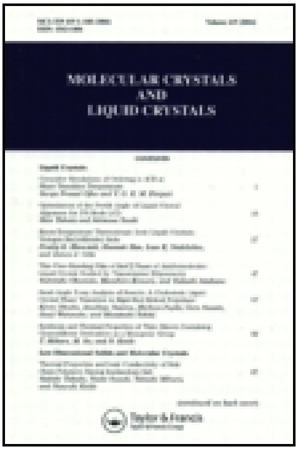

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Color Prediction of Photochromic Organic Compounds: Theoretical Calculations of Ground and Excited States of Spiropyrans, Spirooxazines and Diarylnaphthopyrans

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Color Prediction of Photochromic Organic Compounds: Theoretical Calculations of Ground and Excited States of Spiropyrans, Spirooxazines and Diarylnaphthopyrans

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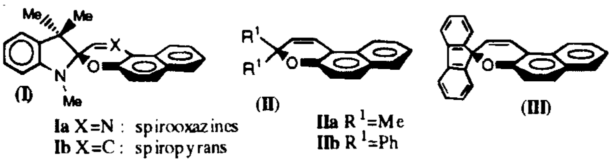
ab initio and semi-empirical geometry optimization in conjunction with modified CS-INDO-CIPSI calculations was performed to predict the λ_{max} of absorption of merocyanines forms of spiro[indoline-naphthoxazine], spiro[indoline-naphthopyran] and diarylnaphthopyrans. The predicted λ_{max} are found in excellent agreement with experimental values providing the geometry used for vertical energies calculation is delocalized, i.e. obtained at the UHF/AM1 and DFT levels.

Keywords: ab initio; DFT; excited state calculations; photochromic compounds

I - INTRODUCTION

Color prediction of photochromic molecules by theoretical methods is of particular interest for the design of variable optical transmission materials. Unfortunately, the description of electronic excited states of large conjugated molecules raises numerous problems and previous theoretical studies have shown that prediction of λ_{max} of absorption of photomerocyanines isomers with traditional methods (AM1, PM3, CNDO/S and INDO/S) was difficult to achieve with good accuracy [1]. To overcome these computational limitations we have used a new method (modified version of CS-INDO-CIPSI) recently developed for the description of electronic excited states of large conjugated molecules [2]. In the present work, the lower electronic transitions were calculated from the most stable conformations of open forms of photochromic spiropyrans, spirooxazines (I), diarylnaphthopyrans (II) and fluorene-chromene (III), determined by semi-empirical (AM1) and *ab initio*



SCHEME 1: Spiro forms of photochromic compounds studied

calculations. The aim of this paper was to check the capability of the modified CS-INDO-CIPSI method for estimating the vertical energies of photochromic molecules.

II - METHODS OF CALCULATION

The geometries of all molecules investigated here were optimized at the semi-empirical Hartree-Fock AM1[3], *ab initio* and DFT levels. Hartree-Fock, density-functional and hybrid Hartree-Fock/density-functional (BP86[5,6] and B3LYP[7] functionals were used) calculations were performed with the Gaussian 94/DFT [4] package. *ab initio* and DFT calculations were carried out employing the 3-21G basis set. The exchange functional used in the various DFT calculations was the gradient corrected functional of Becke (B) [5]. The correlation functional includes the gradient corrected functional of Perdew (P86) [6]. The three-parameter hybrid HF/DF methods used was B3LYP [7]. Geometry were fully optimized without symmetry constraint. However, it was found that AM1 geometries deviate significantly from the main molecular plane compared to *ab initio* geometries. Therefore, semi-empirical optimizations were performed under planar symmetry as constraint in order to produce reliable results. The optimized S_0 geometry obtained as described above were used as starting points to excited states calculations. The vertical transition energies, state dipole moments, and transition dipole moments were calculated with a version of CS-INDO-CIPSI method especially modified in order to compute the excited state of large conjugated molecules. In order to bypass severe limitations inherent to the calculations of electronic states in the case of large conjugated molecule, the σ MOs (bonding and antibonding) are localized while the π system is delocalized. As described in detail in Ref. [2], such strategy allows to reduce the number of two-electron integrals and the size of CI (configuration interaction) matrix.

III - RESULTS AND DISCUSSION

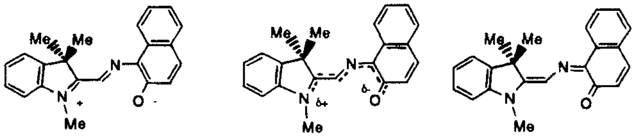
One of the main goal to achieve was the accuracy of the method predicting the λ_{max} of absorption in order to use it as a tool for designing new photochromic pigments. It is therefore necessary to know the energies and the geometries of the several trans isomers of the photomerocyanines to achieve this aim. Unfortunately, except only in a few cases [8], the open-form structure cannot be easily studied experimentally because of its unstability. Several levels of calculations were then used to determine i) the most stable photomerocyanine isomer and ii) the impact of the geometry upon the λ_{max} of absorption.

