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Influence of silyloxy substitution on the photochromic properties of diarylbenzo- and naphthopyrans[§]

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Abstract. Diarylbenzopyrans and their annulated derivatives are a class of photochromic compounds, which have been extensively investigated for photochromism. In fact, some naphthopyrans are employed industrially in ophthalmic lens applications. Photoirradiation of 2,2-diphenylbenzopyran leads to the formation of colored *o*-quinonoid intermediates. The latter revert too rapidly to allow their observation only at low temperatures (173–263 K). Annulation and other strategies are exploited to observe the colored *o*-quinonoid intermediates that persist for a few minutes at room temperature. We have examined photochromism of a set of silyloxy-substituted 2,2-diphenylbenzo- and naphthopyrans to explore how the mesomeric effects transmitted by the strongly e-donating silyloxy group substituted in the ring and at phenyl groups manifest in the spectrokinetic properties of their photogenerated colored *o*-quinonoid intermediates. We show that silyloxy substitution in the benzopyran ring leads to remarkable stabilization of the colored intermediates to enable their persistence at 283 K for a few minutes. In contrast, similar substitution in the C2-phenyl rings destabilizes the colored intermediates.

Keywords. Photochromism; naphthopyrans; chromenes; photochemistry; spectrokinetics.

1. Introduction

There is a surge of interest in recent times in functional materials based on stimuli-responsive molecular systems.[1,2] In particular, design and synthesis of systems that respond to a photon as the stimulus lay the foundation for the development of photochromic materials.[3–9] The latter have dominated contemporary interest due to their applications in a range of domains, e.g., UV-protective goggles, ophthalmic lenses, variable transmission glasses, display systems, smart windows, information recording and storage devices, optical switches, etc.[3–9] Among different classes of photochromic organic systems known so far, those that contain 2,2-diarylbenzopyran unit – termed popularly as chromenes – have been investigated extensively

(Scheme 1).[6,10–12] Indeed, their benzoannulated derivatives, namely, diarylnaphthopyrans, are employed as photochromic dyes in commercial ophthalmic lenses.[13,14]

Mechanistically, photoirradiation of colorless diarylbenzopyrans (closed forms) leads to heterolytic cleavage of the $C(sp^3)$–O bond in their singlet-excited states to generate the so-called *o*-quinonoid intermediates (open forms), cf. Scheme 1.[3,4,6,10–14] An extensive conjugation in the latter confers them with with absorption properties. The colored intermediates may revert to their precursor colorless forms either thermally or upon photoexcitation with light. The parent chromene, i.e., 2,2-diphenyl-2*H*-1-benzopyran (**BP**), without any structural modifications, exhibits absorptions far deep into the UV region and is known to
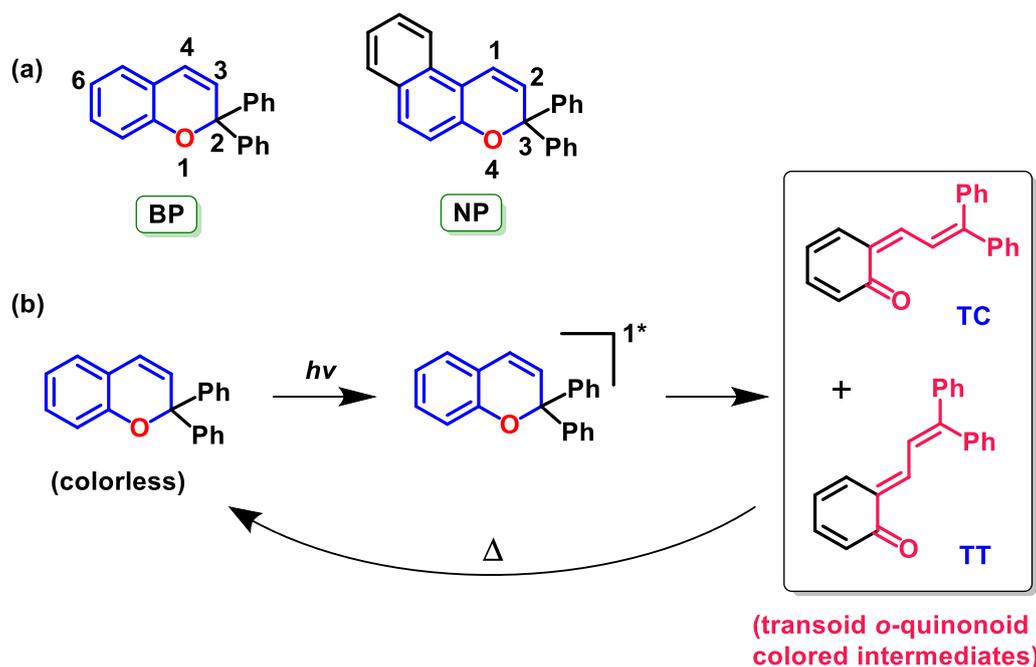

