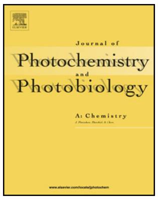
Journal of Photochemistry and Photobiology A: Chemistry 293 (2014) 40–49

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Selective photoisomerization of methyl substituted nitro diphenylbutadienes

Harsha Agnihotri, Veerabhadraiah Palakollu, Sriram Kanvah*

Department of Chemistry, Indian Institute of Technology Gandhinagar, VGEC Campus, Chandkheda, Ahmedabad 382 424, Gujarat, India

ARTICLE INFO

Article history:
Received 21 April 2014
Received in revised form 17 July 2014
Accepted 23 July 2014
Available online 1 August 2014

Keywords:
Regioselective photoisomerization
Intramolecular charge transfer
Solvatochromism

ABSTRACT

A series of *p*-nitro substituted *trans*-diphenylbutadienes is synthesized and their photophysical and photochemical properties are investigated. All the dienes have a very low quantum yield of fluorescence but exhibit remarkable solvatochromic emission shifts attributed to twisted intramolecular charge transfer. Photochemical irradiation of simple *p*-nitro substituted diphenylbutadienes reveals inefficient or no detectable photoisomerization. However, substituting a methyl group on the butadiene chain of *p*-nitro substituted diphenylbutadiene or replacing the nitro group with cyano group yields the corresponding *trans*–*cis* isomers. In the case of simple nitrodienes, strong intramolecular charge transfer character in the excited state aids dissipation of absorbed energy through non-photochemical and non-radiative channels. The steric effect caused by the presence of methyl group lowers the isomerization barrier in methyl substituted dienes leading to a regioselective isomerization.

1. Introduction

Light induced isomerization around a double bond is an important step for many biologically important pigments such as the opsin family of proteins [1,2]. To understand this highly rapid and efficient *trans*–*cis* photoisomerization of all-*trans* retinal to 13-*cis* retinal in bacteriorhodopsin [3] and 11-*cis* to all-*trans* retinal in rhodopsin [2], diphenylpolyenes have been extensively investigated as model compounds. Their utility as model compounds arose in part because of their energy level proximity with retinyl polyenes and visual pigments [4]. Apart from the photochemical processes, the emission and photoswitchable properties of such arylethylene derivatives in solution and solid state have also found utility in a variety of biological [5–9] and materials applications [10–12]. Photoisomerization of 1,4-diphenylbutadiene leads to the formation of the corresponding *cis*–*trans* isomers and *trans*–*cis* isomers and isomerization is presumed to happen *via* perpendicular intermediates [13]. Rigorous mechanistic investigations of photoisomerization of diphenylbutadiene and other polyenes revealed involvement of Bicycle Pedal (BP) and Hula twist (HT) pathways [14–21]. Both BP and HT pathways were utilized to explain the specificity of photoisomerization of the opsin proteins despite the protein imposed volume restrictions [15]. Although detailed photochemical investigations utilizing diphenylbutadiene were communicated, isomerization of substituted diphenylbutadienes [22–24] has received little attention in comparison to their fluorescence spectroscopic investigations [25–31]. In specific, diphenylbutadienes substituted with donor or acceptor groups yields one-photon-one bond isomerization of the C=C bond lying closer to the acceptor group [23,32]. Similarly photoisomerization of *trans,trans,trans* *p*-methoxy-*p*′-nitro substituted diphenylhexatriene derivative yielded a regioselective *cis* isomer [33]. Recent investigations on similar butadiene containing systems reveal significant influence of the methyl group or halogen group on the photoinduced behavior [34,35] and efficient *trans* to *cis* isomerization of dendrimeric diphenylbutadiene derivatives [36,37]. In general, the observations reveal discrete one-bond rotations, barrier to the isomerization and involvement of competing internal conversion processes [13]. In the current work, we seek to examine the effect of methyl substituent and the nature of substituent on the photoisomerization of a series of diphenylbutadiene derivatives (Fig. 1) in acetonitrile at room temperature. Our results show that substituting methyl group on the double bond and replacing nitro group with a cyano group has a significant influence on the photoisomerization of the diphenylbutadienes examined.

2. Experimental

The reagents required for the synthesis of diphenylbutadiene derivatives were obtained from Sigma-Aldrich, Alfa Aeser, Akcros

---

* Corresponding author. Tel.: +91 11 7932419500.
E-mail address: kanvah@gmail.com (S. Kanvah).

http://dx.doi.org/10.1016/j.jphotochem.2014.07.019
1010-6030/© 2014 Elsevier B.V. All rights reserved.

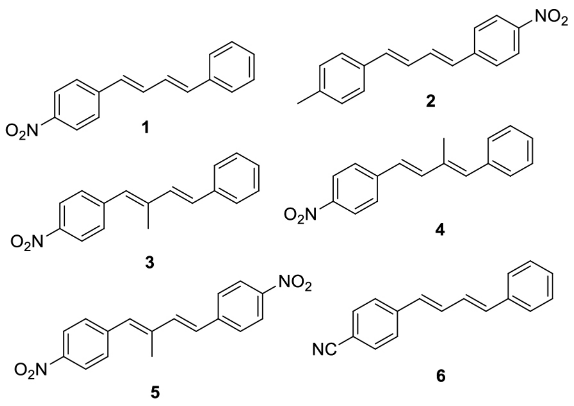


Fig. 1. Structures of diphenylbutadienes investigated.

