

Photophysics of indigo and molluscan purple dyes: why are they photostable?

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Motivation

The color purple has long been used as a symbol of royalty and power in art, fashion, and architecture. The use of molluscan purple in wall paintings and textiles by royalty is dating back up to the 18th century BCE. The use of a rich purple dye is still presently more expensive than gold. The name comes from molluscus snails which in huge quantity were used to dye fabrics in ancient times. 1 gram of this dye is obtained from the secretion of 10,000 of these large sea snails. While the molluscan purple dye is composed of a mixture of various proteins, its color is derived from indigotin, indirubin and their brominated derivatives, including the molecule, 6,6'-dibromoindigotin. Both dyes can exhibit high stability, in particular against photodamage from UV and Visible radiation that allowed them to survive in ancient art for centuries as was recently confirmed for the molecules isolated in Ar matrix experiment [2]. It is also unique in that both indigo and molluscan purple can undergo both an excited-state intramolecular double hydrogen and double proton transfer on the nanosecond timescale followed by a ground state back transfer [3,4]. This mechanism can be traced in potential energy surfaces presented in Fig. 1 and along the Energy profiles – in Fig. 2.

In this study, the excited-state lifetimes of indigo and 6,6'-dibromoindigotin were measured. We combine these results with static calculations of the excited and ground-state potential energy surfaces which elucidate the step-wise mechanism of the ESIPT process. The lifetime measurements reveal that molluscan purple has nearly the same relaxation rate as indigotin providing new insights in the possible relaxation mechanisms of the indigotin family of dye molecules. Resonance Enhanced Multi-Photon Ionization (REMPI) was used to study the dye in the gas phase. The excited-state lifetime for both dyes were measured in the ps time regime using a pump-probe scheme in which the ionization pulse was mechanically delayed relative to the excitation pulse to measure the decay of the excited-state population.

