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The Control of Photochromism of [3H]-Naphthopyran Derivatives with Intramolecular CH- π Bonds

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ABSTRACT

The photochromism of [3H]-naphthopyran derivatives can be switched from T-type to inverse- or P-type through the manipulation of relative thermodynamic stabilities of open isomers with intramolecular CH- π bonds.

Photoswitchable molecules such as azo compounds and dithienylethenes have been extensively investigated over the last years, due to their potential in technological advanced applications ranging from molecular electronics to bioimaging.¹ These applications rely on the capacity of the photochromic compounds to switch reversibly between two states thermally (meta)stable having different properties by light (P-type photochromism).² In contrast, photochromic organic naphthopyrans have attracted much attention due to their industrial application in ophthalmic technology.³ The reversible change of color under solar exposition that ceases after the removal of the illumination constitutes the first required property for the use of naphthopyrans in plastic photochromic lenses (T-type photochromism). Changing the photochromism of naphthopyrans from T- to P-type is very challenging and would offer a new family of photochromes that could be critical of use in advanced applications and constitute an interesting alternative to azocompounds and dithienylethenes. The photochromism of [3H]-naphthopyrans is believed to start with C-O bond cleavage of the closed pyran ring (CF) induced by UV absorption that leads after some internal rearrangement of

double bond to an open colored isomer transoid-cis (TC) which returns thermally to the initial state (Scheme 1).⁴ Under continuous irradiation, TC can eventually produce a transoid-trans open isomer (TT) following an isomerization of one double bond.⁴ The reversible change of color comes from the fact that the TC isomer is the major product under solar or UV irradiation.⁵ In fact, TC and TT isomers differ from their thermal and thermodynamic stabilities. In the case of the reference compound namely the 3,3-diphenyl-[3H]-naphtho[2-1b]pyran at room temperature in toluene solution, TC is less thermally stable by about 3 to 4 orders of magnitude lower compared to TT while its thermodynamic stability is about 8.9 kJ higher than that of TT.⁶ Indeed, a hydrogen-bond is established between proton H₂ and the oxygen of the ketone group stabilizing TC while the same proton in TT is in a repulsive interaction with the naphthalene ring, consequently destabilizing TT. The isomerization of the double bond involved in the formation of TT from TC is rendered more difficult due to the presence of this hydrogen-bond that should be broken in this transformation. Consequently, the photochromism of naphthopyran is controlled by a

hydrogen-bond allowing the accumulation of the most thermodynamic stable open isomer TC. According to this argument, the manipulation of the relative thermodynamic stabilities of open isomers compared to the closed form would in principle modify the thermo and/or photoequilibrium between all species involved in the photochromic processes.

Scheme 1. Photochromic interconversion in [3H]-naphthopyran

Scheme 2. Synthesis of photochromic compounds **1** and **2**

Herein, we report the synthesis and the properties of two naphthopyran derivatives **1** and **2** displaying unusual and intriguing inverse- and P-type photochromism respectively, through the adjustment of relative thermodynamic stabilities of open isomers with CH- π bonds. To the best of our knowledge, the control of the photochromism of naphthopyrans with CH- π bonds is the first time demonstrated and shed further insight into the molecular design of naphthopyrans with specific and innovative properties. Compounds **1** and **2** are namely belonging to benzopyrano[6,5-*c*]carbazole derivatives which differ from one substituent located at the 3-position. **1** has an ethynylphenyl group while this group is replaced by a phenyl substituent in **2**. This little structural change has a tremendous effect on the thermo/photoequilibrium between the closed and open isomers.

