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Published on Web 01/19/2006

# Thioindigo Dyes: Highly Accurate Visible Spectra with TD-DFT

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***Abstract:*** The structure and visible spectra of a large panel of thioindigo dyes and derivatives have been evaluated using a TD-PBE0/6-311+G(2d,p)//PBE0/6-311G(d,p) approach explicitly taking bulk solvent effects into account by means of the polarizable continuum model. The influence of the solvent characteristics, the trans−cis isomerization, and the chemical substitution on the benzene rings have been investigated. In addition, hemi-thioindigo dyes, thiazine-indigo, chromophore-like molecules, and selenoindigo have been considered. Though the relative oscillator strengths of the two allowed visible transitions in the nonplanar cis isomers are not always correctly reproduced by theory, the agreement between theoretical and experimental results is far above expectations. For the 170 cases studied, we obtained a mean unsigned error on the predicted $\lambda_{\max}$ limited to 6.9 nm or 0.03 eV, with only 6 (4) cases for which the difference exceeds 20 nm (0.10 eV). These errors are 1 order of magnitude smaller than what has previously been reported for indigoids. A linear correlation between the central double bond length and the $\lambda_{\max}$ has been established, while the bond length and vibrational frequency of the carbonyl groups do not correlate with the thioindigo color. The higher excitation energies of the cis conformers, compared to the trans structures, result from a less stabilized LUMO in the former case. Indeed, for cis thioindigo, the two electron-rich (in the excited state) carbonyl units lie close to each other.

## I. Introduction

Indigo and its 6,6′-dibromo derivative Tyrian Purple are known since antiquity and were already industrially produced at that time, by extraction from vegetal species and Murex seashells, respectively.[1−4] In the early times of organic chemistry, the synthesis of indigo and its precursor, indoxyle, was performed using various strategies by von Bayer, Heumann and co-workers so that by 1914 only 4% of the world production of indigo had a plant origin. As efficient vat dyes, indigoids (Figure 1) are still today one of the most widely used blue-jeans dyes with a production of ∼15 000 tons per year. The reduced (leuco, colorless) chemical form is highly soluble in water and is used in a large dyeing bath, the color appearing after simple oxidation by air-drying. At the beginning of the 20th century, huge efforts motivated by industrial applications[5] have been performed to synthesize new dyes based on the indigo core. The modifications proposed can be classified into two categories. On one hand, one finds substitution of the outer phenyl rings in 4-to-7 positions by methyl, halogens, methoxy, ... groups.[6] In this way, a large panel of symmetrically disubstituted indigoids have been obtained. On the other hand, modifications of the chromophoric center have been achieved by replacing one or two N−H group(s). An early example of this second category is thioindigo, reported by Friedländer in 1906.[7,8] In thioindigo, one has substituted nitrogen with sulfur atoms (X = S in Figure 1), removing internal hydrogen bonds of indigo and leading to an hypsochromic shift of the maximal wavelength of absorption, and finally allowing a trans−cis isomerism. Remarkably, the hypso-shift was already pointed out by Friedländer in 1908,[9] as he measured the first $\lambda_{\max}$ of thioindigo: 547 nm in chloroform, in quantitative agreement with much more recent data.[10,11] To our knowledge, the first investigations of 4-to-7 substitution effects on thioindigo are due to Ettinger and Friedländer,[12] Formanek,[13] Gindraux,[14] and Hixson and Cauwenberg.[15,16] From World War II to the 1970s, three major groups of researchers studied the UV spectra of

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**10.1021/ja056676h CCC: $33.50**

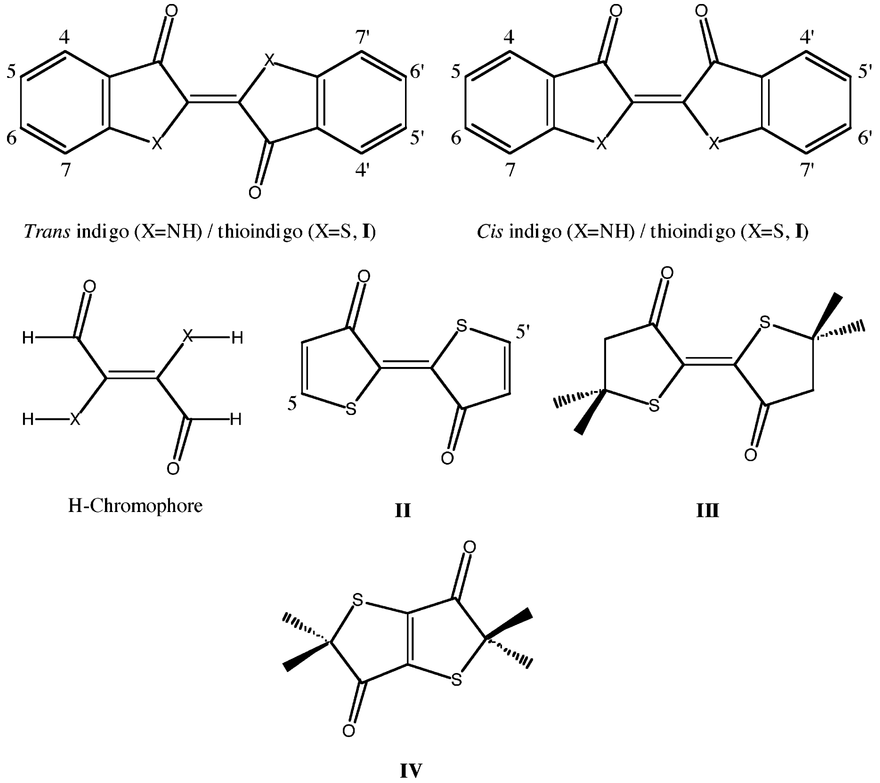

***Figure 1.*** Sketch of trans (top left) and cis (top right) indigoids. The H-shaped chromophore and three molecules representative of the chromophoric system of thioindigo are also depicted.

thioindigo. The major focus of the first group, led by Lüttke, was the determination of the structure of the chromophoric unit of indigoids. Using a combination of (semi-)empirical calculations and innovative chemical synthesis, Lüttke and his collaborators determined the nature of the chromophore, namely the H-shaped molecule depicted in Figure 1.[17−21] They also studied the cis−trans isomerism of chromophore-like molecules **II** and **III** (Figure 1),[11,21−24] as well as the impact of elongation of the conjugation path on the $\lambda_{\max}$ of **III**.[11,25] The second group, directed by Wyman at the National Bureau of Standards of the U.S.A., assessed the variations in the UV/vis spectra, resulting from the trans−cis isomerization of substituted thioindigo.[26−30] Mechanistic studies of the isomerization, which can be achieved by exposure of thioindigo to the appropriate light, as well as fluoresence measurements of thioindigoids, have been performed later on by Wyman[30,31] and others.[32−38] The third contributors, Dokunikhin and Gerasimenko, based in the U.S.S.R., assessed the auxochromic shifts resulting from substitution of thioindigo by chemical groups (nitro, sulfonate, ...).[39−45] Apart from these three groups, several other contributions dealing with the chemistry of thioindigo or closely related compounds are available.[10,46−57] One can especially point out von Heller's cristallographic studies.[58] More recently, thioindigo derivatives

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have been the focus of several works,[59−69] and in particular, thioindigo derivatives substituted by chiral groups are used by Lemieux and its collaborators as dopant in liquid crystal technology,[60,66−68] allowing photoalignement.[70]

