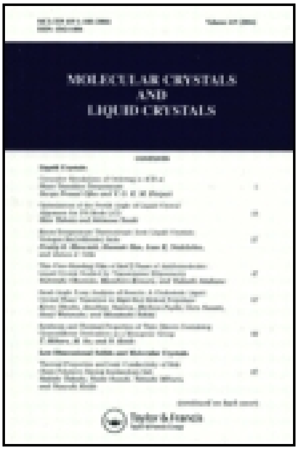

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Investigation of Some Photochromic Structures by Molecular Mechanics and Scf Mo Calculations

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INVESTIGATION OF SOME PHOTOCHROMIC STRUCTURES BY MOLECULAR MECHANICS AND SCF MO CALCULATIONS

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Abstract

In order to predict the geometry and electronic spectra of spiropyrans and spirooxazines, the validity of some semi-empirical methods has been checked. Results show that both AM1 and GenMol give reasonable geometrical values. If CNDO/S and INDO/S calculate well theoretical absorption of closed forms, in contrast, the λmax obtained for opened forms are underevaluated.

INTRODUCTION

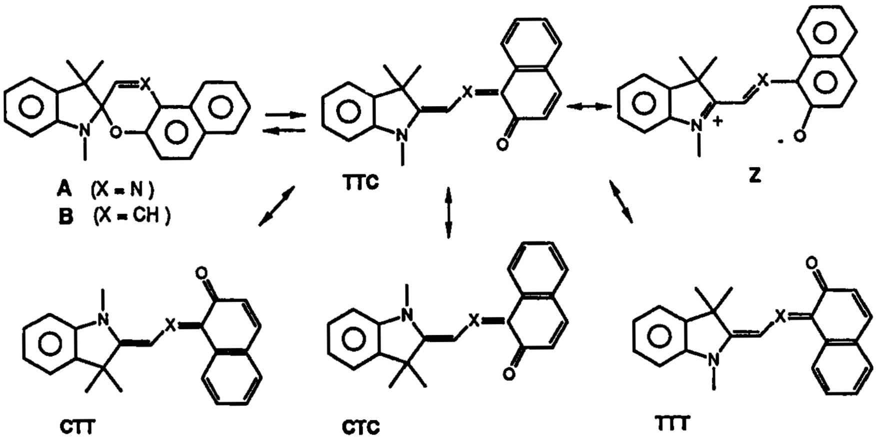
Since our first attempts to use quantum chemistry calculations on photochromic substances[1], a lot of progress has been made and recent papers reported interesting results with calculated models[2,3]. This leads us to investigate how some programs could give a correct description of a series of spiropyrans and spirooxazines, main topic of our research team.

We used a new revision of molecular mechanics program GenMol[4] and classical quantum chemistry methods AM1[5] (from AMPAC), INDO[6], CNDO/S[7] with the Ohno's or Mataga's parametrisations[8], and INDO/CS[9]. Attempts of best correlation was checked on two closed (colourless) and 12 open (coloured) species. Results were evaluated on the criterion of better match of calculated and experimental geometrical values and absorption spectra.

STRUCTURAL APPROACH

If some crystal structures of closed forms are available in the litterature, this is not the case for open forms due to their ephemeric existence. All initial geometries were computed by molecular mechanics program GenMol; then AM1 was used, one time without any

SCHEME 1



optimization to get a comparable value of the energy of formation, and a second time with full optimization to find the geometry of lowest energy according to AM1.

Computed distances and angles of closed forms AFF and BFF by both programs match satisfactorily with experimental values. Bond lengths, valence and dihedral angles are all within 5% of experimental ones.

For open forms, various isomers should be considered. We restricted our study to the four most probable CTT, CTC, TTC and TTT for both A and B.

Two isomers ATTC and ACTC shows near complete flatness while all others where found twisted, the two conjugated parts showing 15 to 55 degrees dihedral angle. In the parent compounds BTTC and BCTC, torsion is due to steric hindrance between the hydrogen in the position 4 and indoline portion.

The two flat A isomers exhibited lower energy than the two others, while in the B series no significant difference could be made between the four isomers. Both GenMol and AM1 are consistent on this point (see Table 1).

TABLE 1 Energies of formation from AM1 calculations in Kcal/mole

	A FF	A TTC	A CTT	A CTC	A TTT	A Z		B FF	B TTC	B CTT	B CTC	B TTT	B Z
GenMol Geometry	105	107	113	104	117	115		93	96	96	97	99	113
AM1 Geometry	85	90	92	89	95	-		78	79	80	79	80	-

Between the two limit tautomers, zwitterionic and quinonïd (respectively Z and TTC in Scheme 1), GenMol leads to a delocalized structure close to the quinoid side. AM1 finds the energy of zwitterionic tautomers AZ and BZ slightly higher than the quinoid ones (Table 1). From both tautomers, AM1 converges towards a delocalized structure quite halfway the two extremes. This is in good agreement with solvatochromic data observed on this kind of compounds[10].