1)Ground state structures (semi-empirical and ab initio calculations)

The photomerocyanines studied here are constituted of two moieties, namely the left (indoline, di-methyl, di-phenyl or fluorene) and the right one (naphthalene moiety), linked by a conjugated system which contains three partial double bonds. Owing to these three central bonds, the photomerocyanine forms can exist either in eight distinct isomeric configuration (**Ia**, **Ib**) or only four distinct isomers in series **II** and **III**. Semi-empirical and *ab initio* calculations show that the *trans* isomers are largely preferred over the *cis* one because of less steric hindrance [9]. The order of stability calculated at the B3LYP/3-21G level of calculation for the *trans* isomers in gas phase is :

Ia : TTC (0)>CTC(1.94 kcal/mol)>>TTT(10.05 kcal/mol >>CTT(11.25 kcal/mol),and IIa : TC(0)> TT(5.1 kcal/mol)

The merocyanines can be represented by a mixture of resonant forms (localized forms), i.e. quinoid or zwitterionic, or delocalized structure (scheme2). The parameter that best expresses the conjugation is found to be the degree of bound alternation, Δr, within the binding chain between the two moieties of the photomerocyanines. Here, Δr is defined as the average sum of the absolute value of the bond-length differences between the adjacent bonds. It is expected that Δr is minimum for a delocalized system (Δr is zero for purely aromatic system like benzene) and gradually increases with increasing quinoidal character.



Zwitterionic Delocalized Quinoïd

SCHEME 2: schematic representation of 1,3,3-trimethylspiro-[indoline-naphthoxazine] photomerocyanines.

The optimized structural parameters of the most stable isomer (TTC or TC) of spiropyrans, spirooxazines (**I**), diarylnaphthopyrans (**II**) and fluorene-chromene (**III**) calculated by various methods are given in Table I. Concerning the naphthalene moiety and the linking chain, the molecular structures of the most stable photochromic isomer were found to be planar except for the compound **III** which deviate slightly from planarity. The planar structure reflects the crystal structure of the open permanent form [8].

From these geometries, it can be seen that the linking chain exhibit an alternation of double-single bonds at the Hartree Fock (HF/3-21G and RHF/AM1) level corresponding to the quinoïd representation depicted in scheme 2. However, inclusion of correlation effect through DFT calculations (B3LYP/3-21G and BP86/3-21G calculations) shifts the structure toward a more delocalized (i.e. more aromatic) rather than quinoidal structure as indicated by the Δr values.

TABLE I : Main geometric parameters of TTC and (for **Ia** and **Ib**) TC (for **II** and **III**) Isomers.

Ia	N_1-C_2	C_2=C_3	C_3-N_4	N_4=C_5	C_5-C_6	C_6=O_7	Δr
RHF/AM1	1.402	1.378	1.375	1.307	1.499	1.242	0.109
UHF/AM1	1.398	1.405	1.349	1.341	1.491	1.247	0.093
RHF/3-21G	1.371	1.350	1.376	1.281	1.489	1.227	0.123
B3LYP/3-21G	1.375	1.377	1.364	1.324	1.486	1.262	0.083
BP86/3-21G	1.384	1.389	1.371	1.343	1.493	1.279	0.083
Ib	N_1-C_2	C_2=C_3	C_3-N_4	N_4=C_5	C_5-C_6	C_6=O_7	Δr
UHF/AM1	1.407	1.387	1.408	1.395	1.477	1.247	0.073
B3LYP/3-21G	1.386	1.373	1.415	1.386	1.485	1.264	0.081
BP86/3-21G	1.394	1.384	1.418	1.401	1.494	1.280	0.070
IIa	C_1-C_2	C_2=C_3	C_3-C_4	C_4=C_5	C_5-C_6	C_6=O_7	Δr
UHF/AM1	1.479	1.377	1.416	1.393	1.479	1.246	0.097
B3LYP/3-21G	1.510	1.357	1.438	1.373	1.498	1.256	0.133
BP86/3-21G	1.517	1.373	1.438	1.388	1.507	1.271	0.123
IIb	C_1-C_2	C_2=C_3	C_3-C_4	C_4=C_5	C_5-C_6	C_6=O_7	Δr
UHF/AM1	1.449	1.398	1.408	1.399	1.479	1.247	0.076
B3LYP/3-21G	1.491	1.370	1.433	1.375	1.496	1.257	0.120
BP86/3-21G	1.483	1.387	1.431	1.392	1.504	1.273	0.104
III	C_1-C_2	C_2=C_3	C_3-C_4	C_4=C_5	C_5-C_6	C_6=O_7	Δr
UHF/AM1	1.467	1.388	1.404	1.400	1.479	1.247	0.082
B3LYP/3-21G	1.484	1.367	1.429	1.377	1.500	1.256	0.120
BP86/3-21G	1.486	1.382	1.428	1.393	1.507	1.272	0.107

This result is consistent with recent calculations[10] which indicated that HF level overestimates the stability of the localized structure. As an example, BP86/3-21G geometry of **Ia** exhibits the more delocalized structure while HF/3-21G and HF/AM1 show a quinoidal structure. It is surprising that delocalized structure is obtained at the unrestricted (UHF) AM1 level. These results cast doubt on the validity of using HF and semi-empirical methods for determining geometries of large conjugated systems. It is interesting to note that a donor substituent, -OMe, induces a more pronounced quinoidal character while a withdrawing substituent, -CN, induces a delocalized structure.