Scheme 1. (a) Structures of parent chromene, i.e., 2,2-diphenyl-2*H*-1-benzopyran (**BP**) and 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (**NP**), and (b) general mechanism of photochromism of diarylpyrans.

exhibit photochromism only at very low temperatures (173–263 K).[11] Indeed, the reversion of the open forms to the closed forms occurs too rapidly in simple diarylbenzopyrans to preclude detection of their photogenerated colored quinonoid intermediates at room temperature. Therefore, modulation of spectrokinetic properties of the photogenerated colored species continues to be a subject of fundamental interest in research on photochromic diarylpyrans.[15–20]

One of the major research interests in our own laboratories has been focused, for quite some time, on modulation of the photochromic properties of diarylpyrans by rational molecular design approach and development of photoresponsive organic[21–28] and metalorganic materials[29] by exploiting diarylpyran as the design element. Over the past decade, we have comprehensively established the profound influence of aromatic annulation,[21] electronic effects transmitted by arylation[22,23]/arylethynylation,[24] toroidal conjugations extant to the systems based on hexaphenylbenzenes,[25] through-space electronic effects in cofacially oriented arenes,[26] helicity as a steric force,[27] *etc.*, on the stabilization of the otherwise fleeting *o*-quinonoid colored intermediates photogenerated from diarylbenzopyrans. Indeed, compelling evidence has emerged from our and previous investigations that strong mesomeric effects exert remarkable influence on the spectral as well as kinetic properties of the photogenerated *o*-quinonoid intermediates to allow their persistence/detection at room temperature.[22–24] Recently, we have shown that

fluoride-triggered ring opening of silyloxy-substituted diarylpyrans into merocyanine colored dyes permits naked-eye sensing of fluoride in sub-ppm levels.[30] In a continuation of these investigations, we deemed it instructive to investigate how the substitution of a very strongly electron-donating group such as silyloxy group (for instance, *tert*-butyldimethylsilyloxy ether, i.e., OTBDMS) at different positions in the chromene nucleus modifies spectrokinetic behavior of the photogenerated colored *o*-quinonoid intermediates. We designed and synthesized *tert*-butyldimethylsilyloxy-substituted, i.e., OTBDMS-substituted, benzopyrans **BP1** and **BP2** and the benzo-annulated analog of **BP2**, namely, naphthopyran **NP2**, to examine how the mesomeric effects transmitted by the silyloxy group(s) at different location(s) of the chromene influence the phenomenon of photochromism, cf. Chart 1. Herein, we report that the silyloxy substitution of benzo-(**BP**) and naphthopyrans (**NP**) compellingly brings about remarkable effects of mesomeric effects in the spectrokinetic attributes of the photogenerated colored *o*-quinonoid intermediates; the position of silyloxy substitution, i.e., directly on the benzopyran moiety (as in **BP1**) and at the *para*-positions of the diphenyl rings (as in **BP2**), manifests in contrasting differences in the persistence of their colored intermediates. Indeed, 6-silyoxychromene exhibits remarkable photochromism at room temperature as a result of stabilization of the photogenerated *o*-quinonoid intermediate.
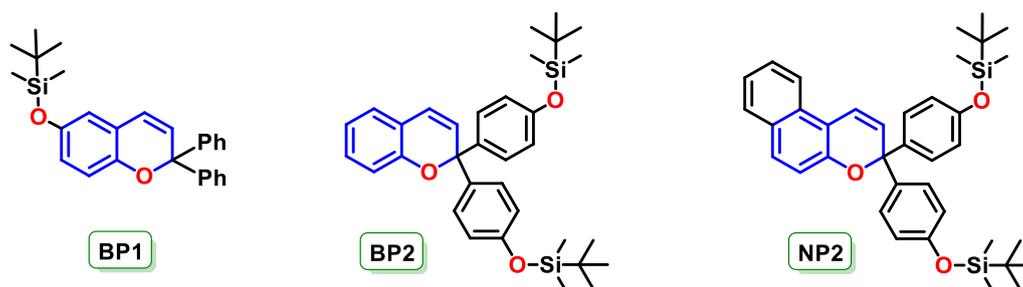
Chart 1.   Structures of the silyloxy-substituted benzo- and naphthopyrans.

