

Photophysics of an Indigo Derivative (Keto and Leuco Structures) with Singular Properties

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Spectral and photophysical properties of the indigo derivative Cibalackrot in keto and reduced (leuco) forms were studied by absorption spectra, fluorescence and pulse radiolysis and compared with the structurally similar indigo. With the keto form of this dye, fluorescence ($\phi_F = 0.76$) and intersystem crossing ($\phi_T = 0.11$) are dominant, whereas with indigo, efficient internal conversion ($\phi_{IC} = 0.99$) is observed, probably involving proton transfer through intramolecular hydrogen bonds. With Cibalackrot, this pathway is blocked, supporting the above model for indigo. With the reduced form of Cibalackrot, more than 98% of the absorbed quanta are dissipated through $S_1 \sim\sim\rightarrow S_0$ internal conversion, which contrasts with leuco-indigo, where fluorescence ($\phi_F = 0.35$), internal conversion ($\phi_{IC} = 0.53$) and intersystem crossing ($\phi_T = 0.12_5$) are found to be competitive. In addition, a synthetic precursor of Cibalackrot (preCiba) was also investigated. This has a rigid molecular structure (with a moiety identical to Cibalackrot and the other to indigo), but intra- or intermolecular proton transfer is allowed between adjacent carbonyl and N–H groups. With this precursor in its keto structure the photophysical parameters are generally very close to those of the keto form of indigo, and different from those of Cibalackrot. A more detailed investigation of the time-decay profiles of preCiba in dioxane (and with added water and D_2O) has shown that these follow biexponential laws with a shorter component of 14–25 ps, which appears associated with a risetime at longer wavelength emissions (and to a positive preexponential at shorter emission wavelengths) and a longer lived (decay) component of 104–130 ps. In the steady-state spectra of preCiba, the variation with temperature reveals a blue shift of the emission maxima, which is interpreted as the presence (simultaneous emission) of two species (keto and enol) in the excited state. Indigo and deuterated indigo are also found to present a similar behavior. The overall data are interpreted as to be due to an excited-state process involving the proton transfer between keto and enol forms. Rate constants with values of $7 \times 10^{10} \text{ s}^{-1}$ for preCiba and $1.6 \times 10^{11} \text{ s}^{-1}$ for deuterated indigo were obtained. This inverse isotope effect is justified on the basis of the proposed model for proton-transfer excited-state deactivation.

Introduction

Indigo and its derivatives, such as purple (6,6'-dibromoindigo), are among the most ancient natural dyes.^{1–4} Indigo has an almost mythical status,⁵ was known by the Hebrews as “tekhelet” (possibly as a mixture with purple) and it is still used to dye “blue jeans”. It is one of the most stable organic dyes, which partially explains both its wide use in antiquity and the premodern era and its longevity as a colorant. This is also the reason it was used in oil paintings by the great masters of the 17th and 18th century, in contrast to other organic colorants, which, with the exception of some necessary irreplaceable lakes, were usually avoided due to their low photostability. This stability has been linked to fast intramolecular proton transfer (ESIPT) via hydrogen bonds between adjacent carbonyl and

N–H groups, keeping the molecule in a stable trans planar configuration, thus preventing cis–trans isomerization.^{6,7} Internal conversion (IC) via ESIPT is thus suggested to dominate the deactivation of the first excited singlet state, with negligible contributions from fluorescence, intersystem crossing (ISC) or photochemical reactions.^{8,9} Alternative interpretations claim that blocking ESIPT still gives rise to the same photophysical behavior,¹⁰ or that with indigo carmine the effect involves intermolecular hydrogen bonding with solvent.¹¹ Thus, an unambiguous mechanism for this high stability is still needed. This study aims to obtain further insights into the detailed nature of this mechanism.

In their keto forms, indigo and its derivatives purple, carmine and indirubin show highly efficient $S_1 \sim\sim\rightarrow S_0$ internal conversion (IC),⁹ whereas with their leuco forms, fluorescence and triplet-state formation are the dominant routes for singlet-state deactivation.⁹

Two different explanations for the predominance of IC are particularly relevant: (1) intramolecular excited-state proton transfer (ESIPT) between adjacent hydrogen-bonded carbonyl and N–H groups; (2) intermolecular hydrogen-bonding between

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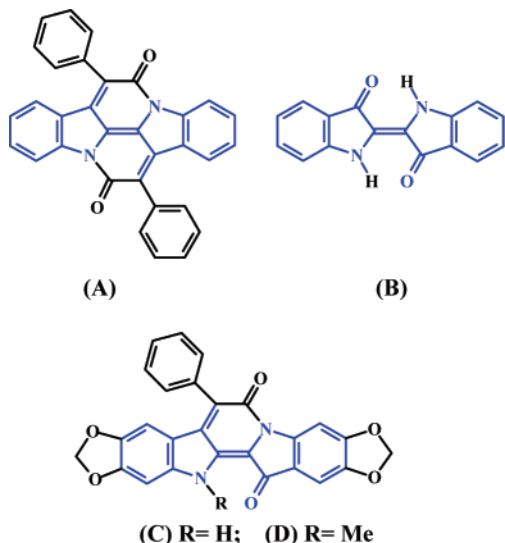
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CHART 1: Cibalackrot (A), Indigo (B), preCiba (C) and Mpreciba (D) Structures, with the Common Core Shown in Blue

the dye and the solvent.^{6,10,11} The presence of hydrogen bonding in indigo has also been suggested as the reason this compound exists in the stable trans form, precluding the competing cis–trans photoisomerization.^{12,13} This is particularly important because when the N–H groups are replaced by sulfur, oxygen or selenium atoms, significant fluorescence and considerable trans–cis isomerization are observed, confirming the peculiar nature of the N–H...O=C– bridge in indigo.^{14–16} In the context of the molecules studied in this work, it is also important to mention that the obvious molecule to preclude ESIPT between the N–H and C=O groups would seem to be a dialkylindigo such as *N,N'*-dimethylindigo.^{17–22} However, in this case the deviation from coplanarity of the dimethyl derivative leads to a strongly twisted structure about the central C=C bond, in contrast with the virtually planar structure of indigo, and it appears that cis–trans photoisomerization becomes a favorable and highly competitive pathway.^{23,24} This presumably occurs together with fluorescence, although this latter process does not appear to have been studied in detail.^{18,24} This (di)methylated indigo derivative (or, in general, *N,N'*-substituted indigo derivatives) cannot, therefore, provide evidence as to whether ESIPT is the reason for the efficient dissipation of the excited-state because cis–trans isomerization becomes the dominant process with it.²⁴

In this study, we reevaluate the importance of ESPT in indigo and its relation to the efficiency of the internal conversion deactivation channel by a strategy involving the study of two molecules in which the twisting of the molecule and proton transfer is partially blocked (compound C in Scheme 1) or totally blocked (compound A in Scheme 1). In addition, a methylated derivative of compound C (compound D in Chart 1) was also investigated. In this case the proton transfer is also excluded. In the case of compound A (see structure in Chart 1) a detailed photophysical study is reported. This compound, known as Cibalackrot, has proton transfer blocked by substitution with the rigid C=C(Ph)–C=O moiety linked to the central indigo nitrogen atom. This leads to photophysical properties that are diametrically opposed to those found for indigo: high fluorescent yields, nanosecond lifetimes, efficient intersystem $S_1 \rightsquigarrow T_1$ crossing (ISC) and negligible $S_1 \rightsquigarrow S_0$ internal conversion (IC). With the synthetic precursor (structure C in Chart 1 and here abbreviated as preCiba) the intramolecular proton transfer

between adjacent carbonyl and N–H groups is allowed whereas with its *N*-methylated analogue (structure D in Chart 1) this pathway is blocked.

