

Structure–property relationships in a series of photochromic thiophene-substituted 3*H*-naphtho[2,1-*b*]pyrans

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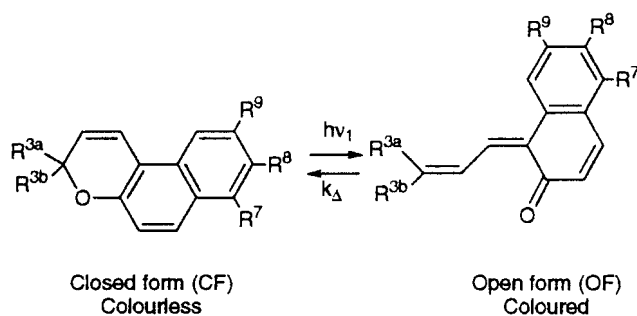
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ABSTRACT: The photochromic parameters of a set of 26 thiophene-substituted [3*H*]-naphtho[2,1-*b*]pyrans were studied by flash photolysis. The experimental results obtained along with molecular modelling approaches (molecular mechanics and quantum calculations) allowed us to propose structure–property relationships. From this approach, the main structural modifications able to induce large variations in electronic absorption, fading rates and coloration ability are discussed. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; thiophene; naphthopyrans; structure–property relationships; electronic absorption; kinetics; theoretical calculations

INTRODUCTION

Photochromism is defined as a light-induced reversible colour change. Owing to their practical or potential applications (variable optical transmission glasses or optoelectronic devices), photochromic compounds have been subjected to extensive investigations.^{1–3} Among the various mechanisms that are displayed by organic photochromic compounds, electrocyclization processes are the most important. Recently, naphthopyrans have been selected owing to their efficient coloration ability, rapid reversibility and good fatigue resistance.^{4–9} Scheme 1 shows the photochromic equilibrium in the naphthopyran series. Ring opening is induced by UV light whereas ring closure is mainly thermal.



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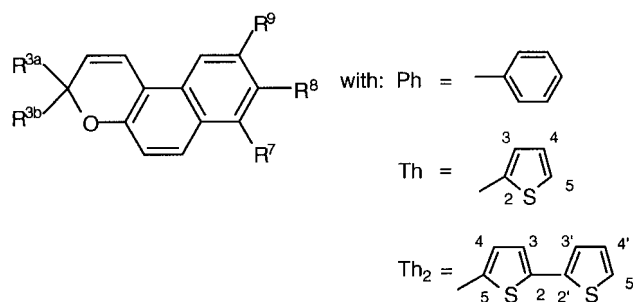
In order to stabilize sufficiently the open form, allowing room temperature photochromism, substituents R^{3a} and R^{3b} must be preferentially aromatic or conjugated. We have recently synthesized a series of 3*H*-naphtho[2,1-*b*]pyrans bearing thiophene substituents^{10,11} in order to obtain photoactivable polythiophenes for organic conductors or semiconductors.^{12,13}

All naphthopyrans described in this paper are shown in Table 1. They can be separated into two main groups: either the thienyl entities are linked to the naphthopyran ring by a carbon chain (1–8) or directly (9–26). In the latter case, the thienyl ring has the possibility to be conjugated with the plane system of the open form.

In this work, we have established structure–property relationships within this series of naphthopyrans using both experimental measurements and theoretical calculations. The results show that the photochromic parameters are closely related to the substitution pattern of the naphthopyran ring.

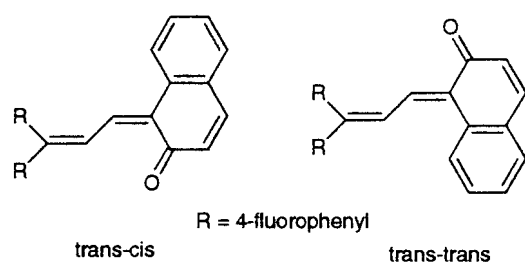
The various photochromic parameters which were taken into account were absorption wavelengths of the closed and open forms (λ_{CF} and $\lambda_{max,OF}$, respectively), rate constants of thermal bleaching (k_{Δ}) and coloration ability or ‘colorability’ (measured as the absorbance A_0 immediately after the irradiation flash).¹⁴ A_0 is expressed by $A_0 = \epsilon_{OF} \Phi_{col} k [CF]_0$ (at low concentration), where k depends on the experimental conditions, ϵ_{OF} is the molar absorptivity of the open form at λ_{max} , Φ_{col} is the photocoloration quantum yield and $[CF]_0$ is the initial concentration of the closed form.

