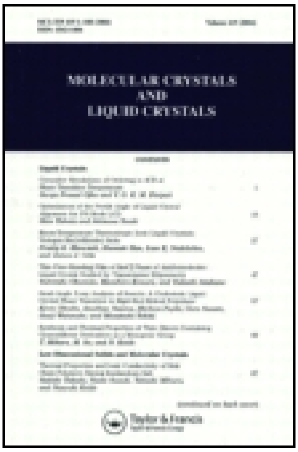

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THE RELATIONSHIP BETWEEN THE STRUCTURE AND THE ABSORPTION SPECTRA OF NAPHTHO[2,1-b]PYRAN

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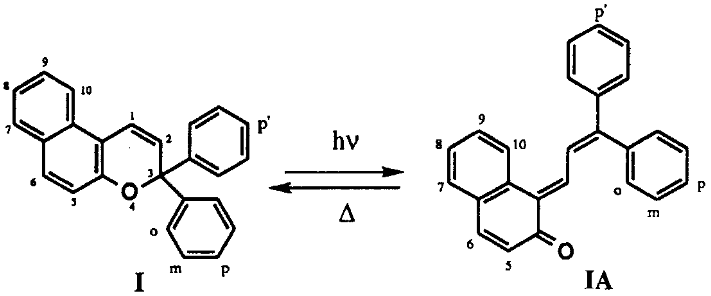
Abstract: The absorption wavelengths of methoxy substituted 3,3-diaryl-naphtho[2,1-b]pyrans in the open and closed forms were calculated and compared to observed values. The observed and calculated absorption wavelengths showed good correlation. The molecular geometries were minimized and electronic spectra were calculated using ZINDO methods.

INTRODUCTION

Naphthopyrans are organic photochromic compounds that are potentially useful in optical applications such as ophthalmic lens, transparencies, plastic films etc. Naphthopyran **I** undergoes a photo-induced ring opening process to the corresponding open form **IA** which is responsible for color formation on exposure to sunlight.



I **IA**

Scheme I Photochromic process in naphthopyrans.

The absorption spectra of these compounds is of great importance and strongly influenced by the position and type of substituents.[1,2,3] The ability to predict the wavelength of absorption and how it is effected by substituents would be a useful tool for synthetic chemists working in the field of photochromism.

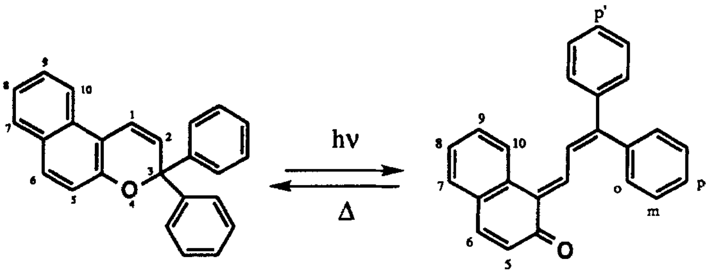
There is no information available in the literature on the calculation of absorption spectra for photochromic naphthopyran dyes. On the other hand, fixed dye spectral calculations have been done using PPP[4,5] as well as other methods. The PPP method is most accurate for compounds with their π-electrons in a planar configuration. Unfortunately the open form of naphthopyrans can not be assumed to be planar. Where the degree of non planarity and the absorption spectra are closely related[6] it would therefore be inappropriate to use PPP for predicting absorption spectra of the open form(s) of naphthopyrans. Recently, Nakamura et al.[6,7] has calculated the absorption spectra of indoaniline dyes by INDO/S on AM1 minimized geometries and showed good correlation between observed and calculated results.

This paper reports the relationship between the calculated and observed absorption maxima for the closed and open forms of photochromic naphthopyrans using ZINDO calculations. In addition, the effect of methoxy substituent on the λ_{max} is discussed.

EXPERIMENTAL

The open and closed forms of naphthopyran derivatives shown in scheme II were selected for calculations. The structures of compounds **I-VI** and **IA-IXA** were minimized using MM2 followed by PM3 methods. The absorption maxima were calculated using the ZINDO program (singlet multiplicity, 22X22 configuration interaction). All these calculations were performed on a CAChe[8] work station.

