# A Theoretical Study of the Indigoid Dyes and Their Chromophore

**Luis Serrano-Andrés* and Björn O. Roos**

**Abstract**: A theoretical study of the electronic spectra of indigo, bispyrroleindigo, and the H-chromophore, thought to be the basic structure leading to the intense absorption in the visible spectrum of the indigoid dyes, has been performed by means of the complete active space (CAS) SCF method and the multiconfigurational second-order perturbation theory (CASPT2). The calculations include excitation energies, oscillator strengths, and transition moment directions for the valence singlet states of the molecules. The assumption that the H-chromophore is responsible for the absorption in the visible spectrum is quantitatively revisited with the help of the modern ab initio methodologies and the main features of these molecules are theoretically analyzed, some of them for the first time.

**Keywords**
ab initio calculations · chromophores · dyes · electronic structure · indigo

## Introduction

In theory, visible absorption spectroscopy is no more important than other spectroscopic methods, but it has been the subject of particular interest over many years, for obvious reasons: we perceive compounds that absorb in the range 400–700 nm (3.10–1.77 eV) as being colored, and compounds that absorb strongly at these frequencies can be used as colorants, dyes, or pigments. Known since ancient times, colorants became industrially important with W. H. Perkin's discovery of the first synthetic dye, mauve, in 1856. It was soon realized that compounds absorbing in the visible region differed from those absorbing at higher energies, namely, near ultraviolet, in that they contained complex combinations of what Witt named chromophores in 1876,[1] that is, one or several groups of unsaturated species responsible for absorption in the low-frequency region of the spectrum.

Empirical theories about color and constitution were developed by spectroscopists at the beginning of this century, but, with the development of the valence bond theory, the concept of resonance was thought to have provided the final explanation for the phenomenon of color. Bury suggested in 1935 that color was actually due to the oscillation of bonding between two Kekulé structures.[1] The initial success of resonance theories led to the elaboration of Knott's rules,[2] which allow solvatochromic shifts to be predicted by examining all possible resonance forms according to stability criteria. The number of exceptions to these rules began to increase, and the first molecular orbital calculations showed that a large number of resonance structures should be included to obtain even a qualitative understanding of the absorption bands. One of the greatest achievements of the semiempirical molecular orbital theories was obtained in 1960's and related to the indigoid-type dyes.

Indigo (also referred to as indigotin, 2,2′-bisindoleindigo, or 2,2′-biindoline-3,3′-dione; **I** in Figure 1) is a blue pigment, which is insoluble in water and which must be first reduced to the water soluble leuco form and then reoxidized to become a blue dye locked within the fiber. It is one of the most ancient natural dyes obtained both in Asia from the so-called indigo plant and in Europe from dyers' woad, and it is still one of the most prevalent dyes used to obtain the blue color of jeans.[3, 4] One of its derivatives, 6,6′-bromoindigo is known as Tyrian purple. It was obtained from glandular secretions of some molluscan species in the Mediterranean Sea in such small quantities that wearing clothes dyed with it became a privilege of Greek kings and Roman emperors. The synthetic form is still used today to obtain violet colors.[3, 4] The structure of indigo was elucidated by von Baeyer between 1866 and 1883, but it was only in 1928 that Reis and Schenider succeeded in determining its *trans* configuration by X-ray analysis.[3] Qualitative and empirical theories of color and constitution were unable to explain the blue color of the indigo dye and the red color of its sulfur-containing analogue (-S- replacing -NH-). Therefore the proposed structure was repeatedly questioned.[3]

Four resonance structures were initially proposed to explain the color of indigo: neutral **I**, two structures with a negative charge on one of the oxygen atoms and a positive charge on the nitrogen of the second moiety, and the so-called quadrupole merocyanine structure with a negative charge on each oxygen and a positive charge on each nitrogen. In the quadrupole structure the benzene ring is explicitly considered to be part of the chromophore. In 1965 Leupold and Dähne[5] applied the extended Hückel molecular orbital method to this problem, and they concluded that the ground state of indigo was best regarded as a resonance structure between the neutral and the quadrupole

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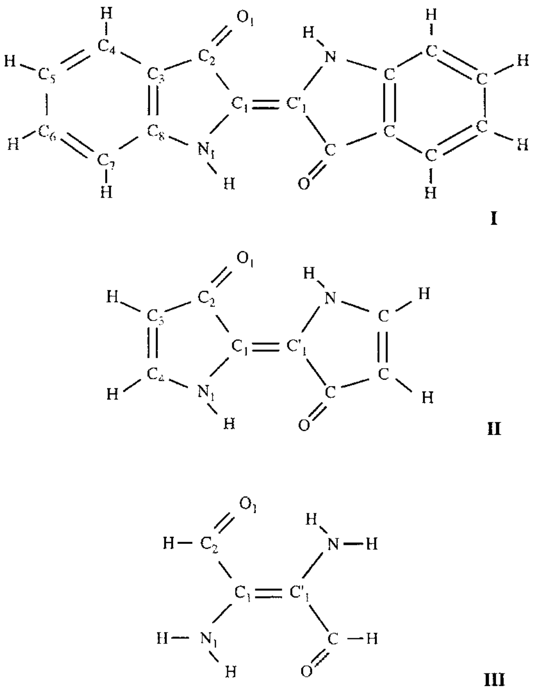

Figure 1. Structure and atom labeling for indigo (I), bispyrroleindigo (II), and the H-chromophore (III) ($C_{2h}$ symmetry).

merocyanine structure a term coined by them. More sophisticated calculations using the Hückel method[6] and later the PPP method,[7, 8] mainly performed by Klessinger and co-workers between 1966 and 1973, suggested that the fundamental chromophore of indigo was the cross-conjugated system **III**, designated as H-chromophore by Dähne and Leupold[9] because of its shape. The structure of the indigo chromophore, identified by purely theoretical methods, was confirmed by Klessinger and co-workers. They synthesized simple models analogous to indigo, such as tetramethylbispyrroleindigo (a tetramethyl derivative of **II**) and other derivatives,[10, 11] in which no additional unsaturated bonds could be formed other than those of the H-chromophore.[1]

Indigo was therefore classified as a donor–acceptor chromogen where the amino groups act as the electron donors and the carbonyl groups as the electron acceptors. The position of the lowest absorption band (and therefore the color) in indigo varies strongly with its environment, ranging from red (540 nm, 2.30 eV) in the gas phase, to violet (588 nm, 2.11 eV) in a nonpolar solvent such as $CCl_4$, to blue in polar solvents such as ethanol (606 nm, 2.05 eV) or in the solid state.[3, 6, 12] The introduction of substituents in the benzene rings has no pronounced effect, probably due to the secondary role of the rings, and the band maxima in a tetrachloroethane solution fall between 570 and 645 nm (2.18 and 1.92 eV)[1] depending on the substituents. Substitutions at the 5,5′-positions (γ from the carbonyl carbon) lead to bathochromic shifts, and substitutions at 6,6′ (γ from the nitrogens) to hypsochromic shifts. This is the case in 6,6′-dibromoindigo, which is purple in polar solvents owing to an absorption at 590 nm (2.10 eV).[12] Replacing the nitrogens in indigo by poorer donating systems like sulfur or oxygen leads to large hypsochromic shifts. There is a rich literature about the synthesis and properties of indigoid dyes and related compounds, but from the structural point of view the most important conclusion is that it is impossible to establish simple qualitative rules for the correlation between the structure and the electronic spectrum of π-electronic molecular systems.[3] In most of cases the use of high-quality quantum chemical methods is unavoidable.

The visible and near-ultraviolet spectrum of indigo in ethanol up to 220 nm (5.64 eV) is composed of four main bands with the following band maxima and extinction coefficients (in parentheses): 2.0 (15800), 3.5–3.9 (10000), 4.4 (26900), and 5.2 eV (19900).[6] The semiempirical studies on the system were limited to the lowest singlet state. The present study tries to perform a complete study of the main features of the indigo molecule by means of the ab initio CASSCF/CASPT2 method.[13, 14] The size and structure of the indigo molecule means that it is necessary to make certain approximations. The π valence electron correlation, involving 22 electrons and 20 orbitals, cannot fully be accounted for at the CASSCF level. It will therefore become necessary to treat part of the π electrons as inactive and use the CASPT2 method for all remaining contributions to the correlation energy.