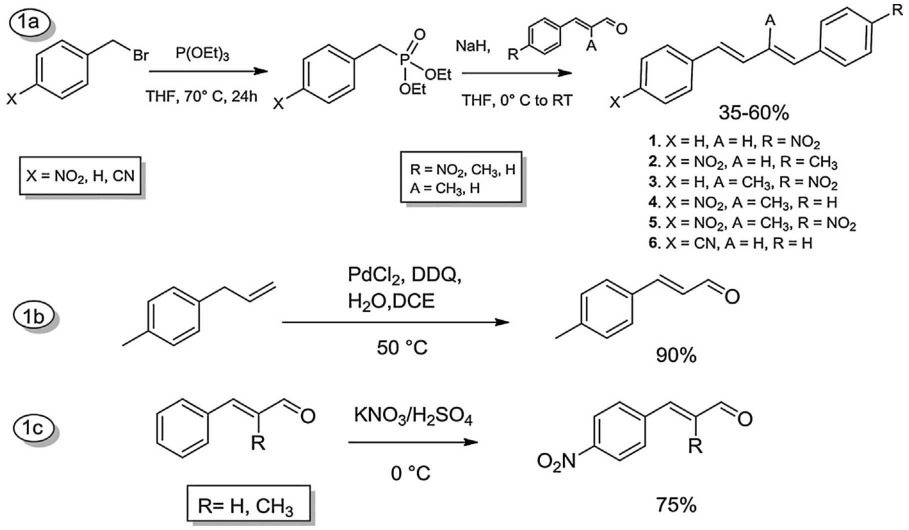
and S.D. Fine Chemicals India. The solvents needed for the synthesis and spectral studies were dried using reported procedures. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with tetramethylsilane as internal standard using a 500 MHz Bruker Avance spectrometer. Absorption spectra were recorded on Analytikjena, Specord 210 model UV–vis spectrophotometer. HPLC was done using Agilent 1260 infinity fitted with Kinetex 5 μm C18 100 Å (250 × 4.6 mm) column. 65% acetonitrile-water eluent conditions at a rate of 1.0 mL/min are used for all the samples. The monitoring wavelengths for detecting the photoproducts are 360 nm and 390 nm. Fluorescence studies were performed using fluorolog-3 spectrofluorimeter and fluorescence quantum yields were calculated using quinine sulfate as a standard [38]. For photochemical irradiation experiments, a sample (3 mL of ~10^{-5} M) in acetonitrile was taken in a 1 cm path length quartz cuvette and irradiated using 125 W medium pressure Hg vapor lamp. 10% copper sulphate pentahydrate solution having 100% transmittance from 330 to 560 nm was used as the cut-off solution filter. Progress of the photoisomerization was monitored using UV–vis. spectroscopy. For characterization purposes, a higher concentration of sample solutions (3 mg in 1 mL of $CDCl_3$) was irradiated for 12–16 h using 125 W medium pressure Hg lamp. Quantum yields of photoisomerization (ϕ_{PI}) were performed using potassium ferrioxalate actinometry [39].

2.1. Synthesis

Diphenylbutadiene derivatives utilized in this investigation were prepared by using Horner–Wadsworth–Emmons reaction [23] (Scheme 1a) in about 35–60% yields. In a typical procedure, triethyl phosphite (5.74 mmol) was added to the THF solution of benzyl bromide (2.3 mmol) and refluxed for 24 h under a N_2 atmosphere. The reaction mixture was cooled to room temperature and further cooled to 0 °C using an ice bath. Sodium hydride (11.5 mmol) was added to this mixture and stirred for 5 min. Aldehyde (2.3 mmol) was subsequently added drop wise to the pale/dark pink colored solution and stirring was continued for additional 30 min. In the case of methyl substituted aldehydes, corresponding (*E*) geometric isomer of α-methyl cinnamaldehyde (Aldrich) was used. Thin Layer Chromatography (TLC) was utilized to monitor the progress of the reaction and the reaction was quenched by adding water. The organic layer was extracted using dichloromethane and concentrated under reduced pressure. The crude reaction mixture so obtained was purified by column chromatography using silica gel, 5% ethyl acetate in petroleum ether. Starting materials, 4-methylcinnamaldehyde required for the synthesis of (**2**) and nitro cinnamaldehyde required for synthesis of (**3**) and (**5**), were obtained by DDQ oxidation of 4-allyl toluene [40] (Scheme 1b) and by simple nitration using a nitrating mixture generated by mixing KNO_3 with H_2SO_4 of α-methyl-cinnamaldehyde (scheme 1c), respectively. Characterization data for all the synthesized dienes were given in the Supplementary information.

3. Results and discussion

A series of diphenylbutadiene derivatives containing nitro and cyano substituents are synthesized and examined for their photochemical isomerization behavior. The synthesized dienes (**1**–**6**) are listed in Fig. 1. Diene (**1**) has a *p*-substituted nitro group on the aromatic ring. Diene (**2**) is a *p*,*p*′ disubstituted diphenylbutadiene containing methyl and nitro groups *para* to each other. Dienes (**3**)–(**5**) have a methyl substitution on the double bond. In Diene (**3**), a methyl group is proximal to the aromatic nitro group and in (**4**) the methyl group is placed distal to the nitro group. Diene (**5**) is the same as (**3**) but have nitro groups on both sides of the double bond in the aromatic ring. Through this arrangement,



Scheme 1. (a) Typical synthetic schemes for the synthesis of substituted diphenylbutadienes. (b) Synthesis of 4-methylcinnamaldehyde [40] and (c) nitration of aromatic cinnamaldehydes.