The preparation of **1** and **2** is outlined in Scheme 2. The building of the naphthopyran scaffold in **1** and **2** was obtained by a “one-pot reaction” with 7-phenyl-7H-benzo[*c*]carbazol-2-ol and the corresponding prop-2-yn-1-ol derivatives in the presence of a catalytic amount of PPTS.⁷ For **2**, the reaction proceeded smoothly and the closed form **CF2** was obtained as pure product in 75 % yield. In the case of **1**, it turned out that the reaction mixture was getting redder and after 24 hours of stirring, analysis with TLC plate revealed a dark red spot as the main product. This was very surprising and was indicative that colored open isomers were stable in the reaction mixture. **1** could be purified by column chromatography with a mixture of petroleum ether and ethylacetate (90/10) as eluent and obtained as dark red

solid in 54% yield. ¹H NMR spectrum at 20°C in toluene solution, revealed amazingly the presence of only two isomers in a ratio 80/20. Four open isomers could be expected for naphthopyrans having a chiral center at the 3-position. The minor isomer was assigned to **CF1** due to the doublet signal at 6.00 ppm ($J = 9.1$ Hz), characteristic of proton H2 of the pyran ring (Figure 2S and Table 1S, ESI). For the major isomer, two pseudo doublets at 9.26 and 9.39 ppm with a coupling constant of 12.2 Hz in AB system were observed. The measured values of coupling constant and the downfield chemical shifts make it possible to attribute these signals to protons H2 (deshielded by C=O) and H1 (deshielded by the concomitant effect of the ethynyl and indolino group) in TC type compound isomers.^{4a,5c-5f} The major isomer was found to be CTC isomer and this assignment was based on recording 2D-Noesy experiment (Figure 6S, ESI).

Figure 1. X-ray molecular structure of CTC isomer

The structure of the CTC isomer was nicely confirmed by X-ray crystallography.⁸ We were very pleased to get the first X-ray molecular structure of one open isomer in naphthopyrans series. It is worthwhile to note that the distance between H2 and the ketone group is about 2.31 Å, the angle C2-H2-O is 122.25° and the dihedral angle between C4a-O-H2-C2 is 21.37°, confirming a strong hydrogen bond is taking place in TC isomer.⁹ The alternate bond lengths of the diene unit between double (C3-C2 = 1.36 Å), pseudo-single (C2-C1 = 1.43 Å) and double bond (C1-C13d = 1.36 Å) are in agreement with a conjugated bridge and a quinoidal structure of the open form.⁸ This is also consistent with the bond length of the conjugated ketone group (1.22 Å).⁹ Due to the repulsive interaction between H1 and the indoline group, an dihedral angle (C13b-C13c-C13d-C1) of 32° between the diene and the pseudo naphthalene units is observed. Thanks to the ethynyl group, the anisole is almost perfectly planar with the conjugated bridge (C2-C3-C1'-C2' = 4.65°) and the phenyl group is slightly more twisted from planarity (C2-C3-C1''-C2'' = 7.53°). Indeed, the twisting of the phenyl group comes from the dedication of this group to be in a strong edge-to-face interaction with the phenyl of the carbazole unit. The geometry of the edge-to-face interaction is as follows: the proton H2'' in interaction to ring centroid distance is 2.70 Å and the dihedral angle between the interacting ring

planes is 51.77° . These bond lengths and angles are typical for strong edge-to-face interactions with face-tilted-T geometry.¹⁰

According to the X-ray structure, the introduction of the ethynyl group at the 3-position leads to a very good conjugation throughout the entire molecule by limiting the steric hindrance at the strict minimum. The concomitant effect of a planar structure highly conjugated and the withdrawing character of the ethynyl group¹¹ with the presence of a strong CH- π bond, led to the first thermoequilibrium between CF1 and CTC wherein the CTC is the most abundant isomer (Figure 2a).

Figure 2. a) Thermal- and photoequilibria for **1**; b) Absorption spectra before and after visible irradiation; c) Absorption spectra of CTC and CTT in the visible range