This work aims at predicting and rationalizing the $\lambda_{max}$ of a series of trans and cis isomers of thioindigo by using ab initio quantum chemical approaches. The major difficulty in determining the color of organic compounds is the astonishing accuracy of the standard human eye, which can distinguish, in some parts of the visible spectra (typically in the green region), differences of coloration corresponding to less than 1 nm $\lambda_{max}$ shifts. In today's quantum chemistry, such an accuracy could only be (possibly) obtained for gas-phase molecules with highly correlated methods, like EOM-CC using high-order excitations and very extended basis sets. This approach is completely out of computational reach for dyes, molecules possessing numerous $\pi$-electrons and used in solution. Nevertheless, in regards to practical industrial applications, the target properties are the relative auxochromic shift amplitudes. When theoretical calculations reach correct estimates of these shifts (±5−10 nm) as well as reasonable $\lambda_{max}$ values (±10−15 nm), they could be regarded as serious competitors to experimental approaches for developing new dyes and/or pigments. Such a "chemical" accuracy for large molecules is still a real challenge for the modelization approaches. In view of the results obtained since the 1960s, the semiemperical methods, which are particularly useful in gaining chemical insights, are not able to consistently deliver quantitative $\lambda_{max}$ of indigoids. For instance, Miehe et al. undershoot the $\lambda_{max}$ of $N,N'$-alkyl indigo by ~100 nm using a PPP-CI approach,[71] whereas INDO/S and CNDO/S approaches underestimate the $\lambda_{max}$ of indigo by 131 and 229 nm, respectively.[72] Recently, Fabian also pointed out the (nonunderstood) failure of the popular ZINDO method for thioindigo: ZINDO predicts the first absorption peak of **I** in the near-UV region (311 nm).[73] Even much more elaborated approaches could be relatively disappointing. For instance, Serrano-Andrès and Roos using CAS-PT2 reproduced very accurately the shape of the spectra of indigo,[74] but their gas-phase $\lambda_{max}$ of 633 nm (1.96 eV)[74] is about 90 nm above the experimental gas-phase values (539,[75,76] 540,[19] or 546 nm[77,78]) although in nice agreement with measurements in polar solvents (606−610 nm in ethanol[17−19,62,79] and 619−620 nm in DMSO[19,76]). On top of that, it is still difficult to routinely apply techniques such as CAS-PT2, EOM-CC, ... on a large set of dyes. Actually, the most promising scheme for evaluating the color of dyes in a systematic fashion is the time-dependent density functional theory (TD-DFT).[80] Indeed, TD-DFT is often found robust and efficient for evaluating the low-lying excited spectrum of conjugated molecules[81−84] and has been the subject of countless applications.[85−96] In addition, bulk solvent effects can be accounted for when using TD-DFT.[97] We are aware of a few previous TD-DFT investigations for indigoids.[73,98−100] Using B3LYP/6-31G(d), Guillaumont and Nakamura,[98] on one hand, and Xue and co-workers,[99] on the other hand, studied indigo derivatives, but the differences reported between gas-phase theoretical and solvated experimental $\lambda_{max}$ are quite large (~60 nm on average). The spectrum of thioindigo was predicted by Fabian[73] using a TD-B3LYP/6-31+G(d)//B3LYP/3-21G scheme: a $\lambda_{max}$ in perfect agreement with vapor experiment[19] (508 nm) was obtained,[101] but the spectral shift between **I** and **III** (Figure 1) was estimated to be −36 nm, only half of the experimental value in the gas phase (−77 nm).[11,19] However, as we pointed out in a recent methodological contribution,[100] these large discrepancies might be related to the use of a small basis set and the complete neglect of solvent effects that are sizable for indigoid dyes, which display strong positive solvatochromism effects.[77,78]

In this paper, we demonstrate the high accuracy of TD-DFT for the spectra of thioindigo dyes, once extended basis sets are selected and bulk solvent effects are accounted for. The method developed is also successfully applied to hemithioindigo, selenoindigo, and molecules representative of the chromophore.

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(101) Fabian compares his theoretical peak with $CHCl_3$ measurements in his paper.

***Table 1.*** Comparison between Theoretical and Experimental $\lambda_{\max}$ (nm)[a]

| | | theory | | experiment | | |
|---|---|---|---|---|---|---|
| structure | solvent | trans | cis | trans | cis | ref |
| **I** | vapor | 520 | | 508 | | 19 |
| | cyclohexane | 540 | | 537/536 | | 11,10/34 |
| | $CCl_4$ | 541 | | 540/541 | | 10/17,19 |
| | benzene | 542 | 489 | 546/545/545/543 | 485/ /486/484 | 11/26,29/31,30,34/40,10 |
| | toluene | 542 | 489 | 542 | 485 | 32 |
| | xylene | 542 | | 545/525/543/544 | | 127,128/49,110/43/13,10,19 |
| | $CHCl_3$ | 544 | 495 | 547/546/550/548/546/548/541 | /490/ / / /491/ / | 9/26,27/129/10/21/11/24 |
| | TCE | 545 | | 551 | | 18,19 |
| | EtOH | 544 | | 543/542 | | 18,19,20/10,11,62 |
| | DMF | 548 | | 543 | | 10,130 |
| **II** | $CHCl_3$ | 494 | 465 | 505/505 | /476 | 21/11 |
| | TCE | 495 | | 506 | | 18 |
| | EtOH | 494 | | 502 | | 18,20 |
| 5,5′-Me-**II** | EtOH | 470 | | 484 | | 18 |
| **III** | vapor | 439 | | 431 | | 22,11 |
| | cyclohexane | 454 | 410 (400) | 450/450 | 394/ | 11,23,24/62 |
| | benzene | 456 | 411 (400) | 452/454/454 | 397/400/ | 11/31/62 |
| | $CHCL_3$ | 456 | 414 (402) | 459/458/458 | /406/ | 11,24/21/62 |
| | EtOH | 455 | 416 (396) | 453/453 | 407/ | 11,23/62 |
| **IV** | cyclohexane | 469 | | 467 | | 24 |
| | $CCl_4$ | 469 | | 466 | | 24 |
| | benzene | 471 | | 467 | | 24 |
| | $CHCL_3$ | 472 | | 467 | | 24 |
| | EtOH | 473 | | 460 | | 24 |

[a] The theoretical values have been computed with the PCM-PBE0/6-311+G(2d,p)//PCM-PBE0/6-311G(d,p) approach.

## II. Computational Details

We have chosen the Gaussian03[102] package of programs to perform the geometry optimizations, vibrational analysis, and excited-state evaluations.

The ground-state geometry of each molecule has been fully optimized. From our previous investigation,[100] it turned out that Adamo and Barone's PBE0[103] hybrid functional combined with the split-valence triple-$\zeta$ polarized 6-311G(d,p) basis set provides adequate ground-state geometries. For thioindigo in benzene, using 6-311G(2df,p) instead of the 6-311G(d,p) for ground-state minimization would only modify the C−S distances by 0.01 Å and the $\lambda_{\max}$ by +1 nm. PBE0 is built on the Perdew−Burke−Ernzerhof pure functional,[104] in which the exchange is weighted (75% DFT/25% HF) accordingly to theoretical considerations.[105] Following each optimization, the vibrational spectrum has been determined and it has systematically been checked that all vibrational frequencies are real.

TD-DFT[80] methodology is then used to compute the low-lying excited states of thioindigo derivatives. Consistent with ref 100, the PBE0/6-311+G(2d,p) level has been chosen. Note that this basis is more extended than in most previous TD-DFT investigations on dyes. Actually, using 6-311+G(d,p) instead of 6-311+G(2d,p) would lead to nonconverged $\lambda_{\max}$,[100] while using 6-311+G(2df,p) instead of 6-311+G(2d,p) does not change significantly the computed $\lambda_{\max}$ (543 nm instead of 542 nm in benzene). As expected for dyes, the electronic excitation responsible for the color of thioindigo present a typical $\pi \rightarrow \pi^*$ character often associated with a large oscillator force. For the trans isomers, the reported $\lambda_{\max}$ always corresponds to the transition energy toward the first dipole-allowed excited state. For some cis isomers, two low-lying excited states, close in energy, present nonnegligible oscillator forces. In that case, both positions are given that with the smallest transition probability between brackets.