2. Experimental

2.1 *General aspects*

All the solvents used for synthesis were distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded with JEOL (400 MHz and 100 MHz, respectively) spectrometers in CDCl$_3$ as the solvent. IR spectra were recorded with Bruker Vector 22 FTIR spectrometer. The ESI mass spectra were recorded with Waters GCT Premier ^{Q}TOF machine. Melting points were determined with a JSGW melting-point apparatus. UV–Vis absorption spectra were recorded with SHIMADZU UV-1800 spectrophotometer. Solution-state photolysis was carried out in a Luzchem photoreactor fitted with 300 nm UV lamps (8 W, 14 lamps).

2.2 *Synthesis and characterization of* **BP1**

A 50 mL round-bottom flask was charged with 4-((*tert*-butyldimethylsilyl)oxy)phenol[31] (0.5 g, 2.23 mmol), 1,1-diphenylprop-2-yn-1-ol (0.51 g, 2.45 mmol), a catalytic amount of *p*-toluenesulfonic acid (0.041 g, 0.22 mmol) and anhyd DCM (20 mL). The contents were stirred at rt under nitrogen gas atmosphere for 4 h. Subsequently, the reaction mixture was washed with a saturated Na$_2$CO$_3$ solution. The organic matter was extracted with DCM (20 mL × 3). The combined organic extract was dried over anhyd Na$_2$SO$_4$, filtered, and concentrated to dryness under vacuum. Purification of the crude material by silica gel column chromatography using 5% DCM in hexane led to the product as a colorless solid in 77% yield (0.71 g).

2.2a 6-((tert-Butyldimethylsilyl)oxy)-2,2-diphenyl-2H-1-benzopyran, **BP1**:
Colorless solid; M.p. 72–74 °C; IR (KBr) cm^{-1} 3055, 2930, 2858, 1631, 1607, 1462, 1360, 1216; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.15 (s, 6H), 0.96 (s, 9H), 6.17 (d, 1H, $J = 10.1$ Hz), 6.50 (d, 1H, $J = 2.7$ Hz), 6.54 (d, 1H, $J = 10.1$ Hz), 6.59 (dd, 1H, $J_1 = 8.68$ Hz, $J_2 = 2.8$ Hz), 6.77 (d, 1H, $J = 8.7$ Hz), 7.22–7.34 (m, 6H), 7.40–7.44 (m, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ-4.5, 18.1, 25.7, 82.3, 116.9, 117.5, 120.5, 121.6, 123.5, 127.0, 127.4, 128.0, 129.5, 144.9, 146.7, 149.5; ESI-MS$^+$ m/z Calcd. for C$_{27}$H$_{31}$O$_2$Si 415.2093 [M+H]$^+$, found 415.2091.

2.3 *Solution-state photolyses of silyloxy-substituted pyrans*

Solutions of the pyrans (**BP1**, **BP2** and **NP2**) in DCM (4 × 10^{-4} M) were taken in 3 mL quartz cuvettes equipped with extended arms, and the solutions were thoroughly purged with nitrogen gas for 10 min. Subsequently, these solutions were cooled to 283 K and subjected to UV irradiation in a Luzchem photoreactor fitted with 300 nm-UV lamps (8 W, 14 lamps) for 3–4 min. Upon exposure to UV irradiation, the colorless solutions were found to undergo ready coloration. The cuvette in each case was removed from the photoreactor, and the UV–Vis absorption spectrum was recorded immediately for the photolysate.