Cibalackrot is thus an indigo derivative where proton transfer is completely blocked, and where cis–trans isomerization is also not possible. The compound's name, Cibalackrot, comes from the German acronym of the naphthyridine dye “Ciba Lake Red” (Color Index C.I. 73095 [6417-51-2]). Its synthesis was described by Engi in 1911 (from the *Gesellschaft fuer Chemische Industrie* in Basel)²⁵ and Posner²⁶ and its basic fluorescent properties studied by Birckner, Hauke and Paetzold.^{27,28} More recently, laser flash photolysis and fluorescence results have been presented.²⁹ Besides these works, only two Japanese patents on it as an electrophotographic photoreceptor^{30,31} and an optoelectronic device³¹ with high-energy conversion efficiency are found in the literature. The substance was, and apparently still is, being used as a red pigment in lakes for lithography. Also, the dye is currently recommended for the bulk dyeing of plastics, producing red fluorescent shades. Cibalackrot is thus structurally related to the (ancient) blue indigo but displays a red color.

Experimental Section

Indigo was synthesized³² or purchased from Aldrich and used as received. Cibalackrot and its synthetic precursor (preCiba) were prepared according to literature methods.^{26,27} A brief description of the synthesis and of spectral identification can be found in the Supporting Information (SI).

Solvents were spectroscopic or equivalent grade. Dimethylformamide (DMF) was distilled and stored over molecular sieves. Deuterated water was purchased from Aldrich and stored under Ar or N₂ inert atmospheres in a freezer. Prior to use it was left for 30 min at room temperature.

The leuco species were prepared by adding 2–3 drops of a concentrated sodium dithionite/NaOH solution (0.15 g of Na₂S₂O₄ in 10 mL of NaOH (1 M)) to the dye in DMF, submitted to constant and gentle bubbling with Ar. The solution was left bubbling for a further 20 min and then sealed in a device described elsewhere.³³

Absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Jobin-Yvon Spex Fluorog 3-2.2 spectrophotometers. Fluorescence spectra were corrected for the wavelength response of the system. Fluorescence quantum yields for the keto form were determined using rhodamine 6G ($\phi_F = 0.88$ in ethanol³⁴) and quinquethiophene ($\phi_F = 0.36$ in dioxane³⁵) as standards. For the reduced (leuco) forms, quaterthiophene ($\phi_F = 0.18$ in dioxane³⁵) was used.

Fluorescence decays were measured using a home-built TCSPC apparatus³⁶ with 465 nm Horiba-JI-IBH nanoLED excitation, Jobin-Yvon monochromator, Philips XP2020Q photomultiplier, and Canberra instruments TAC and MCA and were analyzed using the method of modulating functions of Striker.³⁷ The time resolution of this equipment is 150 ps.³⁶ In some cases, the decays were also measured with picosecond resolution on two different systems that have been detailed elsewhere and whose time resolutions are given as 3 ps³⁸ and 5 ps.³⁹

Triplet–singlet difference spectra were obtained using Applied Photophysics laser flash photolysis equipment pumped by a Nd:YAG laser (Spectra Physics) with excitation wavelength 532 nm.⁴⁰ The time resolution of this equipment is ≈ 50 ns. Transient spectra (300–700 nm) were obtained by monitoring the optical density change at 5–10 nm intervals, averaging at least 10 decays at each wavelength. Hamamatsu IP28 and Hamamatsu R928 photomultipliers were used.

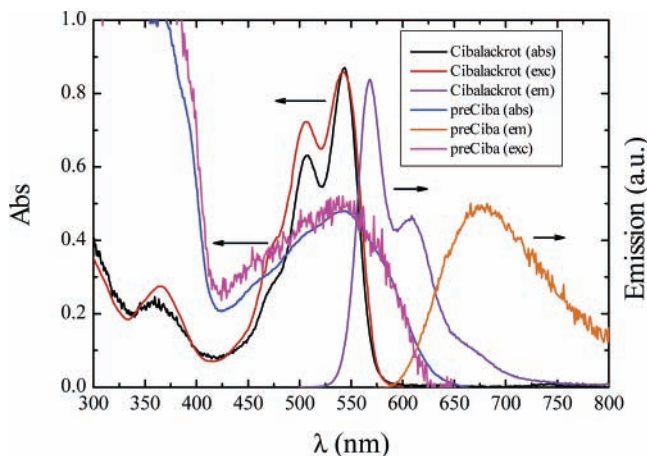


Figure 1. Absorption (abs), excitation (exc) and emission (em) spectra of Cibalackrot and preCiba in dioxane, $T = 293$ K. Note the clear mirror-image relationship between the absorption and emission spectra of Cibalackrot.

Actinometry was carried out using the absorption signal of the reference and Cibalackrot as functions of the laser energy and linear plots were obtained under the experimental conditions used. Examples of these plots are given in the SI.

Triplet molar absorption coefficients for the keto forms in DMF were determined by the singlet depletion technique, using⁴¹

$$\epsilon_T = \frac{\epsilon_S \Delta OD_T}{\Delta OD_S} \quad (1)$$

where ΔOD_S and ΔOD_T are obtained from transient absorption spectra. The ϵ_T value obtained was $34\,100 \text{ M}^{-1} \text{ cm}^{-1}$. The triplet formation quantum yield (ϕ_T) was obtained by comparing the ΔOD at 525 nm of a benzene solution of tetraphenyl porphyrin, TPP, ($\epsilon_T = 6000 \text{ M}^{-1} \text{ cm}^{-1}$ and $\phi_T = 0.82$),⁴¹ used as actinometer, with an optically matched solution (at the laser wavelength) of the compound using⁴²

$$\phi_T^{\text{Cibalackrot}} = \frac{\epsilon_{TT}^{\text{TPP}}}{\epsilon_{TT}^{\text{Cibalackrot}}} \cdot \frac{\Delta OD_{\text{max}}^{\text{Cibalackrot}}}{\Delta OD_{\text{max}}^{\text{TPP}}} \cdot \phi_T^{\text{TPP}} \quad (2)$$

Singlet oxygen yields (ϕ_Δ) and lifetime were obtained on excitation at 532 nm with a frequency-doubled Nd:YAG laser by measuring phosphorescence emission of O_2 (at 1270 nm) in air-equilibrated *N,N*-dimethylformamide (DMF) with a germanium diode, comparing the initial emission intensity (extrapolated to zero time) with solutions of TPP as standard optically matched at the excitation wavelength ($A_{532} \approx 0.2$), using $\phi_\Delta = 0.28$. The ϕ_Δ value for TPP in DMF was obtained using as reference TPP in benzene ($\phi_\Delta = 0.62$).⁴³

Pulse radiolysis experiments were carried out at the Free Radical Research Facility, Daresbury, U.K., using 200 ns to 2 μs high-energy electron pulses from a 12 MeV linear accelerator (LINAC), passed through solutions in a 2.5 cm optical path length quartz cuvette attached to a flow system.^{44,45} All solutions were bubbled with argon for 30–40 min before experiments.