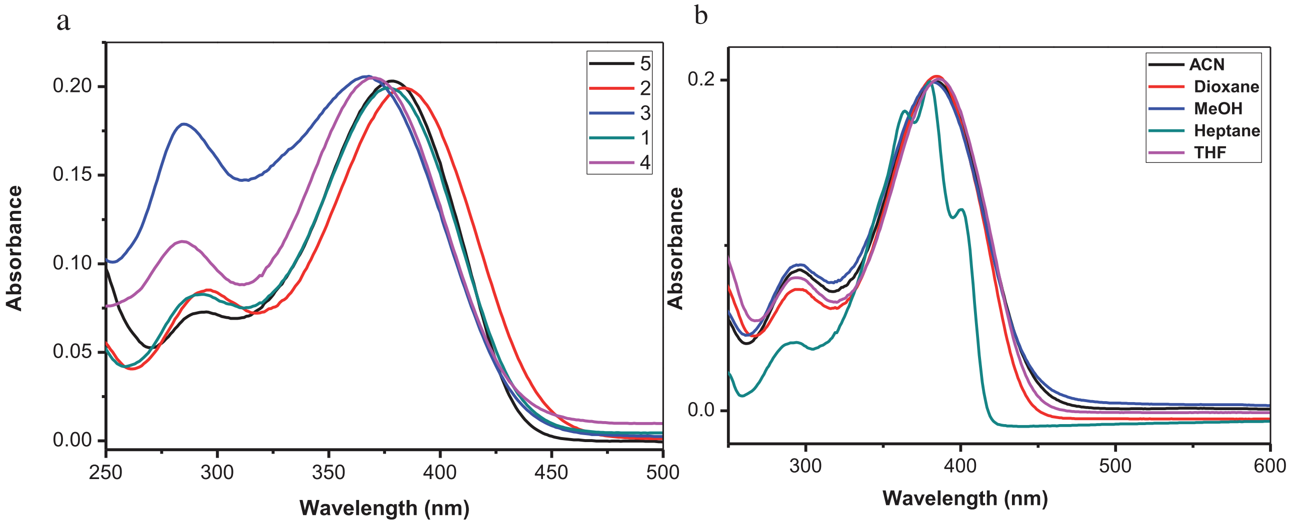


Fig. 2. (**a**) UV–vis absorption spectra of dienes (**1**–**5**) in acetonitrile. (**b**) UV–vis absorption spectra of diene (**3**) in different solvents.

we sought to increase the distance of methyl to nitro group and understand the positioning effect of the methyl group on photoisomerization. Diene (**6**) bears a cyano group instead of a nitro group.

*3.1. Absorption and fluorescence of dienes (**1**)–(**6**)*

Substitution of a strongly electron-withdrawing nitro group leads to significant bathochromic absorption shift as compared to the absorption (328 nm) of unsubstituted diphenylbutadiene [41]. The presence of a methyl group on *p*-position of the aromatic ring (**2**) causes a slight red-shift of λ_{abs} (+6 nm) as compared to (**1**) while introduction of methyl group on the conjugated double bond (**3** and **4**) leads to hypsochromic absorption (up to 10 nm) shifts (Fig. 2a)-Table 1. Presence of an additional nitro group on the aromatic ring (**5**) has a weak influence (~3 nm) on the λ_{abs} as compared to mono-substituted diene (**1**) but has a greater effect (~at least 13 nm) as compared to methyl substituted dienes (**3** and **4**). Enhanced resonance contributes to a red-shift in the absorption while hindered non-planar configuration induced by methyl substitution explains the blue shifted absorbance in (**3**)–(**5**). Thus, among the dienes investigated, diene (**2**) exhibits the largest λ_{abs}. Slight red shifts in absorption maxima are observed in all dienes upon increasing solvent polarity from heptane to acetonitrile (Fig. 2b). All dienes exhibits structured absorption spectrum in non-polar solvent heptane while a smooth structure less spectrum was found in polar solvents such as acetonitrile. These structural and absorption shifts are ascribed to solute-solvent interactions. Table 1 lists the absorption and emission data of dienes (**2**) and (**3**).

All nitro substituted diphenylbutadienes exhibit remarkable solvatochromism that was attributed to the presence of strong intramolecular charge transfer (ICT) states [42,43]. As shown in Table 1, solvent polarity changes from heptane to acetonitrile result in significant bathochromic emission shifts. Shifts of 161 nm for (**2**) and 142 nm for (**3**) were observed along with heavily quenched emission in methanol (Fig. 3a and b). Diene (**2**) exhibits a weak emission band near 600 nm while no such emission band was observed for (**3**) in methanol. In polar solvents, the charge transfer excited state is highly stabilized resulting in a bathochromic and a broad emission spectrum contrary to heptane where a structured emission spectrum is seen. The characteristic long wavelength ICT band in the case of methanol is heavily quenched leading to emission from the locally excited state. This quenching in emission is a consequence of solute and solvent intermolecular hydrogen bonding [25]. The introduced methyl group decreases the conjugation in the butadiene chain. This induced non-planarity still contributes to a significant solvatochromic shift (142 nm). Such behavior is accounted due to the formation of strong intramolecular charge transfer states [44]. Solvent polarity also affects the fluorescence quantum yield. Fluorescence quantum yield (ϕ_f) is greater for medium polar solvents and decreases with increase in solvent polarity because of competing radiationless decay pathways [26,45] such as internal conversion. It is known that nitroaromatic

Table 1
Absorption data of (**1**)–(**6**) in acetonitrile and emission data of (**2**) and (**3**) in varying solvents.

Absorption data of dienes (**1**–**6**) in acetonitrile						
Diene	**1**	**2**	**3**	**4**	**5**	**6**
λ_{abs} (nm)	377	383	367	370	380	343
Absorption and emission data of dienes **2** and **3**						
Solvents	Diene **2**			Diene **3**		
	λ_{abs}	λ_{em}	ϕ_f*	λ_{abs}	λ_{em}	ϕ_f*
Heptane	374	427	0.001	354	423	0.001
Dioxane	384	511	0.08	365	470	0.004
Tetrahydrofuran	386	527	0.16	366	511	0.018
Acetonitrile	384	588	0.067	367	565	0.015
Methanol	382	429, 600 (weak)	0.003	364	433, –	0.002

* Quinine sulfate (0.545 in 1 N H_2SO_4 is used as a standard to measure).

