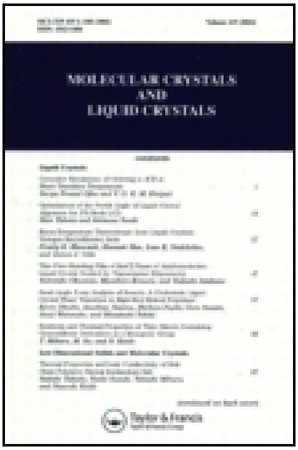

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Color Tunability in Photochromic Naphthopyrans

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Color Tunability in Photochromic Naphthopyrans

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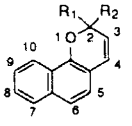
Photochromic naphthopyrans are of particular interest due to their wide use in applications such as switchable eyewear, security devices and novelty items. The spectral properties of the activated form are important in many of these applications. This paper reports the effect of substituents on the visible absorption of the activated form(s). In addition to color, other photochromic properties of naphthopyrans are briefly discussed.

Keywords: Naphthopyran; photochromic; spectra; chromene

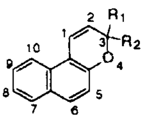
INTRODUCTION

Naphthopyrans (or benzo-fused chromenes) are thermally reversible organic photochromic compounds that have found use in commercial applications such as ophthalmic lenses and novelty items. Becker[1] in 1966, for the first time reported on the photochromism of naphthopyrans. Since that time, significant progress has been made in better understanding the properties of this class of photochromics.[2,3] The absorption characteristics (or color) of the activated state are of great importance to many applications. For example, frequently it is necessary to have compounds with colors covering the entire visible spectrum. Most of the naphthopyrans in their activated form absorb over a narrow range giving discreet colors. Therefore, to cover the entire visible spectrum (make neutral colors like grays and browns) blending of different photochromics is needed.[4] Historically, the color tunability of naphthopyrans had been very limited (primarily yellow to red). Today colors ranging from yellow to blue can be achieved within this family through substituent effects.

Of the three possible isomeric naphthopyrans, only 3H-naphtho[1,2-b]pyran (**A**) and 2H-naphtho[2,1-b]pyran (**B**) have been studied in detail.[2]

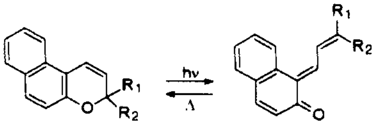


A

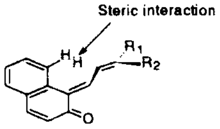


B

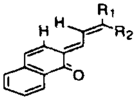
To understand the absorption of the activated form, it is important to know its structure. Naphthopyrans are believed to undergo a photo-induced ring opening process to the corresponding colored species, as shown in the following reaction.



Attempts to characterize the structure of open form(s) have been limited. A chemical trapping study by Becker[5] proves carbon-oxygen bond scission and a low temperature NMR study [6] supports the quinoidal nature of the open form.



A1



B1

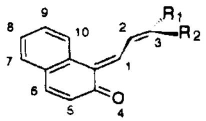
Due to hydrogen-hydrogen steric interaction, the diene portion in the open form of naphtho(2,1-b)pyran (**A1**) is twisted and out of the plane thereby reducing its conjugation with the quinone portion of the chromophore. In contrast, the open form of naphth(2,1-b)pyran (**B1**) is completely planar and well conjugated. Consequently the absorption of **B1** is bathochromically shifted relative to **A1** (476 nm vs. 433 nm when

R_1 and R_2 are phenyl). The steric interaction in **A1** is also responsible for its faster fade vs **B1**.[3]

3H-NAPHTHO[2,1-b]PYRAN (A)

Compounds with R_1 and R_2 equal to phenyl on exposure to UV light, give a yellow color. Due to steric destabilization of the open form, it has a fast fade and low optical density. The optical density is enhanced by substituting a group at the ortho- position of one (or both) of the 3-phenyl rings.[7]

Table1: Substituent effect on naphtho(2,1-b)pyran in polymer



R_1	R_2	R_5 - R_{10}		λ_{max} (nm)
Ph	Ph			432
Ph	p-(MeO)Ph			468
p-(MeO)Ph	p-(MeO)Ph			480
p-(MeO)Ph	p-(MeO)Ph	6-morpholino		461
p-(MeO)Ph	p-(MeO)Ph	6-OMe		461
p-(MeO)Ph	p-(MeO)Ph	6-OAc		467
Ph	Ph	5-OMe		432
Ph	Ph	7-OMe		432
Ph	Ph	8-OMe		473
Ph	Ph	9-OMe		429
Ph	Ph	8-OMe	9-COOPr	468