Results and Discussion

Keto Form. *Absorption Spectra, Emission Fluorescence and Lifetimes in Solution.* Absorption and fluorescence spectra in dioxane (Figure 1) show a small Stokes shift ($\approx 746 \text{ cm}^{-1}$) for Cibalackrot, compatible with its high rigidity, whereas with preCiba a marked Stokes shift of $\approx 3525 \text{ cm}^{-1}$ is observed. Note

from Figure 1 that the preCiba excitation spectrum (collected at different emission wavelengths) matches the absorption spectrum. With indigo, for the keto form, where hydrogen bonding occurs, the Stokes shift is 1080 cm^{-1} , whereas for the leuco form, where the absence of hydrogen bonding allows rotation around the central C–C bonds, it is 3504 cm^{-1} (Table 1).⁹ For preCiba and indigo there is no vibrational structure, in either the absorption or fluorescence spectra, in clear contrast to Cibalackrot. From the marked Stokes Shifts displayed by preCiba, it can be clearly inferred that significant structural variations occur between the ground and lowest excited state. Although the most logical explanation is that we are in the presence of a favored enol structure, because the lactam ring is not completely rigid it is likely that some conformational mobility is still present within the preCiba structure, whereas this is completely prohibited in Cibalackrot. Evidence for significant differences between the excited-state behavior of preCiba and Cibalackrot comes from both the molar extinction coefficients and fluorescence quantum yields (see Table 1 below), which again supports the possibility of preCiba having a less rigid structure.

Triplet-State Characterization by Laser Flash Photolysis and Pulse Radiolysis. The transient triplet-singlet difference absorption spectrum of Cibalackrot was obtained by laser flash photolysis in DMF (Figure 2) and by pulse radiolysis-energy transfer in benzene. In the first case, the transient triplet (excitation at 532 nm) is generated by direct absorption of the dye and two apparent maxima are observed (420 and 590 nm), together with depletion of the ground-state absorption at 540 nm. The decay times at 420 and 580 nm and ground-state recovery at 540 nm had identical rates: $(8\text{--}9) \times 10^3 \text{ s}^{-1}$. In all cases the spectra were assigned to triplet states because (i) they decayed by first-order kinetics (see inset in Figure 2) with microsecond lifetimes and (ii) other possible transients, such as radical ions, were not produced on photolysis. Additionally, for the keto form, the transient was quenched by oxygen.

Triplet states can also be selectively produced⁴⁶ by energy transfer following pulse radiolysis of benzene (Bz) solutions of Cibalackrot (energy acceptor) in the presence of biphenyl (triplet energy donor) as sensitizer, subject to the kinetically demanded concentration ratio $[\text{benzene}] \gg [\text{biphenyl}] \gg [\text{cibalackrot}]$.^{9,47} In our experiments, $[\text{biphenyl}] = 1 \times 10^{-2} \text{ M} \gg [\text{cibalackrot}] = 5.62 \times 10^{-5} \text{ M}$. Similar maxima at 420 and 580 nm were observed to those seen in flash photolysis, confirming assignment to the triplet state, although the first band here is partially masked by the absorption of the biphenyl triplet sensitizer. Similar experiments were performed for preCiba.

In the absence of preCiba, the biphenyl triplet, monitored by its absorption at 360 nm, decayed by first-order kinetics with $k_0 = 5.44 \times 10^4 \text{ s}^{-1}$. In the presence of preCiba, this transient decayed more rapidly ($k_{\text{obs}} = 7.43 \times 10^4 \text{ s}^{-1}$), and again new absorptions were observed to grow-in with maxima at 430 and 650 nm, which were assigned to the preCiba triplet states (see Figure 3). The rates of formation of the transients, monitored at their maxima (430 and 650 nm; see insets in Figure 3), were identical to the rates of decay of the biphenyl triplet absorption at 360 nm. The rate constant for triplet sensitization, k_2 , was obtained from the equation $k_{\text{obs}} = k_0 + k_2[\text{Q}]$ where k_{obs} is the observed rate constant for triplet biphenyl in the presence of the quencher (Ciba or preCiba) and k_0 is the rate constant for biphenyl triplet decay in the absence of quencher. For a preCiba solution in benzene with concentration $5.55 \times 10^{-5} \text{ M}$ we have obtained a rate constant $k_2 = 3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and for Cibalackrot the value was $k_2 = 6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The rates

TABLE 1: Spectral and Photophysical Data for Indigo, Cibalackrot and PreCiba (and MpreCiba) Keto and Reduced (leuco) Forms, $T = 293$ K (ND = Not Determined)

compound	$\lambda_{\text{abs}}^{\text{max}}$, nm	$\lambda_{\text{fluo}}^{\text{max}}$, nm	ϵ_s , $\text{M}^{-1} \text{cm}^{-1}$	ϕ_{T}^f	τ_{T}^f , ns	ϕ_{T}^h	ϕ_{Δ}^g	ϕ_{IC}	k_{F} , ns^{-1}	k_{NR} , ns^{-1}	k_{IC} , ns^{-1}	k_{ISC} , ns^{-1}	Δ_{SS} , cm^{-1}
keto													
Cibalackrot ^a	544	567	21360	0.76	6.10	0.11	0.05 ₈	0.13	0.125	0.039	0.021	0.018	746
indigo ^b	610	653	22140	0.0023	0.14 ^h	0.00117 ^d	0.00117	0.997	0.0164	7.12	7.12	0.084	1080
indigo (Dx)	600	637		0.0025	0.126 ^h				0.0198	7.9			968
indigo deuterated (Dx)	600	637		0.0024	0.125 ^h				0.0192	7.98			968
indigo (Dx:D ₂ O(2%))	600	644		0.0032	-								1139
indigo (Dx:H ₂ O(2%))	600	644		0.0016	-								1139
preCiba ^a	542	670	7170	0.0012	0.118	ND	ND	ND	0.0101	8.464			3525
preCiba (Dx:D ₂ O(2%))	542	678		0.00005 ₇	0.109				0.0052	9.169			3701
preCiba (Dx:H ₂ O(2%))	542	678		0.0005 ₁	0.112				0.0046	8.924			3701
MpreCiba ^a	550	680	2468	0.0006 ₅	0.152	ND	ND	ND	0.0043	6.57			3476
leuco													
Cibalackrot ^a	470 ^c /488	545	16380	0.020	5.94	≈0		≤0.98	0.0034	0.165	≤0.165	≈0	2928/2143 ^e
indigo ^c	442	523	17400	0.348	3.15	0.125		0.527	0.111	0.207	0.167	0.040	3504
preCiba ^a	402	501	22220	0.0012	1.13	≈0		≤0.99	0.0011	0.884			4916

^a In dioxane. ^b Data from ref 9; the solvent is *N,N'*-dimethylformamide. ^c From the excitation spectra. ^d Based on the ϕ_{Δ} (limiting) value. ^e First value considering the maximum obtained from the excitation spectra; second value considering the presumed maximum obtained from the absorption spectrum. ^f Associated errors of $\pm 5\%$. ^g Associated error of $\pm 15\%$. ^h Major (decay) component of a biexponential decay. See text for more details.

