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An Investigation of the Electronic Spectral Properties of the Coloured Photoproducts Derived from Some Photochromic Naphtho[2,1-*b*]pyrans

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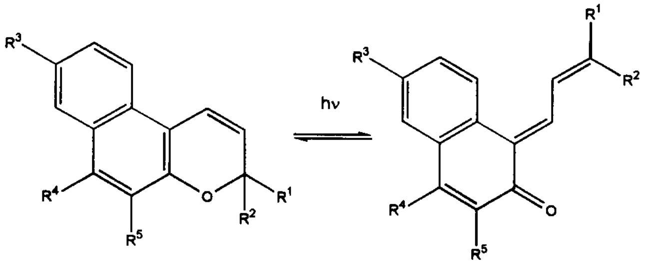
ABSTRACT

Some chromenes are of current interest as photochromic dyes. The results of PPP molecular orbital calculations, after refinement by parameter optimisation, were found to provide a reasonable account of the experimental λ_{max} *values for the ring-opened photoproducts formed from a range of substituted naphtho[2,1-*b*]pyrans. The agreement between experimental and calculated values was less good for two compounds, but this may be explained on the basis of steric constraints which are likely to reduce molecular planarity. The electronic structure of one of the photoproducts and the nature of the electronic excitation process are discussed in terms of the calculated* π*-electron charge densities. © 1997 Elsevier Science Ltd*

Keywords: photochromism, chromenes, electronic spectra, naphthopyrans, PPP-MO calculations.

INTRODUCTION

Organic photochromic materials have been the subject of intense recent investigation because of their wide variety of potential applications, which include ophthalmic and sunglass lenses, optical recording and solar energy storage [1–4]. Interest in chromenes [5] has been stimulated by the emergence of certain derivatives, such as the 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans



1 2

Cpd	R^1	R^2	R^3	R^4	R^5
a	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	H	H	H
b	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	CHO	H	H
c	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	H	H	CO$_2$Me
d	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	H	H	OH
e	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	H	N(CH$_2$)$_5$	H
f	4-NMe$_2$C$_6$H$_4$	4-MeOC$_6$H$_4$	H	H	H
g	4-NMe$_2$C$_6$H$_4$	4-NMe$_2$C$_6$H$_4$	H	H	H
h	2,4-(MeO)$_2$C$_6$H$_3$	4-MeOC$_6$H$_4$	H	H	H
i	3,4-(MeO)$_2$C$_6$H$_3$	4-MeOC$_6$H$_4$	H	H	H
j	4-MeO-1-naphthyl	4-MeOC$_6$H$_4$	H	H	H
k	4-MeO-2-MeC$_6$H$_3$	4-MeOC$_6$H$_3$	H	H	H

(5,6-benzochromenes) (**1**), as a group of organic photochromes of commercial interest. Such compounds are structurally related to spiropyrans, the-photochromism of which is well documented [6]. Absorption of UV light by the naphthopyrans (**1**) causes cleavage of the relatively weak carbon–oxygen bond with the formation of a coloured photoproduct such as **2**. Compound **2** reverts to the naphthopyran (**1**) by a thermally induced ring-closure reaction when the light source is removed.

The PPP-MO approach has emerged as a useful technique for the prediction of the electronic spectra of organic colourants [7–9] and has recently been applied successfully to the coloured photomerocyanine derived from some spirooxazines [10]. The results of an investigation using the PPP-MO approach into the electronic spectra of the coloured form derived from a series of photochromic naphthopyrans are reported. The investigation has established a model which provides a reasonable correlation between calculated and experimental spectral data and which has the potential for use in the design of new photochromic materials.