At each stage, the bulk solvent effects are evaluated by means of the Polarizable Continuum Model (PCM).[97,106] In PCM, one divides the problem into a solute part (thioindigo) lying inside a cavity and a solvent part (in our case, cyclohexane, tetrachloromethane, benzene, toluene, xylene, chlorobenzene, chloroform, tetrachloroethane, ethanol, dimethylsulfoxyde, and dimethylformamide) represented as a structureless material, characterized by its dielectric constant, radius, density, molecular volume, ... Three solvents, namely xylene, tetrachloroethane (TCE), and dimethylformamide (DMF), are not defined in Gaussian03.[102] Therefore we tuned the parameters of related molecules, namely, toluene, dichloroethane, and dimethylsulfoxyde.[107−109] PCM is able to obtain a valid approximation of solvent effects as long as no specific interactions (such as hydrogen bonds, ion pairing, ...) link the solute and the solvent molecules. Such specific interactions are unlikely in a benzene or $CCl_4$ solution but quite probable with EtOH, as hydrogen bonds can be formed with the carbonyl groups or the sulfur lone pairs. Because we study UV/vis spectra, we have selected the nonequilibrium PCM solutions.[97] Indeed the absorption process presents a short characteristic time. Therefore, only the solvent electronic distribution can "adapt" to the new (excited) electronic structure of the solute, while molecular motions of the solvent are frozen during the process.[97]

## III. Results

**A. Chromophore-like Compounds.** In Table 1, the experimental and theoretical $\lambda_{\max}$ of thioindigo and molecules representative of its chromophore are compared. First we note

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(102) Frisch, M. J. et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(103) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158−6170.

(104) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(105) Perdew, J. P.; Ernzerhof, M.; Burke, K. *J. Chem. Phys.* **1996**, *105*, 9982−9985.

(106) Amovilli, C.; Barone, V.; Cammi, R.; Cancès, E.; Cossi, M.; Mennucci, B.; Pomelli, C. S.; Tomasi, J. *Adv. Quantum Chem.* **1998**, *32*, 227−261.

(107) Xylene, as toluene, except for: EPS = 2.27, RSOLV = 3.01, VMOL = 123.7 which have been set following available physicochemical data. Note that, in the older experiments, the relative position of the methyl groups (i.e., ortho, meta, or para) is not given. The above parameters correspond to *p*-xylene which is used in the most recent experiments.

(108) 1,1′,2,2′-Tetrachloroethane, as 1,2-dichloroethane, except for: EPS = 8.20, RSOLV = 2.90, VMOL = 105.2 which have been set following available physicochemical data.

(109) Dimethylformamide, as DMSO, except for: EPS = 36.70, RSOLV = 2.44, VMOL = 69.6 which have been set following available physicochemical data.

that discrepancies of a few nanometers (typically 1 to 2 nm, but up to 9 nm in $CHCl_3$) are not uncommon between different measurements, although some variations could originate in the unit conversion performed on the basis of three-digit $cm^{-1}$ results of refs 26 and 27. One can also conclude that the 525 nm $\lambda_{max}$ reported for **I** by Guha in xylene[49,110] is either a misprint (545) or an experimental error.

For solvated thioindigo, **I**, there is a nice agreement between experimental and theoretical $\lambda_{max}$ for both trans and cis forms: the differences do not exceed 6 nm. Moreover, the hypsochromic shift resulting from trans−cis isomerization is only very slightly underestimated (−53 nm instead −59 nm of in benzene). The more sizable discrepancy, 12 nm, for the gas-phase excitation spectra, could result from the high temperature used to "vaporize" thioindigo (unspecified but probably close to 700 K[76,78] like for indigo). At this temperature, vibrations could substantially deform the planar structure, likely resulting in larger average excitation energies. Quite interestingly, the experimental $\lambda_{max}$ are consistently larger in $CHCl_3$ and TCE than in ethanol and DMF, though the latter present larger dielectric constants. For indigo, the reverse is observed: the excitation energies are smaller in ethanol than in chloroform.[79] The strong solvatochromism effect in indigo has been interpreted as a result of hydrogen bonds between ethanol (and other H-bonds solvents) and the carbonyl groups, weakening the C═O double bond strength and easing the excitation.[79] Therefore, for thioindigo, there is either an unusual solvation process with "polar" chlorine solvents or the formation of hydrogen bonds between sulfur atoms and ethanol that would compensate for the Coulombic (dielectric) effect. Even if the PCM approach is not designed to reproduce such refined effects, it always provides accurate $\lambda_{max}$ in all selected solvents and acceptable solvatochromism shifts for unchlorinated solvents (+8 nm instead of +6/+7 nm between cyclohexane and DMF).

Though smaller than **I**, **II**, **III**, and **IV** present comparable $\lambda_{max}$, as demonstrated by Lüttke.[11,18,21−24] For **II** the theoretical $\lambda_{max}$ are too small by ∼ −10 nm, but the trans−cis shift, which is about half the value of thioindigo, is perfectly reproduced (−29 nm in $CHCl_3$). Adding methyl groups in 5 and 5′ positions increases the excitation energy, as correctly foreseen by our model (−24 nm versus −18 nm in the experiment). **III**, the prototype of the H-chromophore, has been extensively studied in the late 1960s.[11,21−23] In most solvents, the hypsochromic shift only amounts to −90 nm, although **III** possesses only one-third of the $\pi$ electrons of **I**. In the gas phase, PCM-PBE0 predicts a −81 nm displacement, in much better agreement with the −77 nm experimental value than the −36 nm reported by Fabian using gas-phase B3LYP.[73] For the trans conformer of **III**, the agreement between theory and experiment is excellent, the differences for solvated $\lambda_{max}$ being consistently smaller than 5 nm. For the cis isomers, a nonplanar structure with the central CCCC dihedral angle around −6° to −7° is obtained. Consequently, two allowed transitions close in energy are predicted, with the higher-energy transition displaying a smaller oscillator strength. In the measurements, there is only one maximum either between our two peaks or closer to the second one. At this stage it is not possible to determine if our approach overshoots the cis $\lambda_{max}$ by ∼10 nm or does not provide a correct balance between the transition probabilities. For **IV**, the parallelism between Luhmann measurements and TD-DFT results is again exceptional, with discrepancies limited to 5 nm, except in EtOH for which the experimental $\lambda_{max}$ is surprisingly smaller than that in cyclohexane.

**B. Substitution of Thioindigo.** In Tables 2 and 3, we compare theoretical PCM-PBE0/6-311+G(2d,p)//PCM-PBE0/6-311G(d,p) $\lambda_{max}$ with available experiments for 4-to-7 substituted thioindigo. This represents an extended set of 55 substitution patterns with various solvents and conformers, for a total of 100 cases. As for the unsubstituted dye, small discrepancies between experiments (1 to 3 nm) can be noticed. For compounds with multiple available experiments, we use for comparisons the average value of the measurements. However, some of the $\lambda_{max}$ reported by Guha[49,110] jar. Indeed, he reported 494 nm for 7,7′-Me in xylene, whereas other available experiments give 551 nm (in benzene) and 548 nm (in xylene). Likewise, the 540 nm $\lambda_{max}$ for 4,4′-OMe looks too small in regards to the figures in TCE.[111] Therefore, we do not consider the results of refs 49 and 110 in our discussion.

It has often been argued in the literature that the smaller $\lambda_{max}$ for the cis conformers originates from their nonplanar conformation. This assumption is only partially supported by our results. Indeed, we found that most cis thioindigo are planar. Actually, for the present set of dyes, only a substitution in 4,4′ positions leads to an off-planar ground state, regardless of the position and nature of the groups in 5-to-7 (and 5′-to-7′) positions. The central CCCC dihedral angles of nonplanar cis conformers are reported in Table 4. The deformations are always moderate (4°−5°), smaller in $CHCl_3$ than in benzene and almost independent of the substituents nature. Only one methyl group in the 4 position (hydrogen in 4′) is sufficient to induce the twisting, but to a smaller extent. As a consequence of the symmetry breaking, one finds two allowed transitions for cis thioindigo with substituents in 4,4′, whereas the experimentalists report only one transition. However, the ordering of the transition probabilities for these two peaks is molecule-dependent. In the large majority of cases, it is clear that the most hypso peak is in better agreement with experiment, regardless of the relative theoretical oscillator strengths. As it is likely that the positions of the peaks are more adequately reproduced by TD-DFT than the transition probabilities, we systematically select the theoretical hypso-peak for comparisons.