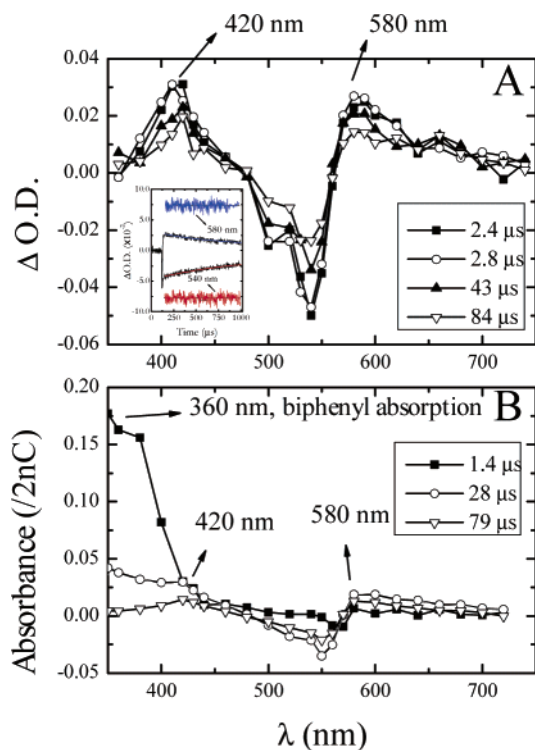


Figure 2. Transient triplet–triplet absorption spectra in DMF obtained by (A) direct excitation with $\lambda_{\text{exc}} = 532$ nm and (B) sensitization (with biphenyl) of Cibalackrot, $T = 293$ K. Shown as inset in (A) are the decays obtained in the depletion (540 nm) and transient maxima (580 nm) together with the residuals from the first-order fittings.

of triplet–triplet energy transfer depend upon the energy difference between donor and acceptor triplet states,⁴⁸ but typically (from spin statistics) have values of the order $2 \times 10^9 \text{ s}^{-1}$.

From the transient spectrum generated by direct excitation, using the singlet depletion method ($\Delta\text{OD}_{\text{S}\epsilon_{\text{T}}} = \Delta\text{OD}_{\text{T}}\epsilon_{\text{S}}$, with $\epsilon_{\text{S}} = 21\,360 \text{ M}^{-1} \text{cm}^{-1}$), it is possible to determine the triplet molar absorption coefficient for Cibalackrot ($\epsilon_{\text{T}} = 34\,100 \text{ M}^{-1} \text{cm}^{-1}$; see Experimental Section), and hence its quantum yield by actinometry with TPP in benzene. A triplet quantum yield value of 0.11 was obtained (see Table 1).

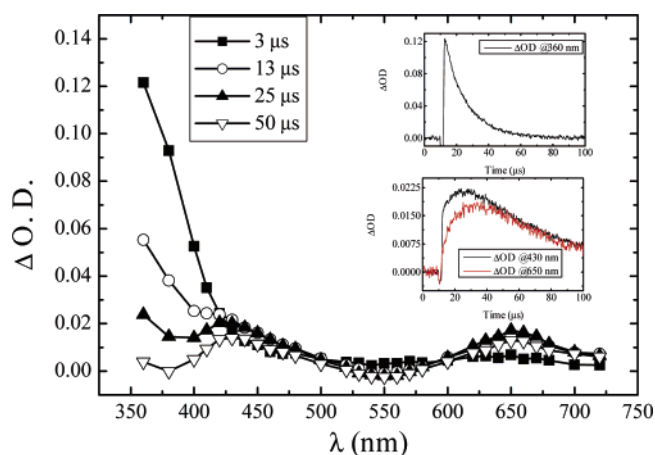


Figure 3. Transient triplet–triplet absorption spectra in benzene obtained by sensitization (with biphenyl) of preCiba, $T = 293$ K. Shown as insets are the decays obtained at the biphenyl maximum (360 nm) and transient maxima (430 and 650 nm).

Singlet oxygen formation quantum yields were obtained following photolysis of aerated DMF solutions of Cibalackrot. Excitations with laser pulses of a frequency doubled Nd:YAG laser (at 532 nm) lead to the characteristic phosphorescence signal of singlet oxygen at ≈ 1270 nm. The ϕ_{Δ} value was then determined by plotting the initial phosphorescence intensity (at 1270 nm) as a function of the laser dose and comparing the slope with that obtained with TPP in DMF as standard (see the Experimental Section for further details). Plots of the compounds can be found in the SI (Figure S2), confirming the good linearity obtained. The resulting data are given in Table 1, from which it can be seen that the singlet oxygen formation yield is ca. one-half the quantum yield value for triplet formation, indicating 50% efficiency of triplet energy transfer to produce singlet oxygen ($S_{\Delta} = \phi_{\Delta}/\phi_{\text{T}}$).

Spectral and photophysical properties for Cibalackrot, preCiba (and its methylated derivative MpreCiba), and indigo are summarized in Table 1.

We note that with Cibalackrot the sum $\phi_{\text{F}} + \phi_{\text{T}}$ is much bigger than with indigo, and that $\phi_{\text{IC}} (1 - \phi_{\text{T}} - \phi_{\text{F}}) \approx 0.19$, indicating that internal conversion loses importance at the expense of the two other channels. This is particularly pro-

TABLE 2: Fluorescence Quantum Yields (ϕ_F) and Lifetimes (τ_F) Together with Radiative (k_F) and Radiationless (k_{NR}) Rate Constants for Cibalackrot in Various Solvents

solvent	ϕ_F^a	$\tau_F,^a$ ns	$k_F,$ ns ⁻¹	$k_{NR},$ ns ⁻¹
dioxane	0.76	6.10	0.125	0.039
DMF	0.70	5.73	0.122	0.052
benzene	0.76	7.38	0.103	0.033
THF	0.70 ₄	6.40	0.11	0.046
ethyl iodide	0.068	0.75	0.09	1.243

^a Associated errors $\pm 5\%$.

nounced with fluorescence, which increases by more than 2 orders of magnitude relative to indigo.⁹ This contrasts with the behavior of keto forms of other indigo derivatives, where internal conversion is always the major singlet deactivation pathway.⁹ Moreover, the low singlet oxygen yield (ϕ_Δ) (see Table 1) reveals that this is not efficiently produced by the compound. This confirms the high stability of the molecule and supports its efficient use both as photoreceptor and in optoelectronic devices.

