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Do substituents make any contribution to the formation of systems where the electronic effects seem to be neutralized? The case of the indigo dye formation

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ABSTRACT: Substituent effects on the fragments, intermediates and indigo dyes have been evaluated using global and local descriptors of the chemical reactivity. In terms of the global electrophilicity, one of the fragments, indoleninone, is classified as the electrophile and the other, indoxyl, as the nucleophile. The resonance, field and polarizability contributions of the substituents play an important role in the description of the fragments' electrophilicity. The interaction of the two fragments, to form the intermediate complex, has been shown to be as a superposition of two molecular planes, one coming from the indoxyl HOMO and the other from the indoleninone LUMO, both oriented by the dipole moment. Also, it has been shown that the complex formation is guided by the most nucleophilic indoxyl compound and not by the most electrophilic indoleninone. In spite of the indigoids having symmetrical structures, the substituent effects described in terms of the resonance, field and polarizability effects have an important effect on the maximum wavelength absorption in the electronic spectra. Copyright © 2005 John Wiley & Sons, Ltd.

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KEYWORDS: indigo dyes; substituent effects; TD-DFT; chemical reactivity indexes

INTRODUCTION

During the 1970s, the structures of five prochromogens, precursors of indigo and dibromoindigo dyes, were elucidated.[1] These precursors were initially found in variable amounts isolated or forming mixtures between them, in the hypobranchial glands of molluscs of the families Muricidae and Thaisidae, especially in the species *Dicathais orbita*, *Murex trunculus*, *Murex brandaris*, *Murex erinaceus*, *Purpura haemastoma* and *Rapana bezoar*.[2] The discovery of these precursors triggered much interest in chemistry, biochemistry and ecology,[3] since no indigo or dibromoindigo were found in the hypobranchial glands of the molluscs.

Chemically, the precursors consist basically of the sodium salt of substituted indoxyl sulfates, which are both brominated and non-brominated at position 6 of the indoxyl aromatic ring. An additional structural variation was found, that is, a different group substitution at C-2 of the indoxyl ring. In this case, the variation consisted in the total absence of substitution or the presence of a thiomethyl or a methylsulfonyl group.[4]

The conversion of the precursors into the indigo or 6,6′-dibromoindigo was found to be produced by an enzyme isolated from the hypobranchial glands.[3,5] This enzyme was able to transform the initial yellow indoxyl sulfate salt (**1**) (see Scheme 1) into an indoxyl (**2**), which, upon oxidation in the presence of oxygen in the solution, formed an orange indoleninone (**3**).[5] Both the oxidized and the reduced forms collide to form a substituted 1,1′-dihydro-[2,2′]biindolyl-3,3′-one, a green dimer intermediate (**4**), which upon exposure to sunlight forms the indigo or dibromoindigo (**5**), depending on the initial substitution at the aromatic ring in the precursor. Our interest in this process is to study the contribution of the substituent effects on the formation of indigoids. Such studies are common in the literature, and most of them tend to quantify these effects on different kinds of reactions.[6–13] However, to the best of our knowledge, there have been no studies dealing with such a process where the interacting systems have similar structures and the final product formed has a structure where the electronic effects seem to be neutralized.

In this paper, we report a study carried out in order to compare the changes in the electronic structure produced

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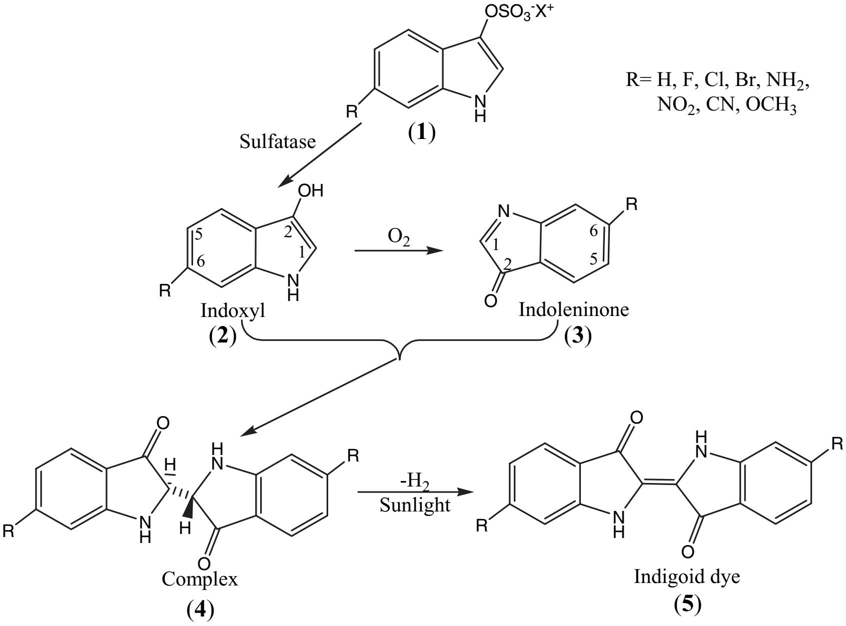