The photochemical interconversion of **1** was carried out in toluene solution at 20°C and followed by UV/Vis and NMR spectroscopies. Before irradiation, the system **1** displays a strong red color centered at 482 nm, ascertained to the absorption behavior of CTC. Knowing the concentration of CTC, an epsilon value of $17800 \text{ mol}^{-1}.\text{L.cm}^{-1}$ at 482 nm was deduced. Upon irradiation with UV light, the absorption didn't change at all. In contrast, upon visible irradiation, a blue shift of the maximum band was observed (Figure 2b). The change of absorbance was indicative that CTC photoisomerized into a less conjugated open isomer. NMR spectrum at the PSS state obtained after 5 min of irradiation, indicates the exclusive formation of CTT isomer (Figure 2, Figure 5S, ESI). The difference of the NMR spectra of CTC and CTT confirmed the presence of CH- π bond between proton $\text{H}_{2''}$ and the phenyl of the carbazole unit in CTC as seen in the X-ray molecular structure. The chemical shift of proton $\text{H}_{2''}$ (6.78 ppm) in CTC is upfield compared to $\text{H}_{2''}$ in CTT (7.70 ppm). This strong upfield effect is the NMR signature of a strong CH- π bond between $\text{H}_{2''}$ and the phenyl of the carbazole in CTC.¹⁰ Similar upfield effect was observed between the chemical shifts of proton $\text{H}_{2'}$ (7.11 ppm) in CTT and $\text{H}_{2'}$ (8.01 ppm) in CTC. This demonstrates that a strong edge to face interaction between the anisole and the phenyl of the carbazole is taking place in CTT isomer as well. In our experiment condition, at PSS state, the photoequilibrium was

comprised of CF1 (10%), CTC (37%) and CTT (53%). Knowing the percentage of all isomers before and after irradiation, it was possible to calculate the absorption property of CTT in the visible region. The absorption maximum of CTT is 453 nm with an epsilon value of $13400 \text{ mol}^{-1}.\text{L.cm}^{-1}$. Compared to CTC, the absorption maximum is blue shifted with a lower epsilon value. This is indicative of a lower conjugation which might result from the fact that the steric repulsion between H-2 and the carbazole is more important in CTT than that between H-1 and the carbazole in CTC. Optimized geometries at CAM-B3LYP /6-311G(d,p) level of CTT and CTC indicate that the dihedral angle between the diene unit and the pseudo naphthalene core (C13b-C13c-C13d-C1) for CTT is 40.8° and 34.4° for CTC (Table 2S, ESI). Therefore, the overlapping of the pi electrons should be less efficient in TT than in TC isomers and might be responsible for the absorption difference observed between CTC and CTT.

Figure 3. a) Photochemical interconversion for **2**; b) absorption spectra before and after UV irradiation; c) Absorption changes at 419 nm upon UV then upon visible light

Under UV irradiation, CTT could be converted back to CTC. After 20 min of irradiation, the photoequilibrium was comprised of CF1 (10%), CTC (75%) and CTT (15%) (Figure 8S, ESI). Moreover, the thermal stability of CTT is amazingly high as after 1 month at room temperature, only 24% of CTT disappeared to give CTC. (Figure 9S, ESI). In order to gain insight into the effect of the ethynyl group and CH- π bonds, we carried out DFT calculation to determine the relative energy between all isomers (Figure 2). The order of stability given in kJ.mol^{-1} was found to be as followed: $\text{CF1} > \text{CTC} (\Delta H = 2.1) > \text{CTT} (\Delta H = 5.7) > \text{TTC} (\Delta H = 18.9) > \text{TTT} (\Delta H = 20.3)$. The order of stability is correlated in some way to the efficiency of the conjugation throughout the whole molecule which is well represented by the dihedral angle between the anisole and the diene unit (C2-C3-C1'-C2')

(Table 3S, ESI). On top of that, CTC and CTT are stabilized by a CH- π bond. There is no wonder why CF1 and CTC are in thermal equilibrium. The small difference in energy between these two forms indicates a barrierless photoisomerization between CF1 and CTC.¹² System **1** is the first example of inverse type photochromism in naphthopyran series in which visible irradiation induces isomerization from CTC to CTT that leads to a blue shift of the absorption and the original absorbance is retrieved by UV irradiation. This original behavior has been possible thanks to the electronic and steric effect of the ethynyl group at 3-position and the important presence of CH- π bond occurring in open isomers.