The photophysical behavior for preCiba resembles that of indigo, yet the structure of the compound is intermediate between those of Cibalackrot and indigo. In fact, the ϕ_F , τ_F and radiative and radiationless rate constants are very similar (at least in terms of order of magnitude) for preCiba and indigo. The fluorescence maximum of preCiba is very similar to that of indigo (670 nm vs 653 nm) whereas the absorption maximum for preCiba is identical to that of Cibalackrot (542 nm vs 544 nm). This clearly indicates the different nature of the ground and excited state in preCiba, and the photophysical properties provide some support for the importance of proton transfer (ESIPT) in the first excited singlet state, with this process taking precedence over the other decay processes: fluorescence, intersystem crossing, and other competitive processes such as cis–trans isomerization.¹⁵ Attempts to observe the transient triplet–triplet spectra of preCiba by direct excitation have been unsuccessful. It has only been possible to sensitize and observe the transient signal of preCiba triplet state with energy-transfer experiments (see Figure 3 and discussion above). This, once more, establishes that $S_1 \rightsquigarrow T_1$ intersystem crossing is a negligible pathway for the deactivation of preCiba lowest singlet state.

In Table 2 the fluorescence quantum yields, lifetimes, and radiative and radiationless rate constants for Cibalackrot in different solvents are shown. It is worth noting that, except with the heavy atom ethyl iodide, photophysical parameters are remarkably insensitive to the solvent (Table 2). Moreover, the constancy of the k_F (≈ 0.1 ns⁻¹) value, its insensitivity to solvent polarity, together with the high value for the molar absorption coefficient (Table 1) provides good evidence that the lowest lying transition is of π, π^* origin.

Study of Reduced Cibalackrot and preCiba Species. From the initial literature on Cibalackrot⁴⁹ it was suggested that, according to its chemical structure, the compound was unlikely to be reduced to a leuco form. However, this does not seem to be true, and the ¹H NMR spectrum of reduced Cibalackrot could be measured with a very low concentration of the dye. Also the absorption, emission and fluorescence excitation spectra in Figure 4A all strongly support the existence of the reduced Cibalackrot species; see the structure of leuco Cibalackrot as an inset in Figure 4A.

One-electron reduced species can be prepared by chemical reduction using alkali metals or strongly reducing systems such as sodium dithionite/NaOH.⁹ Although not perfect, the match

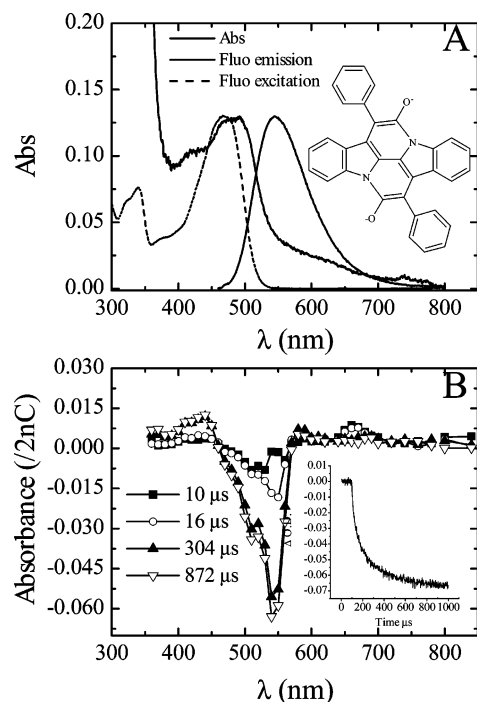
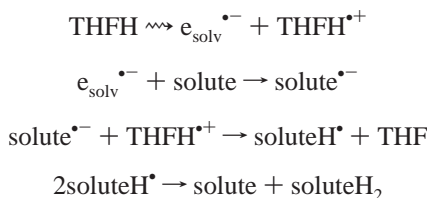


Figure 4. Absorption spectra of the Cibalackrot reduced species obtained through (A) chemically and (B) by radiolysis of THF solution. In (A) also shown are the fluorescence excitation and emission spectra. Show as inset in (B) is the rising component obtained at 440 nm. Show as inset in (A) is the reduced (leuco) structure for Cibalackrot.

between the absorption and the fluorescence excitation spectra is reasonable. Moreover, the maximum is similar to those for other leuco-indigo species.⁹ The emission spectrum is also similar in intensity and relative position of bands to those for indigo and indigo-related molecules.⁹ If the absorption maximum is taken as that from the excitation spectrum, the Stokes shift (Δ_{SS}) of the reduced form of Cibalackrot is similar to that for reduced indigo (see Table 1). The most remarkable observation is the fact that the ϕ_F value for reduced Cibalackrot is ≈ 17 -fold smaller than that of reduced indigo. In addition, we were unable to detect any transient signal by laser flash photolysis of the reduced form of Cibalackrot. This contrasts with the clear, strong signals previously observed with leuco indigo and its derivatives,⁹ suggesting that the $S_1 \rightsquigarrow T_1$ is absent with the Cibalackrot reduced form. With leuco preCiba and Cibalackrot, the low fluorescence quantum yields and lack of triplet absorption suggest that internal conversion is the dominant route. Although we do not yet have a full explanation, two possibilities can potentially explain this difference when compared to indigo. The first comes from the fact that although emission is still predominantly from the π, π^* state, ionization of the OH groups lowers the energy of other excited states, which may be close in energy to S_1 and facilitate relaxation to the ground state. The second has to do with the structural constraints imposed on Cibalackrot and preCiba that are not present in indigo. In the case of the excited state of the leuco form of indigo, rotational isomerism (photosomerization) is allowed, which is likely to produce a highly emissive species. Remember that fluorescence and trans–cis isomerization were observed in the case of indigoid compounds where the N–H groups were replaced by oxygen, sulfur ($\phi_F = 0.71$ and $\phi_T = 0.23$ and therefore with a negligible $\phi_{IC} \approx 0.06$),^{50,51} selenium ($\phi_F = 0.03$),⁵¹ or even carbon (Pechmann's dye⁵²). With these compounds the planar ground-state structure is lost due to the absence of hydrogen bonding between the C=O and the S, O, or Se, instead of N–H groups.⁵¹

The one-electron reduced species can also be produced by radiolysis of tetrahydrofuran (THFH) solutions, which produces predominantly solvated electrons and ions, leading to

SCHEME 1



In addition to producing solvated electrons, radiolysis of tetrahydrofuran also produces the geminate cation $\text{THFH}^{\bullet+}$ which can protonate the solute radical anion according to the reaction in the last equation in Scheme 1.^{53,54}

On kinetic grounds, it is likely that the disproportionation reaction involves at least one radical species rather than two radical anions.

