Mechanistic insights into photochromic 3H-naphthopyran showing strong photocoloration

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3,3-Diphenylbenzo[f]chromene (1) represents an important architectural platform for photochromic systems. Since the practical utility of such chromophores is largely dependent upon the kinetics of coloration and decoloration, elucidating the mechanistic details of these processes is of great value. Toward this end, we studied the photochromic reaction of (3-(2-methoxyphenyl)-3-phenyl-3H-benzo[f]chromene (2) by both time-resolved UV–vis and mid-IR spectroscopies. We found that irradiation of 2 at 365 nm generates long-lived colored transoid-cis isomers with lifetimes of 17.1 s and 17.5 min (at 21 °C) and even longer-lived transoid-trans isomers with a lifetime of 16 h. These experimental results were supplemented with ab initio ground-state and excited-state calculations, and the resulting theoretical interpretation may be useful for the design of new photochromic systems with optimized photofunctionality.

Among the known photochromic compounds, the family of 3,3-diphenyl-3H-naphtho[2,1-b]pyrans (1) has attracted great interest in the field of ophthalmic lens production1–4. Compound 1, exhibiting both P and T type photochromism, has been the subject of fundamental research5–13. In the photochromic reaction under typical conditions two colored species are formed (Fig. 1): transoid-cis TC (which fades rapidly) and transoid-trans TT (which fades more slowly)5. Synthetic changes in the structural pattern of 1 can tune its properties to fulfil the requirements of a particular application.

When the application requires a relatively fast decoloration rate, the presence of the long-lived TT form is unwanted. Efforts are focused then on designing derivatives of 1 with a minimized TT contribution in the photoreaction. Under typical experimental conditions with UV irradiation, the active channel for TT generation is TC → TT photoisomerization, which is a single-twist long amplitude motion11,13 occurring in the excited state (S1). Strong competition of the other TC excited state deactivation channels can minimize the TC → TT photoisomerization yield. For example, if the potential-energy landscape of the initially photoexcited TC S1 state favors a bicycle-pedal motion, the isomerization path might be quickly aborted through S1 → S0 internal conversion populating the form with the geometry close to that of the starting TC form12,13. Such a deactivation path can reduce the TC → TT photoisomerization yield, as reported for derivative of 1 with a methoxy group inserted at the position 1013,14.

The thermal fading rate of colored TC and TT isomers is also a key parameter of photochromic materials based on derivatives of 1. Appropriate substituents in the skeleton of 1 can be used to tune the TC color fading rate which depends on the ground state potential energy landscape15. A key role in this process is played by the cisoid-cis intermediate form (INT) lying midway between the colored TC form (see Fig. 2), and the colorless CF form15. The relationship between the energy barriers ΔEINT-TC and ΔEINT-CF separating the intermediate INT from nearby global and local minima may either decelerate the INT → CF process (favoring the return to the colored TC form) or accelerate the process (favoring the ring-closing reaction). For instance, the ΔEINT-TC barrier for 1 is lower than ΔEINT-CF (Fig. 2), which makes the apparent TC lifetime relatively long (9.3 s at 21 °C in cyclohexane).

The opposite situation (ΔEINT-TC > ΔEINT-CF) has been reported for 3H-naphthopyrans with phenyl substitution at position 215. The apparent TC lifetime is remarkably short (only 30 μs) in solution at room temperature16. On the other hand, one can expect that a slow decoloration would help to achieve a strong photocoloration...
effect in the photostationary state. It is widely accepted that inclusion of a bulky substituent at the ortho position of one of the phenyl rings in 1 would result in a substantial extension of the thermal fading half-life $\tau_{1/2}$, the half-life $\tau_{1/2}$ of the open forms gets longer with increasing size of the ortho substituent (in the order of $H \rightarrow F \rightarrow MeO \rightarrow Me \rightarrow Cl \rightarrow Br \rightarrow I$) in the phenyl ring of 3-aryl-3-(4-pyrrolidinophenyl)naphtho[2,1-b]pyrans. A remarkably slow-decoloration rate remains an intriguing feature for mechanistic and spectroscopic investigations.

