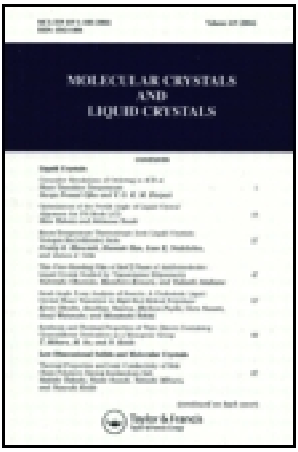

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Color Prevision of Activated Forms of Photochromic Spirooxazines and Chromenes

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COLOR PREVISION OF ACTIVATED FORMS OF PHOTOCHROMIC SPIROOXAZINES AND CHROMENES

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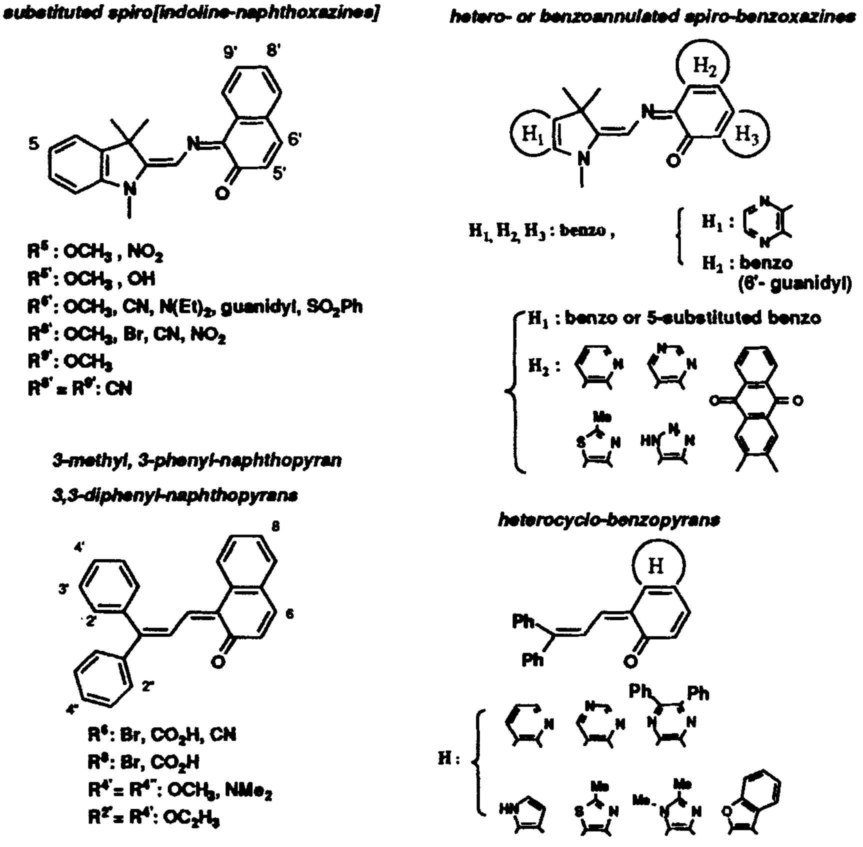
Abstract Different kinds of semi-empirical quantic calculations have been used to model the lower electronic transition of photomerocyanines issued from photochromic spirooxazines and chromenes. PPP-MO leads to satisfying correlations between experimental and calculated λ_{max} of an extended set of compounds. This interesting result allows to predict with a good assumption the effect of a given substitution on the electronic absorption. In contrast, all valence-electrons methods gave deceptive results as well concerning the value of the λ_{max} as concerning the substituent effect on the shift of this λ_{max}. It is suggested that a precise study of the fundamental and excited reaction pathways of the photochromic process could bring decisive informations about the modelling of the electronic absorption of the colored forms of spirooxazines and chromenes.