TABLE 1

Calculated Electronic Spectral Data for Isomers I–IV of the Ring-opened Photoproducts **2a–k** Derived from Naphthopyrans **1a–k**

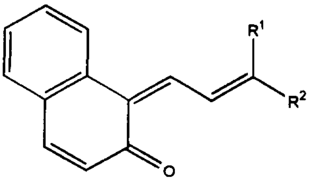
Compound	λ_{max} *(expt)nm*	λ_{max} *(calc.)/nm* (f_{osc})				λ_{max}*(calc.)/nm* (f_{osc})
		Generalised parameters				*Optimised parameters*
		I	*II*	*III*	*IV*	
2a	474	444 (0.97)	444 (0.97)	442 (1.04)	442 (1.04)	477(1.00)
2b	486	452 (1.00)	452 (1.00)	451 (1.02)	451 (1.02)	485(1.02)
2c	486	455 (0.89)	455 (0.89)	452 (1.10)	452 (1.10)	486(1.09)
2d	482	444 (0.90)	444 (0.90)	443 (1.00)	443 (1.00)	477(1.00)
2e	444	422 (1.00)	422 (1.00)	439 (1.01)	439 (1.01)	453(1.01)
2f	504	478 (0.92)	476 (0.95)	470 (1.12)	482 (0.85)	514(0.98)
2g	556	498 (0.98)	498 (0.98)	490 (1.13)	490 (1.13)	523(1.10)
2h	476	466 (0.91)	453 (0.96)	452 (1.04)	452 (1.00)	500(1.00)
2i	480	448 (0.95)	448 (0.95)	446 (1.05)	446 (0.94)	482(0.96)
2j	472	472 (0.96)	[a]	463 (1.15)	[a]	507 (1.02)
2k	468					

[a] No result because of matrix non-convergence.

RESULTS AND DISCUSSION

Naphthopyrans **1a–k** showed characteristic photochromic behaviour when irradiated in solution in toluene with UV light, giving coloured forms which were sufficiently long-lived to allow measurement of λ_{max} values using a diode array UV/visible spectrophotometer. The experimental λ_{max} values obtained for the ring-opened species **2** are given in Table 1. A characteristic feature of the group of compounds is the presence of electron-releasing groups in the *para* positions of the aryl substituents. Comparison of the λ_{max} values obtained for compounds **1a**, **f** and **g** shows that the absorption band (474, 504 and 556 nm respectively) experiences a significant bathochromic shift as the methoxy group is replaced by the more powerfully electron-releasing dimethylamino group. An electron-releasing group in the 6-position (R^4), however, causes a hypsochromic shift, as is demonstrated by the pyrrolidino derivative, **1e** ($\lambda_{max} = 444$ nm).

Initial PPP-MO calculations were carried out on the ring-opened species **2a–j** using a commonly accepted generalised parameter set [8]. The relevant atom numbering system used in the calculations is illustrated in Fig. 1 for compound **2g**. Carbon atoms 7–9 and 11–14 were considered to be alternating alkenes, and the rest to be aromatic. A complication in carrying out calculations on compounds of this type is that, because they are transient species, their molecular geometry is not known with certainty. In principle, the molecules are capable of existing in eight possible geometrical isomeric forms, illustrated as structures I–VIII, when R^1 and R^2 are different, or four



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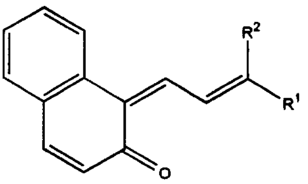

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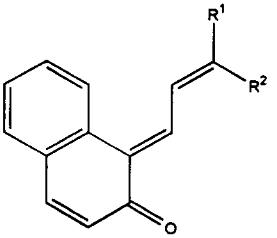

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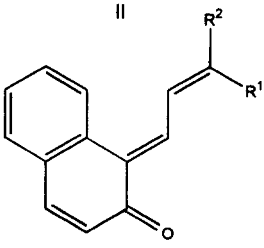

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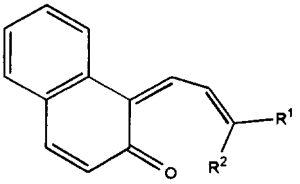

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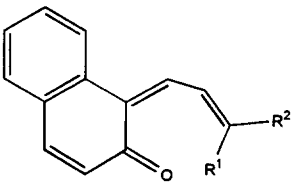

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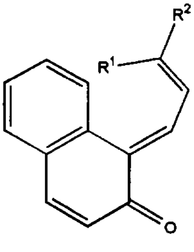

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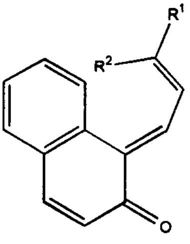