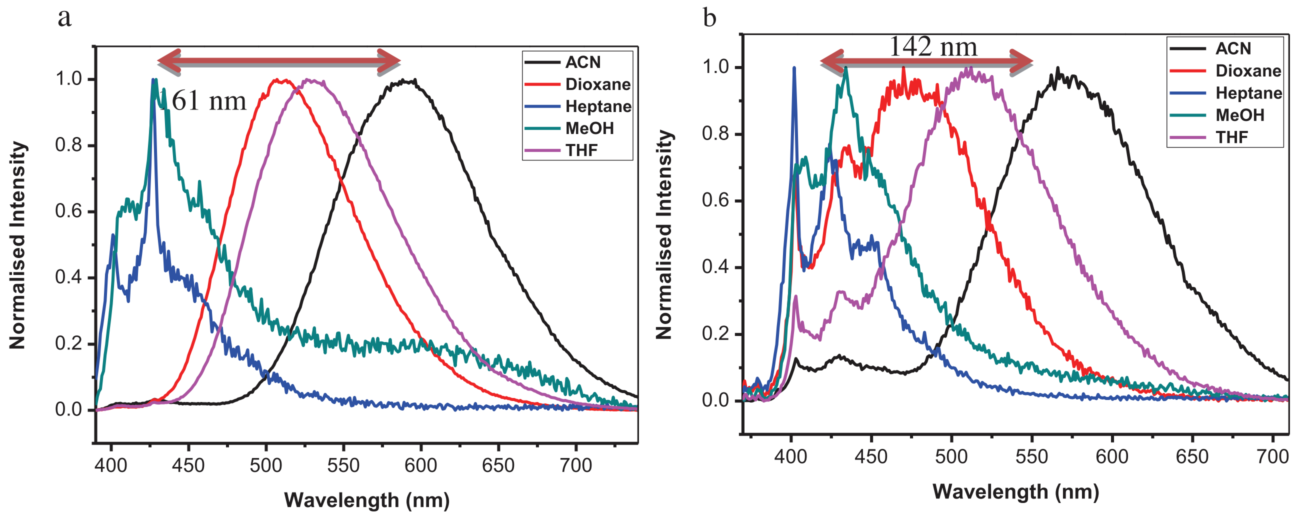


Fig. 3. Fluorescence emission spectra of (a) diene (**2**) and (b) diene (**3**) in solvents of different polarity. The excitation wavelengths are 380 nm for **2** and 360 nm for diene **3**.

compounds are generally weakly fluorescent due to such non-radiative decay processes such as intersystem crossing and internal conversion [25]. The data for other dienes (**1**, **4** and **5**) are provided in Table-S1 have similar observations [26,46].

3.2. *Trans–cis photoisomerization*

Direct photoisomerization of diphenylbutadiene leads to the corresponding *cis* (*c*) and *trans* (*t*) isomers. Technically four different isomers are possible, *trans–trans* (*tt*), *trans–cis* (*tc*), *cis–trans* (*ct*) and *cis–cis* (*cc*). In the case of unsubstituted diphenylbutadiene *tc* and *ct* are indistinguishable [47,13]. (**1**) and (**2**) have H and CH_3 groups in the *para* position of the aromatic ring and exert a feeble donating influence on the overall conjugation. Irradiation of (**1**), containing single nitro group in *para*-position, in acetonitrile at room temperature led to highly inefficient photochemical reaction despite prolonged irradiation. Fig. 4a displays the UV spectra of (**1**) at various time intervals of irradiation in acetonitrile. HPLC peak profiles after irradiation indicate only one peak corresponding to the *tt*-isomer (Fig. 4b). Analysis of the NMR spectra reveals no changes in spectral data of irradiated mixture with respect to pure *tt* isomer (Fig. 4c and d). To ascertain our result, time-dependent NMR study of (**1**) in $CDCl_3$ was performed. The corresponding spectra given in Supplementary information [Fig. S2] reveals no changes to the initial (*tt*) isomer. However, in glassy or polymer matrices, strong UV irradiation gave rise to partial *cis–trans* isomerization involving only one of the two double bonds [48] and gave different EPR spectra upon irradiation at 355 nm or in the range of 420–455 nm. Following these observations, a $CDCl_3$ solution (3 mg in 1 mL) of (**1**) was irradiated using a photoreactor fitted with either 360 nm or 420 nm lamps. Characterization by NMR reveals minimal structural changes to the initial *tt* spectra [Figs. S3 and S4]. The minor peaks observed contribute to less than 3–4% of the overall isomer. Likewise (**2**) containing a methyl group in the *para* position also does not form any significant photoisomers upon photoirradiation (Figs. S5a–d). No such non-detectable photoisomerization is reported for similarly substituted *trans*-stilbene derivatives [49,50]. This could imply that the energy absorbed is released back in non-photochemical channels and non-radiative channels. In this case, electron withdrawing nitro group promotes strongly polarized TICT excited states (through rotation of Ar—NO_2 bonds) and increase the internal conversion and intersystem crossing (ISC) processes characteristic of many aromatic nitrocompounds [51]. The efficient ISC from the charge transfer state competes with formation of the transition state yielding low photoisomerization and fluorescence quantum yields. The lower quantum yields of photoisomerization (ϕ_{PI}) of 0.078 (**3**), 0.098 (**4**) and 0.075 (**5**), obtained using ferrioxalate actinometry, coupled with weaker fluorescence quantum yields imply significant non-radiative processes. To assess the strength of the electron-withdrawing group, (**6**) containing a moderately deactivating electron withdrawing cyano group was synthesized. In contrast to nitro containing dienes (**1**) and (**2**), upon irradiation of (**6**), progressive photoisomerization was noted. UV absorption spectral changes upon irradiation (Fig. S6a) and NMR of pure (Fig. S6b), NMR of photo mixture (Fig. S6c) is shown in the supporting information. Dienes (**3**)–(**5**) have methyl groups on the conjugated double bond. The methyl group in (**3**) is located proximal and in (**4**) the methyl group is distal to the aromatic nitro group. Upon photoirradiation of the diene (**3**), a sharp decrease in absorption intensity was noted (Fig. 5a). Similarly photoirradiated UV spectra of diene **4** show a drop in absorption intensity with increase in time of irradiation (Fig. 5b). Formation of isosbestic point indicates the presence of an equilibrating isomer that is *cis*. HPLC spectra reveal the presence of two components in the photoirradiated mixture for the methyl substituted dienes investigated (Fig. 5c and d). When the methyl group is placed on the aromatic ring (**2**) photostability of the molecule persists. But once the methyl group is placed on the double bond (**3**) or (**4**) molecules undergoes photoisomerization yielding corresponding *cis–trans* (*ct*) isomers.