INTRODUCTION

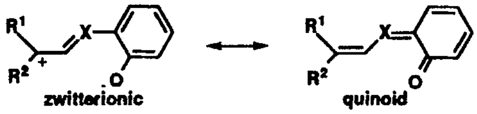
Photochromic spirooxazines and chromenes are of particular interest for the design of variable optical transmission materials due to their intense colorability and their good fatigue resistance.[1] For this kind of application it is necessary to cover whole the visible spectrum using a small number of compounds. The developed color upon UV stimulation depending markedly on the substitution of the molecules, [2-6] methods able to predict the electronic absorption spectra of the colored forms of spirooxazines and chromenes would be of considerable interest to extend the available range of colors but also to design new photochromic pigments.



scheme 1

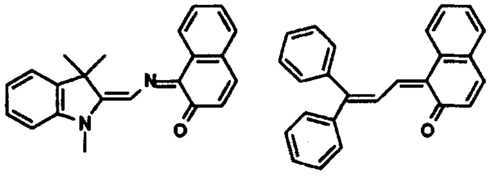
The building of such theoretical models needs, for standardization, reliable experimental data. In order to acquire a better understanding of the structure and substitution effects on the color of photomerocyanines, we synthesized a series of photochromic compounds and studied their photochromic characteristics. [2-9] Completed by literature data, [5,6] a large set of experimental absorption wavelengths for spirooxazines and chromenes are available. In scheme 1 are reported the different compounds used to investigate how some theoretical methods could give a correct description of their spectroscopic characteristic. 5-,5'-,6'-,8'-,9'- substituted spiro[indoline-naphthoxazines] and benzo- or heterocyclo-annulated spirobenzoxazines lead to photomerocyanines with visible absorption ranging from 538 nm to 666 nm in non polar solvent (toluene) or polymer matrix. In the chromene series, 3-methyl-3-phenylnaphthopyran, substituted-3,3-diphenylnaphtopyrans and benzo -or heterocycloannulated benzopyrans allow to create a large range of visible absorption for activated forms, from about 400 nm to 600 nm.

The knowledge of reliable geometries of the studied compounds are also needed to perform modeling calculations. As well for the photomerocyanines of spirooxazines as for the photomerocyanines of chromenes, two geometries corresponding to extreme resonance formula can be considered (scheme 2). Depending on the π-electron repartition, a zwitterionic and a quinoïd representations are possible. For both series experimental results show that, especially in non polar solvent, a quinoïd representation is more reasonable. Solvent effects on electronic absorption undergo a positive solvatochromism, [8, 10-12] i.e., the maximum of the absorption band undergoes a red shift from non-polar to polar solvents. This behaviour indicates that the ground state is less polar than the excited state. A quinoïd-like structure has been confirmed for a permanent open form of a spirooxazine by X-ray diffraction study.[12]



scheme 2

A complication in carrying out calculations on photomerocyanines of this type is due to the existence of different geometrical isomeric forms. In the oxazine series it has been proved by semi-empirical calculations, [13,14] ab-initio calculations, [15] but also by NMR [15,16] and X-ray diffraction experiments [12] that one transoïd isomer is more probable. For that reason our different calculations were worked out on this isomer for the spirooxazine series and on the equivalent isomer of the 3,3-diphenylnaphtopyran series (scheme 3). For the latest, we confirmed by semi-empirical calculations (PM3) the best stability of this isomer. Moreover we can point out that, if the open form of spiro[indoline-naphtoxazines] is quasi planar, in contrast the open form of the chromenes exhibit two phenyl groups twisted out of the mean plan defined by the quinoïd moiety.



scheme 3

Theoretical electronic transitions have been calculated with the help of various quantic semi-empirical methods. It is well known that π-electrons methods lead to convincing results concerning the prevision of color of dyes.[17] PPP-MO method was recently applied to few spirooxazines by Christie *et al* who obtained promizing results.[18] Besides this program, we used also all-valence electrons methods especially devoted to electronic transition calculations. In this work are presented results obtained in the frame of CNDO/S[19], INDO1 (ZINDO)[20] and methods included in AMPAC[21]. For geometries optimizations we used both molecular mechanics through the GenMol program[22] and also quantic semi-empirical methods (AMPAC).

