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Photochromic Behaviour of Bis[4-(N,N-dimethylamino)phenyl]-substituted 3*H*-Naphtho[2,1-b]pyran and 2*H*-1-Benzopyran

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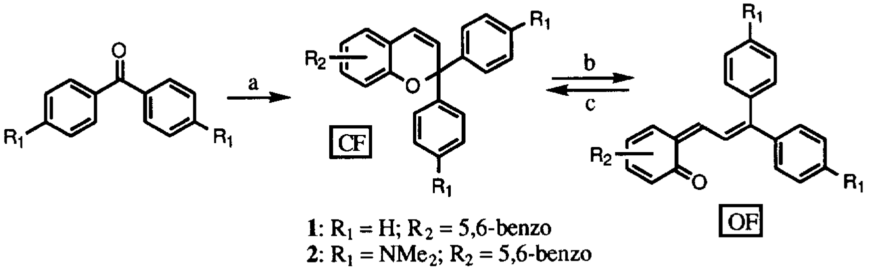
Abstract: The photochromic behaviour of 3,3-bis[4-(N,N-dimethylamino)phenyl]-3*H*-naphtho[2,1-b]pyran (**2**) and 2,2-bis[4-(N,N-dimethylamino)phenyl]-2*H*-1-benzopyran (**3**) has been studied by flash photolysis and compared to 3,3-diphenyl-3*H*-naphtho[2,1-b]pyran (**1**) in order to delineate effects due to the N,N-dimethylamino groups.

3*H*-Naphtho[2,1-b]pyrans and 2*H*-1-benzopyrans have been pre-eminently studied during recent years in view of their interesting photochromic properties and their potential applications in optical materials.[1] We were interested in examining the photochromic behaviour of heterocyclic prototypes **2** and **3**, carrying geminal 4-(N,N-dimethylamino)phenyl groups at the sp^3-carbon atom, as compared to the amino-free analogue **1**. The preparation involves coupling of the propargylic alcohol, derived from Michler's ketone (**2**, **3**) or benzophenone (**1**) and acetylene, with β-naphthol (**1**, **2**) or phenol (**3**) in acid medium.[2-5] The photochromic equilibrium between the uncoloured or closed form (CF) and the coloured (most stable transoid stereoisomer) or open form (OF) is represented in scheme 1.



1: $R_1 = H$; $R_2 = 5,6$-benzo
2: $R_1 = NMe_2$; $R_2 = 5,6$-benzo
3: $R_1 = NMe_2$; $R_2 = H$

SCHEME 1

a: i: Sodium or lithium acetylide / ethylenediamine, THF, r.t.; ii. for **1** and **2**: β-Naphthol, CH_2Cl_2, *p*-TosOH, heat; for **3**: phenol, toluene, Al_2O_3 (weakly acidic), heat; b: hν (UV); c: thermal fading.

The spectrokinetic parameters were determined using a fast scanning spectrophotometer (model 501, Warner and Swasey) after flash photolysis (xenon, 60 J, 50 ms).[6,7] The spectrometer was equipped with a photomultiplier covering a spectral bandwidth between 400 and 650 nm (spectral resolution < 1 nm). Thus, the following parameters could be accessed: the wavelength(s) of the maximum absorption(s) of the open form in the visible (λ_{max}), the absorbance A_0 at this (these) wavelength(s) and the kinetic constant for thermal decolouration (k_Δ). The parameter A_0 defines the 'colorability', which is a measure of the efficiency of the photolysis and, consequently, depends on the photoreaction quantum yield.[8,9] The values of the spectrokinetic parameters are presented in Table 1.

TABLE 1: Spectrokinetic parameters of photochromes **1-3**[a]

Compound	k_Δ (s^{-1})	λ_{max} (nm) (CF)	λ_{max} (nm) (OF)	A_0[b]
1	0.1	303,314, 345[c], 359	432	0.84
2	1.7	302, 316, 347[c], 362	443, 525[c], 600[c]	2.10 (560 nm)[d]
3	10.7	207, 260, 305[c]	460, 565[c], 615[c]	0.82 (595 nm)[d]

a: Toluene, 25°C; b: 2.5 x 10^{-5} *M; c:* λ_{max} *with highest ε-values; d: measured at a wavelength intermediate between the two long-wavelength absorption bands.*

Compounds **2** and **3** exhibit a significant bathochromic shift of the absorption maximum of the coloured form as compared to that of the reference compound **1**. The effect is remarkably higher than for methoxy substituents at the same positions (λ_{max} = 480 nm).[4,10,11] The thermal bleaching is accelerated and the colorability is increased for compound **2** relative to **1**. Comparison of the influence of a naphthopyran ring, as in **2**, with respect to a benzopyran ring, as in **3**, indicates that the open form is more stabilized in **2** and that the colorability is enhanced due to extension of the p-conjugation. In this context, it seemed to be of interest to examine the solvatochromism of **2** in a series of polar and non-polar solvents. The results are collected in Table 2.