In (**3**), methyl substitution results in 100% isomerization site preference for the double bond containing methyl group (Fig. 5a and c). To confirm this observation, *cis–trans* (*ct*) isomer of (**3**) was diligently isolated and the obtained NMR spectrum is shown in Fig. 5e. The calculated coupling constants [$J = 16.0$ Hz for H_c and H_d protons) ratifies our observation of the site of isomerization. It is known that the presence of an electron-withdrawing group could withdraw the electron density from the proximal double bond and facilitate regioselective isomerization [23,24,32]. In this case, electron withdrawing nitro group and steric effects of the methyl group both complement each other. To test if this preference for methyl substituted double bond is certain and to rule out the intervention by the nitro group, isomerization of (**4**) bearing methyl group on the second double bond was investigated. Even in this case, we observed 100% isomerization selectivity for the methyl substituted bond (Fig. 5b and d) yielding *trans–cis* (*tc*)

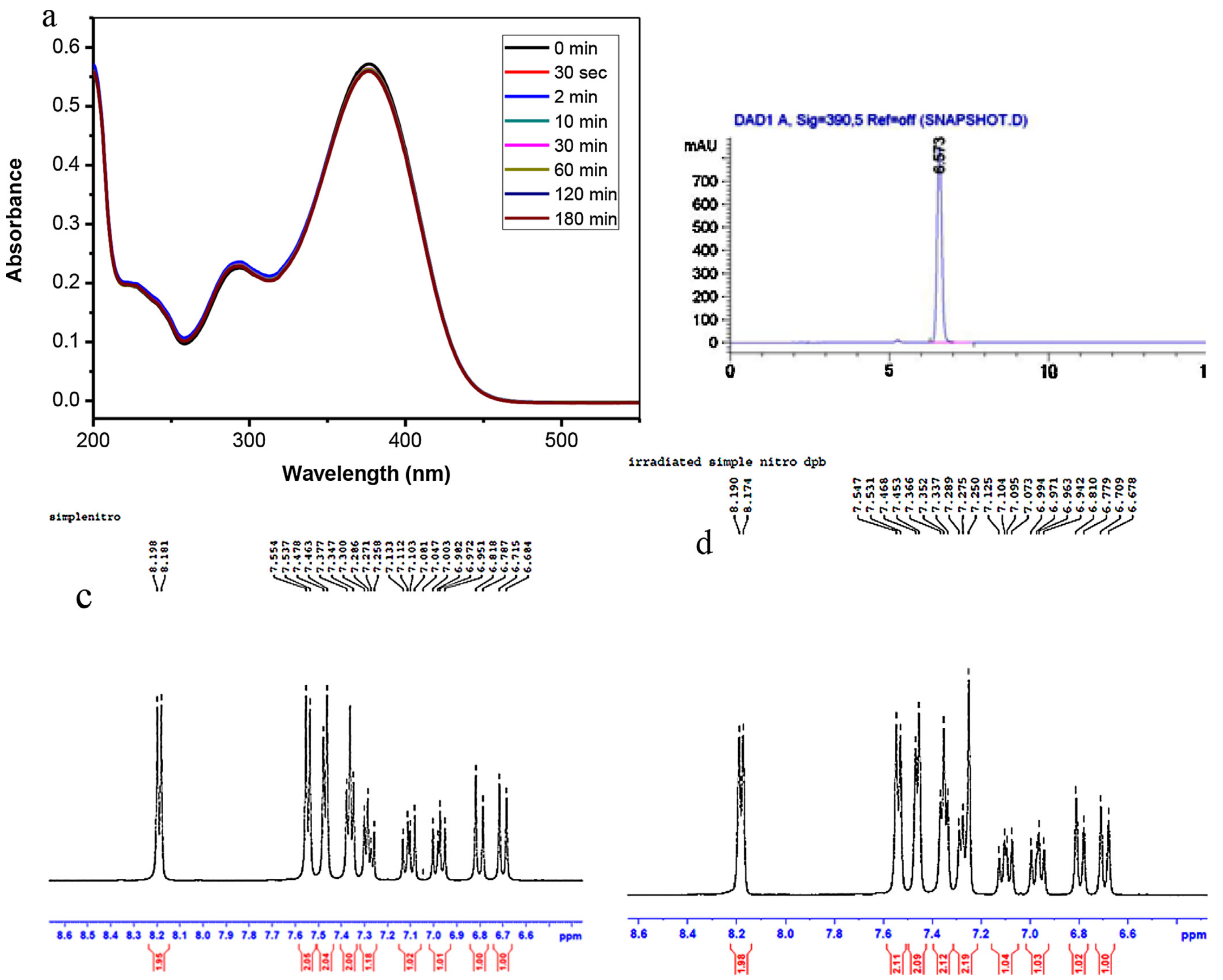


Fig. 4. (a) UV–vis absorption spectral changes upon irradiation of diene (**1**) in acetonitrile at different time intervals. (b) HPLC peak profile of diene (**1**) after irradiation obtained using 390 nm as detection wavelength. (c) ^{1}H NMR spectra of diene (**1**) before irradiation and (d) ^{1}H NMR spectra of diene (**1**) after irradiation.

isomer. Thus simple *p*-nitro substituent (for **1** and **2**) increases the molecular planarity of the butadiene backbone and enhances rapid internal conversion [52] and intersystem crossing processes. These ultrafast non-radiative processes may lead to a photoreactive excited singlet state that favors the decay back to the *trans*-isomer or it may encounter a high potential energy barrier in the singlet-excited state that prevents decay of this species to the ground-state *cis*-isomer. On the contrary, presence of methyl substitution in (**3**)–(**5**) despite the presence of nitro moiety, provides a pre-distortion through steric hindrance and creates no such energy barrier in the singlet excited state and yield the corresponding *cis*-isomers.

