there is a change in the nature of the excited state in N,N'-substituted indigo derivatives, the structural explanation for this is still under discussion, and clearly depends on the substitution. One of the difficulties in the analysis of DFT data for this family of indigo derivatives is the existence of various conformers corresponding to different orientations of the acyl group. DFT calculations on the three conformations where convergence to a local minimum was achieved show that DAI has one conformer that is 10 and 24 kJ/mol more stable than the two others; consequently, a single conformer is observed experimentally (with a maximum 2% contribution from the A conformer that can be marginally detected in fs-TA spectra but not from the time-resolved fluorescence measurements, see below). In contrast, with DBI the conformers are separated by just 4 and 6 kJ/mol, which allows the experimental detection of two conformers. This is illustrated in Fig. 3, where with DAI a single conformer is predicted (Fig. 3 B top and Table 2), while with DBI an ensemble of three conformers (Fig. 3 bottom) should be considered.

This is further complemented by the fluorescence decays collected along the emission band, which are bi-exponential, with two identical decay times but different pre-exponential factors, and is supported by fs-
Table 2
TDDFT data (LC-BPBE/Scaled CAMB3LYP) including the wavelength maxima for the different conformers A and B for DAI and A, B and C for DBI together with the $S_0$–$S_1$ predicted transitions and the relative stability and abundance of the conformers at $T = 298$ K together with the experimental maxima for $S_1$–$S_0$ transition for DAI and DBI in DMSO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r_{S_0}$ (nm)</th>
<th>$S_1$–$S_0$</th>
<th>$f$</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$S_1$–$S_0$</th>
<th>$f$</th>
<th>$\lambda_{max}$ (nm)</th>
<th>Relative stability (kJ/mol)</th>
<th>Relative abundance (%) at 293 K</th>
<th>$r_{S_1}$ (nm)</th>
<th>Exp. $\lambda_{max}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAI (B)</td>
<td>549/551</td>
<td>0.11/0.16</td>
<td>387/390 ($S_0$)</td>
<td>0.12/0.10</td>
<td>636/616</td>
<td>0.12/0.18</td>
<td>98</td>
<td>550</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAI (A)</td>
<td>550/551</td>
<td>0.11/0.16</td>
<td>388/399 ($S_0$)</td>
<td>0.11/0.10</td>
<td>forbidden</td>
<td>520</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-DAI</td>
<td>528/506</td>
<td>0.02/0.06</td>
<td>423/430 ($S_0$)</td>
<td>0.17/0.16</td>
<td>forbidden</td>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAI (A)</td>
<td>564/567</td>
<td>0.11/0.16</td>
<td>398/405 ($S_0$)</td>
<td>0.07/0.09</td>
<td>662/643</td>
<td>0.13/0.19</td>
<td>80</td>
<td>570</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DBI (B)</td>
<td>556/559</td>
<td>0.11/0.15</td>
<td>394/400 ($S_0$)</td>
<td>0.11/0.10</td>
<td>forbidden</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAI (C)</td>
<td>558/561</td>
<td>0.13/0.18</td>
<td>411/412 ($S_0$)</td>
<td>0.11/0.09</td>
<td>628/612</td>
<td>0.13/0.18</td>
<td>15</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-DBI</td>
<td>537/522</td>
<td>0.03/0.09</td>
<td>436/445 ($S_0$)</td>
<td>0.25/0.22</td>
<td>forbidden</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$a$ $S_1$ PES was not probed for isomers that differ by more than 5 kJ/mol from the most stable parent structure.

$b$ Experimental data from Table 1 in dioxane.

$c$ See experimental section for details on the scaling correction.