The present study was performed in the following way. Initially, the valence states of the H-chromophore system (**III**), including $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ singlet states, will be studied. Then, the valence $\pi \rightarrow \pi^*$ spectrum of bispyrroleindigo (**II**), the closest system to indigo where all π valence electrons and orbitals can be included in the active space, will be studied. The final study will be performed on the $\pi \rightarrow \pi^*$ spectrum of indigo itself (**I**). Both the H-chromophore and bispyrroleindigo will be used to test different aspects as the basis-set or active-space selection. The analysis of the results will be used to revisit the H-chromophore hypothesis in a quantitative way, and will permit a better understanding of the basic features of the indigoid dyes.

## Methods and Computational Details

**Ground states geometries**: No gas-phase ground state experimental equilibrium geometries have been reported for the molecules under consideration. Our ground state geometries were therefore optimized at the CASSCF level of theory employing an atomic natural orbital (ANO) type basis set[15] contracted to C,N,O 3s2p1d/H 2s built from the primitive set C,N,O(10s6p3d)/H(4s)[15] for H-chromophore and bispyrroleindigo. The geometry optimization on the indigo molecule was carried out with a basis set contracted to C,N,O 3s2p/H 2s owing to the larger size of the system. The molecules were maintained in a planar arrangement in agreement with findings obtained by X-ray diffraction measurements[16] ($C_{2h}$ symmetry) and were placed in the $xy$ plane. The active spaces employed in the optimizations include the $\pi,\pi^*$ orbitals and electrons, except in indigo where some of them were treated as being inactive. The sizes are: H-chromophore, 8 orbitals and 10 electrons; bispyrroleindigo, 12 orbitals and 14 electrons; and indigo, 12 orbitals and 14 electrons.

**Basis-set and active-space selection**: The large size of the indigoid dyes makes it necessary to limit the size of the basis sets. To study the effect of the basis set reduction on the excited states of these systems, we compiled the results for the $\pi \rightarrow \pi^*$ valence states of the H-chromophore computed with three different ANO-type[17] basis sets (Table 1). As previous experience also shows,[18] the most important quality losses in excitation energies appear when the polarization functions are dropped from the basis set. On the other hand, the change from the basis set C,N,O 4s3p1d/H 2s to C,N,O 3s2p1d/H 2s typically leads to deviations in the excitation energies between 0.1 and 0.2 eV. This latter basis set will be used in the calculations on bispyrroleindigo and indigo.

Table 1. Calculated CASPT2 excitation energies (eV) and oscillator strengths (*f*) for the $\pi \rightarrow \pi^*$ excited singlet states of the H-chromophore in different basis sets [a].

| State | 4s3p1d PT2 | 4s3p1d *f* | 3s2p1d PT2 | 3s2p1d *f* | 3s2p PT2 | 3s2p *f* |
|---|---|---|---|---|---|---|
| $1\,^1B_u$ ($\pi \rightarrow \pi^*$) | 2.40 | 0.127 | 2.47 | 0.130 | 2.85 | 0.156 |
| $2\,^1B_u$ ($\pi \rightarrow \pi^*$) | 6.32 | 0.072 | 6.40 | 0.119 | 6.81 | 0.502 |
| $3\,^1B_u$ ($\pi \rightarrow \pi^*$) | 6.49 | 0.473 | 6.52 | 0.426 | 6.84 | 0.100 |
| $4\,^1B_u$ ($\pi \rightarrow \pi^*$) | 7.43 | 0.054 | 7.37 | 0.085 | 7.86 | 0.094 |
| $5\,^1B_u$ ($\pi \rightarrow \pi^*$) | 7.49 | 0.100 | 7.46 | 0.125 | 7.93 | 0.112 |
| $2\,^1A_g$ ($\pi \rightarrow \pi^*$) | 3.78 | forb. | 3.79 | forb. | 4.25 | forb. |
| $3\,^1A_g$ ($\pi \rightarrow \pi^*$) | 4.82 | forb. | 5.17 | forb. | 5.73 | forb. |
| $4\,^1A_g$ ($\pi \rightarrow \pi^*$) | 5.52 | forb. | 5.32 | forb. | 5.61 | forb. |
| $5\,^1A_g$ ($\pi \rightarrow \pi^*$) | 6.81 | forb. | 6.91 | forb. | 7.27 | forb. |

[a] All ANO-type basis sets, 2s for hydrogen, ref. [17], with additional 1s1p1d diffuse functions.

The indigo molecule has $20\pi,\pi^*$ orbitals and $22\pi$ electrons. To study the $\pi$ spectrum of the molecule it would be desirable to include all the $\pi,\pi^*$ orbitals in the active space for the CASSCF treatment. This is not possible, and therefore some appropriate selection of the space is necessary. The procedure for making the selection is not straightforward, and in the following we show one possible way of dealing with large systems within the present methodology. The bispyrroleindigo will be used first to illustrate the procedure. We will use the natural occupation numbers from a RASSCF calculation as a criterion for the importance of an orbital in the description of an electronic state. The restricted active space (RAS) SCF method[19, 20] was employed to analyze the $\pi \rightarrow \pi^*$ excited states. In the RASSCF method the inactive and secondary space have the same properties as for the CAS wave function. The active space is, however, divided into three subspaces: RAS1, RAS2, and RAS3. RAS1 and RAS3 spaces consist of orbitals in which a certain number of holes and electrons, respectively, are allowed. In the present study we have only considered single excitations from RAS1 to RAS3. In the RAS2 space the arbitrary occupation of the orbitals is retained.

We performed an RASSCF calculation for bispyrroleindigo in which the $\pi$ space was divided into three subspaces: RAS1, including two $a_u$ and two $b_g$ orbitals; RAS2, three $a_u$ and three $b_g$ orbitals; and RAS3, including one $a_u$ and one $b_g$ orbitals. A maximum of one hole and one electron are allowed in RAS1 and RAS3, respectively. Table 2 shows the SCF orbital energies we used as a criterion to divide the RAS space. Also Table 2 contains the natural occupation of the bispyrroleindigo $\pi$ orbitals for both the RASSCF and the CASSCF calculations. A basis set contracted to C,N,O 3s2p/H 2s was employed for these test calculations. In bispyrroleindigo all $12\pi,\pi^*$ orbitals can be included into the CASSCF space. A usual criterion for considering a particular orbital as being important for the description of an excited state is that it should have a CASSCF occupation of higher than 0.05 or lower than 1.95. In bispyrroleindigo the low-lying $a_u$ and $b_g$ orbitals are of minor importance for the six lower $^1B_u$ excited states. This is perfectly reflected in the RAS calculations with the occupations 2.00 or 1.99 in all cases. Both orbitals could then be excluded from the active space if necessary. In general orbitals with occupations of 1.96–1.97 or 0.03–0.04 in the RASSCF calculation are at the limit. Smaller or larger occupancies, respectively, imply that the orbital must be included in the active space. On the other hand, in both the RASSCF and CASSCF calculations, the $2a_u$ orbital seems to be essential in describing the $3\,^1B_u$ state. A CASSCF calculation that does not include this orbital could only be used to compute the lower states. The same study can be performed for the $^1A_g$ states. The RASSCF and CASSCF excitation energies (with respect the $^1A_g$ ground state) and especially the oscillator strengths can differ substantially.

It can be concluded that a RASSCF study of the natural occupation numbers is a useful way to select the orbitals involved in the description of the states. In indigo it is not possible to include all 20 $\pi$ orbitals in the CASSCF active space. Table 3 compiles the results of a RASSCF calculation on the indigo molecule. Here the SCF orbital energies were also used to partition the active space. The two lowest $\pi$ orbitals were considered to be too low in energy and are not included in the active space. The RAS space was divided as follows: RAS1, two $a_u$ and two $b_g$ orbitals, RAS2, five $a_u$ and five $b_g$ and RAS3, two $a_u$ and two $b_g$ orbitals. The results show that the $2a_u$ and $2b_g$ orbitals, which have a constant occupation of 1.99 in all the studied states, can be left inactive. All the orbitals included in RAS2 seem to be important. The four highest orbitals have, however, a low occupation in all the states. It is to be expected that they have only a minor influence. The $3a_u$ and $3b_g$ orbitals are at the limit observed for bispyrroleindigo. They can be included with the ten orbitals of RAS2 in the active space leading to a valence space of 12 orbitals and 14 electron. If the space were too limited, this would be observed when performing the second-order perturbaton. If more active orbitals were required, excitations involving these orbitals would appear as strong intruder states. The same treatment performed for the $^1A_g$ states led to the same conclusions. A similar study was carried out using an SDTQ RASSCF calculation including the valence $\pi$ space in RAS1 and the valence $\pi^*$ space in RAS3. The conclusions obtained led to the same orbital selection.