It should be noted that k_{Δ} and A_0 depend on the

Table 1. The 3*H*-naphtho[2,1-*b*]pyrans studied

Compound	R ^{3a}	R ^{3b}	R ⁷	R ⁸	R ⁹
RC	Ph	Ph	H	H	H
1	Ph	Ph	H	— CHCHC(O)Th	H
2	Ph	Ph	H	— C(O)OCH ₂ CHCHTh	H
3	Ph	Ph	H	— C(O)OCH ₂ Th	H
4	Ph	Ph	H	— C(O)OCH ₂ Th ₂	H
5	Ph	Ph	H	H	— OC(O)CHCHTh
6	Ph	Ph	H	H	— OC(O)CH ₂ Th
7	Ph	Ph	H	H	— OC(O)Th
8	Ph	Ph	H	H	— OC(O)Th ₂
9	Th	Th	H	H	H
10	Th	4-MeO-Ph	H	H	H
11	Th	Me	H	H	H
12	Th	2-F-Ph	H	H	H
13	5-Br-Th	6-MeO-Ph	H	H	H
14	Th	5-Br-Th	H	H	H
15	5-Br-Th	Me	H	H	H
16	Ph	Ph	Th	H	H
17	4-Ph-Ph	Ph	Th	H	H
18	Ph	Ph	Th ₂	H	H
19	4-Ph-Ph	Ph	Th ₂	H	H
20	Th	Th	Th	H	H
21	Th	4-MeO-Ph	Th	H	H
22	Th ₂	Th	H	H	H
23	Th ₂	4-MeO-Ph	H	H	H
24	Th ₂	Me	H	H	H
25	Th ₂	2-F-Ph	H	H	H
26	Th ₂	Th	Th ₂	H	H

irradiation conditions because several photoisomers with different lifetimes can co-exist. For instance, two transoid photoisomers, differing only in their configuration with respect to the double bond (as in Scheme 2), have been identified recently by NMR spectroscopy in the case of 3,3-di(4-fluorophenyl)-[3*H*]-naphtho[2,1-*b*]pyran.¹⁵

**Scheme 2**

Although, UV-visible absorption spectra of the various transoid photoisomers are often similar, their thermal stability can be different. From a kinetic point of view, this latter property leads to a bi-exponential thermal relaxation characterized by two distinct rate constants: a rapid one $k_{\Delta 1}$, and a slower one, $k_{\Delta 2}$. This result agrees with the previous NMR studies showing that the photochromic system globally behaves as if only two photoisomers were involved.¹⁵ Their relative population depends on the irradiation conditions. Under continuous irradiation, a photo-steady state with two interconverting photoisomers is reached. In contrast, in the microsecond range flash photolysis, different relative populations are observed depending on the opening pathways from the excited state. It is this technique which was used in the present study for the determination of k_{Δ} and A_0 of open forms.

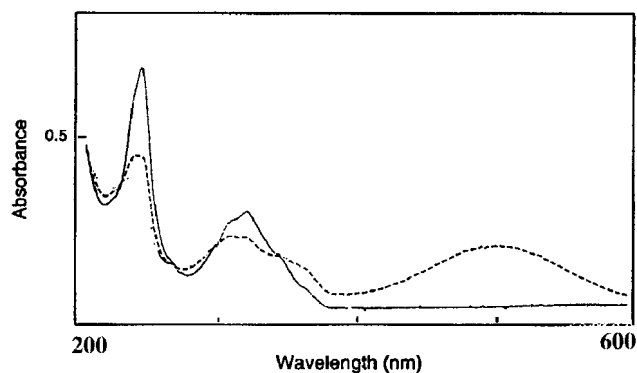


Figure 1. Example of electronic absorption spectra of colourless (solid curve) and coloured forms (dashed curve) of naphthopyran **25** (10^{-5} M in toluene, 20°C)

RESULTS AND DISCUSSION

Characteristic wavelengths of the various UV–visible absorption bands for both closed and open forms were measured. Only bands and/or shoulders within the 300–400 nm range were taken into consideration for the closed form. Indeed, UV irradiation in this region, which is efficient for the photochromic process, leads to only

weak photodegradative effects.² Concerning the open form only the λ_{\max} OF in the visible region was taken into account.

All the experimental results, including rate constants and coloration abilities, are gathered in Table 2.

From a general point of view, Table 2 shows that all the photochromic parameters are very sensitive to the substitution on the naphthopyran ring. There is an important bathochromic shift of the absorption wavelength of the open forms (up to 88 nm) when a bithienyl entity is fixed at position 3, as in molecules **22–26**. Moreover, the closed-form absorption spectra show minor but significant variations with a maximum shift of 20 nm.

On the other hand, a considerable increase in the coloration ability, A_0 , is observed for the product **26** which bears five thiophene rings. Amplitude ratios between rapid ($k_{\Delta 1}$) and slow ($k_{\Delta 2}$) kinetics range from 98:2 for **26** to 25:75 for **21** and **22**. The reference compound (**RC**) shows roughly monoexponential kinetics close to the values of the slowest ones ($k_{\Delta 2}$).