To gain further insight into the trans−cis hypso-shift, we have drawn in Figure 2 the HOMO and LUMO of a typical thioindigo with a planar cis conformer. Indeed, the first dipole-allowed transition presents a strong HOMO → LUMO character for both conformers. As expected, the frontier orbitals show $\pi$ characters, are mainly centered on the H-chromophore, and are similar for both conformers. The excitation related to the $\lambda_{max}$ corresponds to a typical $\pi \rightarrow \pi^*$ transition in conjugated organic molecules: the HOMO lies on the sulfur atoms and the central C═C bond, whereas the LUMO is centered on the single C−C bonds and oxygen atoms. The lower transition energy for the trans thioindigo results from the fact that, in that conformation, each sulfur loosing electron density is stabilized by a nearby C═O unit that gains electron density, while, in the excited state of cis conformers, both now-electron-deficient sulfurs lie close

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(110) Guha, S. K.; Chatterjea, J. N.; Mitra, A. K. *Chem. Ber.* **1961**, *94*, 2295−2305.

(111) If this 540 nm shift is confirmed, this would be the largest solvatochromic (+14 nm) shift between benzene-like solvent and $CHCl_3$/TCE.

***Table 2.*** Theoretical and Experimental $\lambda_{max}$ (nm) for Symmetrically Disubstituted **I**

| | | theory | | experiment | | |
|---|---|---|---|---|---|---|
| substituent | solvent | trans | cis | trans | cis | ref |
| 4,4′-Cl | benzene | 546 | 491 (513) | 548 | 486 | 30 |
| | xylene | 546 | | 545 | | 13 |
| 4,4′-OMe | xylene | 553$^a$ | | 540 | | 110 |
| | TCE | 552$^a$ | | 554 | | 12 |
| 5,5′−F | benzene | 565 | | 559 | | 45 |
| 5,5′-Br | benzene | 564 | 508 | 559/555 | /496 | 34/40 |
| | xylene | 564 | | 556 | | 13 |
| 5,5′-Cl | benzene | 563 | | 559 | | 40 |
| | xylene | 563 | | 548 | | 13 |
| 5,5′-Me | benzene | 556 | | 558 | | 40 |
| | xylene | 556 | | 562/556 | | 49/128 |
| 5,5′-CF$_3$ | benzene | 535 | | 535 | | 45 |
| 5,5′-Et | cyclohexane | 553 | | 546 | | 131 |
| | benzene | 555 | | 558 | | 131 |
| | xylene | 555 | | 555 | | 128 |
| 5,5′-*i* Pr | xylene | 556$^a$ | | 556 | | 128 |
| 5,5′-*t* Bu | cyclohexane | 551$^a$ | | 548 | | 131 |
| | benzene | 553$^a$ | 497$^b$ | 554 | 492 | 30 |
| | xylene | 554$^a$ | | 556 | | 128 |
| 5,5′-NO$_2$ | benzene | 531 | | 513 | | 39 |
| 5,5′-OMe | xylene | 605$^a$ | | 588 | | 110 |
| | TCE | 613$^a$ | | 590 | | 12 |
| 5,5′-OCF$_3$ | benzene | 549 | | 549 | | 45 |
| 5,5′-OEt | benzene | 605 | | 588 | | 42 |
| 5,5′-SCF$_3$ | benzene | 538 | | 548 | | 45 |
| 5,5′-SO$_2$Me | xylene | 534 | | 519 | | 43 |
| 6,6′-Br | xylene | 534 | | 540 | | 13 |
| 6,6′-Cl | benzene | 532 | | 535 | | 30 |
| | xylene | 532 | | 539/538 | | 13/13 |
| 6,6′-NO$_2$ | benzene | 585 | | 567 | | 39 |
| 6,6′-OEt | benzene | 507 | 462 | 515/515/515/516/516/517 | 459/458/ /460/458/459 | 26/29/42/31/30/34 |
| | xylene | 506 | | 519 | | 13 |
| | CHCl$_3$ | 508 | 468 | 521 | 467 | 26 |
| 6,6′-SEt | xylene | 522$^a$ | | 535 | | 13 |
| 6,6′-SO$_2$Me | xylene | 559 | | 558 | | 43 |
| 7,7′-Br | benzene | 546 | | 546 | | 40 |
| 7,7′-Cl | benzene | 546 | 493 | 545/544 | 488 | 40/30 |
| 7,7′-Me | benzene | 545 | | 551 | | 40 |
| | xylene | 545 | | 494/548 | | 49/128 |
| 7,7′-Et | xylene | 543 | | 549 | | 128 |
| 7,7′-*i* Pr | xylene | 551$^a$ | | 549 | | 128 |
| 7,7′-*t* Bu | xylene | 550 | | 549 | | 128 |
| 7,7′-NO$_2$ | benzene | 519 | | 524 | | 39 |

$^a$ *NoAddSph* PCM option. $^b$ Gas-phase geometry optimization.

together and destabilize each other. The same picture holds for the now-electron-rich carbonyls.

In Tables 2 and 3, the agreement between theoretical and experimental values is excellent, especially for halogens and alkyl substituents, whereas sizable differences appear for nitro and methoxy/ethoxy substituents, especially in 5,5′ positions. Figure 3 provides the graphical comparison with limits for the ±10 nm deviations. Considering that this figure is built using different solvents, two conformers, and various substituent natures (alkyl groups, halogens, sulfonates, ...), the TD-DFT accuracy is extremely impressive. For the 78 trans conformers, the mean signed error (MSE) is −0.8 nm (the theory slightly overestimating the experiment), the mean unsigned error (MUE) amounts to 7.0 nm, the median unsigned error (ME) amounts to 5.0 nm, the residual mean square deviation (RMS) is 11.0 nm, and only 20% (16/78) of the estimations differ from the experiment by more than 10 nm. The corresponding values in eV are MSE = 0.001 eV, MUE = 0.028 eV, ME = 0.020 eV, RMS = 0.042 eV. Only two cases with deviations exceeding 25 nm/0.100 eV have been found: 5-OEt,5′-NO$_2$ and 5-OEt,6′-NO$_2$. They correspond to push−pull like molecules with a significant charge transfer between the donor and the acceptor groups, a known difficult case for DFT, which tends to overshoot the amount of transferred charge and consequently underestimate the excitation energy.[112−114] If one considers only trans thioindigoids with, at least, one substituent in the 4 or 4′ position, the MUE amounts to 5.1 nm. The corresponding values are 7.7, 9.3, and 3.9 nm for the 5, 6, and 7 positions, respectively. The larger differences in the 5 and 6 positions primarily originate from the strongly electroactive groups (nitro, ethoxy) in these positions. For the 22 cis molecules, we found similar results: MSE = −2.0 nm (0.011 eV), MUE = 7.2 nm (0.036 eV), ME = 3.5 nm (0.031 eV), RMS = 9.1 nm (0.045 eV), and 23% (5/22) of the dyes for which the theory/experiment disagreement exceeds 10 nm (and only one case the theoretical error is above 0.1 eV). Given the good accuracies obtained for both unsubstituted and substituted thioindigo, it is foreseen that the spectral shifts are also well predicted. Indeed, the evaluation

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(112) Champagne, B.; Perpète, E.; Jacquemin, D.; van Gisbergen, S.; Baerends, E.; Soubra-Ghaoui, C.; Robins, K.; Kirtman, B. *J. Phys. Chem. A* **2000**, *104*, 4755−4763.
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(114) Dreuw, A.; Head-Gordon, M. *J. Am. Chem. Soc.* **2004**, *126*, 4007−4016.