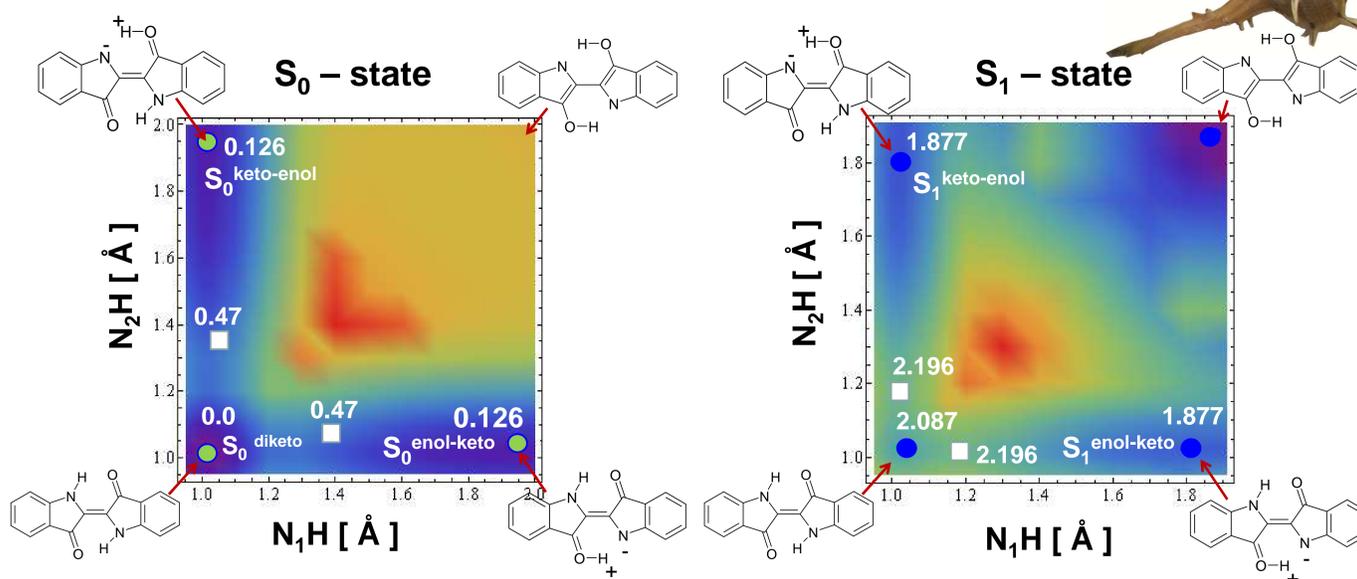


Fig. 1. Relaxed potential-energy surfaces of the electronic ground state (left graph) and the lowest excited state (right graph) of the indigo molecule plotted as a function of the two stretching coordinates N_1H and N_2H . Green circles represent ground-state diketo (global) and single-proton transferred keto-enol (local) minima. Blue circles represent S_1 keto-enol, S_1 enol-keto and S_1 dienol minima. The dashed white line shows the S_1/S_0 conical intersection seam. The results were obtained with the ADC(2)/cc-pVDZ method for the excited state and with the MP2/cc-pVDZ method for the ground state. Relative energies of minima and barriers are given in eV.

Excited-state double hydrogen and proton transfer in:

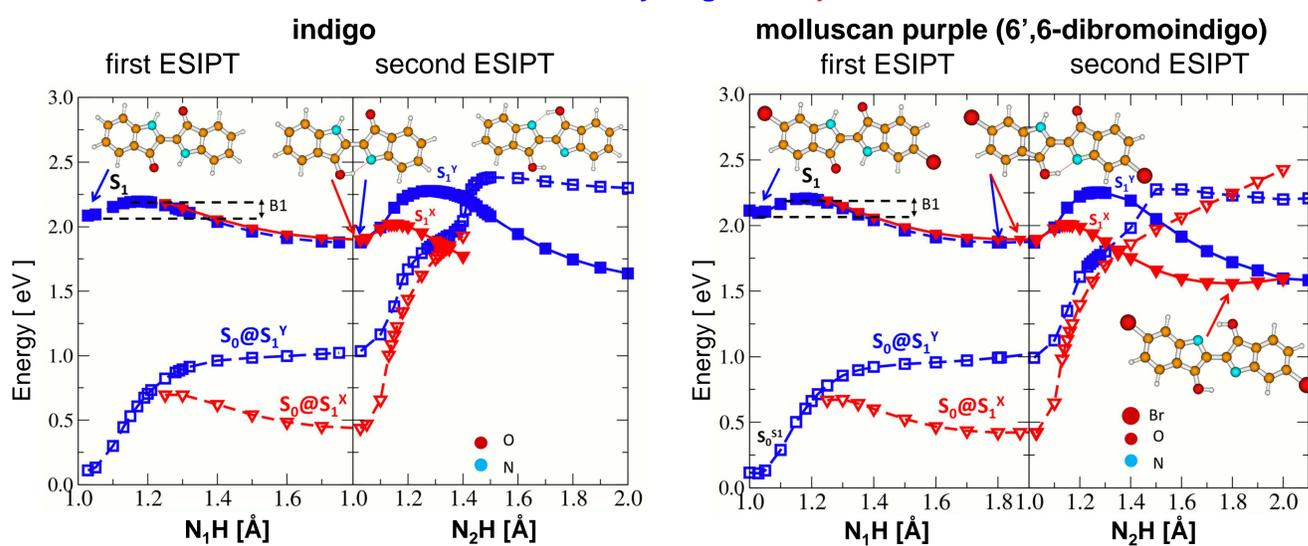


Fig. 2. Two excited-state minimum energy profiles of indigo (left graph) and molluscan purple (right graph), calculated at the ADC(2)/cc-pVDZ level, plotted as a function of N_1H distance (first ESIPT) and N_2H distance (second ESIPT). Solid lines denote minimum-energy profiles of the S_1 state. Dashed lines ($S_0@S_1^X$ and $S_0@S_1^Y$) denote MP2/cc-pVDZ energy profiles of the S_0 state computed at the optimized geometries of the respective S_1 state profile (red triangles for proton transfer (X) and blue squares for hydrogen transfer (Y)). Blue and red arrows in the middle indicate the starting keto-enol geometries for performing the X and Y scans.