In order to visualize some specific structure–property relationships, different diagrams have been considered. Figure 2 shows the diagram of λ_{\max} OF vs λ CF, which was obtained by plotting the wavelength at the λ_{\max} of

Table 2. Photochromic parameters of naphthopyrans **RC** (reference) and **1–26** in toluene^a

Compound	λ CF (nm) ^c	λ_{\max} OF (nm)	A_0	$k_{\Delta 1}$ (s ⁻¹) (amplitude, %)	$k_{\Delta 2}$ (s ⁻¹) (amplitude, %)
RC ^b	(357), 345, (315), 301	432	0.84	0.09 (100)	—
1	(351), 340	465	0.67	0.22 (43)	0.04 (57)
2	(351), 340	455	1.08	0.34 (92)	0.05 (8)
3	(352), 340	448	1.01	0.35 (91)	0.05 (9)
4	(352), (331), (312)	441	1.94	0.38 (90)	0.07 (10)
5	(358), 320	440	0.30	0.23 (81)	0.02 (19)
6	356, 344, 319, 305	436	0.73	0.21 (92)	0.03 (8)
7	359, 344, 320	431	0.70	0.29 (93)	0.04 (7)
8	(356), 341, (326), (312)	432	0.62	0.27 (92)	0.05 (8)
9	353, 342, 318, 304	472	0.60	0.42 (29)	0.16 (71)
10	359, 348, 318, 304	476	0.50	0.41 (40)	0.19 (60)
11	(356), 343, 319, (311)	453	0.53	1.85 (84)	0.20 (13)
12	358, 344, 320, 306	450	0.64	0.06 (42)	0.01 (58)
13	356, 344, 317	476	0.92	0.60 (48)	0.18 (52)
14	356, 344, 318	470	0.84	0.42 (45)	0.18 (55)
15	359, 351, 342, 316	450	0.64	2.13 (93)	0.14 (7)
16	(365), 352, 323	442	1.60	0.25 (91)	0.03 (8)
17	(368), 350, 325, (314)	460	1.30	0.31 (90)	0.05 (10)
18	368, 330	445	0.66	0.28 (90)	0.05 (10)
19	368, 341	450	2.93	0.34 (80)	0.09 (20)
20	(365), 351, 325, (314)	483	1.30	0.63 (92)	0.12 (8)
21	359, (348), 316, 304	483	1.68	0.86 (25)	0.28 (75)
22	(357), (340), 320, (312)	510	1.92	0.49 (25)	0.22 (75)
23	(356), (336), 317, (310)	511	2.16	0.44 (50)	0.15 (50)
24	(358), (336), 316, (308)	495	1.33	2.04 (89)	0.20 (11)
25	(358), (340), 320, (310)	501	1.27	0.05 (35)	0.01 (65)
26	(360), 328	520	3.90	0.67 (98)	0.08 (02)

^a λ CF (nm) are the absorption bands of the closed form in the range 300–400 nm and λ_{\max} OF (nm) is the absorption band of lower energy of the open form. A_0 is the coloration ability; $k_{\Delta 1}$ (s⁻¹) and $k_{\Delta 2}$ (s⁻¹) are the thermal fading rates of the coloured forms. Measurements were performed in toluene at 25°C.

^b The spectrum of the closed form was monitored in ethanol.

^c Shoulders are given in parentheses.

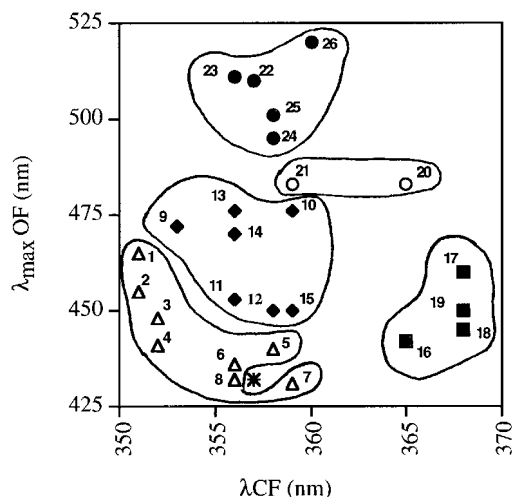


Figure 2. Photochromic parameters of naphthopyrans **1–26** compared to reference compound **RC** (*): $\lambda_{\max}\text{OF}$ (nm) of open forms are plotted vs λ_{CF} (nm) of closed forms. Data are given as point diagrams in which compounds are collected according to their structural characteristics: (Δ) compounds bearing a thiophene or a bithiophene unit linked to the naphthalene moiety through a carbon chain or an ester junction; (\blacklozenge) compounds bearing at least one thiophene unit at the 3-position; (\blacksquare) compounds bearing a thiophene or a bithiophene unit at the 7-position; (\circ) compounds bearing at least one thiophene unit at the 3-position and a thiophene at the 7-position; (\bullet) compounds bearing a bithiophene unit at the 3-position

the open form ($\lambda_{\max}\text{OF}$) against the wavelength corresponding to the minimum energy of the absorption of the closed form (λ_{CF}). When present, shoulders were taken into account.