Table 2. SCF orbital energies (a) and RASSCF (b) and CASSCF (c) occupation numbers for the $\pi$ orbitals in the $^1B_u$ states of the bispyrroleindigo molecule (ANO-type C,N,O [3s2p]/ H [2s] basis set). The excitation energies ($\Delta E$, eV) and oscillator strengths (*f*) also included.

a) SCF energies (eV).

| Orbital | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $a_u$ | −17.29 | −14.22 | −10.96 | −8.35 | 3.44 | 6.48 |
| $b_g$ | −16.09 | −14.45 | −9.57 | 0.40 | 5.01 | 8.76 |

b) RASSCF natural occupation numbers.

| | | RAS1 | | RAS2 | | | RAS3 | | |
|---|---|---|---|---|---|---|---|---|---|
| State | Orbital | 1 | 2 | 3 | 4 | 5 | 6 | $\Delta E$ | *f* |
| $1\,^1B_u$ | $a_u$ | 1.99 | 1.96 | 1.90 | 1.04 | 0.10 | 0.03 | 4.07 | 0.36 |
| | $b_g$ | 1.99 | 1.98 | 1.90 | 1.02 | 0.06 | 0.02 | | |
| $2\,^1B_u$ | $a_u$ | 1.99 | 1.97 | 1.69 | 1.11 | 0.23 | 0.04 | 5.40 | 0.18 |
| | $b_g$ | 1.99 | 1.98 | 1.79 | 1.05 | 0.11 | 0.04 | | |
| $3\,^1B_u$ | $a_u$ | 1.99 | 1.42 | 1.94 | 1.62 | 0.27 | 0.04 | 6.93 | 0.15 |
| | $b_g$ | 1.99 | 1.93 | 1.65 | 1.01 | 0.10 | 0.03 | | |
| $4\,^1B_u$ | $a_u$ | 1.99 | 1.96 | 1.82 | 1.26 | 0.50 | 0.06 | 7.66 | 0.19 |
| | $b_g$ | 1.99 | 1.96 | 1.53 | 0.33 | 0.57 | 0.03 | | |
| $5\,^1B_u$ | $a_u$ | 2.00 | 1.81 | 1.86 | 1.33 | 0.40 | 0.10 | 8.00 | 0.27 |
| | $b_g$ | 1.99 | 1.80 | 1.55 | 0.99 | 0.18 | 0.09 | | |
| $6\,^1B_u$ | $a_u$ | 1.99 | 1.91 | 1.78 | 1.14 | 0.42 | 0.07 | 9.80 | 0.01 |
| | $b_g$ | 1.99 | 1.88 | 1.69 | 0.67 | 0.43 | 0.04 | | |

c) CASSCF natural occupation numbers; C,N,O [3s2p1d]/H [2s] + 1s1p1d.

| State | Orbital | 1 | 2 | 3 | 4 | 5 | 6 | $\Delta E$ | *f* |
|---|---|---|---|---|---|---|---|---|---|
| $1\,^1B_u$ | $a_u$ | 1.98 | 1.95 | 1.90 | 1.05 | 0.11 | 0.06 | 3.71 | 0.16 |
| | $b_g$ | 1.97 | 1.95 | 1.90 | 1.01 | 0.08 | 0.04 | | |
| $2\,^1B_u$ | $a_u$ | 1.98 | 1.94 | 1.70 | 1.12 | 0.24 | 0.07 | 5.43 | 0.14 |
| | $b_g$ | 1.98 | 1.95 | 1.76 | 1.07 | 0.13 | 0.07 | | |
| $3\,^1B_u$ | $a_u$ | 1.97 | 1.34 | 1.90 | 1.69 | 0.23 | 0.07 | 6.83 | 0.09 |
| | $b_g$ | 1.97 | 1.87 | 1.72 | 1.07 | 0.10 | 0.06 | | |
| $4\,^1B_u$ | $a_u$ | 1.97 | 1.91 | 1.82 | 1.46 | 0.59 | 0.10 | 7.72 | 0.23 |
| | $b_g$ | 1.96 | 1.91 | 1.44 | 0.40 | 0.36 | 0.06 | | |
| $5\,^1B_u$ | $a_u$ | 1.97 | 1.84 | 1.77 | 1.13 | 0.25 | 0.10 | 7.79 | 0.01 |
| | $b_g$ | 1.97 | 1.73 | 1.78 | 0.96 | 0.42 | 0.09 | | |
| $6\,^1B_u$ | $a_u$ | 1.97 | 1.90 | 1.68 | 1.25 | 0.48 | 0.08 | 8.20 | 0.17 |
| | $b_g$ | 1.96 | 1.90 | 1.64 | 0.58 | 0.52 | 0.05 | | |

Finally it is interesting to note the small sensitivity of the CASPT2 excitation energies towards the active-space size, once the minimum number of orbitals is included. We performed CASPT2 calculations on the $^1B_u$ states of bispyrroleindigo using the full 12 orbitals/14 electrons active space and a reduced 10 orbitals/10 electrons space, where the $1b_g$ and $1a_u$ orbitals are kept inactive. The previous RASSCF study led us to conclude that these orbitals play a minor role in the description of the states. We use the small 3s2p/2s basis set and no diffuse functions. The computed excitation energies for five $^1B_u$ states for bispyrroleindigo in the 12 orbitals/14 electrons calculation were: 2.31, 4.37, 5.42, 5.64, and 6.09 eV, respectively. For the 10 orbitals/10 electrons calculation the computed excitation energies were: 2.45, 4.33, 5.60, 5.73, 6.14 eV, respectively. These results are within the expected 0.1–0.2 eV accuracy and confirm that the reduction in the active space is appropriate.

**Calculations of the vertical electronic spectra**: ANO-type basis set of higher quality were used in the calculations of the excitation energies. Initially, a basis set contracted to C,N,O 4s3p1d/H 2s from the primitive set

Table 3. SCF orbital energies (a) and RASSCF (b) occupation numbers for the π orbitals in the $^1B_u$ states of the indigo molecule (ANO-type C,N,O [3s2p]/H [2s] basis set). The excitation energies (Δ*E*, eV) and oscillator strengths (*f*) are also included.

a) SCF energies (eV).

| Orbital | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $a_u$ | −17.70 | −14.45 | −14.11 | −10.59 | −10.17 | −8.02 | 1.74 | 3.31 | 5.33 | 6.51 |
| $b_g$ | −16.67 | −14.65 | −13.43 | −10.22 | −9.15 | 0.01 | 2.90 | 3.79 | 7.36 | 7.90 |

b) RASSCF natural occupation numbers.

| | | | RAS1 | | | | RAS2 | | | RAS3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| State | Orbital | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Δ*E* | *f* |
| $1\,^1B_u$ | $a_u$ | – | 1.99 | 1.98 | 1.90 | 1.91 | 1.05 | 0.13 | 0.09 | 0.01 | 0.01 | 3.71 | 0.30 |
| | $b_g$ | – | 1.99 | 1.97 | 1.91 | 1.86 | 0.97 | 0.11 | 0.08 | 0.01 | 0.02 | | |
| $2\,^1B_u$ | $a_u$ | – | 1.99 | 1.97 | 1.32 | 1.90 | 1.60 | 0.18 | 0.11 | 0.01 | 0.02 | 5.52 | 0.18 |
| | $b_g$ | – | 1.99 | 1.97 | 1.87 | 1.69 | 1.08 | 0.11 | 0.12 | 0.02 | 0.02 | | |
| $3\,^1B_u$ | $a_u$ | – | 1.99 | 1.97 | 1.84 | 1.45 | 1.80 | 0.34 | 0.14 | 0.02 | 0.01 | 5.70 | 0.33 |
| | $b_g$ | – | 1.99 | 1.96 | 1.85 | 1.67 | 0.62 | 0.19 | 0.11 | 0.01 | 0.02 | | |
| $4\,^1B_u$ | $a_u$ | – | 1.99 | 1.97 | 1.85 | 1.70 | 1.07 | 0.37 | 0.10 | 0.02 | 0.01 | 6.34 | 0.06 |
| | $b_g$ | – | 1.99 | 1.96 | 1.63 | 1.88 | 0.82 | 0.49 | 0.09 | 0.01 | 0.02 | | |
| $5\,^1B_u$ | $a_u$ | – | 1.99 | 1.96 | 1.86 | 1.56 | 1.49 | 0.29 | 0.20 | 0.02 | 0.02 | 6.48 | 0.15 |
| | $b_g$ | – | 1.99 | 1.97 | 1.85 | 1.63 | 0.76 | 0.23 | 0.14 | 0.01 | 0.03 | | |
| $6\,^1B_u$ | $a_u$ | – | 1.99 | 1.97 | 1.59 | 1.87 | 1.26 | 0.30 | 0.11 | 0.03 | 0.02 | 7.46 | 0.44 |
| | $b_g$ | – | 1.99 | 1.97 | 1.85 | 1.59 | 1.06 | 0.16 | 0.20 | 0.02 | 0.02 | | |