RESULTS AND DISCUSSION

PPP-MO program was applied to twenty two compounds of the spirooxazines series and ten compounds of the chromene series. In the last cases we have forced the two phenyl groups to planarity even if this conformation is not reasonable regarding the steric constraint. On the other hand we adjusted valence state ionization potential and electron affinity values of the nitrogen atom of the azo-methine bridge of the open forms of spirooxazines to have a better agreement between calculated and experimental values. Good relationships between experimental and theoretical wavelengths of absorption have been found : correlation coefficients are respectively O.96 and 0.99 for spirooxazines and chromenes (Figure 1a). Moreover, if substituted spiro[indoline-naphthoxazines] and annulated spirobenzoxazines are considered separatly, correlation is better (Figure 1b). Those interesting results allow a reasonable evaluation of the effect of a given substitution on the electronic absorption of photomerocyanines. For instance, using the found correlation between experimental and calculated values for substituted spiro[indoline-naphtoxazines](λ_{exp} (nm) = 1.672 λ_{calc} (nm) - 376) we can predict the effect of substituents linked on the 5'- to 9'- positions of the quinoïd part. Experimentally, we have shown that a CN group in the 6'-position shifts the λ_{max} to 641 nm (in toluene) instead of 594 nm for the unsubstituted parent compound. According to calculations the shift would be greater (λ_{max} = 661 nm) for a 6'-NO2 substitution. If two electronwidthdrawing groups (CN or NO_2) were placed on both 5'- and 6'-positions, the shift would be over 700 nm. On the other hand, the association of an electron-donnor substituent (OCH_3) linked on the 7'- or 8'-position with a cyano group on the 6'-position would increase the bathochromic shift. These projected data are

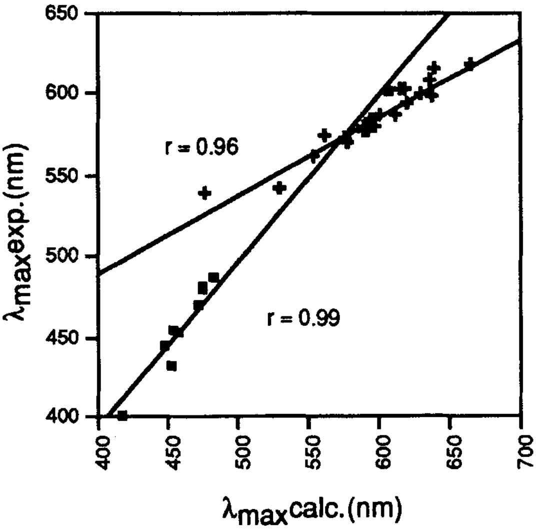


FIGURE 1a

Correlations between experimental and calculated (PPP-MO) absorption wavelengths of photomerocyanines: spirooxazines (+) and 3,3-diphenyl-naphthopyrans (■)

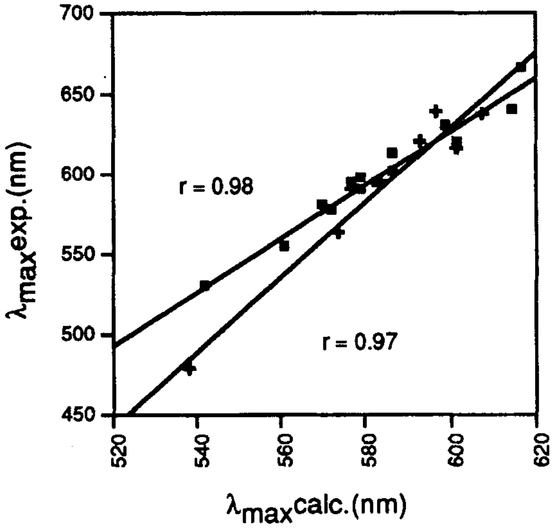


FIGURE 1b

Correlations between experimental and calculated (PPP-MO) absorption wavelengths of photomerocyanines: substituted spiroindoline-naphthoxazines] (■) and annulated spirobenzoxazines (+)

due to the enhancement, by this kind of substitutions, of the charge transfer occuring from the indoline ring to the quinoïd part during the electronic transition.

All valence-electrons methods like CNDO/S and INDO1 are normally able to calculate electronic spectra of planar or non planar molecules and the effect of all structural modifications can be taken into account.