Scheme 1. Indigoid formation process proposed by Benkendorff *et al.*[27]

by a series of electron-withdrawing and electron-donating substituents on the indoxyl **2** and the indoleninone **3** and its effects on the formation of the complex **4** and the indigoid **5**. The substituent effects are discussed in terms of global and local reactivity indices obtained for the fragments, the complex and the indigoid products. Also, we discuss the contribution of these effects to the electronic spectra of indigoids.

MODEL EQUATIONS

The global electrophilicity, ω, of atoms and molecules has been defined by Parr *et al.*[14] as

$$\omega = \frac{\mu^2}{2\eta} \tag{1}$$

in terms of the electronic chemical potential μ and the chemical hardness η.[15] The electronic chemical potential, μ, describes the changes in the electronic energy with respect to the number of electrons and is usually associated with the charge-transfer ability of the system in its ground-state geometry. A very simple operational equation for μ is given in terms of the monoelectron energies of the molecular frontier orbitals HOMO and LUMO, ε_H and ε_L, by $\mu \approx (\varepsilon_H + \varepsilon_L)/2$.[15] In the same way, it is also possible to give a quantitative representation to the chemical hardness concept introduced by Parr and Pearson[16] as $\eta \approx \varepsilon_L - \varepsilon_H$.

The electrophilicity definition given in Eqn (1) introduces, in a balanced way, the propensity of the system to acquire an additional amount of electronic charge $\Delta N_{\max}$, measured by the square of the electronegativity and at the same time the resistance of the system to exchange electronic charge with the environment measured by chemical hardness.[14]

The amount of additional electronic charge, $\Delta N_{\max}$, that stabilizes the electrophile is given by[14]

$$\Delta N_{\max} = -\frac{\mu}{\eta} \tag{2}$$

Hence, while the quantity defined by Eqn (1) describes the propensity of the system to acquire additional electronic charge from the environment, the quantity defined in Eqn (2) describes the charge capacity of the molecule.

COMPUTATIONAL DETAILS

Standard DFT calculations in framework of the B3LYP approach were carried out. The B3LYP hybrid functional including the Becke[17] three-parameter exchange potential with the non-local correlation functional of Lee, Yang and Parr[18] was combined with the 6–31+G(d,p) basis set to optimize all structures considered in this study.

Time-dependent density functional theory (TD-DFT) was used to evaluate the low-lying excited states and the oscillator strengths of the indigo dyes and their fragments. As has been described in the literature,[19–21] TD-DFT generalizes DFT to a time-dependent situation wherein a system is subject to time-dependent perturbation which modifies its external potential. Kohn–Sham equations can be derived by assuming the existence of an effective potential for an independent particle model whose orbitals give the same density as that of the interacting system. Within response theory, transition energies and oscillator strengths can be determined from the response of the charge density to a perturbation. In the present work we used the TD-DFT method combined with the 6–31+G(d,p) basis set employing the B3LYP functional as implemented in the Gaussian 98 program package.[22]

Regional Fukui functions for electrophilic (f_k^-) and nucleophilic (f_k^+) attacks were obtained from a single-point calculation at the optimized structure of the ground state of molecules at the same level of calculation without diffuse function (reviews of the evaluation method of these Fukui functions have been published by Contreras and co-workers[23,24]). Within this approach, the electrophilic and nucleophilic Fukui functions condensed to atoms or groups of them were evaluated in terms of coefficients of frontier molecular orbitals involved and the overlap matrix.[23,24]

To obtain more information on the net atomic charge and the electronic charge density, the study was completed with two different electron population techniques: the natural bond orbital (NBO)[25] analysis and topological analysis of electron charge density and its Laplacian using the atoms in molecules theory of Bader.[26]