For our studies we selected 3-(2-methoxyphenyl)-3-phenyl-3H-benzo[f]chromene (2), Fig. 1, as a candidate for a material with the strongest UV activated coloration. The relatively simple structure of 2 facilitates ab initio quantum-chemical calculations for the excited state, while the stages of the photochromic reaction can be studied in detail with experimental techniques such as the time-resolved UV–vis and mid-IR spectroscopies.

**Experimental**

**Materials.** Compound 1 was purchased from TCI. Compound 2 was synthesized following the procedures described in the Supplementary Information. In the time-resolved spectroscopic investigation cyclohexane of spectroscopic grade from Sigma Aldrich was used for solution preparation.

**Time-resolved UV–vis and mid-IR spectroscopies.** Changes in UV–vis absorption spectra and kinetics were recorded using three configurations.

1. Jasco V-550 spectrophotometer with a modified cell compartment. The solution in 1 cm x 1 cm fused silica cuvette was placed into a temperature-controlled cuvette holder (Flash 300, Quantum Northwest) with stirring switched on. UV LED ($\lambda_{exc} = 365$ nm, Thorlabs M365LP1) was used to induce the photochromic reaction (as in the two other configurations below).

2. Similar arrangement with a temperature-controlled cuvette holder and white light generated by a xenon lamp (Applied Photophysics), equipped with a bundle fiber, as a probing beam. The probing beam was passed through an almost-closed iris to ensure low white light intensity. The UV–vis spectra were recorded by an Ocean Optics FLAME-T-VIS–NIR–ES USB spectrometer at the sampling rate of 10 spectra per second.
Theoretical calculations. The equilibrium geometries of the CF conformers and their isomers in the closed-shell ground state \((S_0)\) were obtained with the MP2 method\(^{23}\) with no imposed symmetry constraints. The energy of the most stable form \(\text{CF}_1\) (Table S1, Supplementary Information) was assumed as the reference energy for higher energy structures. The excited-state \((S_1)\) equilibrium geometries were determined with the second-order algebraic diagrammatic construction ADC(2) method\(^{24–26}\). The correlation-consistent valence double zeta basis set with polarization functions on all atoms (cc-pVDZ)\(^ {27}\) was used in these calculations as well as in the potential energy profiles and surfaces. The vertical excitation energies and response properties of the lowest singlet excited states were calculated using the CC2 methods\(^ {28,29}\). The basis set augmented with the diffuse functions aug-cc-pVDZ was also used to compute vertical excitation energies of the molecular system. All calculations were performed using a biexponential function.

Results and discussion

The stationary UV–vis absorption spectrum of 2 in cyclohexane (Figure S1, Supplementary Information) is similar to that of the reference compound 1\(^ {11}\), reflecting structural similarities between the two derivatives. In the structure of 1, each phenyl ring has two ortho positions that can be substituted by a methoxy group, thus, four respective conformers of 2 are taken into account in the calculations. These conformers of the CF form are in thermal equilibrium in freshly prepared solution (indicated with subscripts: a, b, c, and d, see Table S1). The selection of wavelength at 365 nm induces the electronic transition \(S_0 \rightarrow S_1(\pi, \pi^*)\) separately in each CF form, which opens up along the \(C_3–O_4\) photodissociation pathway, as in 1\(^ {11}\). The photoinduced pyran ring-opening process can lead to the colored-isomers CTC and TTC. All the CF, TC and TT conformers potentially involved in the photoreaction, along with their calculated vertical excitation energies (\(\Delta E_{\text{VE}}\)) simulating UV–vis absorption spectra, are collected in Table S1. The strong \(S_0 \rightarrow S_2(\pi, \pi^*)\) transitions for colored TC forms are slightly redshifted vs. those of TT forms; a similar trend was observed for the parent compound 1\(^ {11}\).