C,N,O(14s9p4d) H(6s)[17] was used to compute the full set of excited states in the H-chromophore system. It was supplemented with a 1s1p1d set of Rydberg type functions (contracted from 8 primitives of each angular momentum type), which were constructed following a procedure described earlier,[13] and were placed at the charge centroid. These diffuse functions are essential for the description of the Rydberg states and for the minimization of spurious interaction between Rydberg and valence states.[14] The calculations of the spectra of bispyrroleindigo and indigo used a basis set contracted to C,N,O 3s2p1d/H 2s plus the additional 1s1p1d diffuse functions. The carbon, nitrogen, and oxygen 1s orbitals were kept frozen in the form determined by the ground state SCF wave function and were not included in the calculation of the correlation energy.

The CASPT2 method[14, 21, 22] calculates the first-order wave function and the second-order energy with a CASSCF wave function constituting the reference function. Thus, initially the multiconfigurational wave functions are determined at the CASSCF level of approximation.[23] Orbitals and transition densities are obtained at this level. Only the dynamic correlation energy is obtained by the second-order perturbation treatment. All the remaining properties are obtained from the CASSCF wave function. Recently, a level shift operator has been introduced[24] to the CASPT2 approach, which removes the effect of intruder states. The description of this technique can be found in the original articles.[24, 25] The method has been given the acronym LS-CASPT2. A value of 0.3 au was used for the level shift in all the computed states. The CAS state interaction method (CASSI) was used to compute transition properties.[26] Intensities were obtained by combining the CASSCF transition moments with CASPT2 evaluated excitation energies, a method that has proven to give accurate results in a number of previous applications.[13, 24] The molecule is placed in the *xy* plane (*x* long axis and *y* short axis of the molecule), and the coordinate origin is the inversion center of the molecule. Transition moment directions are therefore defined as angles from horizontal axis *x* to vertical axis *y* (positive direction).

The selection of the appropriate active space is the crucial step in the CASSCF/CASPT2 approach. In general, the active space should include all orbitals with occupation numbers appreciably different from two or zero in any of the excited states under consideration. This means that all near-degeneracy effects are included in the CASSCF reference function, and consequently there will be no large terms in the perturbation expansion. The limit of 13–14 orbitals that can be included in the active space in present implementations of the CASSCF method sometimes makes it difficult to choose an appropriate active space in studies of a large number of excited states. Table 4 lists the active spaces employed in the present study. For the valence π → π* states the minimum active space should be that including all valence π,π* orbital and electrons. The recommended procedure is to always include diffuse functions in the basis set and Rydberg type orbitals in the active space, as has been done for the H-chromophore. As listed in Table 4, the spaces used for the H-chromophore include the eight valence π orbitals and the three π Rydberg orbitals $3p_z$ ($a_u$ symmetry) and $3d_{xz}$, $3d_{yz}$ ($b_g$ symmetry) for the π → π* states, and two more lone pair n orbitals for the n → π* states. In bispyrroleindigo and indigo only one orbital has been added to the valence space to include one Rydberg orbital. If there is more than one Rydberg orbital belonging to this symmetry, a second calculation can be performed where the initial Rydberg orbital is deleted from the orbital space and is replaced by the second Rydberg orbital. This is the case for the $^1B_u$ states in bispyrroleindigo and indigo. As the lowest Rydberg orbitals are deleted from the orbital space, we are not going to study the Rydberg states in bispyrroleindigo and indigo. All the computed excitation energies use the ground state energy computed as an average root with the same active space.

Table 4. CASSCF wave functions (number of active orbitals and electrons) employed to compute the valence singlet excited states of the H-chromophore, bispyrroleindigo, and indigo.

| Wave function [a] | States | No. conf. [b] | $N_{states}$ [c] |
|---|---|---|---|
| H-chromophore | | | |
| CASSCF(0056)(10) | $^1A_g$ π → π* | 30 592 | 8 |
| | $^1B_u$ π → π* | 30 392 | 8 |
| CASSCF(1156)(14) | $^1A_u$ n → π* | 180 774 | 8 |
| | $^1B_g$ n → π* | 180 774 | 8 |
| Bispyrroleindigo | | | |
| CASSCF(0076)(14) | $^1A_g$ π → π* | 368 432 | 9 |
| CASSCF(0067)(14) | $^1B_u$ π → π* | 367 732 | 9 |
| Indigo | | | |
| CASSCF(0076)(14) | $^1A_g$ π → π* | 368 432 | 9 |
| CASSCF(0067)(14) | $^1B_u$ π → π* | 367 732 | 9 |

[a] In parentheses: number of active orbitals of symmetry CASSCF-($a_g b_u a_u b_g$)(number of active electrons); $C_{2h}$ symmetry. [b] Number of configurations in the CASSCF wave function. [c] Number of states included in the average CASSCF calculation.

All calculations were performed with the MOLCAS-3[27] program package on IBM RS/6000 workstations. It might be worth mentioning that the indigo calculations are among the largest performed with the MOLCAS system. The size of the basis set is 309 ANOs in $C_{2h}$ symmetry.

## Results and Discussion

**The electronic spectrum of the H-chromophore**: In Table 5 the results obtained for the valence π → π* and n → π* excited states of the H-chromophore (**III**) system are compiled (the results

Table 5. Calculated excitation energies (eV), oscillator strengths ($f$), and transition moment directions ($TM_{dir}$, °) for the excited singlet states in the H-chromophore [a].

| State | Excit. energ. CAS | PT2 | $f$ | $TM_{dir}$ [c] | PPP [b] $E$ (eV) | $f$ |
|---|---|---|---|---|---|---|
| $1\,^1B_u$ ($\pi \rightarrow \pi^*$) | 4.66 | 2.40 | 0.127 | +16 | 2.74 | 0.34 |
| $1\,^1B_g$ ($n \rightarrow \pi^*$) | 4.43 | 3.30 | forb. | – | – | – |
| $1\,^1A_u$ ($n \rightarrow \pi^*$) | 4.53 | 3.50 | $6 \times 10^{-5}$ | – | – | – |
| $2\,^1A_g$ ($\pi \rightarrow \pi^*$) | 5.08 | 3.63 | forb. | – | 4.34 | forb. |
| $4\,^1A_g$ ($\pi \rightarrow \pi^*$) | 6.64 | 4.73 | forb. | – | 5.20 | forb. |
| $2\,^1A_u$ ($n \rightarrow \pi^*$) | 6.62 | 4.93 | $4 \times 10^{-4}$ | – | – | – |
| $2\,^1B_g$ ($n \rightarrow \pi^*$) | 6.73 | 5.13 | forb. | – | – | – |
| $3\,^1A_g$ ($\pi \rightarrow \pi^*$) | 7.14 | 5.19 | forb. | – | – | – |
| $2\,^1B_u$ ($\pi \rightarrow \pi^*$) | 8.49 | 6.32 | 0.072 | +23 | 6.22 | 0.14 |
| $3\,^1A_u$ ($n \rightarrow \pi^*$) | 8.94 | 6.23 | $1 \times 10^{-5}$ | – | – | – |
| $3\,^1B_g$ ($n \rightarrow \pi^*$) | 8.94 | 6.26 | forb. | – | – | – |
| $3\,^1B_u$ ($\pi \rightarrow \pi^*$) | 8.71 | 6.49 | 0.473 | −77 | – | – |
| $4\,^1A_u$ ($n \rightarrow \pi^*$) | 10.28 | 6.49 | $3 \times 10^{-4}$ | – | – | – |
| $4\,^1B_g$ ($n \rightarrow \pi^*$) | 10.23 | 6.79 | forb. | – | – | – |
| $4\,^1A_g$ ($\pi \rightarrow \pi^*$) | 9.22 | 7.06 | forb. | – | – | – |
| $4\,^1B_u$ ($\pi \rightarrow \pi^*$) | 9.76 | 7.43 | 0.054 | +29 | – | – |
| $5\,^1B_u$ ($\pi \rightarrow \pi^*$) | 10.58 | 7.49 | 0.100 | +48 | – | – |