For spectroscopic measurements the photochromic compounds were dissolved in spectroscopic grade hexane and absorption spectra of the closed forms were measured on a Varian Cary 3 UV-Visible Spectrophotometer. The same solution was irradiated under a UV lamp for few minutes and the absorption spectrum of the open forms were measured in equilibrium with the closed form.



Compound	Substituent	Compound
I	None	IA
II	5-OMe	IIA
III	6-OMe	IIIA
IV	7-OMe	IVA
V	8-OMe	VA
VI	9-OMe	VIA
VII	o-OMe	VIIA
VIII	p'-OMe	VIIIA
IX	p-OMe, p'-OMe	IXA

Scheme II Structures of compounds used in calculations

RESULTS AND DISCUSSION

Fig 1. shows the optimized structure of compound **I**. Notice how both phenyl rings are positioned out of plane to minimize the interaction between the ortho hydrogens of the phenyl rings.

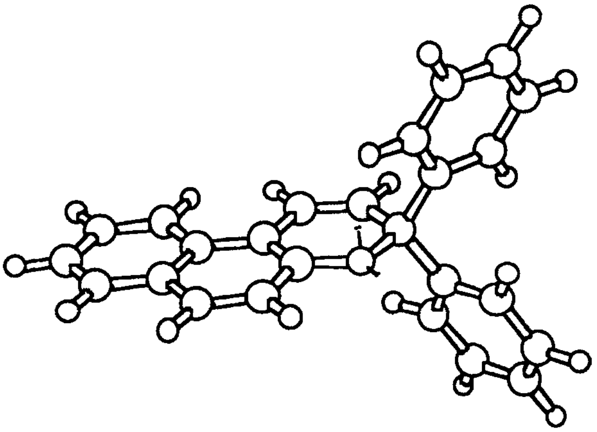


Fig 1. Optimized structure of compound I

The pyran ring is also twisted to minimize internal strain. The absorption maxima obtained by ZINDO calculation on the closed forms (I-VI) are summarized in Table I.

Table I: Observed and calculated maxima (UV) closed form.

Compounds	**λ_{max} (Actual)**	**λ_{max} (Calculated)**
I	347 nm	338 nm
II	338 nm	324 nm
III	358 nm	341 nm
IV	350 nm	340 nm
V	360 nm	345 nm
VI	340 nm	327 nm

Fig 2. shows a good relationship between experimental and calculated absorption maxima. Methoxy substitution at positions 6 and 8 (compounds III and V) are known to give a bathochromic shift in the UV,[2,3] and a similar trend is also observed in the calculated results. Other observed and calculated trends are shown in Fig. 3. A parallel in trends can be easily seen between the experimental and calculated results.

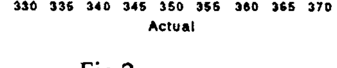


Fig 2.

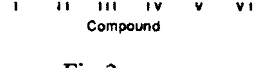
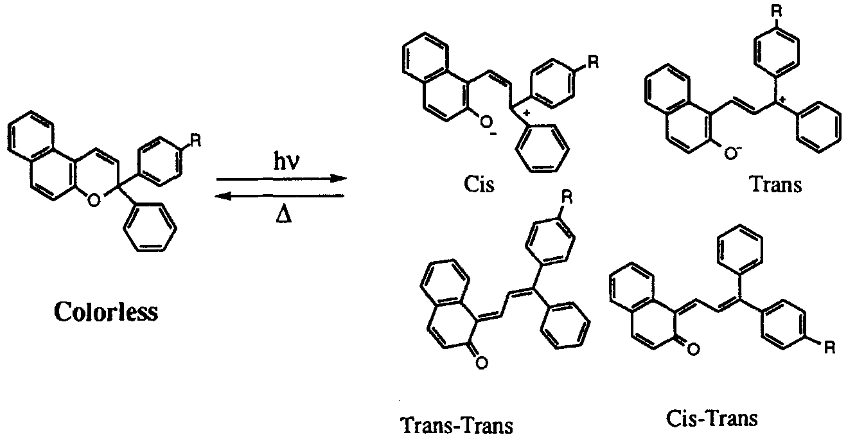


Fig 3.