Thus, methyl substitution on the phenyl ring has little effect on photochemistry, but the photoisomerization is significantly enhanced when the methyl groups are substituted on butadienyl carbon. This enhanced reactivity is primarily attributed to a decrease of torsional barrier [43]. The geometric isomers of (**3**) and (**4**) were identified using ^{1}H NMR by careful calculation of coupling constants of their *cis* and *trans* isomers. NMR spectra of pure *trans*, irradiated mixture and isolated *trans–cis* (*tc*) isomer of **4** are given in Supplementary information (Fig. S7a–c). In case of (**4**), analysis of photo mixture NMR revealed two doublets at 7.47–7.44 ppm (J = 15.5 Hz) and at 6.75–6.72 ppm (J = 16.5 Hz) that correspond to *tt*-configuration and a singlet at 6.72 ppm that corresponds to *tc*. Absence of *cis*-coupling constant in the data indicates that observed changes are caused by the *tc*-isomer (Fig. S7c) resulting from the methyl substituted double bond. To show clearly the impact of methyl on the isomerization, (**4**) in $CDCl_3$ (3 mg/1 mL) was irradiated at various time intervals (Fig. 6; Fig. S7f). The emergence of additional peaks is due to the *tc*-isomer arising from the methyl-substituted double bond. Table 2 gives comparative NMR values and their coupling constants of dienes (**3**)–(**5**).

More importantly, site of photoisomerization migrates with the positioning of the methyl group. To further emphasize the steric influence of the methyl group on the photoisomerization, (**5**) consisting of two nitro groups was synthesized. Despite having two very intense electron-pulling groups on opposite ends of the chain, diene (**5**) does not inhibit the photoisomerization of the methyl-substituted double bond. This shows the prevalence of steric effects (due to methyl) over the electronic effects associated with the nitro group. A comparison of NMR spectra of pure *trans* (Fig. 7a) and irradiated mixture (Fig. 7b) of (**5**) clearly indicates the formation of another *cis* isomer (*cis–trans*). The UV and HPLC data of (**5**) are shown in the supporting information (Fig. S9a and b).