Compounds were divided into five main sets according to their structural features. The set **16–19** which corresponds to compounds bearing a thienyl or a dithienyl entity at position 7 together with a phenyl or a diphenyl group at position 3 exhibit longer absorption wavelength of the closed form. This shift of ca 20 nm ($\sim 1500\text{ cm}^{-1}$) is particularly interesting for application in photochromic glasses where an absorption as close as possible to the visible spectrum is needed. This low-energy absorption band corresponds to a $\pi\pi^*$ electronic transition located on the naphthopyran part. Quantum calculations using the AM1 program¹⁶ show that about 80% of this transition can be interpreted as a HOMO–LUMO electron transfer. Figure 3 shows frontier orbitals of **RC**, **16** and **18**. The results demonstrate that in the last two cases, there is an increasing involvement of the thiophene nuclei in the transition and in the stabilization of the LUMO on adding one, then two thiophene rings.

The higher $\lambda_{\max}\text{OF}$ of the set **22–26** compared with the set **9–15** can be attributed to the effect of replacing one thiophene ring by a dithiophene ring at position 3. This replacement induces a bathochromic shift of ca 40 nm ($\sim 1700\text{--}2200\text{ cm}^{-1}$) of the $\lambda_{\max}\text{OF}$ without any notice-

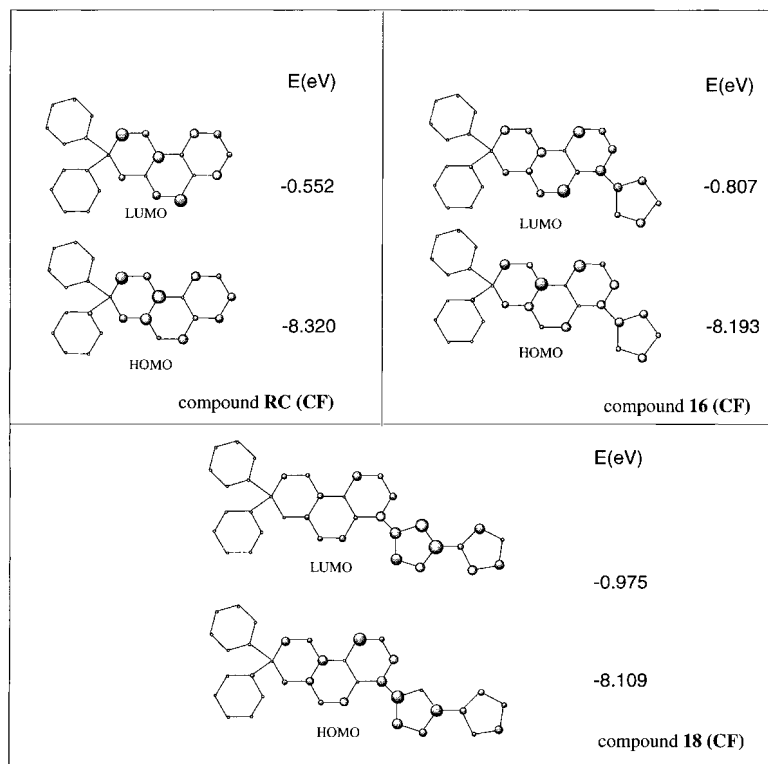


Figure 3. Representation of the frontier orbitals of closed forms (CF) of naphthopyrans **RC** (reference), **16** and **18**. The diameters of the grey balls are proportional to the coefficient of the atomic orbitals involved in the considered molecular orbital. E is the energy (eV) of the orbital