Excited states calculations from the most stable conformations.

The excited- and ground-state geometries are considered to be the same (Franck Condon approximation) since under optical frequencies, no geometric relaxation can occur. The properties of studied molecules are gathered in Table II. For the overall studied molecules, at the CI level, the main component (c.a. 85%) of the first excited state is found to correspond to the one-electron transition between the HOMO and LUMO levels.

If previous theoretical studies have shown that the calculated λ_{max} of photomerocyanine are underevaluated by about 200 nm with traditional methods (AM1, PM3, CNDO/S and INDO/S), our results show that this discrepancy comes, for the major part but not only, from the starting geometry. For instance, the structure **Ia** computed with BP86/3-21G method shows a λ_{max} at 561 nm which is very close to the experimental value, i.e. 578 nm in cyclohexane [11], whereas when it was computed with the HF/3-21G geometry the λ_{max} estimation is rough (490 nm).

TABLE II : Calculated maximum wavelength absorption of photochrome (nm).

Geometry	RHF/AM1	HF	UHF/AM1	B3LYP	BP86	Exptl
Ia	537	490	552	541	561	578
Deviation	7.1	15.2	4.5	6.4	2.9	
Ib	458	439	488	482	507	549
Deviation	16.6	20.0	11.1	12.2	7.6	
IIa	344	328	398	371	374	376
Deviation	8.5	12.8	5.8	1.3	0.5	
IIb	383	366	434	419	430	431
Deviation	11.1	15.1	0.7	2.8	0.2	
III	377	355	447	414	424	453
Deviation	16.8	21.6	1.3	8.6	6.4	
Ia(R=CN)	557	537	584	581	603	641
Deviation	13.1	16.2	8.9	9.4	5.9	
Ia(R=OMe)	454	433	543	529	551	554
Deviation	18.0	21.8	2.0	4.5	0.5	

* Deviation %: λ_{exp}^{max}-λ_{calc}^{max}/ λ_{exp}^{max}

From inspection of the Table II, it is clear that a delocalized geometry (i.e. DFT or UHF/AM1) leads to the best absorption close to the experimental values. Thus, excellent agreement is achieved with DFT(BP86/3-21G) geometry for **Ia** (λ_{max}calc=561 nm) with experimental measurements in non-polar solvent, such as cyclohexane (λ_{max}exp=578 nm). The agreement with experimental data is much better for the diarylnaphthopyrans (deviation less than 1%). It appears that our method seemed to be very attractive regarding the absolute value of the λ_{max} in conjunction with DFT or UHF/AM1 geometry.

The substituent effect is also correctly predicted, especially for the substituents giving high shifts of the λ_{max}, i.e. –CN and –OMe in the 6'-position of the naphthalene unit in indoline naphthoxazine series. The –CN substituent induces a bathochromic shift of λ_{max} ($\delta\lambda_{max}$calc= 42 nm, $\delta\lambda_{max}$exp= 63 nm in toluene) while the methoxy group has a hypsochromic shift ($\delta\lambda_{max}$calc= -10 nm, $\delta\lambda_{max}$exp= -24 nm in toluene).

The transition from the ground to the first excited singlet state results in an increase of the dipole moment for the compound studied. Consequently it is expected, as the solvent polarity increases, that the excited state is stabilized relatively to the ground state and the absorption band is red shifted. This bathochromic shift of the absorption maximum with the increasing solvent polarity is typical of spirooxazines [12]. However, the calculated rise of dipole moment is found much higher for **Ia** than for **IIb** (μ_{S0}=2.6 D; μ_{S1}=7.5 D for **Ia** and μ_{S0}=4.9 D; μ_{S1}=6.5 D for **IIb**) which suggests that this solvatochromism effect should be less important for diarylnaphthopyrans.

IV - CONCLUSION

It was shown that the linking chain between the left and right moieties of the studied photomerocyanines have a tendency toward the bondlength equalization, i.e. delocalized, rather than quinoidal structure. The theoretical longest wavelength maximum, λ_{max}, obtained over seven photochromic molecules indicated that the agreement between experimental and calculated spectra is better with the DFT or UHF/AM1 rather than with HF optimized structures of the molecule. The former show excellent agreement between the experimental and theoretical values. The substituent effect is also predicted by this approach with a satisfactory agreement. From a practical point of view, the UHF/AM1 method offers the best compromise between accuracy and computational time. On the basis of the increasing of the dipole moment between ground and first excited singlet state, it is also predicted that the solvatochromism effect should be more important in spiro[indoline-naphthoxazine] than in diarylnaphthopyrans series.

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