Table 3
Photophysical data for Indigo (IND), DAI, DBI and DBI derivatives in various solvents at room (293 K) and low (77 K) temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\theta_{\tau}$ (K)</th>
<th>$\theta_{f}$ (K)</th>
<th>$\tau_i$ (ns)</th>
<th>$k_{f}$ (ns $^{-1}$)</th>
<th>$k_{ps}$ (ns $^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>IND</td>
<td>DMSO</td>
<td>-</td>
<td>293</td>
<td>293 K</td>
<td>293 K</td>
<td>293 K</td>
</tr>
<tr>
<td>DAI</td>
<td>MCH</td>
<td>0.11</td>
<td>0.06</td>
<td>7.5</td>
<td>0.008</td>
<td>0.125</td>
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<tr>
<td></td>
<td>DMSO</td>
<td>0.055</td>
<td>293</td>
<td>0.28</td>
<td>2.79</td>
<td>0.010</td>
</tr>
<tr>
<td>DBI</td>
<td>MCH</td>
<td>0.11</td>
<td>0.11</td>
<td>12.2</td>
<td>0.008</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>0.001</td>
<td>293</td>
<td>0.07</td>
<td>4.9</td>
<td>0.014</td>
</tr>
<tr>
<td>DAIOMe</td>
<td>DMSO</td>
<td>-</td>
<td>0.009</td>
<td>6.06</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>DBICl</td>
<td>DMSO</td>
<td>-</td>
<td>0.001</td>
<td>0.09</td>
<td>110 (25)</td>
<td></td>
</tr>
<tr>
<td>DIBNO$_2$</td>
<td>DMSO</td>
<td>-</td>
<td>0.005</td>
<td>0.0057</td>
<td>4.01</td>
<td></td>
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</table>

Table 4
Fluorescence decay times ($\tau_i$) and preexponential factors ($a_i$) for DAI, DBI, DBI derivatives in 2MeTHF and Dioxane at $T = 298$ K from ps time resolved fluorescence measurements. $\lambda_{exc}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\tau_i$ (ns)</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$k_{ref}$ (s $^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAI</td>
<td>2MeTHF</td>
<td>33</td>
<td>0.18</td>
<td>0.18</td>
<td>2790</td>
</tr>
<tr>
<td>DBI</td>
<td>2MeTHF</td>
<td>53</td>
<td>0.08</td>
<td>0.89</td>
<td>6000</td>
</tr>
<tr>
<td>DAI</td>
<td>DMSO</td>
<td>24.5</td>
<td>0.6</td>
<td>115</td>
<td>0.4</td>
</tr>
<tr>
<td>DBI Ome</td>
<td>2MeTHF</td>
<td>65</td>
<td>0.93</td>
<td>4500</td>
<td>0.07</td>
</tr>
<tr>
<td>DBI Cl</td>
<td>2MeTHF</td>
<td>94</td>
<td>0.89</td>
<td>3070</td>
<td>0.11</td>
</tr>
<tr>
<td>DBI Cl</td>
<td>DMSO</td>
<td>98.5</td>
<td>0.93</td>
<td>642</td>
<td>0.07</td>
</tr>
</tbody>
</table>

NA not applicable.

$b$ Fluorescence decays and analyses can be found in Fig. 5 in the electronic version of the manuscript.

Table 5
Time Resolved fs-TA data (decay times, $\tau_i$, and pre-exponential factors $a_i$) for DAI, DBI, DBI derivatives in 2MeTHF and DMSO obtained with $\lambda_{exc}$ 530 nm at $\lambda = 611$ nm (for DBI and DBI derivatives) and $\lambda = 598$ nm (for DAI) in the ESA band. (TA Bands and Time resolved Experiments can be found at SI – Fig. S14 to S18).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\tau_1$ (ps)</th>
<th>$a_1$</th>
<th>$\tau_2$ (ps)</th>
<th>$a_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAI</td>
<td>2MeTHF</td>
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<td>0.18</td>
<td>2790</td>
<td>0.02</td>
</tr>
<tr>
<td>DBI</td>
<td>2MeTHF</td>
<td>53</td>
<td>0.08</td>
<td>4980</td>
<td>0.11</td>
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<tr>
<td>DAI</td>
<td>DMSO</td>
<td>24.5</td>
<td>0.6</td>
<td>115</td>
<td>0.4</td>
</tr>
<tr>
<td>DBI Ome</td>
<td>2MeTHF</td>
<td>65</td>
<td>0.93</td>
<td>4500</td>
<td>0.07</td>
</tr>
<tr>
<td>DBI Cl</td>
<td>2MeTHF</td>
<td>94</td>
<td>0.89</td>
<td>3070</td>
<td>0.11</td>
</tr>
<tr>
<td>DBI Cl</td>
<td>DMSO</td>
<td>98.5</td>
<td>0.93</td>
<td>642</td>
<td>0.07</td>
</tr>
</tbody>
</table>

NA not applicable.