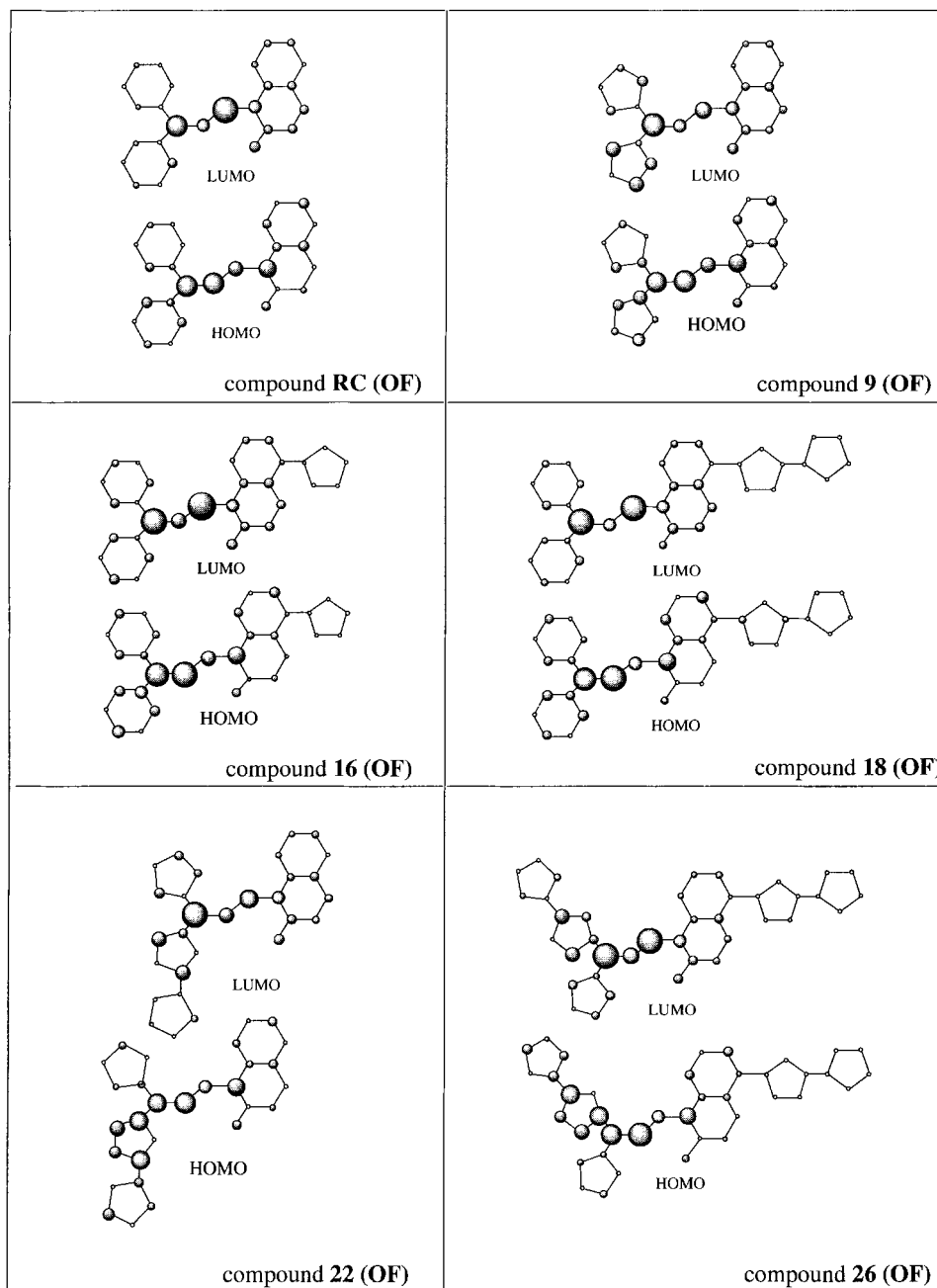


Figure 4. Representation of the frontier orbitals of open forms (OF) of naphthopyrans **RC** (reference), **9**, **16**, **18**, **22** and **26**. The diameters of the grey balls are proportional to the coefficient of the atomic orbitals involved in the considered molecular orbital

able effect on the λ_{CF} . The effect of this replacement can be visualized on the respective couples (**9/22**, **10/23**, **11/24** and **12/25**).

Frontier molecular orbitals that are involved in the visible transition of the open form of compounds **9** and **22** are shown in Fig. 4. The quantum calculations show a high participation of the dithiophene unit (**22**) in the transition, whereas a thiophene fixed at the same position (**9**) is weakly involved. One can also observe a decrease in the energy difference (ΔE) between the LUMO and the HOMO on going from the monothiophenic compound **9**

($\Delta E = 6.51$ eV) to the dithiophenic compound **22** ($\Delta E = 6.34$ eV). This result is in good agreement with the experimental observation (bathochromic shift of λ_{max}^{OF}).

Inside some of these sets, several subgroups can be distinguished according to more precise structural characteristics. For instance, inside the **1–8** set, two subgroups can be distinguished, one corresponding to a junction through the 8-position (**1–4**) (higher λ_{max}^{OF} , lower λ_{CF}) and other to a junction through the 7-position (**5–8**) (lower λ_{max}^{OF} , higher λ_{CF}). In the **9–15** and **22–**

26 sets, the substitution effect of the thiophene ring by a methyl group is highlighted by the behaviour of the couples **9/11**, **14/15** and **22/24**. In these three cases, a bathochromic shift of $\lambda_{\max}\text{OF}$ is observed. Compound **26**, bearing dithiophenes on both the naphthalene part and the Csp^3 atom, shows the higher $\lambda_{\max}\text{OF}$.

These experimental data can be explained by quantum calculations (Fig. 4). The energy difference between the LUMO and the HOMO is slightly weaker for **26** ($\Delta E = 6.31$ eV) compared with **22** ($\Delta E = 6.34$ eV) bearing only one dithiophene at position 3.

Generally, significant variations of $\nu_{\max}\text{OF}$ are reflected in the variations of the calculated $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ (Table 3).