3. Results and Discussion

### 3.1 *Synthesis of silyloxy-substituted pyrans*

All the three silyloxy-substituted benzo- and naphthopyrans were synthesized following the conventional acid-catalyzed cyclocondensation route. **BP1** was accessed by cyclocondensation of 4-((*tert*-butyldimethylsilyl)oxy)phenol[31] with 1,1-diphenylpropargyl alcohol in the presence of PTSA (i.e., *p*-toluenesulfonic acid) as the catalyst, cf. Scheme 2. The synthesis of **BP2** and **NP2** by similar cyclocondensation reactions of phenol and β-naphthol, respectively, with 1,1-bis(4-((*tert*-butyldimethylsilyl)oxy)phenyl)prop-2-yn-1-ol in the presence of PTSA, has been reported from our group.[30]

3.2 *Photochromic behavior of the silyloxy-substituted pyrans*

The absorption spectra of the colorless solutions of the silyloxy-substituted pyrans **BP1** and **NP2** in DCM are shown in Figure 1. The long-wavelength absorption maximum (λ_{max}) and the molar extinction coefficient (ε) at the λ_{max} in each case are collected in Table 1. A perusal of the electronic absorption spectra reveals that
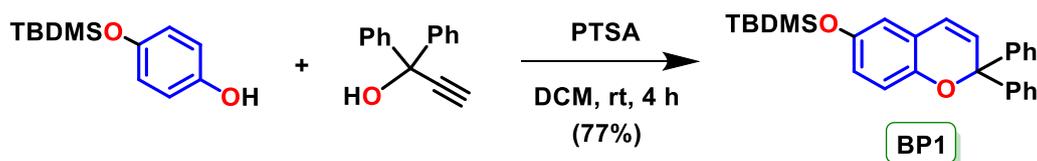
Scheme 2. Synthesis of **BP1**.
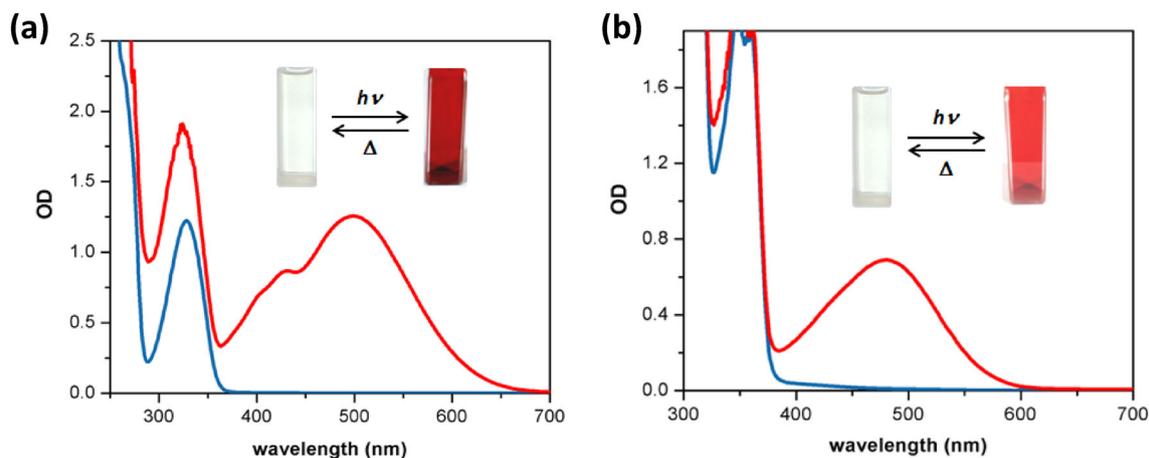
Figure 1. UV–Vis absorption spectra (4×10^{-4} M in DCM) of **BP1** (a) and **NP2** (b) recorded before (blue line) and after (red line) photoirradiation ($\lambda_{ex} = 300$ nm). Notice the changes in the colors of the solutions after steady-state photoirradiation at 283 K.

Table 1. Absorption properties and spectrokinetic data of pyrans and their respective photogenerated colored intermediates.

Pyran	Absorption properties[a,b]		Decay rate[c] $k(s^{-1})$
	Before $h\nu$ (nm) (ε in M^{-1} cm^{-1})	After $h\nu$ (nm)	
BP[d]	310	410, 510 [e]	[f]
NP	348	432	0.021[g]
BP1	328 (3060)	430 (sh), 500 (br)	0.007
NP2	348 (5100)	482 (br)	0.055

[a] Based on absorption spectra of the silyloxy-substituted pyrans in dry DCM solutions (4×10^{-4} M). [b] br = broad band and sh = sharp peak. [c] The decay kinetics for the photogenerated colored species of the silyloxy-substituted pyrans were monitored at 283 K after steady-state photoirradiation of the pyran solutions for 3–4 min and the kinetic data in each case was fitted to a monoexponential function. [d] Spectrokinetic data in ethanol at 295 K, see Ref. [11] [e] The absorption band at 410 nm is stronger in intensity. [f] The decay is too fast for kinetics to be monitored, see Ref. [11] [g] The decay rate is 0.09 s^{-1} in toluene at 298 K, see Refs. [13,15,28]

the absorption due to π, π* transition tapers off well below 400 nm. The same was found to be the case for **BP2** as well.