Figure 4 shows the absorption spectra obtained by chemical reduction and by pulse radiolysis of Cibalackrot in THFH solution. In the chemical reduction case, a band with maximum 440 nm is observed together with the characteristic depletion of the Cibalackrot keto absorption, whereas with pulse radiolysis in THFH there is depletion of the ground-state absorption, confirming a very fast reaction between solvated electron and Cibalackrot that produces the reduced species at the expense of its keto form, as indicated in Scheme 2. Decay of the 440 nm absorption was second order with

$$\frac{2k}{\epsilon l} = 1.89 \times 10^5 \text{ s}^{-1}$$

which, using $l = 2.5 \text{ cm}$, $\epsilon = 21\,360 \text{ M}^{-1} \text{ cm}^{-1}$ (see Table 1), leads to a second-order rate constant of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, in agreement with the close to diffusion controlled disproportionation of the radical.

From the photophysical data of reduced preCiba (see Table 1) it is clear that this shows a behavior similar to that of reduced Cibalackrot with energy dissipation mainly occurring through the $S_1 \rightsquigarrow S_0$ radiationless channel.

Excited-State Dynamics of Indigo, Deuterated Indigo and preCiba. If proton transfer from the N–H to the C=O group in the excited state is the dominant factor contributing for the predominance of internal conversion deactivation over the other S_1 decay pathways, then deuteration of the system would be likely to have an effect on the observed photophysical parameters by inducing a dynamic effect on the H-bonding (or more specifically the N–H bond) involved in the deactivation process. By adding deuterated water (D_2O) in 2% to the media, the amino hydrogen of preCiba is quantitatively exchanged by deuterium. However, as has previously been pointed out in a similar investigation with indigocarmine, this effect could be promoted by either intra- or intermolecular hydrogen-bonding.¹¹

SCHEME 2

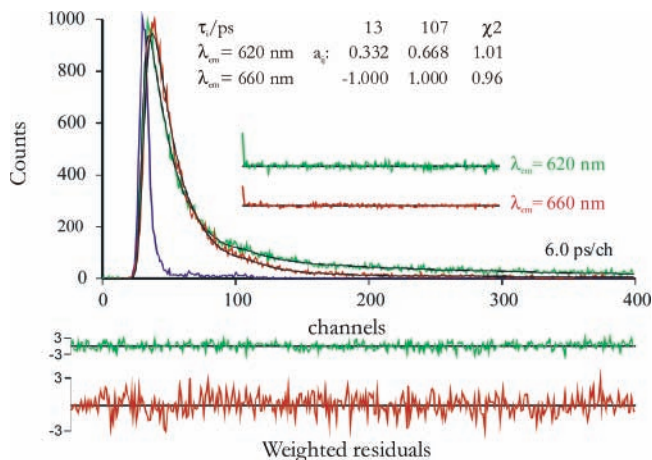
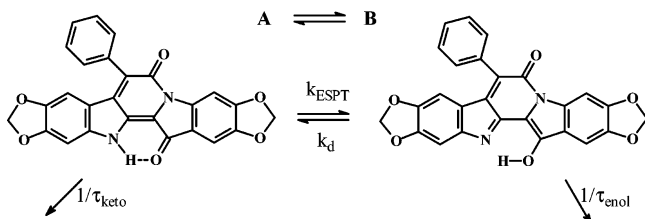


Figure 5. Fluorescence decays of preCiba in Dx:H₂O(2%) collected at the blue-edge and red-edge of the emission band. Shown as insets are the autocorrelation functions, weighted residuals and χ^2 values attesting the good quality of the fittings.

A more detailed analysis of the fluorescence decays has revealed these to follow biexponential rate laws consistent with a two-state model (interconversion between two species: A and B), which in this case presumably involves excited-state proton transfer. This can, however, involve intra- or intermolecular proton transfer (ESPT). The existence of the two-state model does not automatically imply the existence of an excited-state proton transfer but only shows that there are two coupled species in the excited state. However, on the basis of the obtained data in pure (and, in principle, water free) dioxane, intramolecular hydrogen proton transfer should be considered to be the dominant mechanism present.

This process is illustrated below in Scheme 2. In this scheme species A corresponds to keto preCiba species and the B species to its enolic form (resulting from the proton transfer) of preCiba. Remember that we cannot distinguish between intra- (shown process) or intermolecular proton transfer and thus the scheme is valid also if proton transfer is between the keto form of preCiba and the water in the solvent.

The decay profiles in the different mixtures show a long decay-time (varying from 105 to 130 ps) and a second shorter time (varying from 9 to 20 ps) which is associated with a risetime; see Figure 5 for an illustrative example.

Because the decay of the enolic form (B in Scheme 2), i.e., return to the ground-state keto form, is likely to be much faster than k_d (back-proton transfer in the excited state), this means that under these conditions $1/\tau_{\text{enol}} \gg k_d$ and thus this rate constant is an unimportant deactivation pathway for excited preCiba's enolic form. This means that the back-reaction in the excited state, enol \rightarrow keto process (reversibility), is absent. In view of the fact that the lifetime of the keto form is 152 ps (MpreCiba model compound), the decay time of the enol species is 107 ps and that of the keto species is 13 ps (Figure 5), strong evidence is seen that there is no reversibility in the enol-to-keto tautomerism in the excited state. Also note that in the decays in Figure 5, the longer component is due to the enol emission in the keto emission region.

In a two-state model where no reversibility exists (i.e., $1/\tau_{\text{enol}} \gg k_d$ in Scheme 2) the rate constant for the B species formation at the expense of the A species can be given according to eq 3, where τ_2 represents the fast component in the fluorescence decay:⁵⁵

$$k_{\text{ESPT}} = \frac{1}{\tau_2} - \frac{1}{\tau_{\text{keto}}} \quad (3)$$

where τ_{keto} is the decay time of preCiba in the absence of other deactivation processes, i.e., in the present case in the absence of the ESPT. This lifetime can be obtained with model compounds where this process is blocked, for example, by methylation of the N–H group in preCiba. Preliminary results with a methylated preCiba (MpreCiba) show a monoexponential decay with a lifetime of ≈ 150 ps (see Figure 6B). MPreCiba shows similar absorption and emission spectra to those of preCiba, although the decay is monoexponential. This can be seen in Figure 6 and Table 1.

Making use of this lifetime, data in Figure 5 and eq 3, one obtains $k_{\text{ESPT}}(20^\circ\text{C}) = 7 \times 10^{10} \text{ s}^{-1}$. Similar values are obtained in dioxane and dioxane:D₂O (2%) solutions. This extremely fast rate constant is comparable, for example, to those found for conformational relaxation in polyfluorene polymers ($2.5 \times 10^{10} \text{ s}^{-1}$)⁵⁵ or for ultrafast excited-state proton-transfer reactions of 7-hydroxy-4-methylflavylium cation to water which give a rate constant of $2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.³⁸ This cannot compete, however, with the ESPT with 2-(2'-hydroxyphenyl)benzothiazole where this rate constant at RT is ca. $6 \times 10^{12} \text{ s}^{-1}$ or of 3-hydroxyflavone where this value is $4 \times 10^{12} \text{ s}^{-1}$.⁵⁶

We have extended this study to indigo and partially (see SI) deuterated indigo in dioxane. Again, the decays collected in red and blue regions of the emission display an analogous behavior to that found for preCiba. This can be seen in Figure 7.