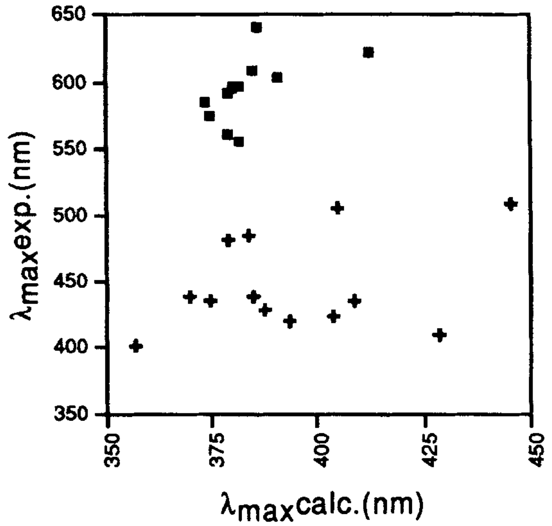


FIGURE 2

Correlations between experimental and calculated (CNDO/S) absorption wavelengths of photomerocyanines: spirooxazines (■) and chromenes (+).

We applied CNDO/S to twelve spirooxazines[14] and thirteen chromenes using two different set of parameters (Ohno and Mataga). 80 CI were included. Figure 2 summarizes data obtained with the combination (GenMol geometry, Mataga parametrization) giving the less deceptive previsions. For spirooxazines we showed previously [14] that the theoretical values are very far from the experimental values (around 400 nm for calculated and 600 nm for experimental) and moreover the substituent effects are not correctly modeled especially for substituents giving high shifts of the λ_{max}. The same kind of the results is obtained with chromenes, showing the lack of any correlation.

The INDO1 method seemed to be very attractive regarding the absolute value of the calculated λ_{max} of the unsubstituted spiro[indoline-naphthoxazine] (calc. = 585 nm, exp. = 594 nm). In fact, the λ_{max} value depends markedly on the number of introduced CI, and the best results are obtained if only 6 CI are taken into account (3π-occupied MO and 3π-unoccupied MO). A bathochromic shift is effectively calculated with a cyano group in the 6'- position, (λ_{max}calc. = 620 nm, λ_{max}exp. = 641 nm) but a bathochromic shift is also predicted with a 6'-OCH_3 group instead of an hypsochromic shift (λ_{max}calc. = 614 nm, λ_{max}exp. = 554 nm), preventing any other prevision.

Finally, concerning all valence-electrons methods, we used the different programs of the AMPAC package (MNDO, AM1, PM3) introducing ten CI. Combination of different optimized geometries with different hamiltonians, applied to a set of twenty seven photomerocyanines of spirooxazine and chromene series leads to bad results. The best correlation coefficient obtained between experimental and calculated λ_{max} are 0.76 for spirooxazines and 0.65 for chromenes. The substituent effects, as for the previous all valence-electrons methods were not correctly modeled with a gap of + 11 % to - 49 % compared to experimental values.

CONCLUSION-PERSPECTIVES

At this stage of the study we can conclude about the evaluation of electronic transitions of photomerocyanines of spirooxazines and chromenes by quantic semi-empirical calculations :

- PPP-MO gives interesting correlation between experimental and calculated λ_{max} and previsions of the developed color are possible. But application is limited to planar molecule and to a set of π-conjugated substituents. Nevertheless it is the first time that predictions can be made on a large scale in the field of photochromic compounds.
- Whole semi-empirical calculations involving all valence-electrons leads to unworkable results. Two reasons can be put forward : excited states are uncorrectly calculated or the chosen conformation of the photomerocyanine is not the good one, or both. A confirmation seems to be brought by an unexpected relationship we found recently [23] between λ_{max} of photomerocyanines of spiro[indoline-naphthoxazines] and the electronic charge of the C-2' of the spiro form. If the electronic transitions were related to the variation of the electronic distribution on the naphthoxazine part, one could expect the same kind of relationship with the electronic charge of the 2'-carbon atom of the open form. We have checked the lack of such a correlation using semi-empirical calculations (AM1, PM3). This means, perhaps, that the supposed structure of the photomerocyanine is not correctly modelled and then the electronic transition is not calculated from the best conformation. In fact it would be necessary to know the photochromic reaction pathway involving both singlet excited state for the opening and ground state for the closure. We have to know the potential surface of the S_1 state to look for particular conformations corresponding to minimum energy along the surface. Calculations using PM3 method with the options TS (Transition State) and Intrinsic Reaction Coordinate are in progress.

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