[a] Basis set ANO C,N,O [4s3p1d], H [2s]. [b] Semiempirical PPP values from ref. [7]. [c] Transition moment directions defined in the text.

with the largest basis set C,N,O [4s3p1d], H [2s] are considered here). Five valence excited states of $^1A_g$ symmetry and four of $^1B_u$ symmetry form the valence $\pi \rightarrow \pi^*$ spectrum of the system. Considering the orbital structure of the system with three double bonds and (2,1)-occupied and (1,2)-empty ($a_u$,$b_g$) $\pi$ orbitals, a simple model based on single excitations would predict nine valence $\pi \rightarrow \pi^*$ states, four with $^1A_g$ and five with $^1B_u$ symmetry. However, the multiconfigurational character of the states, with important contributions from double excitations, destroys such a simple single-excitation description. The $^1A_g$ states are one-photon forbidden, owing to symmetry considerations, and the most relevant features of the spectrum will therefore be produced by transitions to the $^1B_u$ one-photon allowed states. The $1\,^1B_u$ state results mainly from the excitation from the HOMO to the LUMO orbital (cf. Table 6). The analysis of the SCF orbital energies indicates that the HOMO orbital lies around 5 eV higher in energy than the HOMO −1 orbital at this level of calculation. The destabilization of the HOMO orbital with respect to the remaining occupied orbitals, but mainly the low energy of the LUMO orbital, lead to a low-energy HOMO → LUMO excitation and places the $1\,^1B_u$ state at 2.40 eV, within the range of the visible spectrum. The comparison of the Mulliken population analysis of the ground and the $1\,^1B_u$ state confirms that the charge transfer taking place between the nitrogen and the atoms forming the C=O bond is approximately 0.4e. The nature of the $1\,^1B_u$ state shows the importance of the nitrogen atoms as electron donors. When nitrogen is substituted by less electron donating atoms, like sulfur, a substantial shift of the lowest band to higher energies is observed in the indigoid dyes.[3]

The $1\,^1B_u$ state has a computed energy of 2.40 eV and an oscillator strength of 0.64. The following intense $^1B_u$ states are also calculated to be valence $\pi \rightarrow \pi^*$ states with energies of 6.32

Table 6. CASSCF wave function composition, excitation energies (PT2, eV), oscillator strengths ($f$), and net charge transfer per atom for the excited $^1B_u$ states of the H-chromophore, bispyrroleindigo, and indigo [a].

| State | Configuration [c] | $W$ [c] (%) | PT2 | $f$ | Net charge transfer per atom [b] Bz | $C_4$ | $C_3$ | $C_2$ | $C_1$ | $N_1$ | $O_1$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H-chromophore | | | | | | | | | | | |
| $1\,^1B_u$ | H → L | 76 | 2.47 | 0.13 | – | – | – | −0.26 | +0.07 | +0.31 | −0.14 |
| $2\,^1B_u$ | H → L+2 | 21 | 6.40 | 0.12 | – | – | – | −0.18 | −0.01 | +0.06 | +0.14 |
| | H−2 → L | 10 | | | | | | | | | |
| | H−4 → L | 10 | | | | | | | | | |
| $3\,^1B_u$ | H−4 → L | 35 | 6.52 | 0.43 | – | – | – | −0.19 | −0.01 | +0.28 | −0.15 |
| | H → L+2 | 33 | | | | | | | | | |
| | H,H−1 → L,L | 11 | | | | | | | | | |
| Bispyrroleindigo | | | | | | | | | | | |
| $1\,^1B_u$ | H → L | 60 | 2.19 | 0.16 | – | −0.08 | +0.13 | −0.15 | −0.15 | +0.40 | −0.13 |
| $2\,^1B_u$ | H−2 → L | 25 | 4.11 | 0.14 | – | −0.14 | +0.20 | −0.22 | +0.04 | +0.22 | −0.10 |
| | H,H−2 → L,L | 21 | | | | | | | | | |
| | H,H → L,L+2 | 10 | | | | | | | | | |
| | H → L | 10 | | | | | | | | | |
| $3\,^1B_u$ | H−3 → L | 25 | 5.11 | 0.09 | – | −0.10 | +0.10 | −0.20 | −0.03 | +0.17 | +0.07 |
| | H−1 → L | 18 | | | | | | | | | |
| $4\,^1B_u$ | H−2 → L+2 | 32 | 5.30 | 0.23 | – | −0.04 | −0.01 | −0.22 | +0.07 | +0.18 | +0.03 |
| | H → L+1 | 20 | | | | | | | | | |
| Indigo | | | | | | | | | | | |
| $1\,^1B_u$ | H → L | 63 | 1.96 | 0.15 | +0.06 | +0.02 | +0.04 | −0.10 | −0.12 | +0.20 | −0.12 |
| $2\,^1B_u$ | H−4 → L | 20 | 3.49 | 0.05 | +0.02 | −0.08 | −0.02 | −0.08 | −0.02 | +0.16 | −0.06 |
| $3\,^1B_u$ | H−2 → L | 29 | 3.55 | 0.41 | −0.02 | +0.00 | +0.00 | −0.08 | +0.08 | +0.08 | −0.10 |
| | H → L | 12 | | | | | | | | | |
| | H−4 → L | 12 | | | | | | | | | |
| $4\,^1B_u$ | H−2 → L | 20 | 3.59 | 0.01 | +0.04 | −0.04 | +0.16 | −0.10 | −0.10 | +0.10 | −0.12 |
| | H−4 → L | 14 | | | | | | | | | |
| | H−1 → L+1 | 11 | | | | | | | | | |
| $5\,^1B_u$ | H → L+2 | 12 | 3.93 | 0.07 | +0.04 | −0.02 | −0.04 | −0.12 | +0.02 | +0.16 | −0.12 |
| | H,H−3 → L,L | 11 | | | | | | | | | |
| $6\,^1B_u$ | H−2 → L | 17 | 4.71 | 0.12 | −0.02 | +0.02 | +0.08 | −0.12 | −0.04 | +0.12 | −0.10 |
| | H,H−1 → L,L | 16 | | | | | | | | | |
| $9\,^1B_u$ | H−6 → L | 26 | 5.36 | 0.22 | +0.04 | +0.06 | +0.02 | −0.08 | −0.04 | +0.06 | −0.12 |

[a] Basis set: ANO C,N,O 3s2p1d/H 2s. [b] Based on Mulliken partitions; $C_4$ is $C_8$ in indigo (see Figure 1); Bz represents the remaining carbons. [c] Configurations with weight ($W$) larger than 10%; H: HOMO, L: LUMO.

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and 6.49 eV and oscillator strengths of 0.072 and 0.473, respectively. Other $^1B_u$ valence states will lie at higher energies in the spectrum. This state structure can be related to the visible and near-ultraviolet spectrum of indigo.[6] In the gas phase only, the lowest band has been reported at 2.30 eV, close to the value obtained for the H-chromophore, namely, 2.40 eV. In ethanol the band drops to 2.05 eV. This band appears as an isolated band in indigo, while two other bands are close to each other at higher energies (3.7–3.9 and 4.34 eV).[6] As will be shown later the $^1B_u$ transition mainly involves the $C_1$, $C_2$, $N_1$, and $O_1$ atoms (and their symmetry pairs). The addition of new groups to the basic H-chromophore system is not going to strongly affect these orbitals, and consequently the $1\,^1B_u$ transition has similar excitation energies in all three systems. This is not the case for the other transitions. Except for the intensity values, the results for the excitation energies obtained for the H-chromophore by the PPP method[7] basically agree with the CASPT2 results.

A number of $n \rightarrow \pi^*$ excited states were also studied (cf. Table 5) in order to locate them in the electronic spectrum. The two lowest $1\,^1B_g$ and $1\,^1A_u$ states are mainly described by the single excitations from the lone pairs to the LUMO orbital, $13a_g(n) \rightarrow 3b_g$ and $12b_u(n) \rightarrow 3b_g$, respectively. They were computed at 3.30 and 3.50 eV, respectively. The remaining valence $n \rightarrow \pi^*$ states have large contributions for doubly excited configurations. All of them are either one-electron forbidden states or have extremely low intensities.