The photobehavior of all the pyrans was examined in DCM (conc. ca. 4×10^{-4} M) at 283 K. Upon exposure to UV irradiation ($\lambda_{ex} = 300$ nm), the colorless solutions of the pyrans **BP1** and **NP2** were found to undergo ready coloration. **BP1** led to red coloration for which the absorption spectrum exhibited strong and slightly

structured broad absorption with a maximum at 500 nm. In contrast, photoirradiation of **BP2** led to no observable coloration at this temperature. While weak coloration was observed when irradiated at 273 K or lesser, the color was found to appear quickly to preclude spectral acquisition. In the case of **NP2**, however, photoirradiation resulted in red coloration, for which the absorption was found to be broad with maximum centered at 482 nm, cf. Figure 1. The UV–Vis absorption spectra
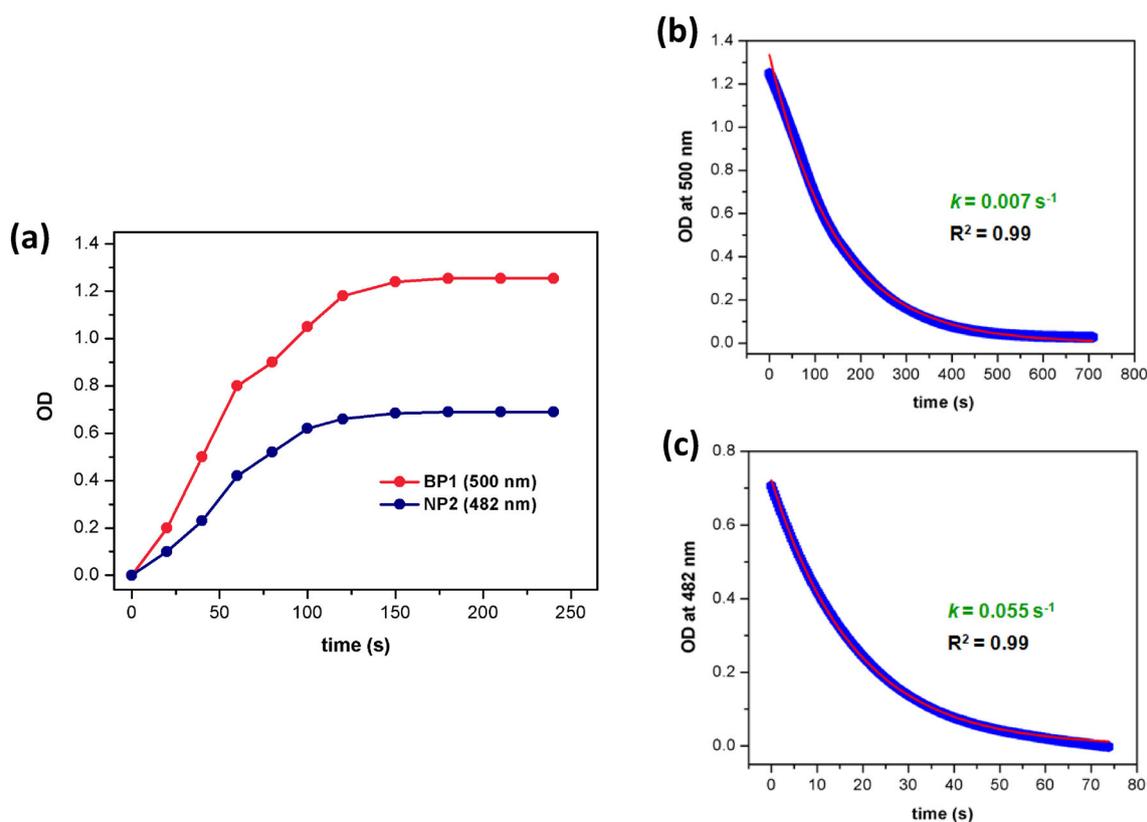
Figure 2. (a) Coloration plots for **BP1** and **NP2** at 283 K. The absorption maximum of the colored species is mentioned in parenthesis in each case. Monoexponential fitting of the thermal decay profiles of the photogenerated colored intermediates of **BP1** (b) and **NP2** (c) in DCM (conc. of pyran = 4×10^{-4} M) at 283 K.

of the colored species generated upon photoirradiation of **BP1** and **NP2** are shown in Figure 1.