Conclusions

We present REMPI spectra, pump-probe spectra, and calculated 1-D traces for sequential double proton and hydrogen transfer along the excited and ground-state potential-energy surfaces of 6,6'-dibromoindigotin, the major chromophore in the ancient dye known as molluscan purple. Other than a blue-shift in the absorption spectra, molluscan purple shares similar photo-relaxation mechanisms with indigotin: a faster sequential double proton transfer along the X trajectory followed by a back transfer, and a slower interconversion from the Y trajectory to the X profile and followed by the same process. While halogenic substitution in other molecular systems has led to changes in the calculated potential energy surfaces and consequently the rate to transfer, in this case bromination had little effect on the excited-state lifetimes of both decay processes compared to the indigotin molecule. The striking similarities between the measured lifetimes and calculated PES for both indigotin and molluscan purple illustrate the hardness of the two dyes to harmful photodamage as well as the importance of modelling analogous molecules to predict the effects of more complex systems.

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Methodology

Ground-state equilibrium geometries and energy profiles were computed with the MP2 method. The excited-state geometries and minimum potential-energy surfaces were calculated with the ADC(2) method, a simplified and cost-effective variant of the coupled-cluster method with single and double excitations. ADC(2) can be considered as an MP2 equivalent for excited states. The cc-pVDZ atomic basis set was used throughout the calculations.

Ab initio calculations of the excited-state (S_1) potential-energy surface indicate that the double proton or hydrogen transfer is sequential, not concerted (see large red barrier along the diagonals of two-dimensional plots (Fig. 1) – both in the ground (S_0 - state) and in the excited state (S_1)).

The molecule being in the diketo form first overcomes the **B1** barrier for the first ESIPT/ESIHT toward the enol-keto form.

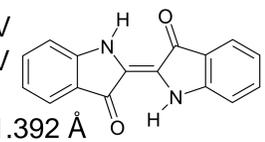
The trajectory of the second PT/HT transfer passes through a second barrier and then encounters a conical intersection that leads back to the ground state. Both – first and second excited-state energy barrier are of the order of 0.1 eV

B1 energy barrier – first ESIT

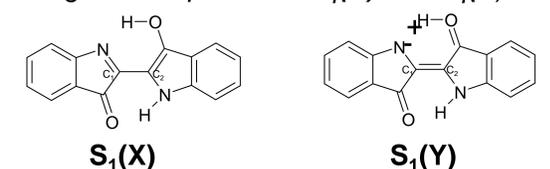
from S_1 (diketo) toward S_1 (enol-keto)
indigo, B1 = 0.109 eV
molluscan purple, B1 = 0.109 eV

S_1 (diketo) → S_1 (enol-keto)

$E_a = 2.087$ eV
 $E_{fl} = 1.98$ eV
 $f_{fl} = 0.3$
 $R(C_1-C_2) = 1.392$ Å



Two isoenergetic enol-keto excited-state structures of Indigo were optimized: $S_1(X)$ and $S_1(Y)$



$E_a = 1.899$ eV
 $E_{fl} = 1.46$ eV
 $f_{fl} = 0.2$
 $\mu_e = 6.8$ D
 $R(C_1-C_2) = 1.454$ Å

$E_a = 1.875$ eV
 $E_{fl} = 0.84$ eV
 $f_{fl} = 0.1$
 $\mu_e = 3.4$ D
 $R(C_1-C_2) = 1.383$ Å

B2 energy barrier, second ESIPT

from S_1 (enol-keto) toward S_1 (dienol)
Indigo B2(X) = +0.124 eV,
molluscan purple, B2(X) = +0.117 eV,

indigo B2(Y) = +0.401 eV
molluscan purple, B2(Y) = +0.382 eV

R2PI experiment gives two excited state lifetimes for each molecule :

	τ_1	τ_2
indigo	1.5 ns	20 ns
molluscan purple	2.5 ns	20 ns

Literature

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