**The electronic spectrum of bispyrroleindigo**: Table 7 shows the computed results for the bispyrroleindigo molecule (**II**). The valence $\pi \rightarrow \pi^*$ spectrum up to 7.4 eV is composed of five $^1B_u$ and six $^1A_g$ states. The lowest $1\,^1B_u$ state is computed at 2.19 eV with an oscillator strength of 0.164. This energy is lower than the 2.47 eV obtained for the same state and basis set in the H-chromophore, but the basic characteristics of the state, intensity, wave function composition, and charge distribution remain similar. Table 6 lists the wave function composition for the $^1B_u$ states in bispyrroleindigo. The $1\,^1B_u$ state is described as the HOMO → LUMO one-electron promotion (60%), and the net charge transfer takes place (in both parts of the molecule) from the nitrogen, $C_1$, and $C_2$ towards the oxygen, and to a minor extent from $C_3$ to $C_4$. The $2\,^1B_u$ state differs in the H-chromophore and bispyrroleindigo. While in the H-chromophore the second $^1B_u$ transition was described by a HOMO → LUMO+2 excitation, where the net charge transfer took place from the oxygen to the carbonyl carbon $C_2$, in bispyrroleindigo it is mainly described by the one-electron promotion HOMO − 2 → LUMO. The charge transfer in this state of bispyrroleindigo is similar to that of the lowest $^1B_u$ state, but the carbons $C_3$ and $C_4$ participate more significantly in the process. As a consequence the excitation energy drops from 6.40 eV in the H-chromophore to 4.11 eV in bispyrroleindigo, although the intensities are similar. The contribution of doubly excited configurations is more important in bispyrroleindigo (cf. Table 6). The state at 4.11 eV can be related to the 3.5–3.9 eV band observed in the experimental spectrum of indigo.[6] In bispyrroleindigo the LUMO orbital has an SCF orbital energy lower than that in the H-chromophore. The composition of the wave function in the low-lying electronic states is dominated by excitations to the LUMO orbital from the different highest occupied molecular orbitals. In the H-chromophore, however, other virtual orbitals are also important. This tendency will continue in indigo, and it will lead to states with lower excitation energy.

Table 7. Calculated excitation energies (eV), oscillator strengths ($f$), and transition moment directions (TM, °) for the excited singlet states in bispyrroleindigo.

| State | Excit. energ. |  |  |  |  | PPP [a] |  |
|---|---|---|---|---|---|---|---|
|  | CAS | PT2 | Exp. [b] | $f$ | TM$_{dir}$ [c] | $E$ (eV) | $f$ |
| $1\,^1B_u$ ($\pi \rightarrow \pi^*$) | 4.41 | 2.19 | 2.35 | 0.164 | +41 | 2.55 | 0.34 |
| $2\,^1A_g$ ($\pi \rightarrow \pi^*$) | 4.60 | 2.72 | – | forb. |  | 2.92 | forb. |
| $2\,^1B_u$ ($\pi \rightarrow \pi^*$) | 6.09 | 4.11 | – | 0.135 | +7 | 4.39 | 0.14 |
| $3\,^1A_g$ ($\pi \rightarrow \pi^*$) | 7.14 | 4.84 | – | forb. | – | 4.69 | forb. |
| $3\,^1B_u$ ($\pi \rightarrow \pi^*$) | 7.49 | 5.11 | – | 0.091 | +25 | 5.57 | – |
| $4\,^1B_u$ ($\pi \rightarrow \pi^*$) | 8.34 | 5.30 | – | 0.227 | −71 | – | – |
| $4\,^1A_g$ ($\pi \rightarrow \pi^*$) | 5.84 | 5.58 | – | forb. | – | 6.06 | forb. |
| $5\,^1A_g$ ($\pi \rightarrow \pi^*$) | 8.34 | 5.76 | – | forb. | – | – | – |
| $6\,^1A_g$ ($\pi \rightarrow \pi^*$) | 7.56 | 5.81 | – | forb. |  |  |  |
| $5\,^1B_u$ ($\pi \rightarrow \pi^*$) | 8.42 | 5.90 | – | 0.006 | −84 | – | – |
| $7\,^1A_g$ ($\pi \rightarrow \pi^*$) | 8.38 | 7.44 | – | forb. | – | – |  |

[a] Semiempirical PPP values from ref. [7]. [b] Absorption in ethanol for 3,3′,4,4′-tetramethylbispyrroleindigo [3]. [c] Transition moment directions defined in the text.

**The electronic spectrum of indigo**: The structure of the indigo molecule and some $N,N'$-substituted indigo dyes in their ground state was studied by Abe et al.[28] at the MNDO level of calculation. Indigo was computed to have an almost planar structure (twisting angle 0.4°), while the other systems had strongly twisted structures both in their *trans* and *cis* forms. We can compare our CASSCF structures to the X-ray diffraction data.[16] It should be noted, however, that large discrepancies are sometimes found between crystal and gas-phase structures, mainly for the double bonds.[29] The CASSCF-computed values for the bond lengths $C_1{=}C_1'$ (1.354 Å) and $C_2{=}O_1$ (1.242 Å) (see Figure 1) are comparable to the experimental measurements of 1.37 and 1.22 Å, respectively.[16] The discrepancy found for the $C_1{-}N_1$ bond is much larger: the computed value is 1.400 Å, while the measured length is 1.36 Å.[16] A semiempirical geometry optimization at the MNDO level gave a bond length of 1.433 Å for the same bond.[28] Closer agreement is found between the CASSCF value (1.487 Å) and the measured value (1.48 Å) for the $C_2{-}C_3$ length.[16]

Table 8 lists the computed and experimental excitation energies for the low-lying $\pi \rightarrow \pi^*$ valence states of the indigo molecule together with the computed oscillator strengths and transition moment directions. Five $^1B_u$ and eight $^1A_g$ form the computed spectrum up to 7.5 eV. The lowest $^1B_u$ excited state is computed at 1.96 eV with an oscillator strength of 0.155. The excitation energy is close to the $^1B_u$ energy in bispyrroleindigo, which shows that the addition of new groups has only a minor influence on a transition that is mainly described by the HOMO → LUMO one-electron promotion (63% of the CASSCF wave function). Figure 2 shows the CASSCF HOMO and LUMO orbitals for the $1\,^1B_u$ state of indigo. The excitation energy to the $1\,^1B_u$ state is somewhat lower than the experimental excitation energy for indigo in gas phase (2.3 eV), but it falls into the expected accuracy range. In ethanol the transition energy is 2.0 eV.[6] The Mulliken population analysis shows that a

Table 8. Calculated and experimental excitation energies (eV), oscillator strengths (*f*), and transition moment directions ($TM_{dir}$, °) for the excited singlet states in indigo.

| State | Excit. energ. CAS | PT2 | Exp. [a] | *f* | $TM_{dir}$ [b] |
|---|---|---|---|---|---|
| $1\,^1B_u$ ($\pi \rightarrow \pi^*$) | 3.63 | 1.96 | 2.0 | 0.155 | +38 |
| $2\,^1A_g$ ($\pi \rightarrow \pi^*$) | 3.71 | 2.64 | – | forb. | – |
| $3\,^1A_g$ ($\pi \rightarrow \pi^*$) | 4.67 | 2.80 | – | forb. | – |
| $2\,^1B_u$ ($\pi \rightarrow \pi^*$) | 6.36 | 3.49 | – | 0.050 | +32 |
| $4\,^1A_g$ ($\pi \rightarrow \pi^*$) | 5.38 | 3.53 | – | forb. | – |
| $3\,^1B_u$ ($\pi \rightarrow \pi^*$) | 5.34 | 3.55 | 3.6–3.8 | 0.411 | –4 |
| $4\,^1B_u$ ($\pi \rightarrow \pi^*$) | 5.16 | 3.59 | – | 0.009 | +4 |
| $5\,^1B_u$ ($\pi \rightarrow \pi^*$) | 5.92 | 3.93 | – | 0.073 | –25 |
| $5\,^1A_g$ ($\pi \rightarrow \pi^*$) | 6.36 | 4.11 | – | forb. | – |
| $6\,^1A_g$ ($\pi \rightarrow \pi^*$) | 6.23 | 4.33 | – | forb. | – |
| $7\,^1A_g$ ($\pi \rightarrow \pi^*$) | 7.16 | 4.41 | – | forb. | – |
| $8\,^1A_g$ ($\pi \rightarrow \pi^*$) | 6.95 | 4.64 | – | forb. | – |
| $6\,^1B_u$ ($\pi \rightarrow \pi^*$) | 7.07 | 4.71 | 4.4 | 0.124 | –8 |
| $7\,^1B_u$ ($\pi \rightarrow \pi^*$) | 7.70 | 5.00 | – | 0.087 | –27 |
| $9\,^1A_g$ ($\pi \rightarrow \pi^*$) | 6.74 | 5.00 | – | forb. | – |
| $8\,^1B_u$ ($\pi \rightarrow \pi^*$) | 7.63 | 5.10 | – | 0.058 | –9 |
| $9\,^1B_u$ ($\pi \rightarrow \pi^*$) | 7.12 | 5.36 | 5.2 | 0.220 | –27 |

[a] Values for indigo in ethanol; ref. [6]. [b] Transition moment directions defined in the text.