For **2**, before irradiation, the closed form absorbs exclusively in the UV region and the solution is colorless. Upon continuous UV irradiation, the solution turns from colorless to yellow. The maximum of the visible band was 419 nm (Figure 3b). After reaching PSS state, the irradiation was removed and the change of absorbance was monitored at 419 nm at room temperature in the dark (Figure 3c). A fast bleaching rate constant ($k = 0.21 \text{ s}^{-1}$) was first observed, counting for 7% of total absorbance, attributed to TC isomers. 93% of the residual absorbance was found to very stable for a long period of time ($k = 1.01 \times 10^{-6} \text{ s}^{-1}$, $t_{1/2} = 380$ hours). The stable coloration was attributed to the absorption of TT isomers. The reaction back from TT to CF2 can be induced photochemically with visible light. This photochemical process involves two consecutive transformations $\text{TT} \rightarrow \text{TC} \rightarrow \text{CF}$, the first one being the rate limiting step.^{5h-i} **2** can be considered as P-type photochromic system in which coloration and bleaching can be obtained photochemically. Even though TT isomers revert back to the closed form thermally; this thermal process is rather slow with half-life comparable to azocompounds.^{1f} To confirm the photoproducts produced under UV irradiation, NMR spectra before and after irradiation at room temperature was carried out. After UV Irradiation, two open isomers were observed and were attributed to TTT and CTT isomers (Figure 10-11S, ESI). At this temperature, short-lived TC species cannot be followed in the NMR time scale. However, they were detected at 228K (Figure 13S, ESI). At PSS, the conversion ratio from the closed form to the open forms was 40% comprising of 26% of TTT and 14% of CTT. The conversion ratio is rather low. The chemical shifts of protons in TTT and CTT are very similar, except those belonging to the anisole and phenyl group at 3-position and in particular H2' and H2'' protons of interest (Table 1S, Figure 13S, ESI). For instance, H2' (6.57 ppm) in TTT is upfield compared to H2' (7.24 ppm) in CTT. For H2'', reverse scenario is observed. H2'' (6.69 ppm) in CTT is upfield compared to H2'' (7.32 ppm) in TTT. As in CTT for **1**, H2' and H2'' in TTT and CTT respectively interact in edge-to-face fashion with the phenyl group of the carbazole unit. To gain more information about the effect of these CH- π bonds in the energy difference between all isomers, we carried out DFT calculation. It can be seen that CF2 is the most thermodynamic stable isomer (Figure 3). More

importantly, thanks to CH- π bond, TT isomers becomes more thermodynamically stable than their TC counterparts. In the reference compound displaying T-type photochromism, reverse scenario is observed in which TC is the most stable open isomer. This finding indicates that P-type photochromic naphthopyrans are obtained for compounds in which TT isomers are the most stable open isomers. In **2**, this has been possible due to the stabilizing energy through intramolecular CH- π bonds in TT isomers that counterbalances in some way the stabilizing energy of CH-O bond in TC isomers.

In conclusion, we showed for the first time that [3H]-naphthopyrans can display unusual inverse or P-type photochromism through the manipulation of relative thermodynamic stabilities of open isomers with CH- π bonds. The relative energy of all isomers is an important parameter that should be taken into account in the design of naphthopyrans with specific properties.¹³ P-type photochromic naphthopyrans rely on the introduction of fused rings in the k-face. Such photoswitchable molecules with improved properties could be an interesting alternative to azomolecules in applications requiring among others a large geometry change upon photoisomerization. The modulation of fused (hetero) rings in the k-face of [3H]-naphthopyrans are underway in our laboratory.