***Table 3.*** Theoretical and Experimental $\lambda_{\max}$ (nm) for Substituted **I**

| | | theory | | experiment | | |
|---|---|---|---|---|---|---|
| substituent | solvent | trans | cis | trans | cis | ref |
| 4,4′-Cl-7,7′-Me | xylene | 549 | | 554 | | 14 |
| 4,4′,5,5′,7,7′-Cl | benzene | 569 | 528 (502) | 564 | 493 | 29 |
| 4,4′-Me-5,5′-Cl-7,7′-OMe | xylene | 597 | | 591 | | 13 |
| 4,4′-Me-5,6,7-Cl[a] | benzene | 549 | 514 (491) | 551 | 493 | 29 |
| 4,4′-Me-6,6′-Cl | benzene | 530 | 481 (506) | 538 | 483 | 26,29 |
| | $CHCl_3$ | 530 | 483 (504) | 541 | 490 | 26,27 |
| 4,4′-Me-6,6′-Cl-7,7′-$^{i}$Pr | xylene | 542[b] | | 549 | | 15 |
| 4-Me-6-Cl-6′-OMe | benzene | 520 | 471 (496) | 527 | 473 | 34 |
| 4,4′-Me-6,6′-Br | xylene | 532 | | 543 | | 13 |
| 4,4′,7,7′-Me | benzene | 545 | 489 (512) | 553 | 493 | 30 |
| | xylene | 544 | | 552 | | 13 |
| 4,4′,7,7′-Me-5,5′-Cl | benzene | 569 | 529 (492) | 568 | 505 | 26,29 |
| | $CHCl_3$ | 569 | 533 (490) | 575 | 515 | 26,27 |
| 4,4′-$^{i}$Pr-7,7′-Me | xylene | 554[b] | | 559 | | 16 |
| 4,5-benzo-4′,5′-benzo | benzene | 558 | 509 (532) | 562 | 500 | 26 |
| | chlorobenzene | 559 | | 558 | | 13 |
| | $CHCl_3$ | 557 | 512 (527) | 559 | 508 | 26,27 |
| 5,5′-Cl-7,7′-Me | benzene | 565 | 510 | 565/563 | 500/499 | 26/30 |
| | xylene | 565 | | 566 | | 13 |
| | $CHCl_3$ | 567 | 516 | 568/565 | 508/ | 26/27 |
| 5,5′-Br-6,6′-OEt | benzene | 524 | 479 | 526 | 467 | 26 |
| | xylene | 524 | | 529 | | 13 |
| | $CHCl_3$ | 525 | 484 | 526 | 476 | 26 |
| 5,5′-Br-6,6′-$NH_2$ | xylene | 503 | | 519 | | 13 |
| 5,5′,7,7′-Me | benzene | 560 | 504[c] | 564 | 491 | 29 |
| | $CHCl_3$ | 563 | | 568 | | 27 |
| 5-$NO_2$ | benzene | 541 | | 540 | | 41 |
| 5-OEt | benzene | 586 | | 561 | | 42 |
| 5-OEt,5′-$NO_2$ | benzene | 603 | | 562 | | 42 |
| 5-OEt,6′-$NO_2$ | benzene | 631 | | 578 | | 42 |
| 6,6′-Cl-7,7′-Me | benzene | 541 | 487 | 543 | 484 | 30 |
| | xylene | 541 | | 545 | | 14 |
| 6-$NO_2$ | benzene | 572 | | 561 | | 41 |
| 6-OEt | benzene | 525 | | 531 | | 42 |
| 6-OEt,5′-$NO_2$ | benzene | 522 | | 527 | | 42 |
| 6-OEt,6′-$NO_2$ | benzene | 558 | | 549 | | 42 |
| 6-$SO_2$Me | xylene | 553 | | 552 | | 44 |

[a] In ref 55, they report this dye as being 4,4′-Me-5,6′,7-Cl. Theoretical simulation for such structure gives a $\lambda_{\max}$ of 551 nm for trans and 514 (492) for cis conformers.
[b] *NoAddSph* PCM option.
[c] Gas-phase geometry optimization.

***Table 4.*** PCM-PBE0/6-311G(d,p) Central CCCC Dihedral Angles (deg) for Nonplanar Cis Thioindigo

| substituent | solvent | angle |
|---|---|---|
| 4,4′-Cl | benzene | 4.6 |
| 4,4′,5,5′,7,7′-Cl | benzene | 4.8 |
| 4,4′-Me-5,6,7-Cl | benzene | 4.9 |
| 4,4′-Me-6,6′-Cl | benzene | 4.0 |
| | $CHCl_3$ | 3.6 |
| 4-Me-6-Cl-6′-OMe | benzene | 2.6 |
| 4,4′,7,7′-Me | benzene | 4.4 |
| 4,4′,7,7′-Me-5,5′-Cl | benzene | 5.6 |
| | $CHCl_3$ | 5.4 |
| 4,5-benzo-4′,5′-benzo | benzene | 5.0 |
| | $CHCl_3$ | 3.2 |

of these shifts (99 points) leads to MUE = 7.4 nm, ME = 4.0 nm, and 20 cases with deviations over 10 nm.

One can compare these estimations with recent TD-DFT investigations of the $\lambda_{\max}$ of dyes or related molecules. For the set of 22 substituted indigos reported in ref 99 for which experimental values are given by the authors, one finds MSE = MUE = 56 nm (all theoretical $\lambda_{\max}$ are too small) and ME = 62 nm. For the $\pi \rightarrow \pi^*$ transitions of 100 sulfur-containing compounds, Fabian obtained an MUE of 0.24 eV (TD-DFT), 0.40 eV (ZINDO), and 0.20 eV (PPP, only planar molecules).[73] The typical TD-DFT error for the excitation energies of fluorescent coumarins and uroanic acid derivatives ranges from 0.2 to 0.5 eV[115] and 0.3 to 0.4 eV,[116] respectively. Nevertheless, in the latter case, CAS-PT2 provides significantly improved estimates. For the 11 thiouracils of ref 117 for which measurements are given, the MUE is 0.24 eV for the first $\pi \rightarrow \pi^*$ singlet excitation. In 2004, Jamorski and Casida found experimental versus theoretical absorption energy differences ranging between 0.10 and 0.30 eV for alkyl-amino-benzonitrile compounds.[118] For a series of chromophores, Masumov and Tretiak obtained MUEs of 0.09, 0.11, and 0.20 eV (depending on the chosen geometry).[119] Recently, Petit, Maldivi, and Adamo reported deviations of 0.30−0.40 eV for transition-metal complexes,[120] while da Silva and co-workers obtained, with a PCM-ZINDO// PCM-B3LYP approach, an MUE of 19 nm and an MSE of 3.8 nm, for six cationic dyes in water.[121] These investigations use different functionals and basis sets, incorporate or not incorporate solvation models, treat various classes of molecules, and

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(121) Hommen de Mello, P.; Mennucci, B.; Tomasi, J.; da Silva, A. B. F. *Theor. Chem. Acc.* **2005**, *113*, 274−280.

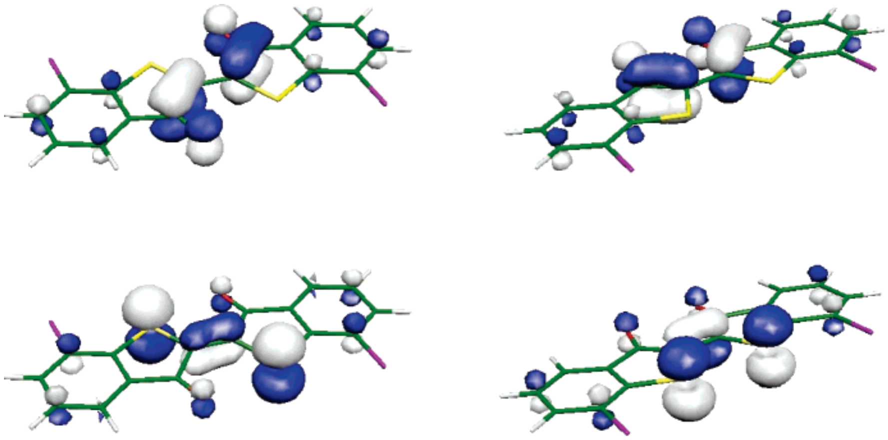

***Figure 2.*** Plot of the HOMO (bottom) and LUMO (top) of trans (left) and cis (right) 7,7′-Cl-thioindigo. They have been obtained at the PCM(benzene)-PBE0/6-311+G(2d,p)//PCM(benzene)-PBE0/6-311G(d,p) level.