VIII

when R^1 and R^2 are identical. Table 1 shows the results obtained from calculations carried out on the four (or two when symmetrical) transoid isomers (I–IV) of compounds **2a–j**. For the purposes of the calculations, planar molecular geometry was assumed in each case. This assumption is clearly unrealistic for cisoid isomers V–VIII because of steric constraints, and the calculations failed in those cases due to matrix non-convergence. For the transoid isomers, single long wavelength absorptions with significant oscillator strengths (0.91–1.00) were predicted. The bond matrix failed to converge in the case of isomers II and IV of the naphthyl derivative **2j**, because in these cases a planar structure is impossible. In general, the calculated λ_{max} and oscillator strength values for the four isomers of each compound are

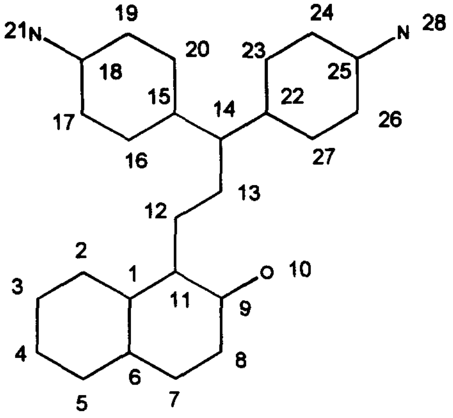

Fig. 1. Relevant atom numbering system for compound **2g**.

similar. This is consistent with results of PPP-MO calculations reported previously for a somewhat simpler ring-opened chromene [11]. Comparison between the experimental λ_{max} values with those calculated in this way shows a reasonably consistent trend although the calculated values are generally hypsochromic of the experimental values. Following a systematic examination of the influence of parameters on the results of the calculations, it was found that much better agreement between the calculated and experimental values could be obtained by assuming the geometry of isomer I, adjusting the valence state ionisation potential and electron affinity values for the carbonyl oxygen atom (O-10) to 16.0 and 1.7 eV, respectively, the alternating carbon–carbon bond β values to −2.35 and −2.50 eV, and the carbonyl bond β value to −2.5O eV. The results of the calculations carried out on compounds **2a–j** using this optimised parameter set are also given in Table 1. In most cases, the calculated λ_{max} values show good agreement with the experimental values. However, compounds **2h** and **j** are predicted to be significantly bathochromic of the experimental values. This is almost certainly due to steric congestion, which forces these molecules to adopt less coplanar geometry. In the case of compound **2h**, this is probably a consequence of the presence of an *o*-methoxy group in one of the 3-aryl rings, which interferes with an *o*-hydrogen atom in the other. There is presumably similar steric congestion as a result of the bulky 3-naphthyl substituent in the case of compound **2j**. Significantly, compound **2i**, an isomer of **2h** in which there is likely to be much less steric congestion, is correctly predicted. Further evidence for the existence of steric congestion arising from *ortho* substituents in the 3-aryl rings is provided by a comparison of compounds **2a** and **k**. The presence of an *o*-methyl group in compound **2k** causes a hypsochromic shift of the absorption band of 6 nm relative to compound **2a**, whereas a small