To study the photochromic reaction by changes in UV–vis absorption spectra, a UV LED light at 365 nm was used for sample excitation, while a xenon lamp was used for probing. Figure 3a shows the kinetics probed at 425 nm upon 60-s exposure a solution of 2 in cyclohexane (Figure S1, Supplementary Information) is comparable (see Supplementary Information). Figure 3b shows the evolution of the transient UV–vis absorption spectra in the time window of 0–2250 s. Global analysis of data (Fig. 3c) reveals three distinct populations: TC1 with the absorption band peaking at 433 nm and a lifetime of 17.1 s, TC2 with the band maximum at 425 nm and a 17.5 min lifetime, and TT with a maximum at 415 nm and a long lifetime. The TT lifetime of 16 h was determined in an additional experiment performed in the time window of 40 h (Figure S2). The respective molar extinction coefficients, \(\varepsilon_{\text{max}}(\text{TC1}) \approx 18,900 \text{ M}^{-1} \text{cm}^{-1}\), \(\varepsilon_{\text{max}}(\text{TC2}) \approx 18,700 \text{ M}^{-1} \text{cm}^{-1}\) and \(\varepsilon_{\text{max}}(\text{TT}) \approx 29,500 \text{ M}^{-1} \text{cm}^{-1}\), are deduced from the simultaneously recorded changes in the UV–vis and mid-IR spectral ranges (see Figure S3, Supplementary Information). Thus, one can estimate from the data shown in Fig. 3 that at the moment of UV irradiation cessation, the conversion of CF population to colored forms is 69% and the concentrations of [TC1], [TC2] and [TT] are: \(1.4 \times 10^{-5} \text{ M}\), \(2.2 \times 10^{-6} \text{ M}\) and \(0.8 \times 10^{-5} \text{ M}\), respectively. In addition, the FT-IR spectroscopy provides a confirmation of our signal assignment to TC and
TT isomers, since the C=O stretching absorption band of TC is located at a lower frequency than that of TT, as has been already observed for the reference compound 1 (TC at 1644 cm⁻¹ and TT at 1655 cm⁻¹ [11]).

Photocycle reproducibility observed for 2 in cyclohexane is similar to that for 1, which is known to have high fatigue resistance (Fig. 4).

Why do TC forms differ in decoloration kinetics? The TC form in 3H-naphthopyrans is photogenerated in a single-photon absorption process[11]. A single TC isomer is generated from compound 1, while four TC isomers from compound 2 should be taken into consideration. The geometries of these conformers are presented in the first column in Table S1. CTCₐ and CTCₖ are energetically more stable than TTC, and TTCₖ. Each of the four TC isomers is a colored species, which, under thermal conditions, fades towards the respective closed CF form via a single cisoid-cis intermediate INT geometry located on the ground-state potential energy pathway. Each of the four S₀-state pathways is characterized by a slightly different energy barriers separating the initial TS pathways, for which the barrier of +0.16 eV is the same for all the considered TC forms (except for the TTC₂d pathway, for which the TS₂d structure (E°₁ = 1.145 eV) is slightly more destabilized due to O…O repulsion). Such a situation (ΔE(INT-CF > ΔE(INT-TC)) favors deceleration of the fading process, since once INT is formed it would rather repopulate the TC form. This may explain long TC lifetimes observed in the experiment for 2 (17.1 s and 17.5 min) in comparison to that of 1 (9.3 s, ΔE(INT-CF = 0.233 eV and ΔE(INT-TC = 0.196 eV)[13,15]). In order to assign each of the two TC lifetimes (17.1 s and 17.5 min) to the respective CTC and TTC families, we should consider their depopulation following the S₀-state energetic profile (Figure S4). While the ΔE(INT-TC) barrier of +0.16 eV is the same for all the considered TC isomers (except for TTCₙ), it is the ΔE(INT-CF) barrier that seems to be critical. Since ΔE(INT-CF) is higher for CTC than for TTC (+0.35 vs. 0.25 eV), the equilibrium of CTCₐ and CTCₖ is responsible for the long 17.5 min time-constant. The short time-constant (17.1 s) should be then ascribed to the TTC forms (equilibrium of TTCₐ and TTCₙ). The respective equilibria (CTC₂ = TTC₂b and TTCₙ = TTC₂d) are confirmed by the relatively low interconversion S₀-state energy barriers of + ~ 0.2 eV.