RESULTS AND DISCUSSION

In the present study we focused our interest on the interaction of indoxyl (**2**) and its oxidized form, indoleninone (**3**), to form the substituted indigo dyes (**5**). Instinctively, it could be assumed that the indoxyl fragment may be considered as the nucleophile and the indoleninone as the electrophile in the complex formation. As our main interest is to evaluate the energetic aspects of the process, we selected only three steps of the process as proposed by Benkendorff *et al.*[27] (Scheme 1). As can be deduced from Scheme 1, indoxyl sulfate salt is the natural compound used as first reactant in the formation process of indigo. The action of a sulfatase on this compound leads to indoxyl, which by oxidation forms indoleninone. In order to obtain the indigo, an intermediate complex is formed. The loss of a hydrogen molecule in the complex, on exposure to sunlight, leads to the indigoid product. To understand the substituent contribution to the formation of indigoids, we will analyze each isolated intermediate taking part in this process.

Indoxyl and indoleninone

The total energy (*E*) and also zero-point energy (*ZPE*) corrections and entropy values (*S*) for the compounds studied are reported in the Supplementary material, available at Wiley Interscience. As was mentioned above, indoleninone and indoxyl are the first intermediates in the formation of indigo, so one of them may be deemed as the electrophilic reactant while the other one can be considered as the nucleophile. To evaluate this quantitatively, we used the global electrophilicity index ω defined in Eqn (1). In Table 1, we present the electrophilicity values for indoxyl and indoleninone (fifth column). Also in Table 1 are included the Fukui functions for electrophilic (f_k^-) and nucleophilic (f_k^+) attacks, which we will discuss later. It may be seen that indoxyl oxidation leads to a good electrophile such indoleninone. Hence substituted indoleninones in Table 1 show higher electrophilicity values than the corresponding indoxyl species. If we focus our analysis on the indoleninone series, we note

Table 1. Static global and local properties of indoleninone and indoxyl in the most reactive centers at its grounds states[a]

R	C-1	C-2	N	ω (eV)	$\Delta N_{\max}$
		$f^+_{\text{indoleninone}}$			
NO_2	0.1117	0.1598	0.1174	4.94	1.639
CN	0.1376	0.1776	0.1368	4.61	1.562
Br	0.1641	0.1844	0.1532	4.04	1.486
Cl	0.1654	0.1851	0.1540	4.01	1.463
F	0.1777	0.1855	0.1601	3.90	1.424
H	0.1629	0.1907	0.1596	3.70	1.392
OMe	0.1798	0.1819	0.1991	3.40	1.371
NH_2	0.1640	0.1892	0.1579	3.25	1.404
		f^-_{indoxyl}			
NO_2	0.1922	0.2038	0.1640	2.74	1.256
CN	0.2068	0.1975	0.1557	1.65	0.873
Br	0.2230	0.1875	0.1461	1.14	0.698
Cl	0.2249	0.1907	0.1484	1.12	0.691
F	0.2364	0.1899	0.1460	1.04	0.661
H	0.2022	0.1995	0.1664	0.92	0.622
OMe	0.2276	0.1560	0.1275	0.85	0.605
NH_2	0.2099	0.1954	0.1598	0.76	0.577

[a] Global electrophilicity (ω) values are given in eV; $\Delta N_{\max}$ values are in electron units. See Scheme 1 for atom numbering.

for the halogen series an enhancement of the global electrophilicity values when the electronegativity of the substituent (R) decreases (compared with R = H as reference). This is especially observed in the halogen substitution. In fact, when the substituent is a fluorine atom, the electronegativity value of which is 3.98 in the Pauling scale, the electrophilicity power is about 3.90 eV, whereas in the case of chlorine and bromine this value is about 4.01 and 4.04 eV, respectively, where the electronegativity is about 3.16 and 2.96. Certainly, this effect is masked by the presence of substituents with important resonance and polarizability effects. In fact, the presence of delocalized π bond and an important dipole moment in indoxyls may be the main factor which would favor the latest effects on the electronegativity. This is observed in the case of NO_2 and CN substitution, which present the highest values of electrophilicity in the indoleninone series, about 4.94 and 4.61 eV, respectively. Maximum charge transfer (ΔN_{max}) is also included in Table 1. Note that the substituted indoleninones have higher values of ΔN_{max} than the substituted indoxyl systems (i.e. indoleninones have a higher charge capacity). This result is consistent with the electrophilicity values for both fragments: substituted indoleninones may act as electrophiles and the substituted indoxyls may act as nucleophiles to form the complex intermediate.