An electron donating group (such as methoxy) at the para position of one of the 3-phenyls gives a bathochromic shift to the λ_{max} of 36 nm. This shift is additive when another methoxy is substituted on the second phenyl ring.[8]

Electron-donating groups have very little effect when substituted on the naphthalene except at the 6 [9,10] and 8 [11] positions. Electron donating groups (such as methoxy [9] and mopholino [10]) at 6-position shifts the color hypsochromically. Compared to hydrogens a weak electronwithdrawing group (such as an acetoxy) at 6- position also gives a hypsochromic shift in color.[12] A methoxy at the 8-position gives the largest bathochromic shift (40nm) and slows the rate of fade.[11] Semi-empirical molecular orbital calculations can successfully predict these trends.[13] An 8-methoxy coupled with 9-carbopropoxy group gives a slight hypsochromic shift but increases the fade rate relative to the single 8- methoxy substitution.[14]

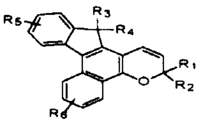
2H-NAPHTHO(1,2-b)PYRAN (B)

Naphtho(1,2-b)pyran **B** with R_1 and R_2 combined to form a adamantyl group, produces an intense yellow color and has reasonable fade at room temperature.[15] Similar to naphthopyran **A**, the effect of R_1 and R_2 going from alkyl to phenyl is a bathochromic shift in color by 30 nm and a slower fade rate. Addition of p-methoxy to one of the phenyls not only further bathochromically shifts the color but also increases the fade rate.[3]

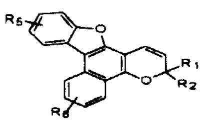
Without a substituent in the 5-position (R_3) the compounds in this series are very slow to fade and can take hours to completly bleach back. Data for R_3 equal to a methyl group indicates the importance of 5-substitution in significantly enhancing the fade, however, a 5-carbomethoxy is much more effective promoter of the fade rate.[3,16] When R_1 and R_2 are p-dialkyl aminophenyl the color can be shifted as far as 618 nm.[17] Conversely, a m-trifluoromethyl gives a hypsochromic shift.[16]

When the 5-substituent is carbomethoxy and the 6-substituent becomes more electron donating in the series: acetoxy, methoxy, and morpholino,[18] the color shifts bathochromically. Similar results are also observed for the 5-position, with electron donation pushing the absorption to longer wavelengths.[19]

The bathochromic shift resulting from 6-phenyl substitution is further enhanced by locking the phenyl in the plane of the naphthopyran with methylene or an oxygen bridge at 5-position. Derivatives of these



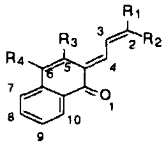
Indeno- fused Naphthopyran



Benzofuro- fused Naphthopyran

indeno-[20] or benzofuro-[21] fused naphthopyrans have typical absorptions in the 560-590 nm region.

Table 2: Substituent effect on naphtho(1,2-b)pyran in polymer



R_1	R_2	R_3	R_4	λ_{max} (nm)	Fade $T_{1/2}$ (sec.)
Adamantyl		H	H	446	300
Ph	Ph	H	H	476	>1800
Ph	Ph	Me	H	482	640
Ph	Ph	COOMe	H	470	54
p-(MeO)Ph	p-(MeO)Ph	Me	H	505	----
p-(MeO)Ph	p-(MeO)Ph	COOMe	Me	505	396
Ph	Ph	COOMe	OAc	470	220
m-(CF_3)Ph	m-(CF_3)Ph	COOMe	OAc	455	218
p-(NMe_2)Ph	Ph	COOMe	OAc	591	----
p-(NMe_2)Ph	p-(NMe_2)Ph	COOMe	OAc	618	----
p-(MeO)Ph	p-(MeO)Ph	COOMe	OAc	509	----
p-(MeO)Ph	p-(MeO)Ph	COOMe	OMe	510	----
p-(MeO)Ph	p-(MeO)Ph	COOMe	Ph	518	----
p-(MeO)Ph	p-(MeO)Ph	COOMe	Morpholino	524	127
p-(MeO)Ph	p-(MeO)Ph	Cl	OAc	462	54
p-(MeO)Ph	p-(MeO)Ph	Me	OAc	506	120
p-(MeO)Ph	p-(MeO)Ph	SPh	OAc	516	42

CONCLUSION

The historical color range limits (yellow to red) in naphthopyrans have been extended (yellow to blue). Naphthopyrans are very tunable to the desired color via substituent effects. The broad range of available colors have made these compounds very useful in commercial applications such as ophthalmic lenses, security devices and novelty items.

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