The absorptions due to colored species are typical of *o*-quinone methide intermediates, which are derived from $C(sp^3)$–O heterolysis of the precursor pyrans in their singlet-excited states, vide infra. For easy comparison, the details of absorption maxima of the colored species generated by irradiation of the parent benzopyran **BP** and the naphthopyran **NP** are also collected in Table 1; while the photogenerated colored species of **BP** exhibits absorption bands at 410 (stronger in intensity) and 510 nm,[11] that of **NP** exhibits a broad band peaking at 432 nm.[15,28] Clearly, the absorption maxima of the colored species of silyoxy-substituted pyrans are different from those of their corresponding unsubstituted pyrans, i.e., **BP** (λ_{max} = 410 and 510 nm) versus **BP1** (λ_{max} = 430 and 500 nm) and **NP** (λ_{max} = 432 nm) versus **NP2** (λ_{max} = 482 nm).

The photogenerated colored intermediates of the silyloxy-substituted pyrans were found to revert to the colorless forms within 2–3 min on standing. For kinetic measurements, the coloration plots to gauge the absorbance at photostationary state (PSS) were

initially developed by recording the absorbances at the long-wavelength λ_{max} of the colored species with increasing durations of irradiation (λ_{ex} = 300 nm). Thus, the solutions of the **BP1** and **NP2** in DCM were exposed to UV radiation at 283 K until the photostationary state (PSS) was reached (Figure 2); as mentioned earlier, the thermal reversion of the colored intermediates of **BP2** was too fast to preclude any build-up of the absorbance. The plots in Figure 2 suggest that the time required to attain PSS is ca. 2–3 min for both **BP1** and **NP2**. The colorability (A_{eq}), i.e., the absorbance at the long-wavelength λ_{max} of the colored species, at PSS was found to be ca. 1.25 (at 500 nm) for **BP1** and 0.69 (at 482 nm) for **NP2**.

For the thermal decay kinetics, the change in absorbance (after attainment of PSS) at the absorption maximum of the colored intermediate with time was followed at 283 K for **BP1** and **NP2** (Figure 2). The decay in each case was best fitted (R^2 = 0.99) to a monoexponential function (Table 1). A brief perusal of the kinetic data in Table 1 reveals slower thermal bleaching rate for the colored species of **BP1** (k = 0.007 s^{-1}) when compared to that of **NP2** (k = 0.055 s^{-1}) at 283 K in

DCM. Further, it turns out that extremely fast thermal reversion rate of the colored species of the benzopyrans **BP** and **BP2** preclude the decay kinetics to be monitored even at 273 K, while that of **BP1** exhibits considerably slow decay rate at 283 K. Insofar as naphthopyrans are concerned, the parent **NP** exhibits photochromism with $k = 0.09$ and 0.02 s^{-1} in toluene (298 K) and DCM (283 K), respectively. Remarkably, faster thermal decay of the colored species of **NP2** did not permit photochromism to be observed at 298 K and the decay kinetics could be followed only at 283 K, yielding a rate constant of $k = 0.055$ s^{-1} in DCM. Clearly, It is the difference in the position of the silyloxy substitution in the diphenylbenzo-/naphthopyran systems that manifests in the observed spectrokinetic behaviors of the photogenerated colored intermediates.

3.3 *Mechanistic rationale for the influence of silyloxy substitution on the spectrokinetic properties*

The mechanism of photochromism of diarylbenzo-/naphthopyrans has been investigated in detail.[28] As shown in Scheme 1, photoirradiation leads to C(sp^3)–O bond heterolysis in the singlet-excited state, forming TC and TT isomers of the *o*-quinonoid species, which are mainly responsible for the observed color; the reported quantum yield for this ring opening in the case of **NP** is as high as 90%.[32] Of the two isomeric forms of the *o*-quinonoid species, the TT isomer is a result of two-photon absorption by the diphenylbenzopyran through initial formation of the TC isomer. Therefore, the TT isomer is likely to be generated only minimally when the precursor diphenylbenzopyran is subjected to photoirradiation for short durations. At relatively shorter durations of photoirradiation, it is the TC isomer that is generated predominantly and is largely responsible for the observed color.[32–34]