[b] Fluorescence decays and analyses can be found in Fig. S10–21.

5

TA data (see discussion below). It is worth noting that a value of 21.77 kJ/mol in hexadecane has been reported in the literature for rotational isomerization around the single bond involving the anthrly and ethenic groups of the $S_1$ state of 2-vinylanthrene. Here, the presence of two rotamers was confirmed by the bi-exponential nature of the fluorescence decays (see discussion below) [39,40].

Table 2 summarizes the TDDFT calculations on the absorption and emission wavelength maxima for the trans and cis conformers and different conformers of DAI and DBI. With both the LC-BPBE (data directly obtained from the calculations and CAMB3LYP (where a scaling factor is added, see experimental section and refs. [6,17,33]), the obtained values are very close (in nm) to the experimental values. It is worth noting that a second allowed band in these derivatives corresponds to a transition to $S_2$. Observing Figs. 1 and 2 and Table 2 the shoulders in the main absorption bands (≈500–530 nm and ≈400–430 nm) are likely to be due to the pre-existence of a small quantity of the cis-isomer. This effect is more pronounced in non-polar solvents.

The $\pi^*\rightarrow\pi$ nature of the lowest energy absorption band can be seen in Fig. 4, where a sizeable delocalization to the acyl carbonyl is only observed with the HOMO. The lowering of the HOMO energy is responsible for the blue shift observed in all the acyl derivatives (Table 1).

The $\pi^*\rightarrow\pi$ excitation transforms the central C–C double bond into a single one, allowing the relative rotation of the two isatin-like moieties. This leads to a peaked Conical Intersection (CI), which provides a competitive deactivation path to fluorescence. The cis or trans ground state isomers produced will depend on the momentum and point of deactivation in the CI branching coordinate. At the CI the two isatin-like half-moieties are found nearly perpendicular to each other and the C=O group nearly planar with the indole moiety, Fig. 5. The structures were optimized in the $S_1$ PES following a rotational negative eigenvalue of the Hessian, until the gap $S_0$–$S_1$ became zero (or very close to zero; in any case always below a threshold value of 0.01 eV).
3.3. Photochemical studies

For indigo, due to the ground-state hydrogen bonds between the N–H and the C═O groups, the molecule is in a stable and planar form precluding rotation (and isomerization) around the central carbon-carbon bond [2,6,41]. With DAI and DBI, this is no longer a limitation and photoisomerization is possible. Indeed, the formation of cis was confirmed in DAI in the present study upon irradiation with a 150 W Xe lamp but found absent in DBI (see Fig. 6) in these conditions.

For DBI the spectra resulting from the photoisomerization process were obtained with a high energy fs-TA sapphire-titanium laser (see experimental section). The data is presented in Figs. SI1-3 for DBI, DBIOMe and DBICl respectively. In the case of DBINO₂ no spectra could be obtained due to sample degradation.

Moreover, from Fig. SI1 it can be seen that in the non-polar solvent 2MeTHF trans-cis isomerization is present and therefore the cis form is observed. However, in polar solvents such as DMSO there is no evidence for photoisomerization both for DAI and DBI due to an over stabilization of the trans form relative to the cis form [17].

This high requirement in energy for isomerization with DBI can be understood by the much higher steric hindrance of this compound reflected in the structural parameters (DFT) N–C═C–N and C–N–C–R (R Me or Ph) dihedral angles of respectively 5.2 and 13.4 for DAI and 9.3 and 20.0 for DBI, Fig. 7. Dynamic factors, namely the viscosity of the solvent, may also play a role in precluding the isomerization of DBI which indeed involves extra rotations of the phenyl group, which are not
relevant with the methyl derivative (DAI).