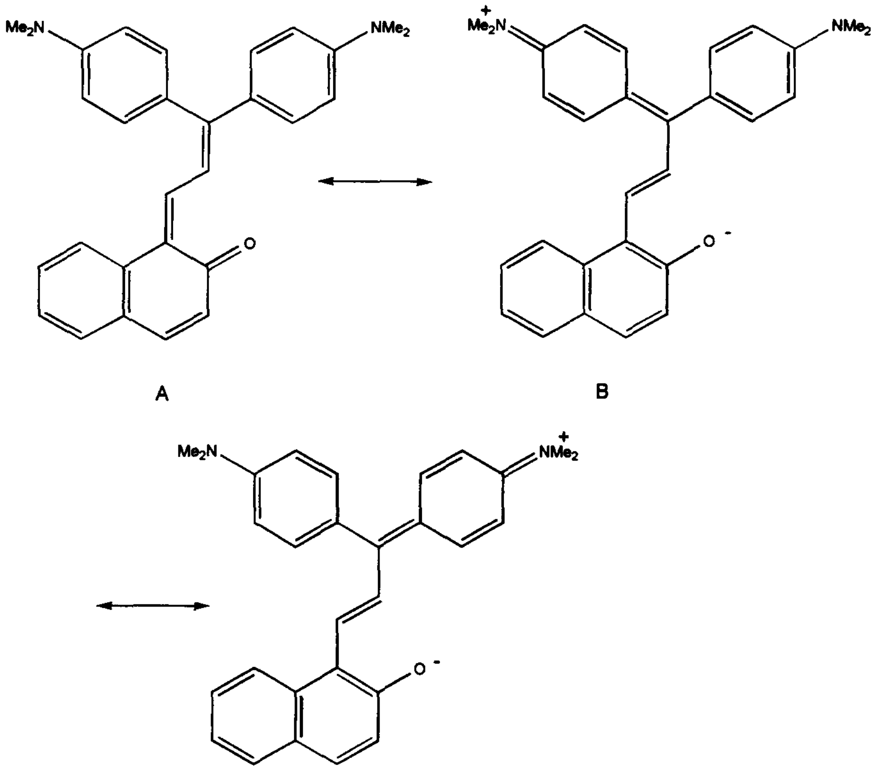

Fig. 2. Resonance forms of compound **2g**.

bathochromic shift might have been expected as a result of the weakly electron-releasing electronic effect of the methyl group.

The results of the PPP MO calculations provide an insight into the π-electronic charge distribution in the photoproducts derived from the naphthopyrans, both in their ground states and in the first excited states. A valence-bond (resonance) representation of the structure of compound **2g** (isomer I) is given in Fig. 2. There has been some conjecture concerning the relative contributions of the 'neutral' form A and zwitterionic or charge-separated forms B and C to the overall structure of these species. Calculated π-electron charge densities for the ground state and of the first excited state of isomer I of compound **2g** are given in Table 2. The ground state charge densities are generally consistent with the valence bond approach illustrated in Fig. 2. For example, they show reduced charge density on the amine nitrogen atoms (N-21 and N-28) and a corresponding increased charge density on the carbonyl oxygen (O-10), consistent with important and equal contributions from structures B and C. Carbon atoms 7–9 and 11–14 in the ground state are polarised, as expected from the valence bond approach.

TABLE 2
Calculated π-electron Charge Densities for the Ground State and First Excited State of Compound **2g** (isomer I) (numbering system as shown in Fig. 1)

	Ground state	*1st excited state*
1	0.99	1.02
2	1.01	1.00
3	1.00	1.03
4	1.01	1.01
5	1.00	1.01
6	1.01	1.03
7	0.98	1.04
8	1.00	1.04
9	0.87	0.92
10	1.27	1.33
11	0.98	1.04
12	0.93	1.09
13	1.04	0.92
14	0.95	1.05
15,22	1.06	1.03
16,20,23,27	0.98	0.99
17,19,24,26	1.11	1.08
18,25	0.98	0.99
21,28	1.71	1.63

The first excited state charge densities suggest substantial further charge transfer from N-21 and N-28 to O-10. In addition, the 'alkene-type' carbon atoms effectively experience an inversion of charge density as a result of excitation.

EXPERIMENTAL

UV/visible spectra

UV/visible spectra of the ring-opened species **2a–k** were obtained by irradiation of solutions of the naphthopyrans **1a–k** in toluene at 365 nm using a flash gun. The spectra of the coloured solutions were recorded immediately using a Hewlett Packard 8452A diode array spectrophotometer.

PPP-molecular orbital calculations

A standard PPP-MO procedure was used within the fixed β approximation [7]. A generalised set of parameters was used and modifications carried out as described in Section 2. Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship [12] and electronic excitation energies were refined by a limited configuration interaction treatment involving nine singly excited configurations obtained by promoting an electron from the three highest occupied molecular orbitals to the three lowest unoccupied molecular orbitals.

CONCLUSIONS

A method for the prediction of the electronic absorption spectra of the ring-opened form of naphtho[2,1-*b*]-pyrans using the PPP-MO approach has been devised which provides a reasonable correlation with experimental data for a series of substituted derivatives. Deviations between experimental and calculated values in certain cases may be explained by steric constraints which enforce non-planarity. The method has potential value in investigations into extending the available shade range of colours available from chromenes, and as an aid to the design of new related molecules with photochromic properties.

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