At this point we had no clear evidence to decide which of the two sets of geometries, from GenMol and AM1, could be more satisfactory. The only experimental data available for open forms are the λmax in the visible spectrum, so we choose to perform absorption spectra calculations on previously obtained structures.

EVALUATION OF THE ELECTRONIC SPECTRA

Evaluating which species are responsible for the color of photochromic solutions is generaly a chalanging task; anyway, in toluene at room temperature and a few seconds after irradiation, the main compound should be the more stable thermodynamicaly. Open forms of spiropyrans are set aside because of the too many possible isomers. In spironaphtoxazines series, the two less stable isomers are not considered that let only the two flat ATTC and ACTC ; but incidentaly these two are supposed to have the same calculated absorption spectra what we verified. Then, calculations of only the TTC isomer of open forms of naphtoxazines should be convenient for our purpose.

To complete the study, a series of opened forms of substituted naphtoxazines that we recently synthetized in our laboratory was added (scheme 2). For each one, we calculated the two geometries obtained by GenMol and AM1, and both where submitted to calculation of absorption spectra.

For closed structures AFF and BFF, results are in reasonable agreement with experience; the spectra is the sum of absorption of the two perpendicular parts of the molecule. Fig. 1 shows an example of concordance between calculated and experimental spectra.

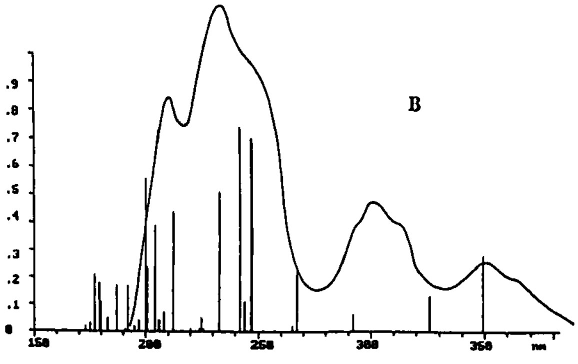
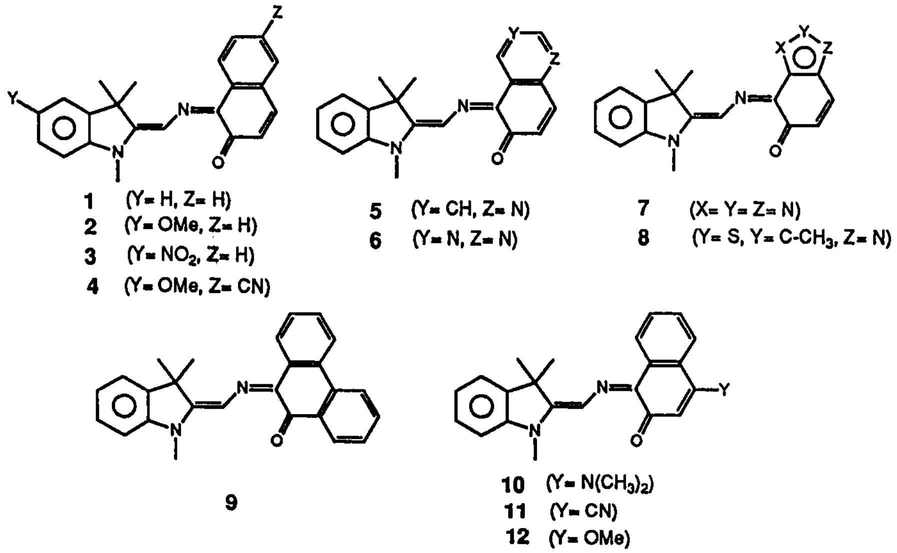


FIGURE 1. Experimental and calculated electronic absorption spectra of compound B (AM1 geometry INDO with the Mataga formulae).

SCHEME 2



1 (Y= H, Z= H)
2 (Y= OMe, Z= H)
3 (Y= NO_2, Z= H)
4 (Y= OMe, Z= CN)

5 (Y= CH, Z= N)
6 (Y= N, Z= N)

7 (X= Y= Z= N)
8 (Y= S, Y= C-CH_3, Z= N)

9

10 (Y= $N(CH_3)_2$)
11 (Y= CN)
12 (Y= OMe)

For open forms **1** to **12**, calculated λmax are in anyway underevaluated by about 200 nm. Nevertheless, we tried to find a correlation between experimental and calculated values of λmax. Results are summarized in Table 2. In every case, λmax of the compound **1** (without substituent) is taken as reference. For compounds **2** to **12** we have reported the Δλmax (i) = λmax (i) - λmax (**1**), i = 2, 12. In the last column, ΣE_{rr} represents the total errors of the considered method with respect to experience. For this set of compounds, the main band corresponding to the upper wavelengths, is a $\pi\pi^*$transition.