3.4. Photophysical studies

Photophysical data, including fluorescence quantum yields (φF) at T 293 K and T 77 K, lifetimes and rate constants for the radiative (kT) and radiationless (kNR) processes, at T 293K, are given in Table 3. For indigo the τF value is associated to the longest component in the decays, i.e., the enol species formed upon excitation and decay of the keto form [19,35,36]. The φF values for DAI and DBI derivatives were found to be always lower in polar solvents when compared to non-polar ones (up to one order of magnitude), which is further mirrored by the short fluorescence lifetime values. In the polar solvent DMSO, DAI and DBI have the lowest fluorescence quantum yields (~10-3) and lifetimes (in the ps time range), whereas in non-polar solvents (MCH and 2MeTHF) the φF values are one order of magnitude higher and the τF values are now also higher and within the ns time range (Table 3). This has implications in the radiationless rate constant values, which are 2–3 orders of magnitude higher than the radiative rate constant values in polar solvents. This effect has previously been reported with thioidindigo derivatives, and explained by a more accessible CI (in polar solvents) and an increased stabilization of the trans form [17]. The fluorescence quantum yields at 77K increase by approximately one order of magnitude relative to those at RT. This suggests that rotation around the central C–C bond is now blocked both for DAI and DBI making the access to the CI less effective, such that fluorescence is now a much more effective deactivation channel.

3.5. Time resolved fluorescence and fs-TA transient data

A more detailed analysis of the time resolved fluorescence decays and fs-TA spectra and decays was performed with DAI and all the DBI derivatives, which can be seen in Tables 1 and 2 and in SI (Fig. S14 to S19 for fs-TA data and Fig. S20 to S21 for the fluorescence decays).

As was found with related systems, such as 2-VA [40], the time dependent intensity profiles collected along the emission band of DAI and DBI derivatives are given by a sum of discrete exponentials:

\[ I(t) = \sum_{i} a_i e^{-\lambda_i t} \]

where A* is the excited indigo derivative (DAI or DBI), \( \lambda_i \) is the reciprocal of the decay times, \( \tau_i \), and \( a_i \) the associated pre-exponential factors.

Table 4 shows that a single exponential properly fits the decays for DAI, with values of a few ns (from ~2.8 ns to 7.95 ns). This contrasts with indigo, where the decay times associated with the keto and enol forms are in the range 5–20 ps (keto) and 120–150 ps (enol). However, with DBI and its derivatives, the behavior is different, and bi-exponential fluorescence decays are observed, which shows two components/species are present in the excited state. Since the excitation spectra match the absorption spectra, this suggests that the two components are the result of an excited state process, which is due to the presence of at least two conformers separated by ~5 kJ/mol, probably the species A and B in Table 2. The B species irreversible evolution to the A species form in the excited state produces the shorter component (τ1 80–280 ps in Table 4) associated with the long decay component of the A conformer (τ2 in Table 4). This leads to the more stable conformer A, with an interconversion rate constant kNR, which is given by:

\[ k_{NR} = \frac{1}{\tau_{short}} \left( \frac{1}{\tau_{long}} + \frac{1}{\tau_{short}} \right) \]

Values for kNR are given in Table 4. The pre-exponential factors of the decays follow the relative abundances of each conformer. From Table 4 it can be seen that the interconversion rate constant, kNR, is in the 10^5 s^-1 to 10^10 s^-1 range.

As discussed above, the S_1 state dominant deactivation channel requires a structure with the two isatin-like half moieties perpendicular to
Fig. 8. Illustration of the two proposed mechanisms (A and B) of the dynamics for fluorescence bleaching from excitation geometries to CI.

each other and at least one C=O nearly planar with the isatin-like moiety, see Fig. 5.

Fig. 8 schematically illustrates two mechanisms (A and B) for the deactivation of S1. With mechanism A, the A conformer (see Fig. 3) deactivation involves a single rotation around the central C-C bond on going from S1 to S0. In this mechanism no further rotation is observed, i.e., the carbonyl co-planarity with each one of the isatin-like moieties is already present. In the case of mechanism B in Fig. 8, besides the rotation around the C-C bond (present in mechanism A) an additional rotation of the acyl group (not present in mechanism A) is also occurring. Mechanism B in Fig. 8 corresponds to the deactivation of B conformers (for DAI and DBI in Fig. 3) from S1 to S0.

The requirement of carbonyl co-planarity with the isatin-like moiety can only be achieved (without acyl rotation) with the A conformer (mechanism A), whereas in the case of mechanism B (the only found possible for DAI) it corresponds to the longer component observed in the time resolved fluorescence measurements. The two mechanisms (A and B in Fig. 8) can be observed for DBI, where the longer component is associated with the deactivation of S1 through mechanism B and the shorter to mechanism A. The associated pre-exponentials factors match the abundances of the corresponding isomers in Fig. 3 and Table 2.