The importance of resonance and polarizability effects of the substituents is well known, where electronic transmission is facilitated by delocalized π bonds, through space and polarized bonds.[28] In order to analyze quantitatively substituent effects on the electrophilicity of the indoleninone, we adopted the Taft and Topsom's model.[28,29] This model decomposes the substituent effects into field (σ_F), resonance (σ_R) and polarizability (σ_α) effects on similar compounds. Such analysis leads to

$$\begin{aligned}\omega_{\text{indoleninone}} &= 1.510\sigma_{R+} + 0.260\sigma_{R-} + 0.309\sigma_F \\ &\quad + 1.710\sigma_\alpha + 3.697 \qquad (3) \\ n = 8 \quad R^2 &= 0.997 \quad SD = 0.047\,\text{eV}\end{aligned}$$

The good correlation obtained shows for indoleninone that the resonance and polarizability effects contribute similarly to the electrophilicity power with a slight dominance of the polarizability effect, in agreement with the analysis presented above. The field effects, as can be seen, make a small contribution. These conclusions are consistent with the maximum charge ΔN_{max} that the system may acquire from the environment, which presents a high value when the resonance and polarizability effects are important as in the cases of NO_2 and CN substituents.

However, in the indoxyl series, the conclusions should be considered carefully because the electrophilicity values are lower and, in the absence of an accurate definition of nucleophilicity, we will assume for our discussion that low electrophilicity values may be considered as nucleophilicity descriptors.[30] The application of Taft and Topsom's model leads to

$$\begin{aligned}\omega_{\text{indoxyl}} &= 0.775\sigma_{R+} + 1.537\sigma_{R-} - 2.176\sigma_F \\ &\quad + 4.690\sigma_\alpha + 0.915 \qquad (4) \\ n = 8 \quad R^2 &= 0.950 \quad SD = 0.220\,\text{eV}\end{aligned}$$

In this case, the field effect seems to make the most important contribution to the nucleophilic character of indoxyl set, whereas the polarizability effect contributes in the opposite way to the nucleophilicity power [(Eqn (4)].

After comparing the electrophilicity values of both substituted indoleninone and indoxyl systems, it is interesting to determine the most electrophilic and nucleophilic center of both compounds. Apparently, only observing the structures of these molecules, the centers C-1, C-2 and N are competitive in both compounds. In order to slice between these centers, which is the most electrophilic or nucleophilic, we calculated the condensed electronic Fukui functions f^+ for indoleninone and f^- for indoxyl at site k (k = C-1, C-2 and N; see Scheme 1 for atom numbering). The results are also summarized in Table 1, from which it can be deduced that C-1 and C-2 are the more active sites for nucleophilic attacks in the indoleninone set. Unfortunately, because of similar values obtained for this Fukui function, we cannot deduce which is the most electrophilic one center. On the other hand, the Fukui function for electrophilic attacks, i.e. f^- in indoxyl, shows that the C-1 center is slightly more nucleophilic than the C-2 center. With the same objective, we analyzed the net atomic charge on these atoms using NBO population analysis. The results are given in Table 2. Here, the C-2 atom seems to be the most favorable site for a nucleophilic attack on indoleninone. Furthermore, the NBO analysis shows that the C-1 atom

Table 2. Net NBO atomic charge on the most reactive centers

		Q (e^-)		
Compound	R	C-1	C-2	N
Indoleninone	H	0.0081	0.5017	−0.3843
	F	0.0190	0.4992	−0.3882
	Cl	0.0163	0.4991	−0.3854
	Br	0.0157	0.4990	−0.3846
	NH_2	0.0088	0.5005	−0.3840
	NO_2	0.0127	0.5009	−0.3751
	CN	0.0153	0.4994	−0.3792
	OMe	0.0170	0.4930	−0.3917
Indoxyl	H	−0.1463	0.2506	−0.5803
	F	−0.1498	0.2538	−0.5791
	Cl	−0.1442	0.2529	−0.5776
	Br	−0.1415	0.2517	−0.5771
	NH_2	−0.1482	0.2500	−0.5786
	NO_2	−0.1170	0.2494	−0.5704
	CN	−0.1262	0.2502	−0.5731
	OMe	−0.1552	0.2529	−0.5847