Regarding the whole results it appears that some substituent effects are unknown. This is true for compounds **10** to **12** substituted in the β-position with respect to the oxygen. This lack of precision must be mainly attributed to the configuration selection in our CI method. The $\pi\pi^*$ orbitals involved do not include the C-Y atomic orbitals in the calculation of the λmax. Thus excluding **10-12**, a reasonably good correlation can be made between experimental and calculated values of λmax (Fig. 2).

It should be noted that AM1 optimized structures give a much higher dispersion on the results than GenMol optimized ones. The combination GenMol-CNDO with Mataga formulae is definitely the most reliable method in this series.

TABLE 2 Experimental and calculated wavelength absorption of the studied opened forms of spirooxazines - Δλmax (i) = λmax (i) - λmax (1).

$$\Sigma E_{rr} = \sum_{i=2}^{i=9} (\Delta\lambda i_{calc.} - \Delta\lambda i_{exp})$$

Abbrevations for the methods and parametrisation :
C. = CNDO/S, H = Ohno, M = Mataga, I = INDO/S, I.CS = INDO/CS.

		λmax (nm)	Δλmax (nm)											
		1	2	3	4	5	6	7	8	9	10	11	12	ΣE_{rr}
Experience		594	+13	-11	+8	-4	+1	+1	+27	-20	-35	+47	-40	-
GenMol Geometries	C.H.	366	+5	-6	+9	0	-1	-7	+25	-2	-1	+3	+1	48
	I.H.	385	+4	-5	+13	0	-1	-9	+33	-4	-3	+5	0	58
	C.M.	380	+5	-6	+11	-1	+2	0	+33	-5	-1	+6	+2	42
	I.M.	404	+7	-9	+19	+1	+3	0	+42	-6	-3	+8	+1	56
	I.CS.	401	+3	-15	+10	+2	+6	+2	+29	-	-	+10	+2	-
AM1 Geometries	C.H.	374	+16	-11	+14	+4	+8	+20	+68	-6	-2	+6	-4	98
	I.H.	394	+7	-11	+19	+2	+12	+15	+60	-12	-3	+11	-5	89
	C.M.	391	+6	-9	+15	+3	+10	+27	+50	-10	-1	+10	-5	91
	I.M.	417	+9	-9	+21	+4	+16	+28	+62	-3	-4	+16	-6	120
	I.CS.	411	+5	-6	+19	+7	+16	+21	+48	-	-	+15	-6	

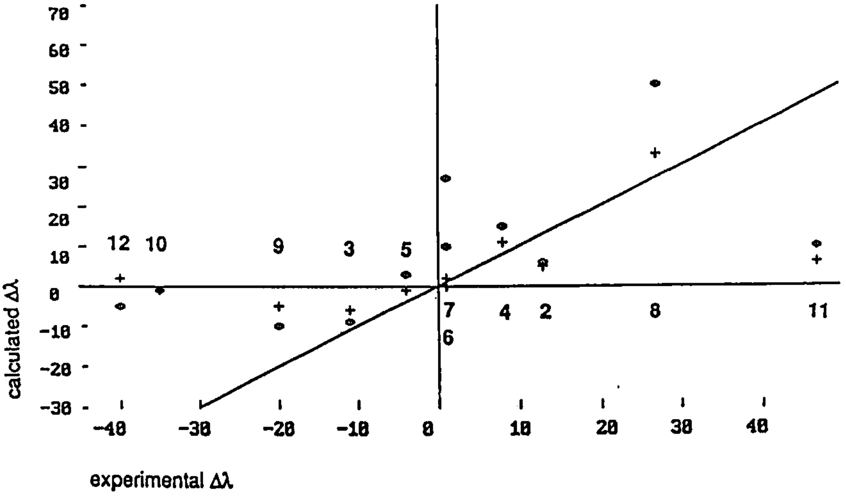


FIGURE 2 Correlation between experimental and calculated Δλmax (nm) for compounds **2** to **12** (Δλmax (i) = λmax (i) - λmax (1). λmax (i) are calculated with CNDO/S (Mataga formulae) from GenMol geometries (+) or AM1 geometries(o).

In conclusion, these semi-empirical methods represent an efficient help for the study of closed forms of spiro-photochromic compounds. On the other hand, they are inadequate to study open forms. We think that better results should be obtained using a selection of configurations based on a perturbational method (CIPSI).

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