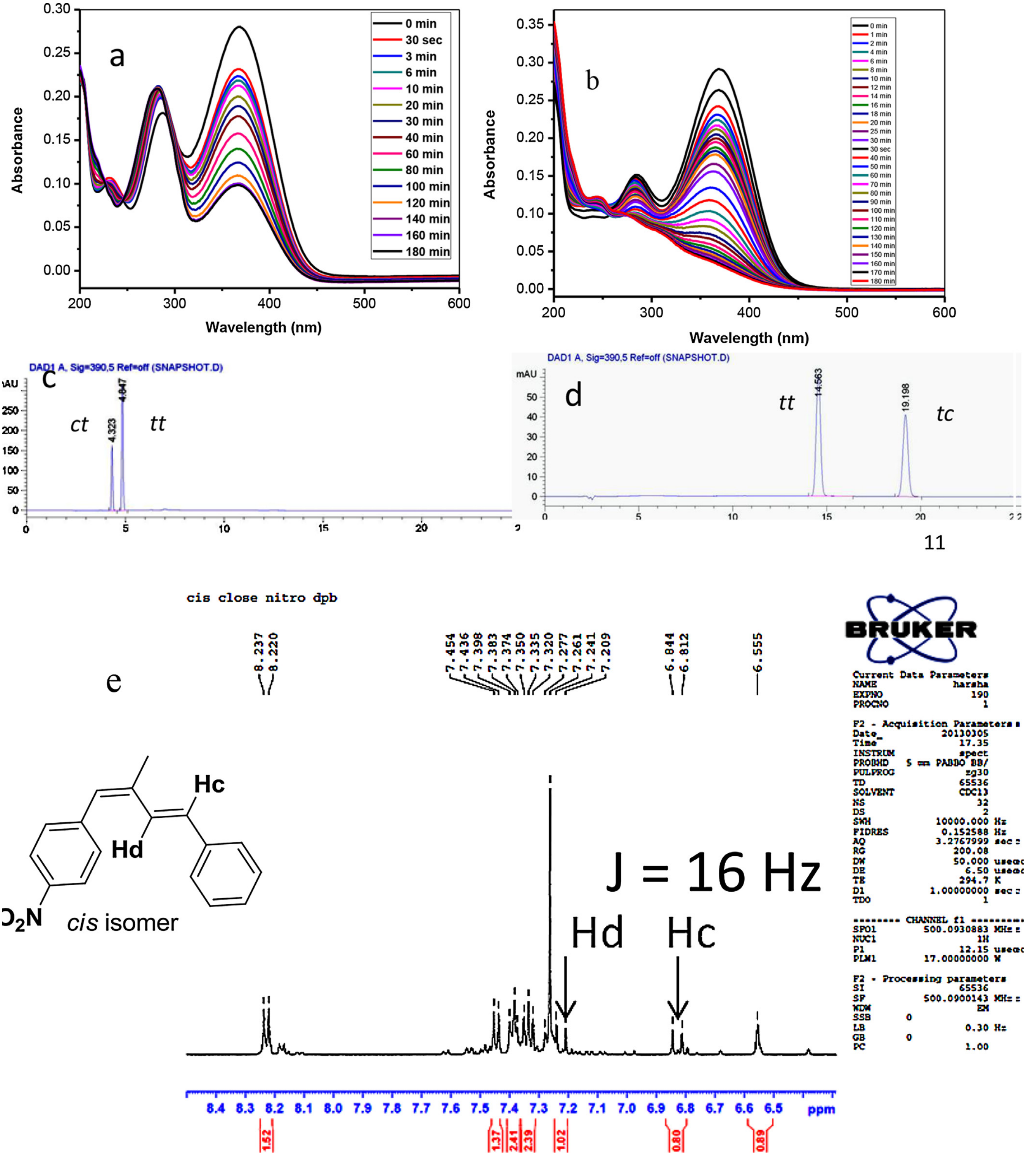


Fig. 5. UV–vis absorption spectral changes on irradiation of (a) diene (**3**) and (b) diene (**4**) in acetonitrile at various time intervals. HPLC spectra of (c) diene (**3**) and (d) diene (**4**) after irradiation; HPLC data was obtained using 390 nm as detection wavelength (e) ^{1}H NMR spectra of *cis*-**3** in CDCl$_3$.

Coupling constants δ 6.86–6.83 (d, *J* = 16.0 Hz *ct*) and 7.34–7.30 (d, *J* = 16.5 Hz *ct*) confirm that only the methyl attached double bond converts to the *cis* configuration. This observation is also confirmed by COSY spectra of photomixture of **5**. The interaction between *trans*-hydrogens of the corresponding isomers was observed in COSY spectra. The cross peaks depicted in the COSY spectra of pure *trans* of diene **5** (Fig. 8a) shows the interaction between two *trans* hydrogens (H$_a$ and H$_b$). The COSY spectra of irradiated **5** (Fig. 8b) has two such cross peaks (squares), the smaller one indicates interaction between H$_a$ and H$_b$ of *trans*–*trans* isomer and larger one indicates interaction between H$_c$ and H$_d$ of *trans*–*cis* isomer. COSY spectra of (**3**) and (**4**) are also given in the Supplementary information (Figs. S8a and b and S7d and e).

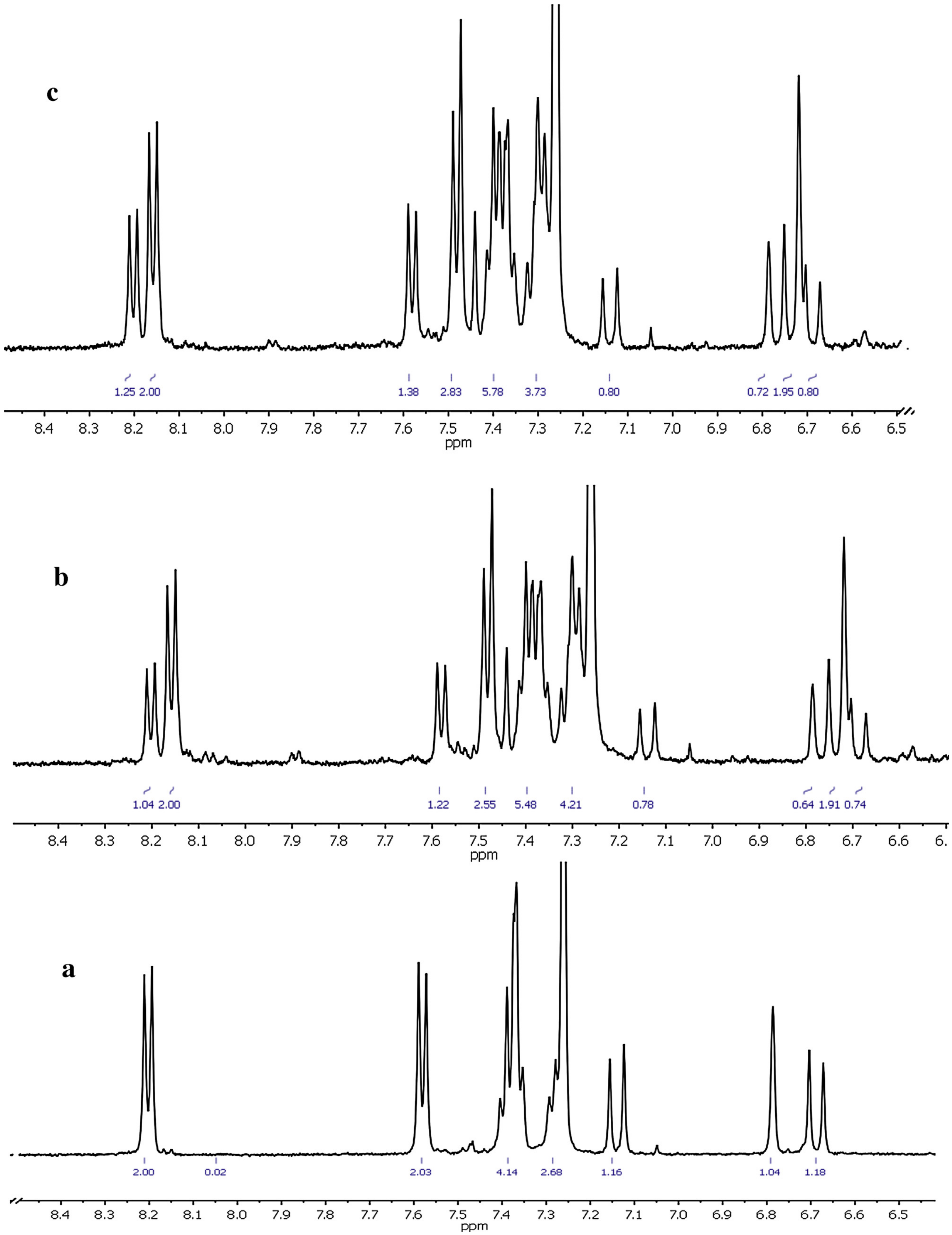


Fig. 6. ^{1}H NMR spectra of diene (**4**) at (a) 0 (b) 30 and (c) 120 min of irradiation.

