Triplet Indigo

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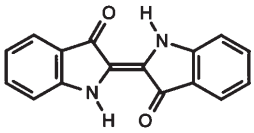
The Triplet State of Indigo**

J. Sérgio Seixas de Melo, Hugh D. Burrows, Carlos Serpa, and Luis G. Arnaut*

Indigo is one of the most emblematic molecules for the color blue, and is believed in many cultures to be charged with unique talismanic properties.[1] The vivid color and high stability of this dye have led to an almost mythical status, from the "tecklet" of the Hebrews (believed to be a mixture with Tyrian Purple), through the blue of Napoleon Bonaparte's army uniforms, to its current application as the dye for denim in blue jeans.[1] Indigo is also associated with the genesis of the German chemical industry.[2] However, in spite of the numerous reports on the properties and applications of indigo (and analogues)[1,3–7] some mysteries remain to be solved. Of particular importance is the characterization of the triplet state. Although triplet states of thioindigo derivatives have been characterized and shown to be involved in *cis–trans* photoisomerization,[8] and both thioindigo and indigo quench the triplet state of tin(IV) porphyrins,[9] no sensitized processes or evidence of a long-lived triplet are seen in the latter case. We have therefore characterized this elusive indigo species in terms of its energy and quantum yield of intersystem crossing using two different and complementary techniques, namely, energy-transfer pulse radiolysis and time-resolved photoacoustic calorimetry (PAC). We believe this has important implications for the properties and applications of the compound.



It has recently been shown that indigoid derivatives quench oxygen at the diffusion limit and that some of them act as excellent radical traps.[10] Moreover, yields of singlet-oxygen sensitization ($\phi_\Delta \approx 10^{-3}$–$10^{-4}$) have been obtained for indigo and several substituted derivatives, including Tyrian Purple (6,6′-dibromoindigo); thus the triplet energy of indigo lies above that of singlet oxygen (0.94 eV, 91 kJ mol^{-1}).[11,12] Due to the absence of a triplet signal for the 12 indigo derivatives studied, it was not possible to measure $S_1 \rightarrow T_1$ intersystem-crossing yields (ϕ_{ISC}), but it can be assumed that the ϕ_Δ values provide a lower limit for these.[11] For indigo itself the value obtained for ϕ_Δ ($\approx \phi_{ISC}$) was 0.0012.[11] In this particular case, a very weak signal (in the 450–700-nm region) was observed and attributed to the transient triplet–triplet absorption of indigo.[13] However, this was too weak to determine the triplet molar extinction coefficient or the ϕ_{ISC} value.[13]

In the present study, we determined the triplet energy of indigo by energy-transfer pulse radiolysis and then studied the singlet-to-triplet intersystem-crossing yield using PAC. We recently used the same strategy to fully characterize the triplet states of some important conjugated organic polymers in benzene solution.[14]

Determination of the triplet-state energy involved the triplet–triplet energy-transfer method developed by Bensasson and Land whereby, on pulse radiolysis of benzene solutions containing relatively high concentrations [$(1–10) \times 10^{-3}$ M)] of appropriate aromatic sensitizers (A) having long-lived triplet states, these can accept the triplet energy from benzene (B) and then transfer it to appropriate solutes (S) at much lower concentrations.[15–17] In addition, if the sensitizer A has a high quantum yield of $S_1 \rightarrow T_1$ intersystem crossing, triplet states of S are selectively generated in nearly quantitative yields.

Following pulse radiolysis of solutions of indigo (S) in benzene with tetraphenylporphyrin (TPP) and aromatic sensitizers (A) with different triplet energies (Figure 1), observation of indigo triplet–triplet absorption indicates that energy transfer has occurred and S has a lower triplet energy than A.