in the indoxyl series has a negative net charge, so the most probable site for electrophilic attacks is the C-1 atom in the indoxyl series. However, the question that we should pose now is, why does the C-1 atom of indoxyl prefer an interaction with C-1 of indoleninone? Two answers can be addressed: first, the orientation of the dipole moment of both compounds points to the direction of the interaction of these centers. It worth noting that in the case of the indoleninone series, the dipole moment orientation is more sensitive to the substituent effects than in the indoxyl series, which can affect the interaction force. Second, as the indoleninone set has an electrophilic character, the LUMO may be the molecular orbital involved in the interaction, whereas for the nucleophile, the HOMO should be the interacting molecular orbital. Let us consider the unsubstituted indoleninone and indoxyl (R = H) and analyze its frontier molecular orbitals (see Figure 1). It appears that the interaction between these compounds probably occurs with a superposition of the two molecular planes. Steric hindrance prevents an interaction between the C-2 and C-1 atoms of both compounds in order to form a symmetric complex, stabilized by a double hydrogen bond between the nitrogen atom and carbonyl oxygen. One can suggest (i) a previous proton transfer from the indoxyl enol group to the nitrogen atom of indoleninone before the interaction or (ii) first the interaction between the fragments and then a proton transfer. Because of the stability of the complex formed (see below), it was difficult to localize both processes. However, we can confirm that the interaction in this case occurs without an activation energy barrier. In fact, a simple scan calculation of the association between indoxyl and indoleninone, just varying the interacting bond distance, shows no energy barrier. Hence the process should occur without the formation of a transition state, which explains the absence of the activation energy barrier (see Fig. 2).

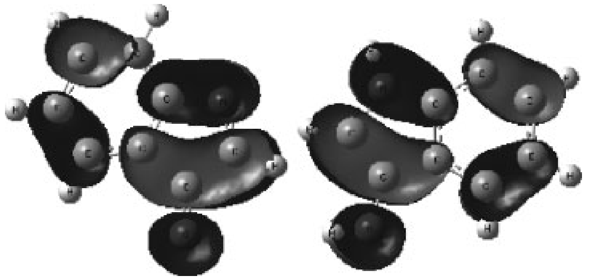

Figure 1. Indoleninone LUMO (left) and indoxyl HOMO (right)

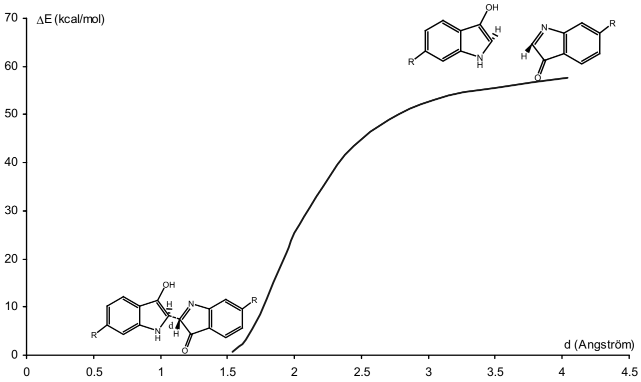

Figure 2. Potential energy curve corresponding to the complex formation between indoleninone and indoxyl

The association enthalpy of the compounds under consideration is shown in Table 3. The basis set superposition error (BSSE) which affects these binding energies was estimated using the counterpoise method of Boys and Bernardi.[31] The substituent effects are significant when one considers the values of the association enthalpy. The variations are between $-27.3\,\mathrm{kcal\,mol^{-1}}$ for $R = NO_2$ and $-36.0\,\mathrm{kcal\,mol^{-1}}$ when the substitution is NH_2 group (1 kcal = 4.184 kJ). The first conclusion that can be addressed from these results indicates that the complexation may be seen as the interaction of the most nucleophilic indoxyl compound (for $R = NH_2$, $\omega = 0.76$ eV; see Table 2) with the indoleninone. This is in accordance with the explanations given above and confirms that such interactions are led by the indoxyl dipole moment orientation. In fact, the NH_2-substituted indoxyl is the most nucleophilic one, presenting a complexation enthalpy of about $-36.0\,\mathrm{kcal\,mol^{-1}}$, whereas the NO_2- and CN-substituted indoxyls, the weak ones, present low values of $\Delta H_{\mathrm{complex}}$ of about -27.3 and $-29.1\,\mathrm{kcal\,mol^{-1}}$, respectively. Applying Taft and Topsom's model to quantify the substituent effects on the formation of the complex, an excellent correlation is obtained:

$$\begin{aligned}\Delta H_{\mathrm{complex}} &= -0.200\sigma_{\mathrm{R}+} + 3.863\sigma_{\mathrm{R}-} + 3.215\sigma_{\mathrm{F}} \\ &\quad + 10.944\sigma_{\alpha} - 32.085 \\ n = 8 \quad R^2 &= 0.980 \quad \mathrm{SD} = 0.665\,\mathrm{kcal\,mol^{-1}}\end{aligned} \tag{5}$$

This correlation shows that, for indoxyl and indoleninone complexation, the polarizability effect is dominant, which promotes strong interactions between these entities

Table 3. Calculated values for the complexation enthalpy between indoleninone and indoxyl (these values include the BSSE corrections)

R	$\Delta H_{\mathrm{complex}}$ (kcal mol^{-1})
H	−32.1
F	−33.8
Cl	−32.6
Br	−31.1
NH_2	−36.0
NO_2	−27.3
CN	−29.1
OMe	−35.9

to form a covalent bond. The resonance and field effects have similar contributions, but are small in comparison with the polarizability effect contributions.

