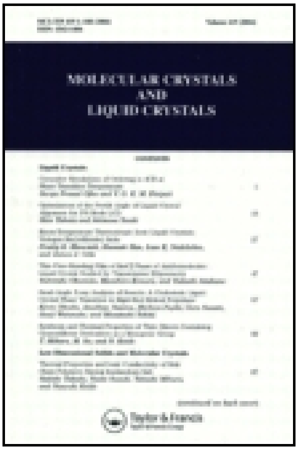

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Comparison of Photochromic Behaviour Between Spiroxazines and Spiropyrans: Theoretical Calculations of Ground and Excited States

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Version of record first published: 24 Sep 2006.

To cite this article: Vincenzo Malatesta , Luca Longo , Roberto Fusco & Giancarlo Marconi (1994): Comparison of Photochromic Behaviour Between Spiroxazines and Spiropyrans: Theoretical Calculations of Ground and Excited States, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 235-239

To link to this article: http://dx.doi.org/10.1080/10587259408037819

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 235–239
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Printed in the United States of America

COMPARISON OF PHOTOCHROMIC BEHAVIOUR BETWEEN SPIROXAZINES AND SPIROPYRANS: THEORETICAL CALCULATIONS OF GROUND AND EXCITED STATES

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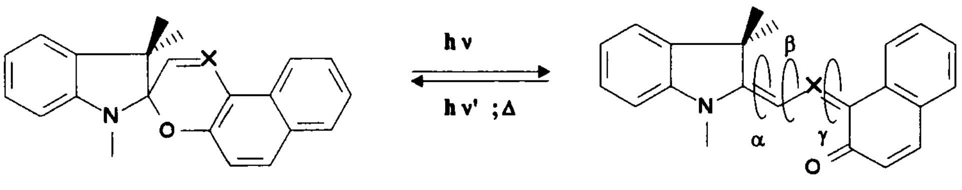
Abstract. MOPAC/AM1 and CNDO/S calculations have been performed on a spiro[indoline-naphthoxazine], a spiro[indoline-naphthopyran] and their open merocyanine(s) form. The energies were fully optimized and the bond orders, charge distribution and energies of both ground and excited states evaluated. The theroretical absorption spectra were calculated and found in good agreement with the experimental ones.

INTRODUCTION

Spiro-oxazines (I) and spiropyrans (II) exhibit photochromism both in solution and polymer matrices as they undergo, upon UV light excitation, isomerization from the colourless spiro to an intensly coloured ring open merocyanine (MC) form (1), SCHEME 1,:



(I) X = N ; (II) X =CH

(MC)

SCHEME 1

Several cis/trans isomers of the near-planar merocyanine form are possible with those having a cisoid configuration about the central bond (β=O$^{\bullet}$) being the least stable. A few theoretical studies have been carried out on spiropyrans (2,3) and spiro-oxazines (4,5). In our previous investigation (4) on (I) and some of its derivatives in the ground states, non-optimizeed geometries were used for MCs. We have now examined also their excited states and included in our study a spiro[indoline-naphthopyran] (II) that is characterized by a resistance to photochemical fatigue lower than that of (I) (1) We have performed MOPAC/AM1 calculations with full geometry optimization on (I), (II) and their most stable merocyanine isomers i.e. those having CTT, TTC, TTT and CTC configurations, in both the ground state (So), first excited singlet (^{1}S) and triplet (T) states in order to evaluate stabilities, bond orders, charge distribution and excitation energies. The results indicate that the merocyanine forms of (I) and (II) have a quinoid structure. CNDO/S calculations were also carried out on the spiro and ring open forms and their absorption spectra calcultated.

THEORETICAL METHODS

The AM1 modification of the MNDO-Hamiltonian has been used for all calculations. For (I) the experimental determined structural parameters (6) were used whereas for (II) standard literature parameters were adopted. The geometries were fully optimized. In the CNDO/S calculations (7), these geometries were used as starting points. The approximation adopted for the Coulomb repulsion integrals was that of Mataga-Nishimoto. The size of the configuration was fixed to 120 singly and doubly excited configurations in a space of 7x7 promotions.