The experiment is subject to the kinetically required concentration ratio $[B] \gg [A] \gg [S]$. Efficient triplet–triplet energy transfer requires that the aromatic sensitizer has a higher triplet energy than the solute under study.[18] Using this methodology we tested several acceptors for sensitization of indigo and found that indigo quenches the triplets of biphenyl (2.94 eV),[13,19] naphthalene (2.63 eV),[13] perylene (1.53 eV), TPP (1.42 eV), and rubrene (1.14 eV). Assuming that these all involve energy transfer and since indigo is known to sensitize singlet oxygen (0.94 eV), this puts the triplet above 0.94 and below 1.14 eV, that is, (1.0 ± 0.1) eV [or (1.04 ± 0.10) eV]. Further indications of the triplet energy come from the rates of energy transfer from sensitizers to indigo. With the highest energy sensitizers, rates are close to diffusion control. However, as the energy gap between triplet sensitizer and acceptor decreases, the rate also decreases, and, as has previously been shown by Sandros and Balzani et al., is

[*] Dr. J. S. Seixas de Melo, Prof. Dr. H. D. Burrows, Dr. C. Serpa, Prof. Dr. L. G. Arnaut
Department of Chemistry
University of Coimbra
3004-535 Coimbra (Portugal)
Fax: (+351) 239-827-703
E-mail: sseixas@ci.uc.pt
Homepage: https://woc.uc.pt/quimica/person/ppgeral.do?idpessoa=23

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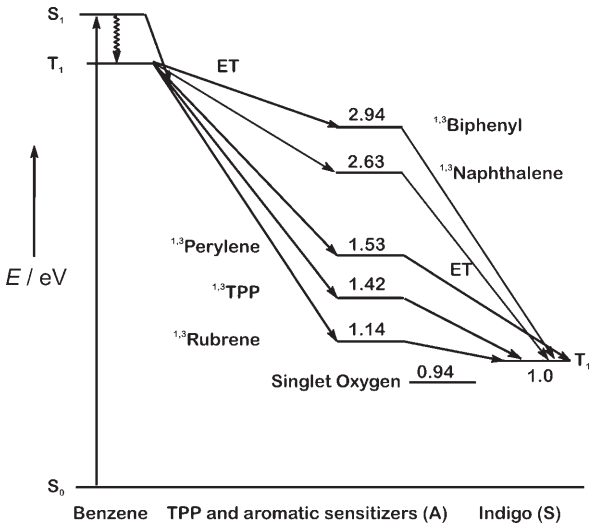

Figure 1. Diagram for an energy-transfer pulse radiolysis experiment leading to the formation of the triplet state of indigo (S) by sensitization with different energy donors (A).

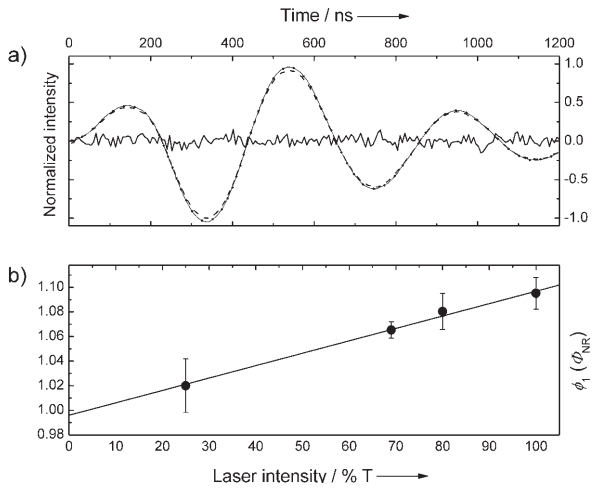

Figure 2. a) PAC waves for 80% laser intensity: reference wave (MnTPP, dashed line), sample wave (full line), calculated wave obtained from fitting with a single fast exponential decay (dotted line that overlaps with the sample-wave line) and residuals (sample wave−calculated wave)×10; sample and reference in dioxane at 293 K; b) fraction of fast energy deposited as heat by the sample at different laser intensities.

related to this energy separation.[20,21] From the measured second-order rate constants for energy transfer from rubrene ($2.8\times10^7\,\mathrm{M^{-1}s^{-1}}$) and by using the Sandros equation,[20] a triplet energy of 1.0 eV was calculated.