Additional information on the excited-state deactivation processes in DAI and DBI was obtained from femtosecond (fs)-transient absorption (TA) measurements. Time-resolved transient absorption difference spectra (fs-TA) for these compounds in 2MeTHF were obtained with excitation at 530 nm and recorded in the 440-750 nm range for DBI within a time window of 227 ps and between 415 and 750 nm for DAI within a time window of 8 ns (Fig. 9).

From the fs-TA spectra of DAI and DBI, no bleaching of the ground-state absorption was observed and positive TA bands at 415–500 nm, with maxima at ~430 nm for DAI (TDDFT predicts a S1→S0 band for the CI form at 466 nm) and ~460 nm for DBI (S1→S0 at 476 nm from TDDFT), together with absorptions at 550–650 nm (maxima ~598 nm for DAI and 611 nm for DBI, predicted by TDDFT to be an S1→S0 at 570 nm for DAI and S1→S0 at 626 nm for DBI) and 700–750 nm (maximum at ~730 nm for DBI but not detected in DAI) also corroborated by TDDFT which predicts a very weak S1→S0 band at 731 nm and 734 nm for DAI and DBI respectively. For a summary of these predicted and experimental transitions see Table SII. These were attributed to the transient excited state absorptions of these two compounds at the CI geometry. Due to the orthogonality of the two half isatin-like moieties the singlet and triplet states should be nearly iso-energetic making it impossible to attribute the nature of the transients to excited state singlet or triplet absorption. Nevertheless it is worth reporting that for DAI the existence of a triplet state has been reported previously [26,42].

![Fig. 9. fs-TA spectra for DAI (left) and DBI (right) obtained with pump @ 530 nm in 2MeTHF at T = 293 K.](image-url)
and therefore cannot be completely ruled out as a competitive deactivation path of the excited state of this compound.

The data resulting from the fs-TA decays is given in Table 5. The decay times are very similar, but not identical, to those obtained from time resolved fluorescence data (Table 4). It is interesting to note that DAI presents two decay components, with the shorter component with a contribution (seen by the associated pre-exponential factor) smaller than the longer one. The absence of the shorter component in the fluorescence decays, and therefore the mono-exponential decay (Table 4) of DAI is due to the relative poor abundance of the associated conformer A (2% in Table 2) relative to conformer B (see Table 2). In the case of the fs-TA, the absorption of this conformer is observed.

With DBI, where the opposite is observed, the largest contribution comes from the fastest component. The relative contributions follow the relative abundances of the A and B conformers. The fact that the independent analysis at different wavelengths shows essentially identical amplitudes (a_i) and decay times (t_i) in the fs-TA of DBI further supports the involvement of two conformers in the excited state behavior of this compound.

4. Conclusions

In this work, we present the spectral and photophysical properties of various indigo derivatives in which the hydrogen in the N–H groups has been replaced by acetyl (DAI, N,N'-diacetyldiindigo) and benzoyl (DBI, N,N'-dibenzoindolyl) groups. This precludes the excited state proton transfer in these compounds, thus allowing the observation of different deactivation routes (conformational changes) from the excited state. With DAI, rotation around the central carbon-carbon bond allows formation of the cis isomer, whereas with DBI, steric hindrance introduce geometric restrictions that leads to the presence of two conformers. This was confirmed by time-resolved fluorescence, fs-transient absorption and TDDFT calculations. In polar solvents the radiationless rate constants were found 2–3 orders of magnitude higher than the radiative rate constants, which were explained by a more accessible conical intersection of DAI and DBI derivatives.

Author contribution statement

Daniela C. Nobre performed the overall photophysical measurements including the different spectra (absorption and emission), the time-resolved fluorescence and fs-TA experiments with the support of Carla Cunha.
Alessandro Porciello, Federica Valentini, Assunta Marrocchi, and Luigi Vaccaro were responsible for the synthesis of the compounds. Luigi Vaccaro was also responsible by the design of the compounds and writing of the experimental procedures relative to the synthesis and analytical characterization of the compounds.
Adelino M. Galvão was responsible by the TDDFT calculations with the help of Daniela C. Nobre and J. Sergio Seixas de Melo.
J. Sergio Seixas de Melo was responsible by the idea, rationalization and writing of the manuscript.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

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References