Based on the mechanistic picture described above, influence of the silyloxy substitution in modifying spectrokinetic behavior of the photogenerated colored intermediates of **BP1-2** and **NP2** can now be reconciled. It should be understood that the electron-donating OTBDMS group substituted in the benzopyran nucleus and C2-diphenyl rings should stabilize/destabilize the *o*-quinonoid species by mesomeric effect. The colored *o*-quinonoid intermediate of the parent unsubstituted diphenylbenzopyran exhibits absorption maximum at 410 nm with a shoulder at 510 nm. In contrast, **BP1** with a silyloxy substituent at position C6 brings about dramatic change in that the photogenerated colored intermediate exhibits a broad and intense absorption with maximum centered at 500 nm. Furthermore, the persistence observed is remarkable. While the

intermediate of the parent chromene can only be observed at low temperatures, that of **BP1** survives at 283 K for a few minutes; in fact, the colored species is comparatively more longer lived that that of **NP**. In stark contrast, **BP2** leads to the colored intermediate that has a fleeting existence. The intermediate could be observed for such a substitution only when dealing with benzoannulated benzopyran, namely naphthopyran **NP2**. It is noteworthy that even in this case, the species is short-lived compared to that of the parent diphenylnaphthopyran, cf. Table 1. In general, benzoannulation is the strategy by which the transient colored species of **BP** is stabilized as to be observed at room temperature. Diphenylnaphthopyran, i.e., **NP**, leads to colored *o*-quinonoid intermediate that is observable at 298 K. It turns out that the silyloxy substitution in **NP2** now renders the decay of the intermediates quite faster. It thus emerges that ring substitution versus C2-phenyl substitution of the silyloxy group exerts drastic influence on the spectrokinetic properties of photogenerated *o*-quinonoid intermediates. Although the effects of a variety of substituents on the photochromism of benzopyrans have been comprehensively unraveled in the literature,[28] dramatic influence as that revealed by the silyloxy group uncovered herein is unknown. This is clearly a consequence of OTBDMS group, which acts a powerful electron-donating group. The observed photochromism has a practical implication in that the silyoxybenzopyrans themselves can now be directly employed to develop polymeric materials containing covalently-linked photochromes for ophthalmic lens applications.[35,36] The silyl group is advantageous from this point of view.

