The Interaction of Excited Thioindigo with Hydroxylic Compounds and its Implications on the Photostability of Indigo

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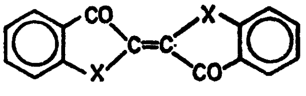
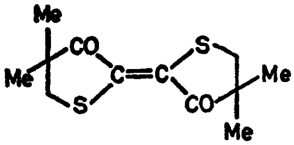
Summary The quenching of the fluorescence of *trans*-thioindigo and the inhibition of its photoisomerization to the *cis*-isomer by phenols support the idea that the photostability of indigo is due to a proton-transfer in the excited singlet state.

THE unique stability of indigo (I; X = NH) and its ring-substituted derivatives to photochemical *cis–trans* isomerization has been attributed to hydrogen-bonding.[1]



(I)



(II)

Although the presence of the hydrogen atoms is clearly essential for photostability, since the corresponding *NN'*-dialkyl and *NN'*-diacyl derivatives are known to isomerize readily,[2,3] a consideration of the energies involved (the energy of the light absorbed is *ca.* 48 kcal whereas only *ca.* 10 kcal can be accounted for from the stabilization of two hydrogen bonds) raises serious doubts about this explanation. The purpose of this communication is to propose that the photostability of indigo is due to the transfer of one or both protons from nitrogen to oxygen in the first excited singlet state, a reaction which is so fast that it takes precedence over all the other processes (fluorescence, *cis–trans* isomerization and/or intersystem crossing) normally shown by molecules of this type upon excitation. The greatly enhanced (*ca.* 10^6 times) acidity of Ar–NH– groups and the similarly increased basicity of Ar–CO– groups in the first excited singlet state is well known[4] and such proton-transfer phenomena have been reported for salicylic acid derivatives[5] and some hydroxy-benzazoles,[6] based on fluorescence measurements.

Since indigo does not fluoresce, it is difficult to see how direct experimental verification could be obtained for the proposed mechanism. As an indirect approach, a study of the reactions of excited *trans*-thioindigo (I; X = S), selected as the prototype of a "protonless indigo",† with phenol and *p*-nitrophenol was undertaken, since phenols (in the ground state) could be expected to exhibit chemical behaviour similar to the weakly acidic excited Ar–NH– groups. The effect of ethanol on thioindigo and of phenol on Luettke's aliphatic "precursor" thioindigo (II) were also studied to some extent, in order to evaluate the effect of eliminating the aromatic rings in either reactant. Fluorescence and photochemical *cis–trans* isomerization were the two excited-state processes of thioindigo that were investigated by spectroscopic techniques.[2,3]

From the Stern–Volmer type plots[8] in the Figure it is clear that both phenols are equally effective in quenching the fluorescence of the dye, presumably by the formation of a donor–acceptor "encounter complex". From the slope of this line (125·5) and the observed lifetime for the excited singlet of thioindigo in benzene ($1{\cdot}34 \times 10^{-8}$ s),‡ it is possible to calculate the quenching rate constant ($k_q = 9{\cdot}34 \times 10^9$). The closeness of this value to that calculated from the Debye equation ($1{\cdot}08 \times 10^{10}$)[9] suggests that the quenching is diffusion-controlled. The observation that both phenols quench the fluorescence at identical rates also supports this conclusion. While phenol inhibits the photochemical *cis–trans* isomerization of thioindigo at approximately the same rate, the effectiveness of *p*-nitrophenol as an isomerization inhibitor is more than 50% greater (slope: 192·5), indicating that the latter must, in addition, also be interacting with another, lower-lying excited state (possibly the triplet) that is involved in the isomerization process.