Supporting Information Available: Experimental procedures, spectroscopic data and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (1) Selected reviews and books on photochromism and applications (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Molecular Switches, Ed: Feringa, B. L.) Wiley-VCH: Weinheim, **2001**; (c) Tian, H. and Feng, Y. *J. Mater. Chem.* **2008**, *18*, 1617. (d) Tian, Z.; Wu, W. A.; Li, D. Q. *ChemPhysChem* **2009**, *10*, 2577. (e) Russew, M-M. and Hecht, S. *Adv. Mater.* **2010**, *22*, 3348; (f) Beharry, A. A. and Woolley, G. A. *Chem. Soc. Rev.* **2011**, *40*, 4422. (2) Bouas-Laurent, H. and Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639. (3) Reviews on photochromic naphthopyrans (a) Van Gemert, B. in *Organic Photochromic and Thermochromic Compounds*, Eds: Crano, J. C. and Guglielmetti, R. J. Kluwer Academic/Plenum Publishers, New York, **1999**, *1*, ch. 3. (b) Hepworth, J. D. and Heron, B. M. *Functional Dyes*, Ed: Sung-Hoon Kim, Elsevier, Amsterdam, **2006**. (c) Corns, N. S.; Partington, S. M.; Towns, A. D. *Coloration Technology* **2009**, *125*, 249. (4) (a) Delbaere, S.; Luccioni-Houze, B.; Bochu, C.; Teral, Y.; Campredon, M.; Vermeersch, G. *J. Chem. Soc.-Perkin Trans. 2* **1998**, 1153. (b) Ottavi, G.; Favaro G.; Malatesta, C. J. *Photochem. Photobiol., A, Chem.* **1998**, *115*, 123. (5) selected references: a) Guo, K. P. and Chen, Y. *J. Mater. Chem.* **2010**, *20*, 4193. (b) Frigoli, M.; Pimienta, V.; Moustrou, C.; Samat, A.; Guglielmetti, R.; Aubard, J.; Maurel, F.; Micheau, J. C. *Photochem. Photobiol. Sci.* **2003**, *8*, 888. (c) Venec, D.; Delbaere, S.; Micheau, J. C.; Frigoli, M.; Moustrou, C.; Samat, A.; Vermeersch, G. *Photochem. Photobiol., A* **2006**, *181*, 174. (d) Tulyakova, E. V.; Fedorova, O. A.; Micheau, J. C.; Paramonov, V.; Lokshin, V.; Vermeersch, G.; Delbaere, S. *ChemPhysChem* **2011**, *12*, 1294. (e) Gabbutt, C. D.; Heron, B. M.; Instone, A. C. *Tetrahedron*, **2006**, *62*, 737. (f) Ortica, F.; Smimmo, P.; Favaro, G.; Mazzucato, U.; Delbaere, S.; Venec, D.; Vermeersch, G.; Frigoli, M.; Moustrou, C.; Samat, A.; *Photochem. Photobiol. Sci.* **2004**, *3*, 878. (g) Frigoli, M. and Mehl, G. H. *Chem. Comm.* **2004**, 2040. (h) Oliveira, M. M.; Salvador, M. A.; Delbaere, S.; Berthet, J.; Vermeersch, G.; Micheau, J. C.; Coelho, P. J.; Carvalho, L. M. J. *Photochem. Photobiol., A, Chem.* **2008**, *198*, 242. (i) Coelho, P. J.; Salvador, M. A.; Oliveira, M. M.; Carvalho, L. M. J. *Photochem. Photobiol., A, Chem.* **2005**, *172*, 300. (j) Sallenave, X.; Delbaere, S.; Vermeersch, G.; Saleh, A.; Pozzo, J-L. *Tetrahedron Lett.* **2005**, *46*, 3257.

- (6) (a) Demadrille, R.; Rabourdin, A.; Campredon, M.; Giusti, G. *J. Photochem. Photobiol., A, Chem.* **2006**, *168*, 143. (b) Gabbutt, CD.; Heron, M.; Instone, A. C.; Kolla, S. B.; Mahajan, K.; Coelho, P. J.; Carvalho, L. M. *Dyes and pigments*, **2008**, *76*, 24. Relative energies of all isomers for the reference was calculated by DFT calculation (ESI).
- (7) Frigoli, M.; Moustrou, C.; Samat A.; Guglielmetti R. *Eur. J. Org. Chem.* **2003**, 2799.
- (8) X-ray data file are available in Cambridge database under deposition number CCDC 885269.
- (9) Desiraju, G. *Chem. Res.* **1991**, *24*, 290.
- (10) Jennings, W. B.; Farrell, B. M.; Malone, J. F. *Acc. Chem. Res.* **2001**, *34*, 885.
- (11) Lucas, X.; Quinˆonero, D.; Frontera, A.; Deya`, P. M. *J. Phys. Chem. A* **2009**, *113*, 10367.
- (12) M. Rosaria di Nunzio, P. L. Gentili, A. Romani, G. Favaro, *J. Phys. Chem. C* **2010**, *114*, 6123.
- (13) Song, L.; Yang, Y.; Zhang, Q.; Tian H.; Zhu, W. *J. Phys. Chem. ,* **2011**, *115*, 14648.