It worth noting that the stabilization of the complex is affected by the formation of a hydrogen bond between the oxygen atom at the indoleninone carbonyl group and the hydrogen attached to the nitrogen atom in the indoxyl fragment. The substituents may contribute to force hydrogen bond formation; however, the symmetry of the complex formed suggests a partial decrease of these effects. For this purpose, a population analysis in Bader's atoms in molecules (AIM) theory was performed. The objective is to localize the bond critical points (bcps) of the hydrogen bonds and to evaluate the effects of the substituent on its electronic charge density (Table 4). The hydrogen bonds in these complexes can be classified as moderate bonds,[32–34] which can attest that the method used in our calculations describes such interactions well. Further, the electronic charge density values (see Table 4) obtained in the bcps of the hydrogen bond formed between NH and carbonyl oxygen atom show that these interactions have an electrostatic character [see the values of the charge density ρ and its corresponding energy $H(\rho)$ in the bcps]. Note that the strongest interactions are observed where the resonance substituent effect is important, i.e. for NH_2 and OMe substituents. In the case of NO_2 and CN, where this effect is practically absent, these interactions are feeble. These results are observed in both the bcp charge density and the hydrogen bond distance, reinforcing our initial hypothesis.

Indigoid dyes

The aim of this part is to analyze the contribution of substituent effects to the indigoids' electronic spectra as the final product of the process shown in Scheme 1. This subject has been widely discussed in the literature, analyzing the substituent effects on the absorption spectra.[3,4,27] The experimental data for a large set of substituted indigoids were obtained from Sadler.[35] The author concluded that the resonance effects are the most important in the maximum wavelength absorption changes. The TD-DFT calculations obtained are in agreement with the experimental data. In fact, when we plot the theoretical maximum wavelength absorption of the selected compounds versus the experimental values, we obtain a good correlation (see Figure 3). This result may be a useful proof to show that the TD-DFT method is appropriate to predict excited states in these systems. Note that in Fig. 3 we have also included the 5,5′-difluoroindigo and 5,5′-dichloroindigo that are of great interest in the dyestuffs industry. These compounds were excluded in the previous discussions in order to simplify the analysis.

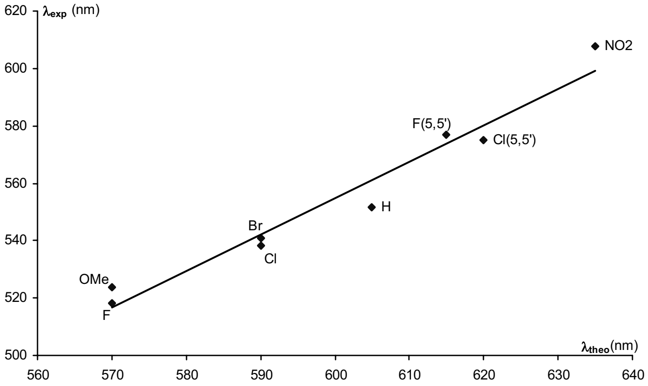

Figure 3. Linear correlation between the experimental values of the maximum absorption wavelength and the theoretical values ($R = 0.979$)

Let us inspect in more detail the information presented in Table 5. When we compare the experimental λ_{max} values with the theoretical values, the difference between them is about 50 nm. This difference may be attributed to the solvent dielectric constant where this property has been measured. Sadler proposed the existence of different resonance forms for substituted indigoids.[35] According to Sadler, these resonant structures appear when the system is excited. The inspection of the difference between HOMO and LUMO energies shows that these changes are governed by the gap between these molecules. The first excitation is essentially an electron transfer from the

Table 4. Hydrogen bond lengths d(NH—O) in the complex and electronic density charge ρ(NH—O) and the energy $H(\rho)$ in the critical bond points of these bonds