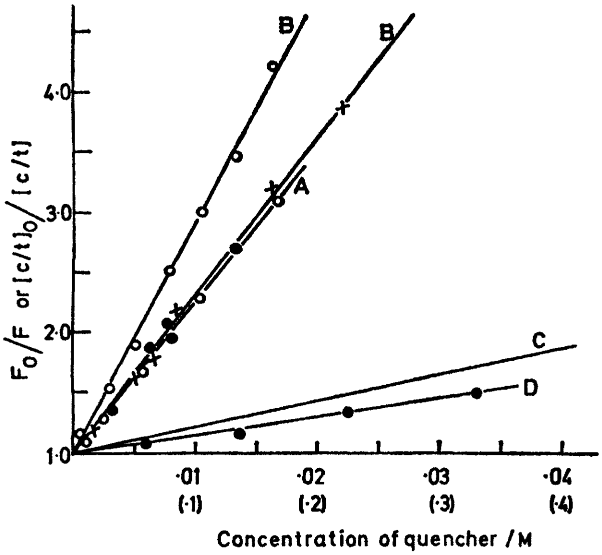


FIGURE. *Stern–Volmer type plots for:* A, *Fluorescence quenching of thioindigo by phenol* (○) *and* p-*nitrophenol* (●); B, *Inhibition of* cis–trans *isomerization of thioindigo by phenol* (X) *and* p-*nitrophenol* (○); C, *Fluorescence quenching or* cis–trans *isomerization inhibition of thioindigo by ethanol* (*lower concentration scale*); D, *Inhibition of* cis–trans *isomerization of Luettke's "precursor"* (II) *by phenol* (*lower concentration scale*). *Solvent: benzene. Concentrations of* cis *and* trans *isomers were determined by absorption* (*at* 565 nm) *or fluorescence* (580—600 nm). *Photochemical* cis–trans *isomerizations were carried out with the apparatus described previously,*[3a] *using Corning filters of appropriate wavelength ranges.*[3b]

The lines C and D in the Figure (plotted against the lower concentration scale) show the relative slowness of the inhibition of the *cis–trans* isomerization reactions, if either of the reactants is aliphatic. Although the data for ethanol are only approximate (because of the formation of a ground state complex at the high concentrations required), it is clear from the slopes of the lines [2·2 for ethanol and 1·4 for (II)] that the rate of formation of the complex is greatly diminished, if either the donor (–CO–) or the acceptor (–OH) groups are not conjugated with an aromatic ring. (It should be noted that the Stern–Volmer slopes obtained for quenching of different substrates by the same quencher are comparable only if the lifetimes of the excited species are similar. However, since the molar extinctions of *trans*-thioindigo and of (II) are of the same order of magnitude,[3b,10] conclusions may reasonably be drawn from the observed large differences in the slopes of the Stern–Volmer plots pertaining to these two compounds.)

While these results do not provide proof for the occurrence of excited state proton-transfer in indigo, nonetheless they are completely consistent therewith. Since in indigo the potentially acidic protons are held in close proximity to the potentially basic carbonyl oxygen atoms by means of hydrogen-bonding in the ground state,[11] the occurrence of intramolecular proton-transfer would seem exceedingly likely upon excitation.§ The results with thioindigo indicate that excited state donor–acceptor complexes formed by indigoid dyes will neither isomerize nor fluoresce during their relaxation to the ground state, a behaviour exhibited only by indigo (and its ring-substituted derivatives) in the absence of external quenchers. Thus one may conclude that, although the photostability and lack of fluorescence exhibited by indigo may seem anomalous, when viewed from the standpoint of ground-state chemistry, these properties are consistent with the behaviour of related systems in the excited state.

The author thanks Professor W. Luettke for samples of non-aromatic thioindigo dyes, Professor D. G. Whitten for suggesting the Stern–Volmer treatment of the results, and both of them and Professor A. Weller for discussions.

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† It has already been reported that the conjugate acid cation obtained by dissolving thioindigo in conc. sulphuric acid behaves very much as indigo does in inert solvents;[7] hence this selection appears well justified.

‡ The author is indebted to Professor W. R. Ware for this measurement.

§ Quantum mechanical (HMO) calculations are also consistent with the proposed excited-state proton transfer. (W. Luettke, personal communication.)

¶ Attempts at bringing about *trans*→*cis* isomerization of indigo by flash photolysis have also failed. (D. G. Whitten, personal communication.)

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