TABLE 2: Spectrokinetic parameters of photochrome **2** in various solvents at 25°C

	DMSO	MeOH	MeCN	Toluene	1,4-Dioxane	Cyclohexane
k_Δ (s^{-1})	5.4	5.8	11.0	1.7	2.8	1.9
λ_{max} (nm)[a]	485,565,650	477,560,635	465,550,628	443,525,600	445,525,596	425,505,571
A_0[b]	1.70	1.60	1.10	2.10	1.30	0.61

a: All absorption bands at longest wavelength have the highest ε-values; b: 2,5 x 10^{-5} *M; determined at* λ_{max} *with highest ε-value.*

Using the Brooker χ_R parameter, defined for a polyenic or quinonic electron distribution,[12] a linear correlation is evident for the three bands in the visible spectrum, corresponding to frequencies ν_1, ν_2 and ν_3 (Figure 1). The equilibrium between the uncoloured (CF) and coloured (OF) forms is shifted to the coloured form in polar solvents due to a thermochromic phenomenon, i. e. thermal cleavage of the C-O bond is facilitated by a more pronounced polarization in polar solvents. The observation of a positive solvatochromism for compound **2** indicates that the open coloured form is not zwitterionic (merocyanine-type), but rather quinonic. In general, as the polarity of the solvent is increased, the visible absorption maximum shifts to shorter wavelengths for merocyanine-type molecules.[13] Our finding is consistent with a weakly polar ground state having a small charge delocalization.[14] The increased fading rate for amino substituents in *para*-position of the phenyl groups (compare **1** and **2**) confirms our observation. This result is nevertheless surprising because a zwitterionic dipolar form, more specifically the carbocation, formed after cleavage of the C_{sp^3}-O bond, could have been stabilized by the 4-(N,N-dimethylamino)phenyl substituents due to the electron-donating character of the amino groups.

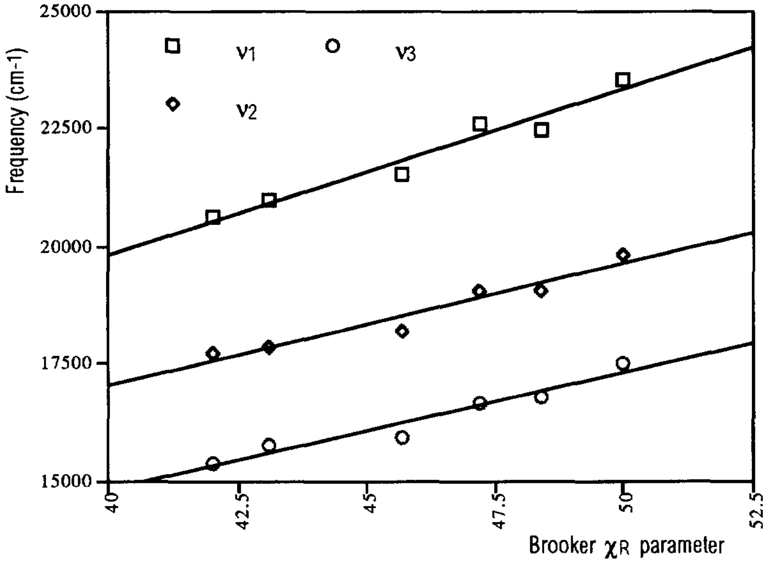


FIGURE 1

In summary, introduction of geminal 4-(N,N-dimethylamino)phenyl groups at the sp^3-carbon atom in 3*H*-naphtho[2,1-b]pyran and 2*H*-1-benzopyran allowed to delineate their influence on relevant photochromic features. The large bathochromic shift of the absorption maximum of the coloured form is accompanied by a positive solvatochromism (as shown for photochrome **2**) indicating an electronic distribution of the quinonic type. The values of the colorabilities and the thermal bleaching constants relate to the degree of conjugation in the coloured forms of compounds **2** and **3**.

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2. **1**: 62%, recryst. from hexane, mp: 158°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm): 6.26 (d, J = 9.9 Hz, 1H), 7.19 (d, J = 8.9 Hz, 1H), 7.23 (m, 2H), 7.29 (m, 1H), 7.30 (m, 4H), 7.31 (m, 1H), 7.44 (m, 1H), 7.48 (m, 4H), 7.65 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm): 118.43, 119.60, 121.40, 123.68, 126.69, 127.10 (4C), 127.60 (2C), 127.79, 128.17 (4C), 128.59, 129.90. **2**: 49%, purification by flash chromatography (Et_2O), mp: 223°C. ^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm): 2.90 (s, 12H), 6.66 (d, J = 8.8 Hz, 4H), 7.16 (d, J = 8.8 Hz, 1H), 7.22-7.27 (m, 2H), 7.33 (d, J = 8.8 Hz, 4H), 7.43 (m, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm): 40.84 (4 C), 112.21 (4C), 118.75, 118.88, 121.63, 123.54, 126.66, 128.38 (4C), 128.74, 128.94, 129.71. **3**: 55%, purification by flash chromatography (hexane: CH_2Cl_2 1:1), mp: 144°C. ^{1}H-NMR (600 MHz, C_6D_6): δ (ppm): 2.93 (s, 12H), 6.12 (d, J = 9.8 Hz, 1H), 6.55 (d, J = 9.8 Hz, 1H), 6.68 (d, J = 8.9 Hz, 4H), 6.80 (dt, J = 7.4 Hz and 0.9 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.98 (dd, J = 7.4 Hz and 1.5 Hz, 1H), 7.10 (dt, J = 7.9 Hz and 1.5 Hz, 1H), 7.30 (d, J = 8.9 Hz, 4H). ^{13}C-NMR (150 MHz, C_6D_6): δ (ppm): 40.41 (4C), 111.82 (4C), 116.31, 120.49, 121.12, 122.18, 126.24, 127.91, 129.04 (4C).
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