For naphthopyrans the photochromic process involves a change from the closed to the open form(s). The open form can be drawn as either a zwitterionic, quinoidal or radical species. Several of the possible metastable open forms, some quinoidal and some zwitterionic, are shown in scheme III.



Scheme III Structures of some possible open forms

The metastable nature of the open form makes it very difficult to obtain any structural information experimentally. Low temperature NMR studies reported earlier by our group tentatively supports the quinoidal structure.[9] For simplicity, the trans-trans quinoidal form was chosen as the starting point in these theoretical calculations for the prediction of absorption spectra.

An optimized structure of open form (IA) is shown in Fig 4. The diene portion of the open form is out of the plane of the naphthalene ring in order to avoid a steric interaction with the hydrogen at position 10. The terminal phenyls are twisted and out of plane due to a steric interaction between the ortho hydrogens as seen before in the closed form.

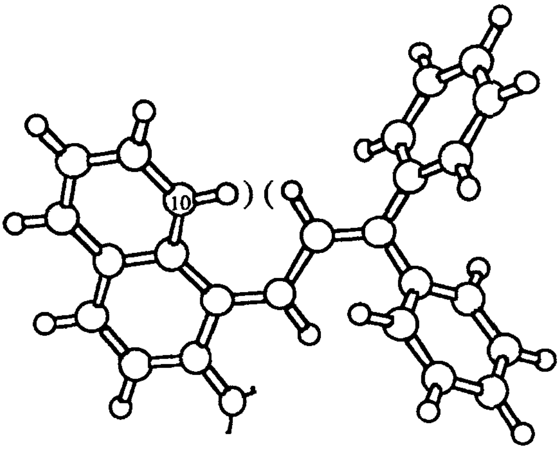


Fig 4. Optimized structure of compound **IA**

Table II summarizes the calculated and observed results obtained the open forms of the naphthopyrans I-IX. The relationship between calculated and observed λ_{max}s for the open forms of methoxy substituted naphthopyrans is shown in Fig 5. The bathochromic shifts due to alkoxy substitution at the para position(s)[1] (**VIIIA** vs **IA**, **IXA** vs **IA**) of phenyl or 8 position[2] (**VA** vs **IA**) are experimentally known. A similar trend is also observed in the calculated values. The hypsochromic shift due to a 6-alkoxy substituent is also observed in both the experimental[3] and the calculated λ_{max}. Fig 6 compares the observed and calculated results.

Table II Observed and calculated maxima of open forms.

Compounds	**λmax (Actual)**	**λmax (Calculated)**
IA	423 nm	428 nm
IIA	423 nm	429 nm
IIIA	418 nm	422 nm
IVA	436 nm	425 nm
VA	460 nm	435 nm
VIA	420 nm	427 nm
VIIA	426 nm	428 nm
VIIIA	449 nm	434 nm
IXA	466 nm	440 nm

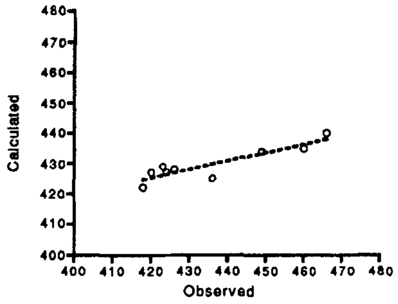


Fig 5.

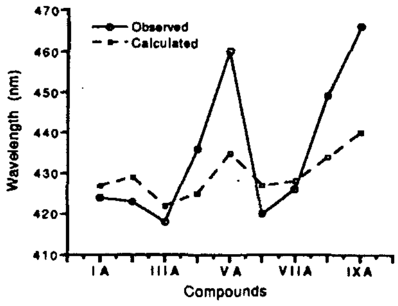


Fig 6.

CONCLUSION

The predicted absorbances in the UV are in good agreement with actual values. Trends in the computed visible spectra are consistent with experimental values although the differences in some cases are fairly large. These data have shown that computational chemistry may a useful tool in directing synthetic efforts.

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