To support the idea that the high value of the ΔE(INT-CF) barrier is a decisive parameter in longer fading time of CTC forms, we analyzed the geometries of the transition state TS₁ structures. Indeed, the presence of a methoxy group is the cause of the O…O repulsion in TS₁ₓ (E°₂ = 1.185 eV, see Table 1) or 10H…OCH₃ steric hindrance in TS₁ₜ (E°₂ = 1.223 eV). The ortho-methoxy substituent increases the electron density on that aromatic ring, which has a stabilizing effect on the cisoid-cis INT geometry through increased π-stacking of the aryl and naphthalenone moieties. This is responsible for a higher ΔE(INT-CF) barrier in the case of INTₕ and INTₜ (+0.341 eV and +0.364 eV) vs. INTₑ and INTₙ (+0.254 eV and +0.203 eV).

Mechanism of the TC→TT photoisomerization reaction in the singlet excited state. The act of photon absorption by each TC isomer activates the two double bonds present in the C₉=O=C₇–C₈=C₇ bridge linking the naphthalene skeleton with the diphenylmethene rotor. This double bond activation allows free rotation about these bonds in the singlet excited state. As already shown for 1 derivatives[13], this rotation can...
be classified as a single-twist mechanism (rotation around the C14=C1 bond) or as a bicycle-pedal motion (if the concerted rotation about both double bonds takes place). Both mechanisms are visualized in the excited-state potential energy surface spanned over the two double bonds (Fig. 5). The single-twist motion can be seen as a motion along the X axes (C14=C1 rotation) from the green dot representing the initial TC geometry (upper left corner of the contour plot) towards the red dot (TT form, in the upper right corner). This motion meets the excited state S1 TW minimum for which C13–C14=C1–C2 dihedral angle is usually a little less than 90°, but it should be considered as the active channel in TC→TT photoisomerization. Alternatively, the bicycle-pedal motion is followed along the diagonal of the plot—from the TC form (green dot, upper left corner) towards the bottom right corner. This path encounters the S1 BP minimum midway through, which may deactivate through S1→S0 internal conversion to repopulate eventually the initial TC geometry in the S0 state. Inspection of the contour plots in Fig. 5 and energetics in Table S2 shows that the relative energies of S1 TW are below S1 BP thus the photoisomerization TC→TT is expected to be efficient, as observed in the experiment.

According to theoretical calculations, the replacement of the methoxy group in 2 by a methyl substituent has a low impact since its potential energy surface is also tilted towards the S1 TW minimum (see Table S3). Consequently, this system should also easily produce the TT form.