Nevertheless, it is interesting to note that the participation of the frontier orbital of a dithiophene

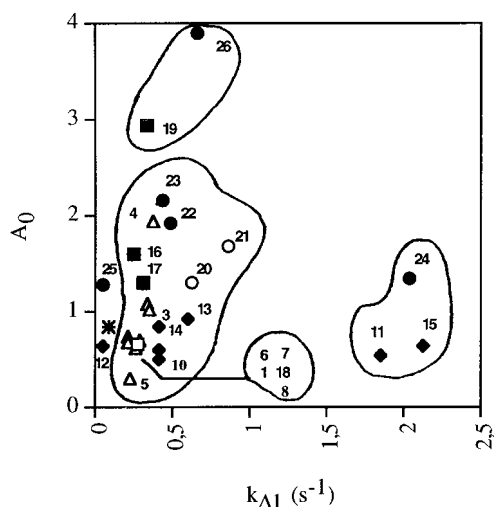
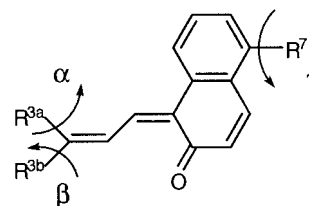


Figure 5. Photochromic parameters of naphthopyrans **1–26** compared with reference compound **RC** (*): coloration abilities A_0 are plotted vs the fading rates $k_{\Delta 1}$ (s^{-1}). Data are given as point diagrams in which compounds are collected according to their structural characteristics: (Δ) compounds bearing a thiophene or a bithiophene unit linked to the naphthalene moiety through a carbon chain or an ester junction; (\blacklozenge) compounds bearing at least one thiophene unit at the 3-position; (\blacksquare) compounds bearing a thiophene or a bithiophene unit at the 7-position; (\circ) compounds bearing at least one thiophene unit at the the 3-position and a thiophene at the 7-position; (\bullet) compounds bearing a bithiophene unit at the 3-position

linked on the naphthalene part is weaker than the participation of a dithiophene linked on the sp^3 carbon atom. This behaviour is certainly due to a decrease in the conjugation of the dithiophene with the whole π system of the molecule. Indeed, in the most stable conformation calculated by molecular mechanics (GenMol program¹⁷), the twist angles of the dithiophenes from the mean plane of the molecule are 14 and 30° for a substitution of the Csp^3 atom and a substitution of the naphthalene ring, respectively (Table 4). Besides, whatever the nature of the aromatic group fixed at the 3-position (phenyl, thienyl or dithienyl), this group is more conjugated (torsion angles from 7 to 25°) than an aromatic group (thienyl or dithienyl) fixed at the 7-position (torsion angles from 30 to 33°). This observation is confirmed by the lack of participation of thiophene or dithiophene nuclei linked at position 7 to the frontier orbital involved in the transition of weaker energy (see compounds **16**, **18** and **26** in Fig. 4). In contrast, the participation of the phenyl, thienyl or dithienyl nuclei (increasing participation in this order) fixed at the 3-position to the same orbital is more evident.

A second diagram (Fig. 5) is obtained by plotting A_0 vs $k_{\Delta 1}$. The arbitrary choice of $k_{\Delta 1}$ instead of $k_{\Delta 2}$ or any

Table 4. Torsion angles ($^\circ$) between the mean plane of substituents R^{3a} , R^{3b} , R^7 and the mean plane of the open form of naphthopyrans (from molecular mechanics, program GenMol¹⁷)



Compound	R^{3a}	R^{3b}	R^7	α	β	γ
RC	Ph	Ph	—	38	23	—
9	Th	Th	—	41	7	—
16	Ph	Ph	Th	37	25	33
18	Ph	Ph	Th ₂	37	23	33
22	Th	Th ₂	—	32	13	—
26	Th	Th ₂	Th ₂	34	14	30

Table 3. Comparison of the experimental wavelengths of absorption of open forms [$\lambda_{\max}\text{OF}$ (nm)] of naphthopyrans with the energy difference [ΔE (eV)] between LUMO and HOMO orbitals

Compound	$\lambda_{\max}\text{OF}$ (nm)	ν_{\max} (cm^{-1})	E_{LUMO} (eV)	E_{HOMO} (eV)	ΔE (eV)	ΔE (cm^{-1})
RC	432	23148	−1.46	−8.21	6.75	54000
16	442	22727	−1.44	−8.21	6.77	54160
18	445	22471	−1.45	−8.22	6.77	54160
9	472	21186	−1.60	−8.11	6.51	52080
22	510	19607	−1.66	−8.00	6.34	50720
26	520	19230	−1.69	−8.00	6.31	50480

linear combination of both does not change the main conclusions. Four main groups can be distinguished:

- 11**, **15** and **24** exhibit rapid rate constants related to the presence of a methyl group at position 3 which destabilizes the open form;
- 12** and **25** are characterized by a slow thermal bleaching rate related to the presence of a 2-fluorophenyl substituent at position 3;
- 19** and **26** show a strong coloration ability, probably owing to the simultaneous presence of a diphenyl or dithienyl substituent at position 3 together with a dithiophene at position 7;
- the other compounds studied have intermediate values of A_0 and $k_{\Delta 1}$.