From these decays and again making use of the methylated preCiba lifetime and eq 3, one obtains a value of $k_{\text{ESPT}} = 8.4 \times 10^{10} \text{ s}^{-1}$ for indigo and $1.6 \times 10^{11} \text{ s}^{-1}$ for deuterated indigo. According to the proposed mechanism the proton transfer involves the formation, in the excited state, of the N–H(D)–O–C species at the expense of the N–H(D)–O=C keto species; i.e., it involves the breaking of a N–H(D) bond with formation of an H(D)–O bond. These bonds have force constants of 914 kcal/(mol Å²) (N–H) and 1006 kcal/(mol Å²) (O–H).⁵⁷ When the force constant at the transition state (in the present case the enol form) becomes larger than that in the initial state (keto form), then the electronic potential energy is smaller for the compound with the heavier atom ($E_{\text{D}} < E_{\text{H}}$), which leads to $k_{\text{H}} < k_{\text{D}}$, i.e., the inverse isotope effect. As a consequence, the proposed mechanism is totally compatible with the obtained rate constants for the indigo and deuterated indigo compounds: $k_{\text{D}}/k_{\text{H}} = 1.9$.

Moreover, in the case of preCiba, we can obtain an approximate value of the activation energy for this proton-transfer process by plotting the logarithm of the reciprocal of τ_2 vs $1/T$ (Arrhenius plot). This fast process showed Arrhenius type behavior, with an activation energy value of 11 kJ/mol in dioxane solution.

It is also worth mentioning that with the steady-state emission spectra in dioxane (and in dioxane:H₂O and dioxane:D₂O) upon increasing temperature there is a blue shift in the maxima and more importantly, an increase in the emission intensity (see Figure 8).

This behavior is clearly compatible with the two-state model proposed above. The blue shift (and the increase in the total fluorescence intensity) can be interpreted in terms of the situation where we are in the presence of two emissive species, and which is dependent on the rate constants of the process (Scheme 2 above) and is likely to be an activated process. This provides an explanation for the unexpected increase in intensity with temperature.

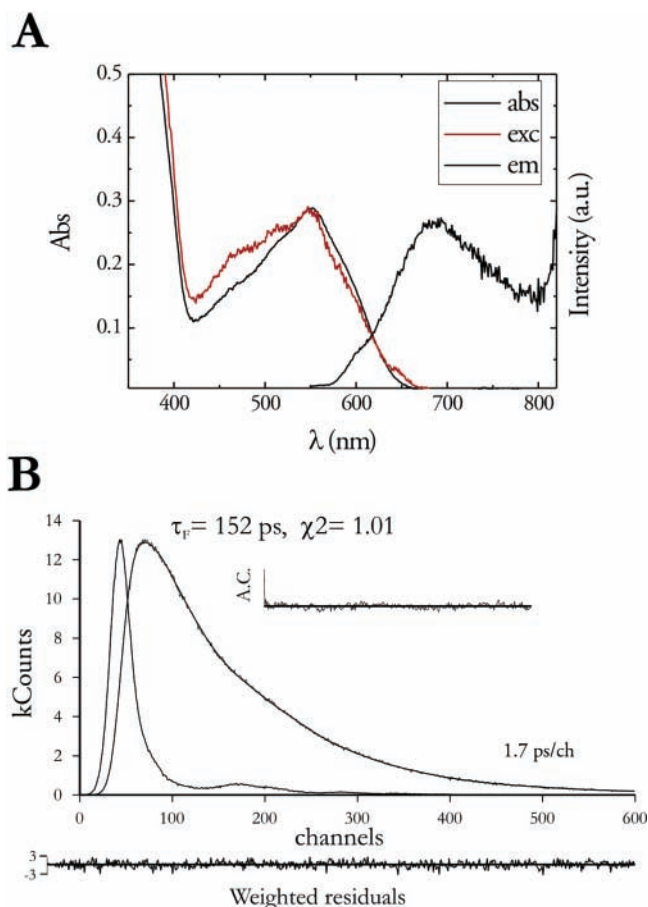
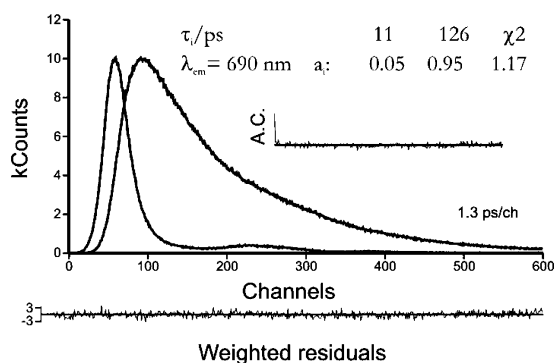
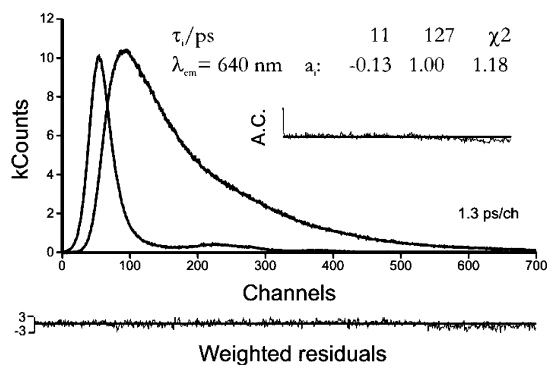


Figure 6. (A) Absorption (abs), excitation (exc) and emission (em) spectra of methylated preCiba (MpreCiba) in dioxane, $T = 293$ K. (B) Fluorescence decay of MpreCiba in Dioxane obtained with $\lambda_{\text{exc}} = 595$ nm and $\lambda_{\text{em}} = 670$ nm. Shown as insets are the autocorrelation function, weighted residuals and χ^2 value, attesting the good quality of the fitting.

The plot of the logarithm of the intensity vs the reciprocal of the temperature (Figure 8B) in fact shows that we are in the region of nonreversibility (low-temperature limit regime) in a Stevens–Ban-like plot.⁵⁸ From these plots the activation energy can be obtained. The value (~ 10 kJ/mol) is in perfect agreement with that obtained from the time-resolved experiments.