RESULTS AND DISCUSSION

In Table 1 are reported the heat of formation ΔHf for (I) and (II) in the closed spiro form for the ground states (So), the first excited singlet (^{1}S) and triplet (T) states along with the dipole moment μ values. Where available the ΔHf for both the non-optimized and relaxed (optimized) geometry are reported.

TABLE1 - Heats of formation, ΔHf, and dipole moments for the So, ^{1}S and T states of the spiro forms of (I) and (II).

PHOTOCHROME	S_o	^1S	T	ΔE_s	ΔE_T	μ (Debye)
(I)	65.2 ^{a}	175.5	112.9	110.3	47.7	0.87
	65.2^b	145.6	101.4^b			
(II)	60.9^a	181.6^a	108.5		47.6	1.10
		139.9^b		79.9		

^{a} X-ray or non-optimized geometry; ^{b} optimized geometry.

Table 2 and 3 report the ΔHf for the four most stable isomers of the merocyanine form of (I) and (II) in the ground state, first excited singlet and triplet states.

TABLE 2. Heats of formation, ΔH_f, for the four most stable isomers of merocyanine of (I) in the So, ^{1}S and T states.

ΔH_f (Kcal/mol)								ENERGY GAP (Kcal/mol)	
ISOMER		α	β	γ	So	^{1}S	T	ΔE_s	ΔE_T
CTC	a	0	180	0	113.1				
	b	-8	151	-9	77.7	154.6	121.5	76.9	
	c	9	-157	45			101.4		23.7
TTC	a	180	180	0	108.5				
	b	-177	-167	4	77.3	161.3	120.8	84.0	
	c	172	-176	85			96.5		19.2
CTT	a	0	180	180	149.3				
	b	-7	160	170	76.9	159.0	127.3	82.1	
	c	11	178	85			94.9		18.0
TTT	a	180	180	180	148.9				
	b	176	159	171	77.2	162.8	124.1	85.6	
	c	-178	-178	89			98.7		21.5

α ,β, γ in degrees; [a] planar; [b] optimized; [c] optimized

TABLE 3 - Heats of formation, ΔH_f, for the four most stable isomers of merocyanine of (II) in the So, ^{1}S and T states.

ΔH_f (Kcal/mol)								ENERGY GAP (Kcal/mol)	
ISOMER		α	β	γ	So	^{1}S	T	ΔE_s	ΔE_T
CTC	a	0	180	0	146.4				
	b	5	-117	1	70.1	157.8	103.9	87.7	
	c	-77	-179	24			93.5		23.4
TTC	a	180	180	0	124.9				
	b	-177	-119	2	70.2	157.5	100.5	87.3	
	c	-178	-179	89			94.4		24.2
CTT	a	0	180	180	176.9				
	b	-9	131	172	70.0	156.9	102.1	86.9	
	c	-19	-177	88			93.9		23.9
TTT	a	180	180	180	159.7				
	b	178	138	168	70.7	157.8	103.7	87.1	
	c	99	178	113			93.3		22.6

α ,β, γ in degrees; [a] planar; [b] optimized; [c] optimized

For the spiro-oxazine there seems to be a slight preference for the CTT conformer. However the ΔH_f values are nested around 77 Kcal/mol. No strong geometrical preferences are evident in the case of the merocyanine isomers of the spiropyran (II). The calculated ΔH for the ring opening reaction is ca. 12 and 10 Kcal/mol for (I) and (II) respectively in good agreement with the 5.2 Kcal/mol measured for (I) in toluene(8). In general the triplet energy is rather low: ca. 23 and 21 Kcal/mol for the merocyanines of (II) and (I) respectively. The analysis of the bond orders for the chain linking the indoline and naphthalene moieties in MC shows that there is an alternation of double-single bonds as that depicted in SCHEME 1 for both (I) and (II) and this indicates that the merocyanine have essentially a quinoid structure in the ground state. Upon passing from the ground to the excited states there is a shift of bonds towards the carbonyl group to give more polar electronic configurations in keeping with the reported positive solvatochromism (8, 9) of (I) and (II).