A more detailed analysis inside each group allows us to highlight more peculiar features. Within groups **11**, **15** and **24**, **12** and **25**, and **19** and **26**, the compound with a dithienyl group at position 3 displays the highest coloration ability (**24–26**). In the more scattered fourth group (d), the more colourable compounds are those with three or four aromatic rings (phenyl or thienyl, as in **16–18**, **20–23** and **25**), while the less colourable compounds are those with only two aromatic rings (**9**, **10**, **13** and **14**). The fairly high coloration ability of compounds **2–4** is related to the presence of an ester group $-\text{C}(\text{O})\text{O}-$ at position 8. The $k_{\Delta 1}$ value depends of the substitution on the sp^3 carbon; thus, a decrease is observed with benzene rings, whereas an increase is expected with thiophene nuclei (compounds **RC** vs **9**, **16** vs **20** and **19** vs **26**).

CONCLUSION

Structure–property relationships obtained from experimental data within a sufficiently wide and homogeneous series could allow the direct synthesis of compounds with more predefined photochromic properties. A theoretical approach using molecular mechanics or quantum calculations affords a better understanding of the observed phenomena. These calculations can help to make qualitative predictions concerning the variation of the absorption wavelength of the open form. This study, which was performed using 26 naphthopyrans bearing one or several thiophene or dithiophene units, allowed us to elucidate some peculiar relationships. For instance, a shift of the absorption wavelength of the colourless form (λ_{CF}) can be obtained by linking a thiophene entity at position 7 or 8 (linked to the naphthalene ring either directly or through an ester junction). In order to increase the absorption wavelength of the coloured open forms ($\lambda_{\text{max}}\text{OF}$), highly conjugated substituents (diphenyl or dithienyl) have to be attached at position 3. Modelling of the fading rate is then easily achieved on varying the substitution at position 3 (methyl to accelerate or 2-fluorophenyl to decelerate). The variation of A_0 is related

to the total number of aromatic rings borne by the molecule either on the sp^3 carbon atom or on the naphthalene part: the higher this number, the greater is the coloration ability.

EXPERIMENTAL

Photochromic compounds **RC** and **1–26** were prepared using experimental conditions as described in Refs 10 and 11. For each compound are given the formula, the molecular weight (MW, g) and the melting-point (mp, °C).

RC, $\text{C}_{25}\text{H}_{18}\text{O}$, MW = 334.420, m.p. = 158; **1**, $\text{C}_{32}\text{H}_{22}\text{O}_2\text{S}$, MW = 470.592, m.p. = 158; **2**, $\text{C}_{33}\text{H}_{24}\text{O}_3\text{S}$, MW = 500.618, m.p. = 147–148; **3**, $\text{C}_{31}\text{H}_{22}\text{O}_3\text{S}$, MW = 474.580, m.p. = 136–137; **4**, $\text{C}_{35}\text{H}_{24}\text{O}_3\text{S}_2$, MW = 556.706, m.p. = 111–112; **5**, $\text{C}_{32}\text{H}_{22}\text{O}_3\text{S}$, MW = 486.591, m.p. = 167–168; **6**, $\text{C}_{31}\text{H}_{22}\text{O}_3\text{S}$, MW = 474.580, m.p. = 116–117; **7**, $\text{C}_{30}\text{H}_{20}\text{O}_3\text{S}$, MW = 460.553, m.p. = 214; **8**, $\text{C}_{34}\text{H}_{22}\text{O}_3\text{S}_2$, MW = 542.679, m.p. = 170; **9**, $\text{C}_{21}\text{H}_{14}\text{OS}_2$, MW = 346.473, m.p. = 138–139; **10**, $\text{C}_{24}\text{H}_{18}\text{O}_2\text{S}$, MW = 370.472, m.p. = 126; **11**, $\text{C}_{18}\text{H}_{14}\text{OS}$, MW = 278.374, m.p. = 56; **12**, $\text{C}_{24}\text{H}_{15}\text{OFS}$, MW = 358.429, m.p. = 116; **13**, $\text{C}_{24}\text{H}_{17}\text{O}_2\text{SBr}$, MW = 449.368, m.p. = 117; **14**, $\text{C}_{21}\text{H}_{13}\text{OS}_2\text{Br}$, MW = 425.369, m.p. = 175; **15**, $\text{C}_{18}\text{H}_{13}\text{OSBr}$, MW = 357.270, m.p. = 79; **16**, $\text{C}_{29}\text{H}_{20}\text{OS}$, MW = 416.543, m.p. = 82; **17**, $\text{C}_{35}\text{H}_{24}\text{OS}$, MW = 492.641, m.p. = 92; **18**, $\text{C}_{33}\text{H}_{22}\text{OS}_2$, MW = 498.669, m.p. = 170; **19**, $\text{C}_{39}\text{H}_{26}\text{OS}_2$, MW = 574.766, m.p. = 176; **20**, $\text{C}_{25}\text{H}_{16}\text{OS}_3$, MW = 428.599, m.p. = 150; **21**, $\text{C}_{27}\text{H}_{20}\text{O}_2\text{S}_2$, MW = 452.598, m.p. = 116; **22**, $\text{C}_{25}\text{H}_{16}\text{OS}_3$, MW = 428.599, m.p. = 122; **23**, $\text{C}_{26}\text{H}_{20}\text{O}_2\text{S}_2$, MW = 452.598, m.p. = 134; **24**, $\text{C}_{22}\text{H}_{16}\text{OS}_3$, MW = 360.500, m.p. = 103; **25**, $\text{C}_{27}\text{H}_{17}\text{OFS}_2$, MW = 440.548, m.p. = 133; **26**, $\text{C}_{33}\text{H}_{20}\text{OS}_5$, MW = 592.851, m.p. = 98.