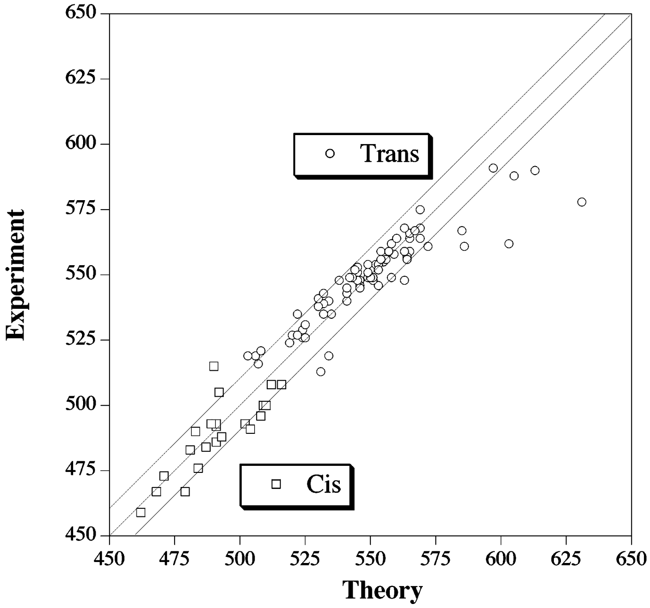

***Figure 3.*** Comparisons between experimental and theoretical $\lambda_{max}$ in nm for the set of thioindigos of Tables 2 and 3. The open circles (squares) indicate the trans (cis) conformers. The central line indicates a perfect match between experiment and theory, whereas for the molecules inside the two side lines, the discrepancies are limited to 10 nm.

are not always mainly focused on the first electronic transition. Consequently a fair comparison is difficult. Nevertheless, it is clear that the PCM-PBE0/6-311+G(2d,p)//PCM-PBE0/6-311G-(d,p) model is extremely adequate for investigating the absorption spectra of thioindigo derivatives: the errors are between one-third and one-tenth of what was foreseen based on previous investigations. Of course, the observed absolute accuracy results from a careful choice of functional and basis sets for a well-identified transition in a specific chromophore. Therefore, the transferability of the absolute accuracy to other systems might be questionable, even though it is probable that the accuracy on the computed substitution shifts could apply to similar compounds.

It is often useful to relate simple chemical descriptors to excitation spectra. In Figures 4 and 5, we compare the theoretical $\lambda_{max}$ of trans molecules with the DFT-optimized double bond lengths included in the H-chromophore, i.e., C═O and C═C.[122]

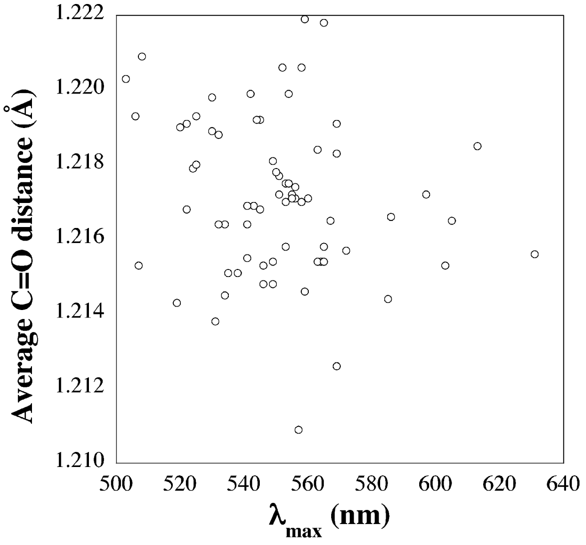

***Figure 4.*** Comparison between theoretical $\lambda_{max}$ (in nm) and the optimized average C═O bond length (in Å).

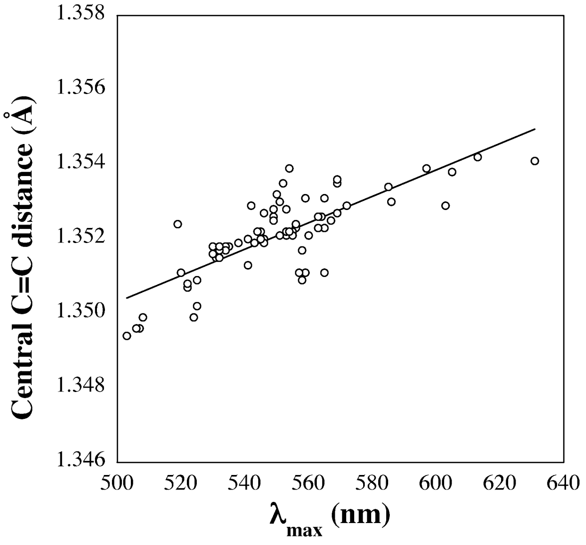

***Figure 5.*** Comparison between theoretical $\lambda_{max}$ (in nm) and the optimized central C═C distance (in Å).

Due to the rigidity of the molecule, the substitution of the outer phenyl rings has only a limited impact on these distances. Indeed, the shortest (longest) bonds are 1.211 (1.222) Å and

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(122) For nonsymmetrical thioindigo, the average C═O bond length is reported.

***Table 5.*** Comparison between PCM-PBE0/6-311+G(2d,p)//PCM-PBE0/6-311G(d,p) and Experimental $\lambda_{max}$ (nm) for a Series of Trans Thioindigo-like Dyes

| | | theory | | experiment | | |
|---|---|---|---|---|---|---|
| substituent | solvent | trans | cis | trans | cis | ref |
| **V** | vapor | 548 | | 530/527 | | 19/133 |
| | cyclohexane | 566 | 512 (487) | 555 | 473 | 133 |
| | $CCl_4$ | 567 | | 558 | | 17,19 |
| | benzene | 568 | 514 (487) | 562 | 485 | 133,31 |
| | toluene | 568 | 515 (487) | 562 | 485 | 126 |
| | xylene | 568 | | 563 | | 19 |
| | $CHCL_3$ | 569 | 519 (484) | 564 | 495 | 133 |
| | TCE | 569 | | 570 | | 18,19 |
| | EtOH | 568 | 525 (481) | 562/559/559 | /478/ | 18,19/62/133 |
| **VI** | vapor | 464 | | 455 | | 133 |
| | cyclohexane | 480 | | 476 | | 62,133 |
| | benzene | 482 | | 480 | | 62,133 |
| | $CHCL_3$ | 481 | | 482 | | 24,62,133 |
| | EtOH | 481 | | 478 | | 62,133 |
| **VII** | cyclohexane | 513 | 466 (502) | 508 | 457 | 34 |
| | benzene | 515 | 468 (502) | 514/512 | 465/467 | 29/34 |
| | xylene | 515 | | 517/478 | | 13/52 |
| | EtOH | 516 | | 510 | | 55 |
| 5′-Br-**VII** | cyclohexane | 528 | 476 (509) | 517 | 464 | 34 |
| | benzene | 529 | 476 (509) | 517 | 462 | 34 |
| | xylene | 529 | | 521/524 | | 13/52 |
| **VIII** | benzene | 517 | | 505 | | 34 |
| | xylene | 517 | | 545 (508) | | 13 |
| **IX** | acetonitrile | 517 | | 509 | | 64 |
| **X** | cyclohexane | 592 | 497 | 580 | 474 | 34 |
| | benzene | 595 | 499 | 591 | 483 | 34 |
| **XI** | cyclohexane | 638 | | 617 | | 34 |
| | benzene | 642 | | 623 | | 34 |
| **XII** | DMSO | 447 | | 450 | | 56 |
| 7,7′-Cl-**XII** | DMSO | 444 | | 450 (480) | | 69 |
| **XIII** | $CHCL_3$ | 433 | | 448 | | 24 |

1.349 (1.354) Å for C═O and C═C, respectively. Obviously, there is no simple relationship between the C═O bond length and the position of the first absorption peak (a linear regression gives $R = 0.20$), whereas a reasonnable linear correlation is found with the C═C bond length ($R$ =0.78). For indigo, the C═O stretching frequency has been used to study the hydrogen bond strength which influence directly $\lambda_{max}$.[123] However, as can be seen in Figure 6, the lack of internal hydrogen bonds in thioindigo makes this frequency a poor color indicator ($R = 0.06$). Of course, other vibrational modes might serve more efficiently as descriptors. But such modes either present a negligible IR intensity (as the central C═C stretch) or are difficult to analyze because they lie in a region of the spectrum in which many displacements contribute to the observed intensity (typically for outer benzene distortion modes).