In the case of systems with negligible volume changes, time-resolved PAC measures directly the heat released in the decay of transients formed by pulsed laser excitation.[22–24] This is the case for the formation of indigo's triplet state. The energy balance for the formation of the triplet state requires that the energy of the laser pulse ($E_{h\nu}$) minus the sum of the energies released as heat in the formation of the triplet ($\phi_1 E_{h\nu}$) and the energy lost radiatively ($\phi_F E_{\nu\max}$) must equal the energy stored in the triplet state [Eq. (1)].[24]

$$\phi_{ISC}\,E_T = (1-\phi_1)\,E_{h\nu} - \phi_F\,E_{\nu\max} \qquad (1)$$

Here $E_{\nu\max}$ is taken as the energy at the maximum fluorescence intensity, assumed to have a Gaussian shape[13] ($E_{\nu\max}=1.90$ eV), and $E_{h\nu}=2.33$ eV at 532 nm. In our PAC experiments we measure separately the heats released following the excitation of a sample and of a calorimetric reference under identical conditions, including the same optical density at the excitation wavelength. From the deconvolution of sample and reference signals, we obtain the fraction(s) of heat released in the formation of the sample transient(s). In the case of indigo, the triplet is formed very rapidly (within a few hundred picoseconds)[13] and contributes to a prompt fraction of released heat (ϕ_1), but its decay in deaerated solutions is too slow ($\tau_T\approx30$ μs)[13] to be detected in our experiment. Thus, with ϕ_1 measured by PAC, knowledge of the energies of the excited states involved (S_1 and T_1), and the yield of fluorescence (ϕ_F), it is possible to determine the quantum yields of the nonradiative processes.[24]

Figure 2 shows the photoacoustic waves of indigo and the calorimetric reference (MnTPP) in dioxane,[24] together with the plot of the measured fraction of heat released in nonradiative processes versus the doses of excitation light. For high laser intensities the intensity of the sample wave is higher than that of the reference because biphotonic processes are occurring in the sample, as expected from the observed formation of the indigo triplet, decay kinetics, and triplet–triplet absorption spectra.[13] The biphotonic effects are conveniently eliminated by carrying out the experiment at different laser intensities and extrapolating to zero light intensity. In the present case, the very low ϕ_{ISC} poses a formidable challenge for measuring the heat deposited in formation of the triplet state of indigo. An accurate measurement is still possible thanks to sensitivity of our front-face PAC cell, and by extrapolating to zero light intensity we obtain a value of $\phi_1=0.995\pm0.011$ at the 90% confidence level (see Figure 2). Based on the value of 1.04 eV obtained for the triplet energy of indigo and $\phi_F=0.0023$,[13] we obtain $\phi_{ISC}=0.0066$. Considering the experimental uncertainty associated with these measurements, this value is in good agreement with the value obtained for $\phi_\Delta=0.0012$, which is a lower limit for the singlet-to-triplet intersystem-crossing yield of indigo.[11] We note that the error limits imposed by the energy-transfer studies on the triplet energy of indigo (0.94–1.14 eV) and the fraction of heat measured by PAC for the formation of this transient require that $0.006\le\phi_{ISC}\le0.007$.

If the energy of the singlet is taken as the intersection of the absorption and fluorescence spectra (635 nm, 1.95 eV), an S_1–T_1 energy splitting of (0.91 ± 0.10) eV is obtained. From the ϕ_{ISC} and τ_F[11–13] values we can obtain the k_{ISC} value ($k_{ISC}=\phi_{ISC}/\tau_F=4.7\times10^7\,\mathrm{s^{-1}}$). Both the singlet–triplet splitting and rate of intersystem crossing are close to those of typical aromatic hydrocarbons.[25] This provides the important information that the lowest excited singlet and triplet states of indigo must be of π,π* origin.

With the determination of the triplet energy and intersystem-crossing quantum yield reported here, we have written one more page in the "book" of the fascinating molecule

indigo. In particular, the combination of inefficient intersystem crossing and low triplet energy in indigo, coupled with fast internal conversion of the singlet state, is likely to be an important factor contributing to the high stability of this compound.

Experimental Section

Absorption and emission spectra, used for optical matching and obtaining singlet energies and fluorescence data, were recorded on Shimadzu UV-2100 and Horiba-Jobin-Ivon-SPEX Fluorolog 3-22 spectrometers, respectively.

Pulse radiolysis experiments were carried out at the Free Radical Research Facility of the Daresbury Laboratory, typically with 50-ns, ca. 7.5-Gray pulses from a 12-MeV linear electron accelerator. Transient absorption difference spectra were observed by using a xenon source and gated diode array or photomultiplier for detection. Details of the setup are given in references [26,27].

Time-resolved photoacoustic calorimetry (PAC) measurements were performed on a home-built apparatus whose design, experimental method, and data analysis have been described elsewhere.[24]

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