Spectrokinetic measurements. For the determination of λ_{CF} , measurements were made in 10^{-5} mol l $^{-1}$ toluene solutions using a Beckman DU 7500 spectrophotometer (optical path 5 mm). For the determination of $\lambda_{\text{max}}\text{OF}$, A_0 and k_{Δ} , 5×10^{-5} mol l $^{-1}$ toluene solutions were used. The flash photolysis apparatus was monitored by a Warner and Swasey rapid spectrometer, allowing us to record visible absorption spectra of the coloured forms in the 400–700 nm range (acquisition time 1 ms, repetitivity 1.25 ms).¹⁸ Flashes (duration 50 μs) were generated by two xenon tubes with a quartz envelope. The energy of the flashes was 60 J for the whole polychromatic emission spectrum. For measurements, thermostated (25 °C) 100 mm cells were used. The light from the analysis lamp (50 W, quartz–iodide) was filtered using a Schott GG400 high-pass filter.

In a preliminary experiment, the visible absorption spectrum and the $\lambda_{\text{max}}\text{OF}$ of the open form were determined. In a second experiment, the initial absorbance A_0 was measured and then the decrease in the

absorbance with time was monitored. The rate constants ($k_{\Delta 1}$ and $k_{\Delta 2}$) were calculated using a bi-exponential model.

Modelling. Molecules were built and their geometry optimized using the molecular mechanics program GenMol.¹⁷ Quantum calculations were performed with the AMPAC program using AM1 as hamiltonian.¹⁶ The chosen options were 1SCF, PRECISE, C.I. = 6 for closed form, C.I. = 8 for open form, MECI, SINGLET, CIS-TATE = 6.

REFERENCES

1. Dürr H, Bouas-Laurent H. (eds). *Photochromism: Molecules and Systems*. Elsevier: Amsterdam, 1990.
2. Crano JC, Kwak WS, Welch CN. In *Applied Photochromic Polymer System*, McArdle CB (ed). Blackie: New York, 1992; Chapt. 2.
3. Crano JC, Guglielmetti RJ (eds). *Organic Photochromic and Thermochemical Compounds*. Kluwer Academic/Plenum Publishers: New York, vol. 1, 1998 and vol. 2, 1999.
4. Van Gemert B. In *Organic Photochromic and Thermochemical Compounds*, vol. 1, Crano JC, Guglielmetti RJ (eds). Kluwer Academic/Plenum Publishers: New York, 1998; Chapt 3.
5. Van Gemert B, Bergomi M, Knowles D. *Mol. Cryst. Liq. Cryst.* 1994; **246**: 67–73.
6. Pozzo JL, Lokshin V, Guglielmetti R. *J. Chem. Soc., Perkin Trans. 1* 1994; 2591–2595.
7. Pozzo JL, Lokshin V, Samat A, Guglielmetti R. *J. Photochem. Photobiol. A: Chem.* 1998; **114**: 185–191.
8. Pozzo JL, Samat A, Guglielmetti R, Lokshin V, Minkin V. *Can. J. Chem.* 1996; **74**: 1649–1659.
9. Chamontin K, Lokshin V, Rossolin V, Samat A, Guglielmetti R. *Tetrahedron* 1999; **55**: 5821–5830.
10. Moustrou C, Rebiere N, Samat A, Guglielmetti R, Yassar AE, Dubest R, Aubard J. *Helv. Chim. Acta* 1998; **81**: 1293–1302.
11. Rebiere-Galy N. Thesis, Marseille, 1998.
12. Yassar AE, Moustrou C, Youssoufi H, Samat A, Guglielmetti R, Garnier F. *J. Chem. Soc., Chem. Commun.* 1995; 471–472.
13. Yassar AE, Moustrou C, Youssoufi H, Samat A, Guglielmetti R, Garnier F. *Macromolecules* 1995; **28**: 4548–4553.
14. Appriou P, Garnier F, Guglielmetti R. *J. Photochem.* 1978; **8**: 145–165.
15. Delbaere S, Luccioni B, Bochu C, Teral Y, Campredon M, Vermeersch G. *J. Chem. Soc., Perkin Trans. 2* 1998; 1153–1157.
16. Dewar MJS, Zoebisch EG, Healy EG, Stewart JJP. *J. Am. Chem. Soc.* 1985; **107**: 3902–3909.
17. Pepe G, Siri D. In *Modeling of Molecular Structure and Properties*, Rivail JL (ed). Elsevier: Amsterdam, 1990; 93–101.
18. Pottier E, Dubest R, Guglielmetti R, Tardieu P, Kellmann A, Tfibel F, Levoir P, Aubard J. *Helv. Chim. Acta* 1990; **70**: 303.