**Conclusions**

The synthesized compound 2 shows exceptional properties among the members of 3H-naphthopyran family. In the photochromic reaction its colored isomers are formed with longer lifetimes in comparison to that of the reference compound 1. Under UV irradiation a high accumulation of colored forms is observed in a photostationary
Figure 5. Minimum-potential-energy surface of the lowest excited electronic state of the TC-molecule: (a) CTC\textsubscript{a}, (b) CTC\textsubscript{b}, (c) TTC\textsubscript{c} and (d) TTC\textsubscript{d}, plotted as a function of $\theta_1$(C\textsubscript{14}=C\textsubscript{1}) and $\theta_2$(C\textsubscript{2}=C\textsubscript{3}) torsional angle coordinates. Green circle represents the Franck–Condon region of the ground-state $S_0$\textsubscript{TC} local minimum and red circle represents the ground-state $S_0$\textsubscript{TTC} local minimum. Blue circles represent various types of the excited-state minima: $S_1$\textsubscript{TC}—the minimum initially populated after $S_0$\textsubscript{TC} photoexcitation, $S_1$\textsubscript{BP}—achieved through the bicycle-pedal motion, and $S_1$\textsubscript{TW}—reached by single-twist motion mechanism. The results were obtained with the aid of the ADC(2)/cc-pVDZ method, for the excited state, and with the MP2/cc-pVDZ, for the ground state.
state. The mechanism of the colored TC form fading process can be analyzed using the energetic landscape of the thermal TC → INT → CF reaction. The determined ΔEINT-CF energy barrier seems to hamper CF repopulation and extends the apparent TC lifetime. Thus, the experimentally determined long lifetime of 17.5 min can be assigned to slow TC→INT processes, while the short lifetime of 17.1 s to TC→CF conformers. The theory suggests also that all TC isomers can undergo photoisomerization by the single-twist mechanism around the C14=C1 angle. The photogenerated TT form is long-lived—the population decay occurs with a single time-constant of 16 h at 21 °C. The proposed photochromic reaction mechanism explains the strong coloration effect observed for 2. Theoretical investigations should be considered as an efficient tool for designing new 3H-naphthopyrans derivatives with optimized properties. In other words, the implementation of a promising substituent in 3,3-diphenyl-3H-naphtho[2,1-b]pyran skeleton can be first theoretically tested for desired photochromic properties prior to the synthesis efforts.

Data availability
The datasets generated during the current study are available from the corresponding author on request.