In Table 4 are reported the dipole moments for the most stable isomers of the merocyanine forms of (I) and (II).

TABLE 4 - Dipole moments of the S_0, ^1S and T states of the most stable merocyanine forms of (I) and (II).

ISOMER		DIPOLE MOMENT (Debye)		
(I)		So	^1S	T
CTC	b	2.6	3.3	6.6
	c			3.4
TTC	b	1.8	1.9	7.4
	c			3.5
CTT	b	3.5	3.5	6.7
	c			3.2
TTT	b	4.2	5.0	8.0
	c			4.6
(II)		So	^1S	T
CTC	b	2.2	2.3	3.7
	c			3.2
TTC	b	1.9	1.8	3.7
	c			3.3
CTT	b	3.1	4.4	3.2
	c			4.2
TTT	b	3.5	5.1	3.8
	c			2.8

[b] optimized geometry; [c] relaxed triplet.

For the merocyanines of (I) the transition from the ground to the first excited singlet results in an increase of the dipole moment for the CTC and TTT isomers, whereas the relaxed triplet of CTC and TTC have dipole moment values larger than those of the ground states. In the case of (II) the dipole moment of the ^1S state is larger than that of S_0 for CTT and TTT isomers. The triplet state has again μ values larger than the ground state ones. The calculated spectra for (I) and (II) in the closed spiro form predict a low energy region having two transitions at 335 and 314 nm respectively whose intensity fits well with the observed bands at 350 and 320 nm. In the shorter wavelengths region we find a transition at 240 nm corresponding to the 250 nm band of the experimental spectrum. In the case of (II) a good agreement is also found for the lower energy part of the UV spectrum whereas a more structured spectrum is calculated for the region between 290 and 310 nm. As for the merocyanine forms of (I), based on the intensities ratio and distance between the two lowest bands, the calculated spectral pattern of the TTC isomer seems to fit better the experimental spectrum (fig 1).

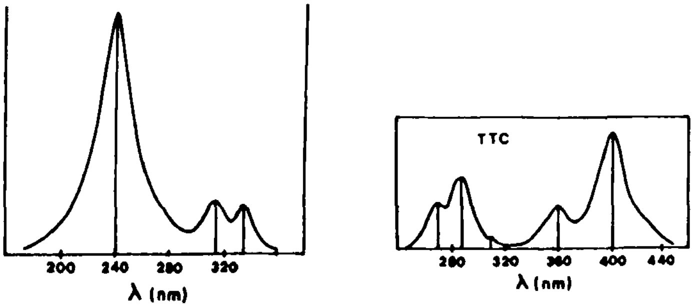


FIGURE 1. Calculated spectra of (I) for spiro form (left) and TTC merocyanine isomer (right).

By a similar reasoning its seems that for the merocyanines of (II) the CTC and TTC isomers should be better represented in the experimental spectrum than the CTT and TTT ones. The TTC isomer was indicated as the most probable isomer in the ring opening of (II) [(3)]. The CNDO/S method although it gives a reasonable sequence of the bands appears unable to describe properly the transition energies in the visible region of the spectrum probably because of the large charge-transfer and/or zwritterrionic character of the actual molecular wave functions. However the approach that we have adopted (ground state optimization + semiempirical calculations on the excited state) seems to enable one to predict which of the merocyanines isomers contributes most largely to the experimental spectrum.

ACKNOWLEDGEMENTS

We thank M.U.R.S.T. for the financial support.

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