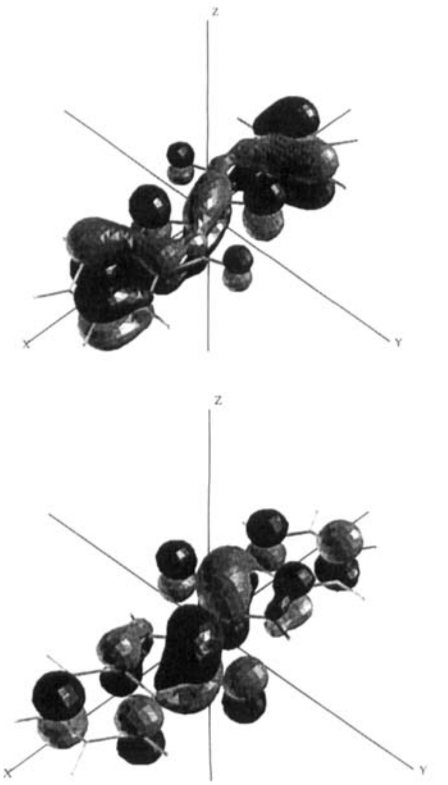

Figure 2. Molecular orbital composition for the HOMO (top) and LUMO (bottom) CASSCF orbitals of the $1\,^1B_u$ excited state of the indigo molecule. The surface value for the orbitals is 0.03 au. Positive parts of the orbitals are shaded with a darker gray tone.

charge transfer has taken place basically from the nitrogen (+0.20e) to the oxygen (–0.12e), $C_1$ (–0.12e), and $C_2$ (–0.10e) in each of the two subunits of the molecule, with minor contributions from the other atoms. These values are lower than those computed for the H-chromophore and bispyrroleindigo. One qualitative conclusion that can be drawn from the analysis of the CASSCF molecular orbitals is that the HOMO orbital is a strongly bonding orbital for the two central carbon atoms $C_1$ and $C'_1$ (see Figure 2), while the LUMO orbital is antibonding for the same atoms and strongly bonding for $C_1-C_2$. As the $1\,^1B_u$ state is mainly described by the HOMO → LUMO excitation, it can be easily predicted that the basic change in geometry taking place in the excited state will be the elongation of the central double bond $C_1{=}C'_1$, which probably will become almost a single bond, and the decrease in the $C_1-C_2$ bond length. This structure closely resembles the so-called leuco form of indigo, that is, the reduced colorless system used to lock the dye in the fiber.[3]

Figures 3 and 4 show the differences in electron density between the ground state and the most intense $^1B_u$ states. The negative charge flow from the nitrogens (darker zones) towards the oxygens and $C_1$ and $C_2$ carbons (brighter zones representing increase in charge) is the common feature in all the studied states. The loss of charge for the central $C_1-C'_1$ bond appears in all the states, although it is less important in the $1\,^1B_u$ transition. The contribution of the benzene rings to the transitions differs in the various $^1B_u$ states. The $1\,^1B_u$ transition shows more electron density transfer among the benzenoid carbons than was expected. The resemblance between the excitation energies of bispyrroleindigo and indigo suggest, however, that this plays a secondary role. The participation of these carbon atoms is minor for the $3\,^1B_u$ transition, which is computed to be the most intense transition in the spectrum. The remaining transitions have different contributions from the ring carbons, but in all of them most of the charge transfer is within the central atoms of the molecule.

The effect of substitutions on the visible band of indigo can be studied by means of the electron density plots. The picture of the $1\,^1B_u$ transition in Figure 3 shows that on excitation the electron

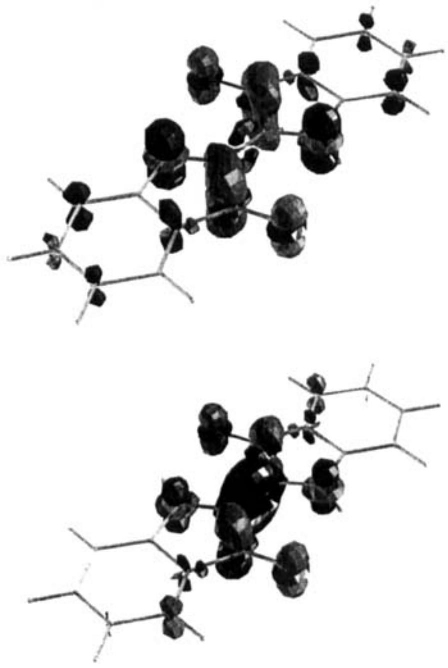

Figure 3. Electron density differences between the ground state and the $1\,^1B_u$ (top) and $3\,^1B_u$ (bottom) excited states in indigo. The surface value is 0.004 au. Darker zones have a larger density in the ground state. Lighter zones have a larger density in the excited state.

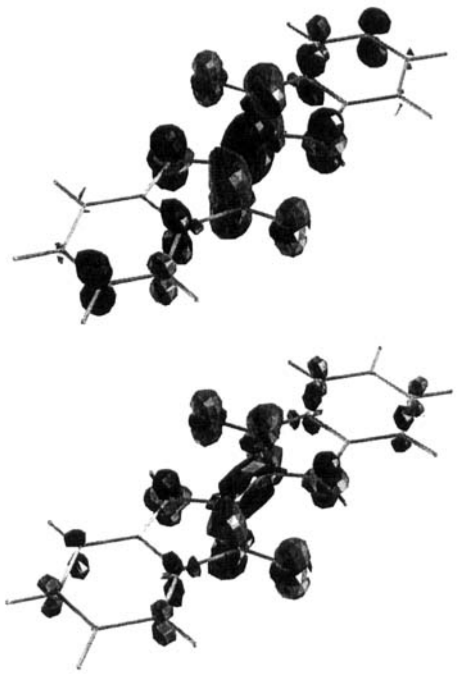

Figure 4. Electron density differences between the ground state and the $6\,^1B_u$ (top) and $9\,^1B_u$ (bottom) excited states of indigo. The surface value is 0.004 au. Darker zones have a larger density in the ground state. Lighter zones have a larger density in the excited state.

density decreases in the 5,5'- and 7,7'-positions and increases in the 6,6'-positions, while no difference is observed in 4,4'-positions. Electron donors, such as halogens or methoxy groups, are predicted to cause a bathochromic shift with respect to the unsubstituted indigo molecule if they are at the 5,5'- or 7,7'-positions and a hypsochromic shift if they are at the 6,6'-positions. This is the case for Tyrian purple (6,6'-dibromoindigo), which has its visible band at higher energies than indigo. The effects are also observed when chlorine or methoxy groups are the substituents.[3] The effect of electron acceptors such as the nitro group is the reverse of that of electron donors.

The second feature observed in the ultraviolet–visible spectrum of indigo in ethanol is a broad band stretching from 3.5 to 3.9 eV. Our calculations show that there are four $^1B_u$ states at close energies. The $3\,^1B_u$ state at 3.55 eV has the largest computed intensity. The composition of its wave function (cf. Table 6) is similar to the $2\,^1B_u$ state in bispyrroleindigo computed at 4.11 eV and is described mainly by the excitation HOMO − 2 → LUMO, with net charge transfer from $N_1$ and $C_1$ to the carbonyl groups. The larger oscillator strength computed for indigo is probably due to the absence of important doubly excited configurations, which appear in the $2\,^1B_u$ state of bispyrroleindigo. The other three $^1B_u$ states computed at 3.49, 3.59, and 3.93 eV all have smaller intensities than $3^1B_u$. The third observed band of indigo spectrum at 4.4 eV is the most intense one. We relate this band to the computed $6\,^1B_u$ state at 4.71 eV with an oscillator strength of 0.124. It is important to note that the oscillator strength is computed as the total area of the band and, though the peak at 4.4 eV is the most intense of the experimental spectrum[6] in ethanol, it is also a sharp band, while the $3^1B_u$ transition is observed as a broad band. The contribution of the benzene ring carbons to the charge transfer processes is larger for the $6\,^1B_u$ transition, but, in any case, the excitation energy and the intensity are similar to the values for the $3^1B_u$ band in bispyrroleindigo. Two $^1B_u$ states are computed at 5.00 and 5.10 eV with low intensity and important contributions of doubly excited configurations. Finally, the $9^1B_u$ state is computed at 5.36 eV with an oscillator strength of 0.220, and can be assigned to the band observed in the spectrum of indigo at 5.2 eV. This $9\,^1B_u$ state is probably related to the $4\,^1B_u$ state in bispyrroleindigo computed at 5.30 eV.