	Complex		
R	d(NH—O)	ρ(NH—O)	$H(\rho)$
H	2.2672	0.0148	−0.0004
F	2.2683	0.0147	−0.0004
Cl	2.2717	0.0146	−0.0005
Br	2.2923	0.0141	−0.0006
NH_2	2.2539	0.0152	−0.0003
NO_2	2.2864	0.0142	−0.0006
CN	2.2828	0.0143	−0.0005
OMe	2.2554	0.0152	−0.0003

Table 5. Gap and theoretical (λ_{theo}) and experimental (λ_{exp}) wavelengths of the substituted indigoids

Compound		λ_{theo} (nm)	Gap (eV)	λ_{exp} (nm)
Indigoids (6,6′)	H	551.5	2.46	605
	F	523.7	2.59	570
	Cl	538.5	2.52	590
	Br	540.8	2.51	590
	NH_2	670.7	2.11	—
	NO_2	607.9	2.24	635
	CN	568.3	2.37	—
	OMe	518.3	2.65	570
Indigoids (5,5′)	F	576.7	2.36	615
	Cl	575.2	2.38	620

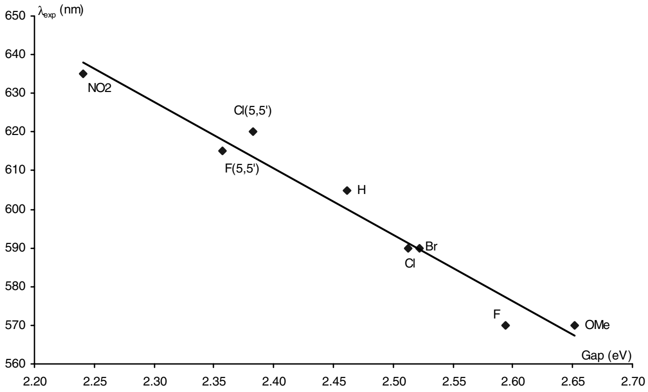

Figure 4. Linear correlation between the experimental values of the maximum absorption wavelength and the indigoid dyes gap ($\varepsilon_{LUMO}-\varepsilon_{HOMO}$) ($R=0.981$)

HOMO to the LUMO orbital. Excluding the NH_2- and OMe-substituted indigoids, where the donating resonance effects are important, the gap presents an excellent correlation with Taft and Topsom's substituent parameters:

$$\begin{aligned}\text{gap} &= -0.060\sigma_{R+} + 0.057\sigma_{R-} + 1.044\sigma_F \\ &\quad - 1.510\sigma_\alpha + 2.461 \qquad (6)\\ n &= 6 \quad R^2 = 0.999 \quad \text{SD} = 0.007\,\text{eV}\end{aligned}$$

From Eqn (6), we can observe that the resonance effects do not make an important contribution to the change in the energy gap. The field effects appear to be the most important to increase the gap, whereas the polarizability effects seem to be responsible for the energy gap decrease. The last effect produces a hypsochromic shift of λ_{max}, using as a reference the unsubstituted indigoid (R = H). When the resonance effect is important, as in the case of NH_2, the gap is diminished, resulting in a bathochromic shift of the λ_{max} (gap = 2.11 eV, λ_{theo} = 670.7 nm). In contrast, in the case of the OMe, where the field and resonance effects are competitive, the λ_{max} shift is hypsochromic (gap = 2.65 eV, λ_{theo} = 518.3 nm). This result probably shows the importance of the field effect on the absorption spectra. Summarizing, we can conclude that the λ_{max} shift depends on the gap, which is confirmed by the good correlation obtained between the gap and experimental λ_{max} values (see Fig. 4).

CONCLUSION

Substituent effects on indoxyls, indoleninones, the complex intermediates and the indigoid systems have been discussed. In terms of the global electrophilicity, indoleninones are classified as electrophiles and indoxyls as nucleophiles. Although the electrophilic site in indoleninone is not clearly identified using the electrophilic Fukui function, the nucleophilic site in indoxyl is clearly established. The NBO analysis is in agreement with these results. The interaction between these fragments, in order to form the complex, is governed by the indoxyl nucleophilic character. The planar superposition of indoxyl and indoleninone is the most probable route for the complex formation, being stabilized by hydrogen bond interactions.

The substituent effects on the indigoid dyes have been discussed in terms of the shift of maximum wavelength absorption in the electronic spectra. Our results show a good correlation between the gap of the indigoids and the experimental λ_{max} values. It seems that the substituents' polarizability and field effects play an important role in the maximum wavelength absorption.