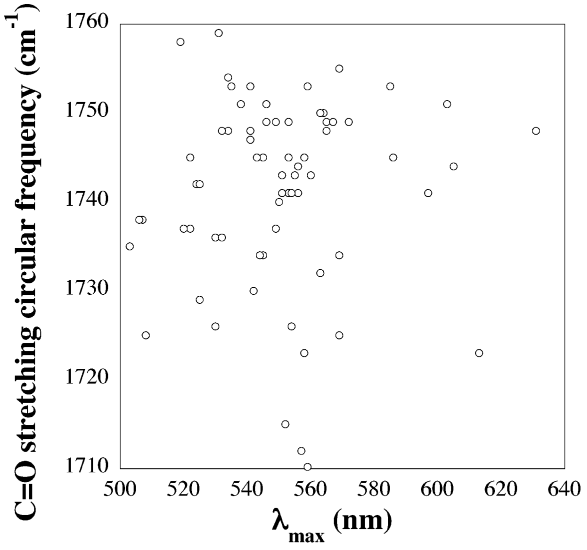

***Figure 6.*** Comparison between theoretical $\lambda_{max}$ (in nm) and the theoretical C═O vibrational frequency (in cm$^{-1}$).

**C. Related Compounds.** Our original methodological study has been performed on unsubstituted thioindigo.[100] As the H-shaped chromophore (Figure 1) does not include the outer phenyl rings, the selected level of theory is adequate for the substituted thioindigo, as we have seen above. However, once the chromophoric moiety is modified, new methodological investigations are required. As Supporting Information, we provide such a complete basis set/functional[103,124,125] study for selenoindigo (**V**). It turns out that the PCM-TD-PBE0/6-311+G-(2d,p)//PBE0/6-311G(d,p) approach is still adequate for **V**. However, we want to underline that further modifications of the chromophoric center could lead to different conclusions. For instance, the description of the internal hydrogen bonds in indigo might require other basis set(s) or functional(s).

In Table 5, the experimental and theoretical spectra of the thioindigo-derived molecules (Figure 7) are compared. These systems are representative of the numerous chemical modifications obtained by (i) changing the heteroatom in the chromophore (**V** and **VI**), (ii) removing one sulfur atom (hemithioindigo dyes, **VIII** and **VIII**) or adding a third one (**IX**), and (iii) keeping the same chromophoric system but adding $\pi$ electrons (**X** and **XI**). In addition, we have also considered

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[123] Weinstein, J.; Wyman, G. M. *J. Am. Chem. Soc.* **1956**, *78*, 2387−2390.
[124] Baker, J.; Pulay, P. *J. Chem. Phys.* **2002**, *117*, 1441−1449.
[125] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

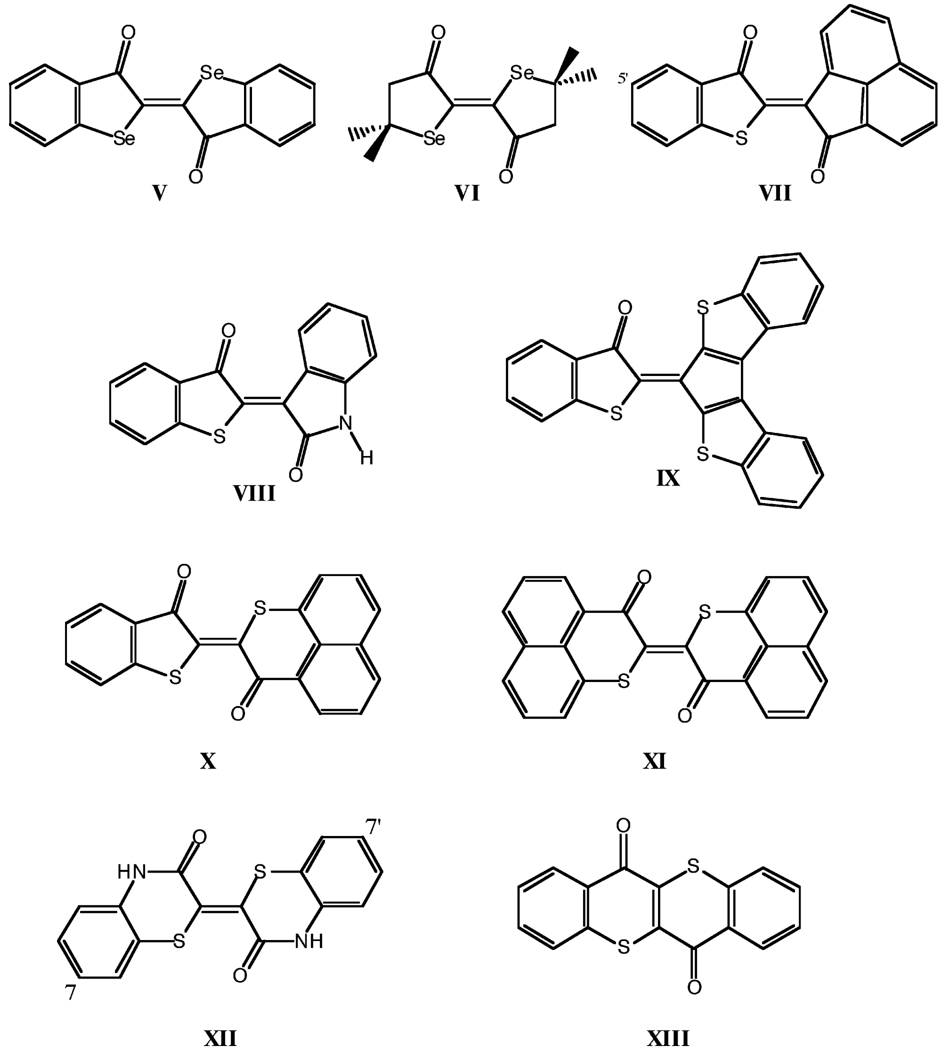

*Figure 7.* Representation of the derivatives of the thioindigo family.

thiazine-indigo (**XII**) and thioepindolidione (**XIII**), a conjugated molecule that presents the same molecular weight as thioindigo but with a chromophoric structure similar to **IV**.

As for the values reported in Table 1, our gas-phase $\lambda_{\max}$ for **V** and **VI** are too large, but the experimental and theoretical results become comparable once solvent effects are included. The substitution of sulfur by selenium induces a bathochromic shift of the spectra (+18 nm in $CHCl_3$) that is slightly overestimated (+25 nm). As for the corresponding thioindigoids, the hypsochromic shift when going from **V** to **VI** is well reproduced (−88 nm instead of −82 nm in $CHCl_3$). For cis selenoindigo (**V**), Ross, Blanc, and Matticoli measured a $\lambda_{\max}$ of 485 nm in toluene.[126] In the same solvent, we find a nonplanar cis form with a dihedral C—C═C—C angle of 5.4° and a $\lambda_{\max}$ of 515 (487) nm. As in some thioindigos, the ordering of the oscillator forces is inverted but the second peak is in perfect agreement with experiment. If the 515 and 487 nm peaks are indeed related to transitions to the LUMO, two occupied levels (HOMO-2 and HOMO) play an important role in both excitations.