To understand the contrasting spectrokinetic behavior of the *o*-quinonoid colored species generated by irradiation of **BP1** (with OTBDMS substitution at the C6 position) and **BP2/NP2** (with OTBDMS substitution at C2 phenyl rings), let us look at their resonance structures shown in Scheme 3. It may be noticed that the stabilization exerted by the strongly electron-donating OTBDMS group by resonance delocalization is almost similar for the two differently-substituted silyloxybenzopyrans, i.e., **BP1** and **BP2**. In the *o*-quinonoid intermediate of **BP2**, the quinonoid oxygen is likely to carry more negative charge as opposed to that in the intermediate of **BP1**. As shown in Scheme 2, the relatively higher charge in the resonance delocalized oxy-anion of the intermediate of **BP2** may facilitate *faster* reversion to the colorless form than that in the case of **BP1**. The same applies to the case of **NP2** as well, wherein the extended benzannulation may suppress the rate slightly to enable observation at 283K.
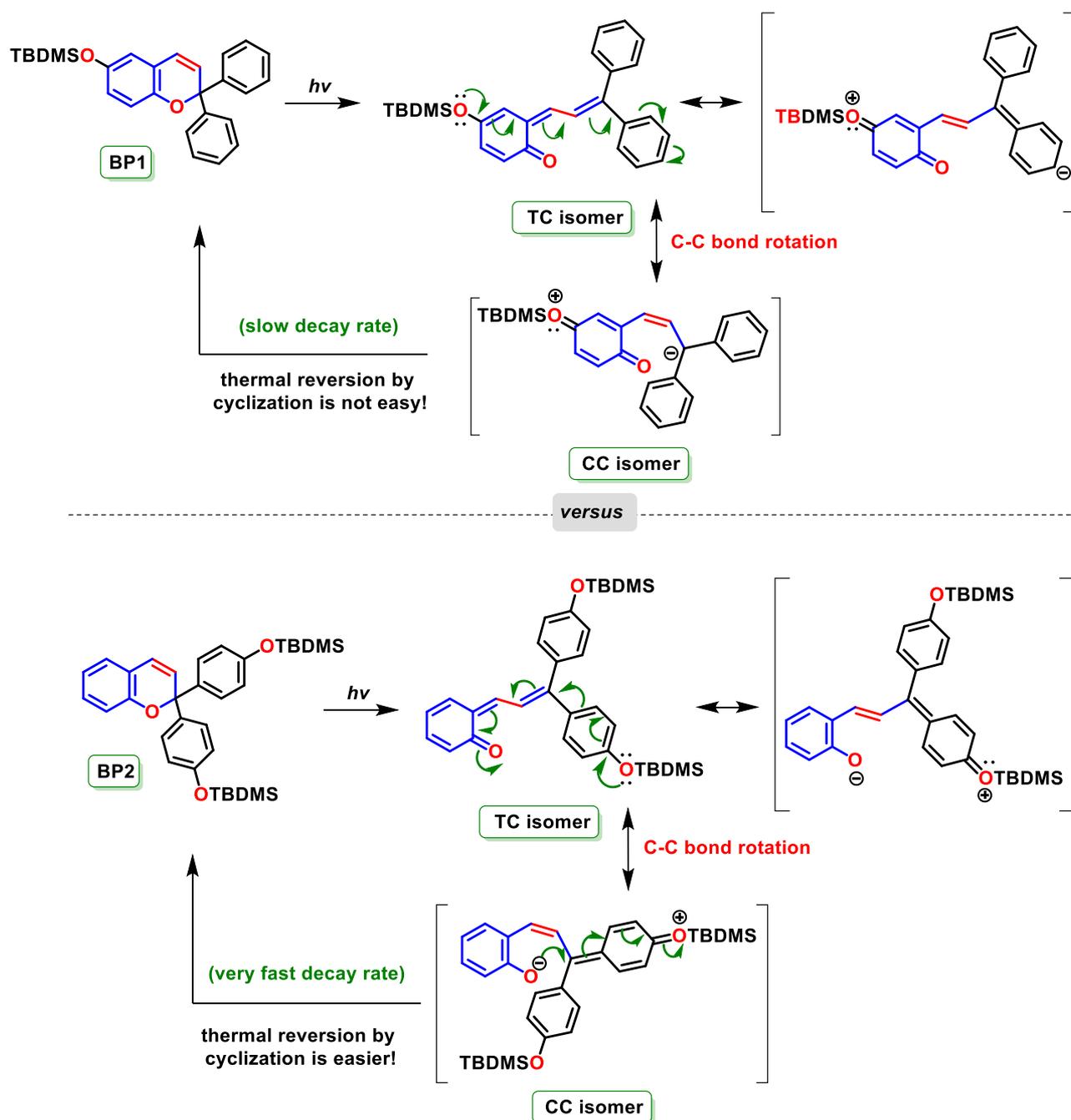
Scheme 3. Influence of silyloxy substitution on *o*-quinonoid the colored intermediates of **BP1** and **BP2**.

4. Conclusions

A set of benzo- and naphthopyrans (**BP**s and **NP**s) substituted with silyloxy groups in the benzopyran nucleus and in the C2-phenyl rings has been synthesized, and their photochromism examined. Photolysis of **BP1** leads to 'naked-eye' observable coloration that persists for a few minutes at 283K, while the color change is simply not observable in the case of **BP2**. Benzannulation as in **NP2** permits the transient colored intermediate to be observed but is significantly unstable than that of the parent diphenylnapththopyran **NP**. Clearly, the silyloxy substitution of the benzopyran ring brings about dramatic modification of the spectrokinetic properties of diphenylbenzopyran. The observed effects can be readily reconciled from mesomeric effects that operate differently in the differently substituted benzopyrans. Although photochromism has been investigated tremendously in a variety of substituted chromenes, we are unaware of such a significant modification of properties

by simple substitution as that uncovered herein with silyloxy substitution. The results have a direct bearing in that the photochromic polymeric materials containing covalently-bound chromens can now be developed for ophthalmic lens applications.[35,36]

Supplementary Information (SI)

UV–Vis absorption spectra and monoexponential fitting of the thermal decay profile for photogenerated colored intermediates of **NP,** ^{1}H and ^{13}C NMR spectra and ESI-MS spectrum of **BP1**. Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgements

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