Supplementary material

The total energy (E) and also zero-point energy (ZPE) corrections and entropy values (S) for the compounds studied here and the Cartesian coordinates for the whole series are available in Wiley Interscience.

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REFERENCES

1. Fouquet H, Bielig HJ. *Angew. Chem. Int. Ed. Engl.* 1971; **10**: 816–817.
2. Baker JT. *Endeavour* 1974; **33**: 11–17.
3. Benkendorff K, Bremner JB, Davis AR. *J. Chem. Ecol.* 2000; **26**: 1037–1050.
4. Baker JT, Sutherland MD. *Tetrahedron Lett.* 1968; 43–46.
5. Baker JT, Duke CC. *Aust. J. Chem.* 1973; **26**: 2153–2157.
6. Khuong KS, Beaudry CM, Trauner D, Houk KN. *J. Am. Chem. Soc.* 2005; **127**: 3688–3689.
7. Kassaee MZ, Arshadi S, Ahmadi-Taheri N. *J. Mol. Struct. (Theochem)* 2005; **715**: 107–115.
8. Simon-Manso Y. *J. Phys. Chem. A* 2005; **109**: 2006–2011.
9. Barbour JB, Karty JM. *J. Phys. Org. Chem.* 2005; **18**: 210–216.
10. Ishiwata A, Ito Y. *Syn. Lett.* 2003; 1339–1343.
11. Lamsabhi AM, Bouab W, Esseffar M, Alcami M, Yanez M, Abboud JLM. *New J. Chem.* 2001; **25**: 509–517.
12. Firdoussi AE, Esseffar M, Bouab W, Lamsabhi AM, Abboud JLM, Mo O, Yanez M. *New J. Chem.* 2003; **27**: 1741–1747.

13. Esseffar M, Bouab W, Lamsabhi A, Abboud JLM, Notario R, Yanez M. *J. Am. Chem. Soc.* 2000; **122**: 2300–2308.
14. Parr RG, Szentpaly LV, Liu S. *J. Am. Chem. Soc.* 1999; **121**: 1922–1924.
15. Parr RG, Yang W. *Density Functional Theory of Atoms, Molecules*. Oxford University Press: New York, 1989.
16. Parr RG, Pearson RG. *J. Am. Chem. Soc.* 1983; **105**: 7512–7516.
17. Becke AD. *J. Chem. Phys.* 1993; **98**: 5648–5652.
18. Lee C, Yang W, Parr RG. *Phys. Rev. B* 1988; **37**: 785–789.
19. Stratmann RE, Scuseria GE, Frisch MJ. *J. Chem. Phys.* 1998; **109**: 8218–8224.
20. Casida ME, Jamorski C, Casida KC, Salahub DR. *J. Chem. Phys.* 1998; **108**: 4439–4449.
21. Bauernschmitt R, Ahlrichs R. *Chem. Phys. Lett.* 1996; **256**: 454–464.
22. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98*. Gaussian: Pittsburgh, PA, 1999.
23. Contreras RR, Fuentealba P, Galvan M, Pérez P. *Chem. Phys. Lett.* 1999; **304**: 405–413.
24. Fuentealba P, Pérez P, Contreras R. *J. Chem. Phys.* 2000; **113**: 2544–2551.
25. Reed A, Weinstock RB, Weinhold F. *J. Chem. Phys.* 1985; **83**: 735–746.
26. Bader RFW. *Atoms In Molecules: a Quantum Theory.* Clarendon Press: Oxford, 1990.
27. Benkendorff K, Bremner JB, Davis AR. *Molecules* 2001; **6**: 70–78.
28. Taft RW, Topsom RD. *Prog. Phys. Org. Chem.* 1987; **16**: 1–45.
29. Hansch C, Leo A, Taft RW. *Chem. Rev.* 1991; **91**: 165–195.
30. Domingo LR, Aurell MJ, Pérez P, Contreras R. *Tetrahedron* 2002; **58**: 4417–4423.
31. Boys SF, Bernardi F. *Mol. Phys.* 1970; **19**: 553–559.
32. Garza J, Ramirez J-Z, Vargas R. *J. Phys. Chem. A* 2005; **109**: 643–651.
33. Vargas R, Garza J, Dixon DA, Hay BP. *J. Am. Chem. Soc.* 2000; **122**: 4750–4755.
34. Vargas R, Garza J, Friesner RA, Stern H, Hay BP, Dixon DA. *J. Phys. Chem. A* 2001; **105**: 4963–4968.
35. Sadler PW. *J. Org. Chem.* 1956; **21**: 316–318.