Eight excited $^1A_g$ $\pi \rightarrow \pi^*$ states have been computed for indigo. The two low-lying $^1A_g$ excited states can be approximately described as the classical combination $A^-$ and $A^+$.[30] The $2\,^1A_g$ valence state at 2.64 eV is mainly composed by the HOMO − 1 → LUMO (50%) and HOMO → LUMO + 1 (11%) excitations. For the $3^1A_g$ state at 2.80 eV the corresponding contributions are 11 and 24%, respectively. In addition there is a significant participation of doubly excited configurations in both cases. The low-lying $^1A_g$ valence excited states in the H-chromophore and bispyrroleindigo have similar characteristics.

The transition moment directions for the $^1B_u$ states of the three systems studied were also computed. The long-axis direction is defined as 0° and the short-axis direction as ±90°. To our knowledge there is no experimental information available on this property. For all three systems the low-lying transition was computed to be basically long-axis polarized, although in indigo the value of the angle (+ 38°) indicates almost intermediate polarization. In the H-chromophore and bispyrroleindigo the most intense computed absorption has a clear short-axis polarization, but not in indigo where all the transitions are long-axis polarized. Previous experience indicates[30, 31, 32] that the effect of a solvated or crystalline environment on the value of the transition moment directions of the valence states is only small, typically ±10–20°.

## Conclusions

The electronic spectra of the indigoid dyes H-chromophore (**III**), bispyrroleindigo (**II**), and indigo (**I**) have been computed by using the CASSCF/CASPT2 method. Excitation energies, oscillator strengths, and transition moment directions for the different valence states have been included in the calculations. The study supports the old hypothesis[3, 6, 7] that the H-chromophore structure is responsible for the lowest transition observed in the visible spectra of indigoid dyes close to 2 eV. The structure containing the complete pyrrole-type rings as in bispyrroleindigo is, however, the basic model that gives a quantitative agreement with the $1\,^1B_u$ indigo transition in the visible spectrum. The CASPT2-computed excitation energies and intensities also show that bispyrroleindigo is a good model for the intense $^1B_u$ transitions observed in the indigo spectrum up to 5.2 eV. Additional states having a benzenoid-type character appear in indigo with low intensity. The computed spectrum for indigo has four medium to intense $^1B_u$ transitions at 1.96, 3.55, 4.71, and 5.36 eV. They can be assigned to the observed features in the spectrum of indigo in ethanol at 2.0, 3.5–3.9, 4.4, and 5.2 eV, respectively. The present study confirms the ability of modern quantum chemistry to provide accurate and quantita-

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tive answers to problems in chemistry and photophysics involving molecules of medium to large size such as indigo and related systems, which were previously too large for ab initio methods. This was the case for dyes and large and complex molecules in general. We can now look to a future in which ab initio methods will provide a useful tool for the dye industry.

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[1] J. Griffiths, *Color and Constitution of Organic Molecules*, Academic Press, London, **1976**.

[2] E. B. Knott, *J. Chem. Soc.* **1951**, p. 1024.

[3] H. Zollinger, *Color Chemistry. Syntheses, Properties and Applications of Organic Dyes and Pigments*, 2nd ed., VCH, Weinheim, Germany, **1991**.

[4] J. Kirk-Othman, *Encyclopedia of Chemical Technology*, Wiley, New York, **1993**.

[5] D. Leupold, S. Dähne, *Theor. Chim. Acta.* **1965**, *3*, 1.

[6] M. Klessinger, W. Lüttke, *Tetrahedron.* **1963**, *19 Sup. 2*, 315.

[7] M. Klessinger, *Tetrahedron.* **1966**, *22*, 3355.

[8] E. Wille, W. Lüttke, *Chem. Ber.* **1973**, *106*, 3240.

[9] S. Dähne, D. Leupold, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 984.

[10] W. Lüttke, M. Klessinger, *Ber.* **1964**, *97*, 2342.

[11] W. Lüttke, H. Hermann, M. Klessinger, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 598.

[12] M. Okawara, T. Kitao, T. Hirashima, M. Matsuoka, *Organic Colorants. A Handbook of Data of Selected Dyes for Electrooptical Applications*, Elsevier–Kodansha, Amsterdam–Tokyo, **1988**.

[13] B. O. Roos, M. P. Fülscher, P. Å. Malmqvist, M. Merchán, L. Serrano-Andrés, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy* (Ed.: S. R. Langhoff), Kluwer, Dordrecht, The Netherlands, **1995** , p. 357.

[14] B. O. Roos, K. Andersson, M. P. Fülscher, P.-Å. Malmqvist, L. Serrano-Andrés, K. Pierloot, M. Merchán, in *Advances in Chemical Physics: New Methods in Computational Quantum Mechanics, Vol. XCIII: 219*, (Eds.: I. Prigogine, S. A. Rice), Wiley, New York, **1996**.

[15] K. Pierloot, B. Dumez, P.-O. Widmark, B. O. Roos, *Theor. Chim. Acta* **1995**, *90*, 87.

[16] E. A. Gribova, G. S. Zhdanov, G. A. Golder, *Kristallografiya* **1956**, *1*, 53.

[17] P.-O. Widmark, P.-Å. Malmqvist, B. O. Roos, *Theor. Chim. Acta* **1990**, *77*, 291.

[18] M. P. Fülscher, B. O. Roos, *Theor. Chim. Acta* **1994**, *87*, 403.

[19] J. Olsen, B. O. Roos, P. Jørgensen, H. J. Aa. Jensen, *J. Chem. Phys.* **1988**, *89*, 2185.

[20] P.-Å. Malmqvist, A. Rendell, B. O. Roos, *J. Phys. Chem.* **1990**, *94*, 5477.

[21] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, K. Wolinski, *J. Phys. Chem.* **1990**, *94*, 5483.

[22] K. Andersson, P.-Å. Malmqvist, B. O. Roos, *J. Chem. Phys.* **1992**, *96*, 1218.

[23] B. O. Roos, in *Advances in Chemical Physics; Ab Initio Methods in Quantum Chemistry—II* (Ed.: K. P. Lawley), Wiley, Chichester, England, **1987**, Chapt. 69, p. 399.

[24] B. O. Roos, K. Andersson, *Chem. Phys. Letters* **1995**, *245*, 215.

[25] B. O. Roos, K. Andersson, M. P. Fülscher, L. Serrano-Andrés, K. Pierloot, M. Merchán, V. Molina, *J. Mol. Struct. (Theochem)* **1996**, *388*, 257.

[26] P. Å. Malmqvist, B. O. Roos, *Chem. Phys. Letters* **1989**, *155*, 189.

[27] K. Andersson, M. P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, J. Olsen, B. O. Roos, A. J. Sadlej, M. R. A. Blomberg, P. E. M. Siegbahn, V. Kellö, J. Noga, M. Urban, P.-O. Widmark, *MOLCAS Version 3*, Dept. of Theor. Chem., Chem. Center, Univ. of Lund, P. O. B. 124, S-221 00 Lund, Sweden Lund **1994**.

[28] J. Abe, Y. Nagasawa, H. Takahashi, *J. Chem. Phys.* **1989**, *91*, 3431.

[29] L. Serrano-Andrés, R. Lindh, B. O. Roos, M. Merchán, *J. Phys. Chem.* **1993**, *97*, 9360.

[30] L. Serrano-Andrés, B. O. Roos, *J. Am. Chem. Soc.* **1996**, *118*, 185.

[31] L. Serrano-Andrés, M. P. Fülscher, *J. Am. Chem. Soc.* **1996**, *118*, 12190.

[32] L. Serrano-Andrés, M. P. Fülscher, *J. Am. Chem. Soc.* **1996**, *118*, 12200.