For the hemithioindigo (**VII**, **VIII**, and **IX**), one finds a good match between PBE0 results and measurements, although the effect of the bromine substitution is overshot. For the cis vat scarlet G, **VII**, Rogers et al.[29] and Haucke and Paetzold[34] measured $\lambda_{\max}$ of 465/467 nm in benzene, whereas we obtained 468 (502) nm with the correct ordering of oscillator strength. For **VIII**, Haucke gave one absorption (505 nm), whereas Formanek, in a similar solvent, reported two (508 and 545 nm). Our 517 nm $\lambda_{\max}$ goes more in support of Haucke's results. For **IX**, Miziguchi predicted at the ZINDO/AM1 level the $\lambda_{\max}$ to be 393 nm instead of 509 nm. On the other hand, our procedure leads to quantitative agreement (517 nm). Although possessing much more $\pi$ electrons than **I** and being planar, **IX** shows a $\lambda_{\max}$ at a shorter wavelength. This is because the first dipole-allowed transition related to an HOMO−LUMO excitation (see Figure 8) takes place at 805 nm but presents a negligible oscillator force (0.0002). The 517 nm peak mainly corresponds to a HOMO-1 → LUMO transition, with a small

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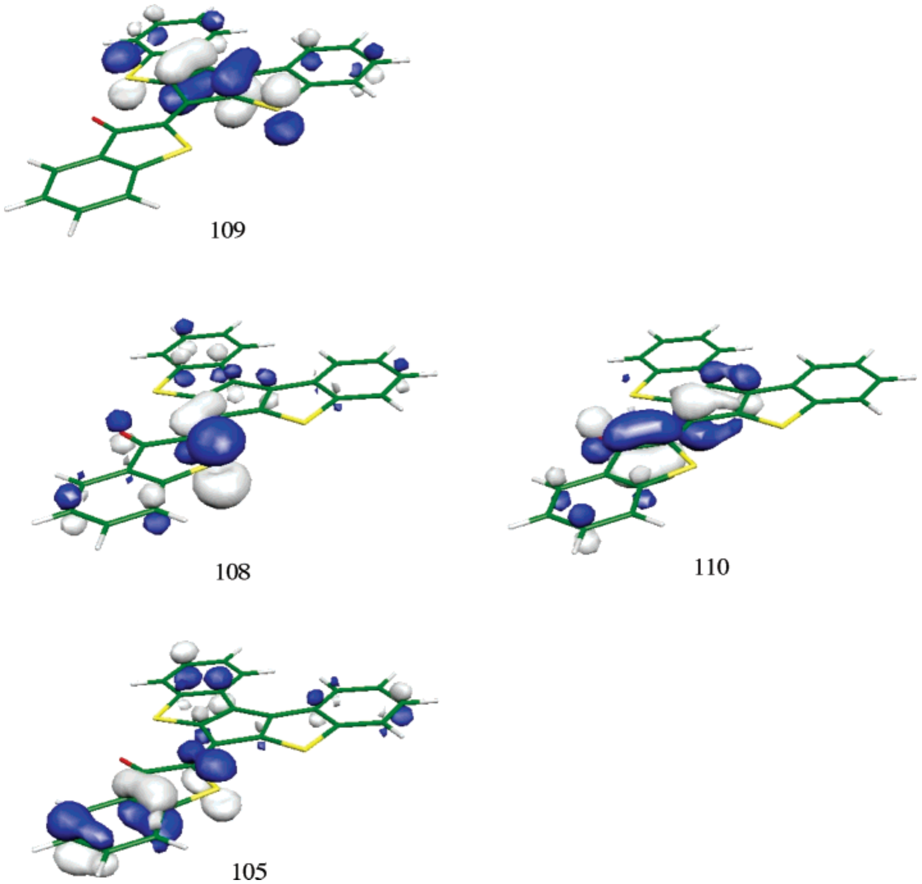

***Figure 8.*** Sketch of the selected molecular orbitals of **IX**. The HOMO label is 109 (top left); the LUMO label is 110 (right).

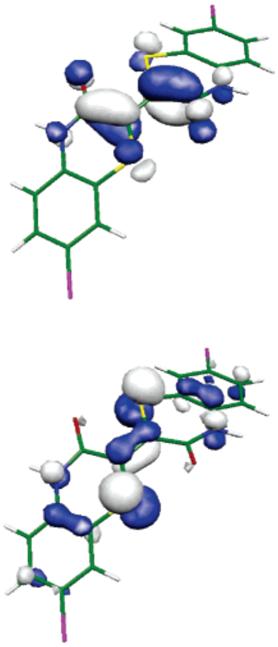

***Figure 9.*** Representation of the HOMO (bottom) and LUMO (top) of 7,7′-Cl-thiazine-indigo.

HOMO-4 → LUMO contribution. As can be seen on Figure 8, the HOMO-1 and LUMO of **IX** are very similar to the HOMO and LUMO of **I**, given the symmetry breaking.

In **X** and **XI**, one has replaced one or two of the five-member rings by six-member rings and added extra phenyl rings, leading to a bathoshift in both theory and experiment. Nevertheless, it is obvious that the increase of $\lambda_{max}$ obtained when extending the conjugation system in the **II** → **I** → **X** → **XI** series is slightly overshot by theory. The experimental **II**($CHCl_3$)−**XI**(benzene) shift is +121 nm, whereas we predict +150 nm. Such a scaling problem of DFT for large conjugated compounds has been reported previously for excited-state energies as well as the related nonlinear optics properties (see refs 112, 114, and references therein). For thiazine-indigo (**XII**), we are in perfect agreement with both experiments, though Senju and Miziguchi assigned the 480 nm shoulder[69] to the 0−0 transition, which we do not support. Note that the X-ray diffraction finds planar 7,7′-Cl-**XII**,[69] whereas we found a bent compound in DMSO, indicating strong solid-state effects. For **XII**, imposing the planarity would result in a +14 nm bathoshift. The HOMO and LUMO of trans 7,7′-Cl-thiazine-indigo (Figure 9) look like those of thioindigo (Figure 2), but with a tiny electronic density on the sulfur atoms in the LUMO that nevertheless slightly destabilizes the electron density on the oxygen of the carbonyl group, increases the energy of the LUMO, and could explain the smaller $\lambda_{max}$ of **XII** compared to **I**. The first absorption of thioepindolidione occurs at higher energies than the corresponding chomophore **IV**, which is quite counterintuitive. This effect is reproduced by theory but is overestimated (39 nm instead of 19 nm).

## IV. Conclusions

We have evaluated the visible spectra of a large panel of thioindigoids with PCM-TD-DFT using the PBE0 functional and extended atomic basis sets. Two problems occur, namely, the incorrect description of relative oscillator strengths in some cis isomers and the overshooting of the $\pi$-conjugated path elongation effect. Having said that, the agreement between theoretical and experimental $\lambda_{\max}$ is exceptional. Indeed, for the 170 cases treated in this study, the required accuracy for the design of new dyes has been reached: the mean signed error is 1.2 nm and the mean unsigned error is 6.9 nm, whereas the rms deviation amounts to 9.8 nm, although our set includes trans and cis isomers, substituted thioindigo, model, and large molecules. These figures are 1 order of magnitude smaller than expected from previous TD-DFT investigations. This high absolute accuracy results from a careful methodological choice for a well-indentified transition in a given chromophoric class, and the computational approach should therefore not be used for other compounds without checking and/or adaptations. Nevertheless, the accuracy on the computed substitution shifts, which is more likely to be transferable, is completely comparable. Consequently, this work demonstrates that once sufficiently extended basis sets are used and bulk solvent effects are accounted for, TD-DFT can be an adequate tool for quantitative predictions of the $\lambda_{\max}$ of dyes, even without statistical posttreatment.

It was found that the majority of the cis thioindigoids are planar and their hypso-character originates from repulsion of electron densities in the excited state. The central double bond length appears to be a good indicator of the color of substituted thioindigo (the reverse assertion might be an instant tool when in the lab), whereas the C=O length and stretching frequency do not correlate with the $\lambda_{\max}$.

We are currently extending this investigation to indigoids and other classes of dyes to confirm the transferability of our methodology.

**Acknowledgment.** D.J. and E.P. thank the Belgian National Fund for Scientific Research for their research associate positions. J.P. acknowledges the FRIA (Belgian "Fonds pour la formation la Recherche dans l'Industrie et dans l'Agriculture") for his PhD grant. The calculations have been performed on the Interuniversity Scientific Computing Facility (ISCF), installed at the Facultés Universitaires Notre-Dame de la Paix (Namur, Belgium), for which the authors gratefully acknowledge the financial support of the FNRS-FRFC and the "Loterie Nationale" for the convention number 2.4578.02 and of the FUNDP.

**Supporting Information Available:** Complete ref 102 and methodological study for *trans*-selenoindigo. This material is available free of charge via the Internet at http://pubs.acs.org.

JA056676H