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References
1. Crano, J. C., Flood, T., Knowles, D., Kumar, A. & Van Gemert, B. Photochromic compounds: Chemistry and application in ophthalmic lenses. Pure Appl. Chem. 68, 1395–1398. https://doi.org/10.1351/pac199668071395 (1996).
2. Hepworth, J. D. & Heron, B. M. In Functional Dyes (ed. Kim, S. H.) 85–135. Elsevier (2000).
3. Corns, S. N., Partington, S. M. & Towns, A. D. Industrial organic photochromic dyes. Color. Technol. 125, 249–261 (2009).
4. Towns, A. In Applied Photochemistry: When Light Meets Molecules (eds Giacomo, B. & Serena, S.) 227–279 (Springer International Publishing, 2016).
5. Delbaere, S. et al. Kinetic and structural studies of the photochromic process of 3H-naphthopyrans by UV and NMR spectroscopy. J. Chem. Soc., Perkin Trans. 2, 1153–1157. https://doi.org/10.1039/A80996F (1998).
6. Ottavi, G., Favaro, G. & Malatesta, V. Spectrokinetic study of 2,2-diphenyl-5,6-benzo(2H) chromene: A thermoreversible and photo reversible photochromic system. J. Photochem. Photobiol. A 115, 123–128 (1998).
7. Görner, H. & Chibisov, A. K. Photoprocesses in 2,2-diphenyl-5,6-benzo(2H)chromene. J. Photochem. Photobiol. A 149, 83–89. https://doi.org/10.1016/S1010-6030(02)00902-3 (2002).
8. Gentili, P. L., Danilov, E., Ortiz, E., Rodgers, M. A. J. & Favaro, G. Dynamics of the excited states of chromenes studied by fast and ultrafast spectroscopies. Photochem. Photobiol. Sci. 3, 886–891 (2004).
9. Delbaere, S. & Vermeersch, G. NMR characterization of allenyl-naphth in the photochromic process of 3,3-diphenyl-3H-naphtho[2-1, b]pyran. J. Photochem. Photobiol. A 159, 227–232 (2003).
10. Herzog, T. T., Kyseck, G., Ploetz, E. & Cordes, T. The photochemical ring opening reaction of chromene as seen by transient absorption and fluorescence spectroscopy. Photochem. Photobiol. Sci. 12, 1202–1209. https://doi.org/10.1039/C3PP50020A (2013).
11. Brazevic, S., Nizinski, S., Szabla, R., M. F. & Burdzinski, G. Photochromic reaction in 3H-naphthopyrans studied by vibrational spectroscopy and quantum chemical calculations. Phys. Chem. Chem. Phys. 21, 11861–11870. https://doi.org/10.1039/C9CP01451A (2019).
12. Brazevic, S., Baranowski, M., Sikorski, M., Rode, M. F. & Burdzinski, G. Ultrafast dynamics of the transoid-cis isomer formed in photochromic reaction from 3H-naphthopyrans. ChemPhysChem 21, 1402–1407. https://doi.org/10.1002/cphc.202000294 (2020).
13. Brazevic, S. et al. Control of the photo-isomerization mechanism in 3H-naphthopyrans to prevent formation of unwanted long-lived photo products. Int. J. Mol. Sci. 21, 7825. https://doi.org/10.3390/ijms2127825 (2020).
14. Inagaki, Y., Kobayashi, Y., Mutoh, K. & Abe, J. A simple and versatile strategy for rapid color fading and intense coloration of the photoreversible photochromic system. J. Photochem. Photobiol. A 159, 227–232 (2003).
15. Gabbutt, C. D., Heron, B. M. & Instone, A. C. The synthesis and electronic absorption spectra of 3-phenyl-3-(4-pyrrolidino-2-substituted phenyl)-3H-naphtho[2,1-b]pyran derivatives: synthesis, NMR characterisation and spectrokinetic studies. Dyes Pigm. 81, 85–90 (2009).
16. Pardo, R., Zayat, M. & Levy, D. Effect of the chemical environment on the light-induced degradation of a photochromic dye in ormosil thin films. J. Photochem. Photobiol. A 198, 232–236 (2008).
17. de Azavedo, O. D. C. C. et al. Synthesis and photochromism of novel pyridyl-substituted naphthopyrans. J. Org. Chem. 85, 10772–10776. https://doi.org/10.1021/acs.joc.0c01296 (2020).
18. Zayat, M. & Levy, D. Photochromic naphthopyrans in sol–gel ormosil coatings. J. Mater. Chem. 13, 727–730 (2003).
19. Gabbutt, C., Heron, B. M. & Instone, A. C. Control of the fading properties of photochromic 3,3-diaryl-3H-naphtho[2,1-b]pyrans. Heterocycles 60, 843–855 (2003).
20. Möller, C. & Plesset, M. S. Note on an approximation treatment for many-electron systems. Phys. Rev. 46, 618–622. https://doi.org/10.1103/physrev.46.618 (1934).
21. Häggest, C. In Advances in Quantum Chemistry Vol. 50 (ed. Jensen, H. J. A.) 37–60 (Academic Press, 2005).
22. Schirmer, J. Beyond the random-phase approximation: A new approximation scheme for the polarization propagator. Phys. Rev. A 26, 2395–2416. https://doi.org/10.1103/PhysRevA.26.2395 (1982).
23. Trofimov, A. B. & Schirmer, J. An efficient polarization propagator approach to valence electron excitation spectra. J. Phys. B: At. Mol. Opt. Phys. 28, 2299–2324. https://doi.org/10.1088/0953-4075/28/12/003 (1995).
24. Dunning, T. H. Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. 90, 1007–1023. https://doi.org/10.1063/1.463153 (1989).
25. Christiansen, O., Koch, H. & Jorgensen, P. The second-order approximate coupled cluster singles and doubles model CC2. Chem. Phys. Lett. 243, 409–418. https://doi.org/10.1016/0009-2614(95)00841-Q (1995).
26. Häggest, C. & Weigend, F. CC2 excitation energy calculations on large molecules using the resolution of the identity approximation. J. Chem. Phys. 113, 5154–5161. https://doi.org/10.1063/1.1290013 (2000).
27. TURBOMOLE V7.1 2016, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
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Author contributions
The following co-authors contributed in particular with; B.G. synthesis, M.R. theoretical calculations, conceptualization, writing original draft and G.B. spectroscopic experiments, formal analysis, supervision, funding acquisition, conceptualization, writing original draft. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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