It is also worthy of note that there is a decrease of the total fluorescence intensity when D₂O or water is added to dioxane. This ratio drops by a factor of 2 (ϕ_{F} (preCiba, Dx) = 0.0012 and (ϕ_{F} preCiba, Dx:D₂O(2%)) = 0.00057), with similar results observed with water and D₂O (see Table 1). Although this change in the ϕ_{F} value cannot be directly related to each species in Scheme 2, because it involves the total emission of both species, it does suggest that water (or D₂O) is strongly involved in the deactivation processes of preCiba. A possible explanation for this decrease of the fluorescence yield and red shift with addition of water (or D₂O) may be that the additional water bridge would stabilize the locally formed excited-state species. However, the same is not true with indigo and the partially deuterated indigo. In these cases, the addition of D₂O increases the ϕ_{F} value whereas the addition of water decreases the ϕ_{F} value relative to dioxane. The behavior here strongly implies the involvement of proton transfer in the nonradiative decay. Comparison between the results with preCiba where no rotational isomerism is allowed, and indigo where this is possible, suggests that with the latter compound water (or D₂O) can be involved in the bonding between the N–H and the carbonyl groups, either by facilitating rotational isomerism in the excited state or by changing the rate for the proton process (from an

Indigo



Deuterated Indigo

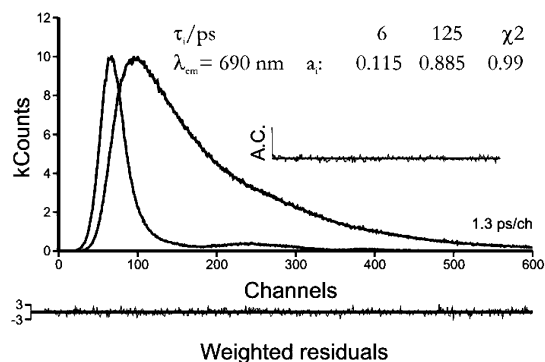
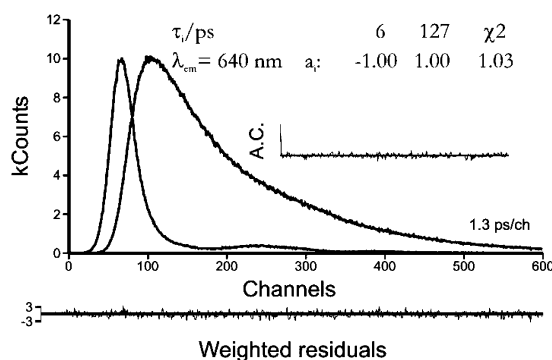


Figure 7. Fluorescence decays for indigo and (partially 31% indigo, 47% 1-deuterioindigo and 22% 1,1'-dideuterioindigo; see SI) deuterated indigo in dioxane obtained at 640 and 690 nm.

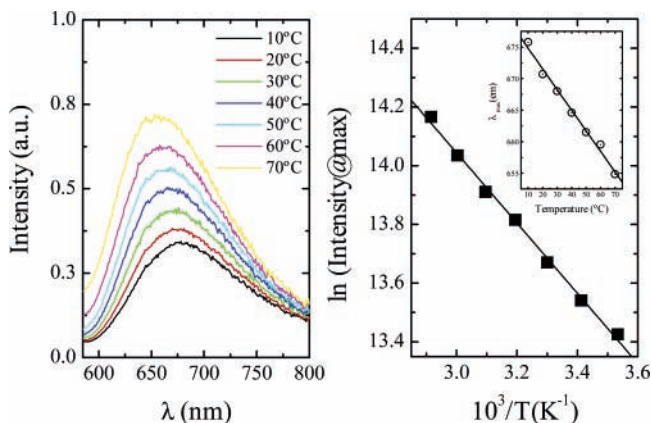


Figure 8. (A) Fluorescence emission of preCiba in dioxane as a function of temperature and (B) Arrhenius type plots of the fluorescence intensity (maxima) as a function of the reciprocal of temperature. The inset shows the dependence of the fluorescence wavelength maxima (in nm) with the temperature.

intra- to intermolecular process). This strongly supports the view of the importance of hydrogen bonding on the nonradiative decay. It is relevant that the fluorescence quantum yield in indigo is ca. an order of magnitude greater than in preCiba; see Table 1.

The above results indicate that deuteration only affects the nonradiative pathway. In their study of intramolecular hydrogen bonding of 4,4',7,7'-tetramethylindigo in the S_1 state using picosecond time resolution, Kaiser and co-workers¹⁰ found no evidence of proton transfer from the NH to the C=O group. Combination of this observation with our results suggest that proton transfer in the nonradiative decay of the excited state

must be followed by an extremely rapid back transfer in the ground state.

The peculiar behavior displayed by MpreCiba is also relevant to this discussion. In this case we also observe a significant Stokes Shift (identical to that of preCiba; see Table 1), which would indicate that the N-CH₃ bond is affecting (differently) the potential energy curves in the ground and excited state of this compound. Due to the very small extinction coefficient it is likely that the electronic transition is less localized in the aromatic chromophore than in the cases of indigo and Cibalackrot.

In summary, on the basis of the observations here with the compounds preCiba and Cibalackrot, and further comparison with indigo, we believe that excited proton transfer is responsible by the fast deactivation of the S_1 state in indigo, mainly through the internal conversion channel. When ESPT is blocked as with Cibalackrot, this channel loses importance at the cost of an increase in the fluorescence. Moreover, for preCiba, which has a structure intermediate between indigo and Cibalackrot, some of the characteristics, such certain spectroscopic properties (e.g., absorption maxima) are similar to those of indigo, whereas others (emission maxima and the Stokes Shift) are remarkably different; most importantly, their photophysical properties clearly resemble very closely those of indigo, providing very strong support for the role of ESPT in the photophysics of indigo.

Conclusions

We have fully characterized the spectroscopic and photophysical properties of the keto and leuco forms of the rigid indigo derivative Cibalackrot in solution. With the keto form a remarkable increase of the fluorescence quantum yield (and

decrease of the internal conversion dissipation channel) was observed compared with indigo. Cibalackrot is an indigo analogue that cannot undergo intra- or intermolecular proton transfer due to the rigid C=C(Ph)-C=O linked to the central nitrogen. This compound was found to display the characteristic photophysics of aromatic hydrocarbons: high fluorescent yields, nanosecond lifetimes, efficient intersystem crossing, etc.⁵⁹ The behavior is opposite to that previously observed with indigo⁹ and with preCiba. In both cases, and as a result of the availability of the proton from the N-H group, intramolecular proton transfer between the carbonyl and N-H groups is allowed and their photophysics is found to be essentially controlled by the internal conversion deactivation channel.

A more detailed investigation of the decay profiles with collection at the blue and red parts of the emission of the fluorescence band of indigo, deuterated indigo and preCiba has revealed that the decays are biexponential and that at longer emission wavelengths these appear to be associated with both rise and decay times indicating that two excited species exist, which is consistent with a keto-excited form giving rise (by fast proton transfer) to the enol-form of indigo. Evidence is presented which supports the idea that intramolecular (and possibly some intermolecular) proton transfer can explain the high efficiency of internal conversion in indigo.

With the reduced form of Cibalackrot, its spectral and photophysical data are clearly different from that found for the reduced form of indigo, with the fluorescence quantum yield 1 order of magnitude lower and the radiative rate constant 2 orders of magnitude lower. This indicates a less effective radiative channel with leuco Cibalackrot, possibly due to more efficient nonradiative decay.

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Supporting Information Available: Synthesis and characterization of the compounds, singlet oxygen phosphorescence plots, and a decay signal plot. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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