Table 2
Comparative NMR values and their coupling constants of dienes (**3**)–(**5**).

Diene	*Trans–trans* (tt)	Photomixture	*Trans-cis*(tc) or *Cis-trans* (ct)
3	δ 7.00–6.97 (d, 1*H*, 16.0 Hz), δ 6.79–6.76 (d, 1*H*, J = 16.0 Hz), δ 6.67 (s, 1*H*)	δ 7.24–7.21 (17.0 Hz ct), δ 7.00–δ 6.97 (d, J = 16.0 Hz tt), δ 6.84–δ 6.81 (d, J = 16.0 Hz ct), δ 6.79–δ 6.76 (d, J = 16.0 Hz tt), δ 6.67 (s, tt), *6.55 (s ct)*	7.24–7.20 (d, J = 16.0 Hz), 6.84–6.81 (d, J = 16.0 Hz), 6.55 (s)
4	δ 7.15–7.12 (1*H*, d, J = 16.0 Hz), δ 6.78 (s,1*H*), δ 6.70–6.67 (1*H*, d, J = 16.0 Hz)	δ 7.47–7.44 (d, J = 15.5 Hz tc), δ 7.15–7.12 (d, J = 16.0 Hz tt), δ 6.78 (s tt), δ 6.75–6.72 (d, J = 16.5 Hz tc), δ 6.72 (s tc), δ 6.70–6.67 (d, J = 16.0 Hz tt)	δ 7.47–7.44 (d, J = 15.5 Hz), δ 6.75–6.72 (d, J = 16.5 Hz), δ 6.72 (s)
5	δ 7.14–7.11 (d, 1*H*, 16.0 Hz), δ 6.81–6.78 (d, 1*H*, 15.5 Hz), δ 6.79 (s, 1*H*)	δ 7.34–7.30 (d, J = 16.5 Hz ct), δ 7.14–7.11 (d, J = 16.0 Hz tt), δ 6.79–6.76 (d, J = 15.5 Hz tt), δ 6.79 (s tt), δ 6.86–6.83 (d, J = 16.0 Hz ct), δ 6.71 (s ct)	δ 7.34–7.30 (d, J = 16.5 Hz), δ 6.86–δ 6.83 (d, J = 16.0 Hz), δ 6.71 (s)

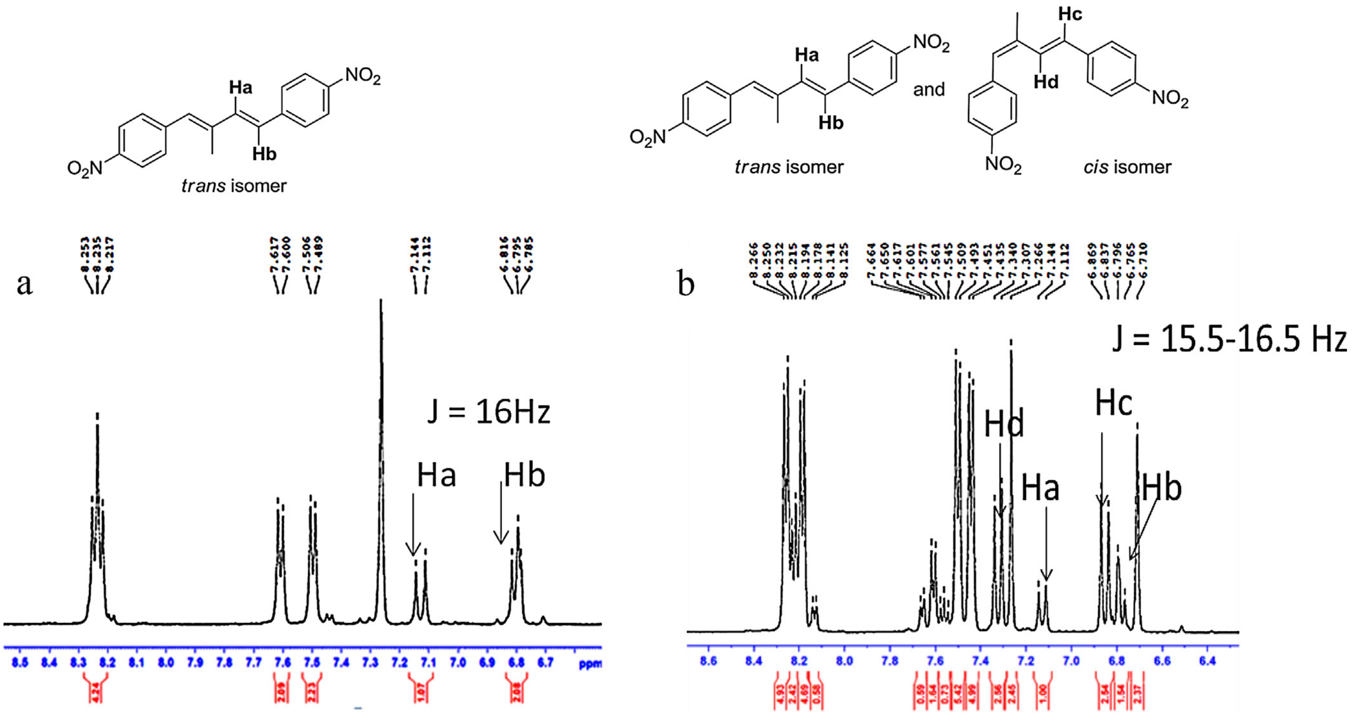


Fig. 7. ^{1}H NMR spectra of diene (**5**) (a) pure *trans* isomer before irradiation (b) after irradiation.

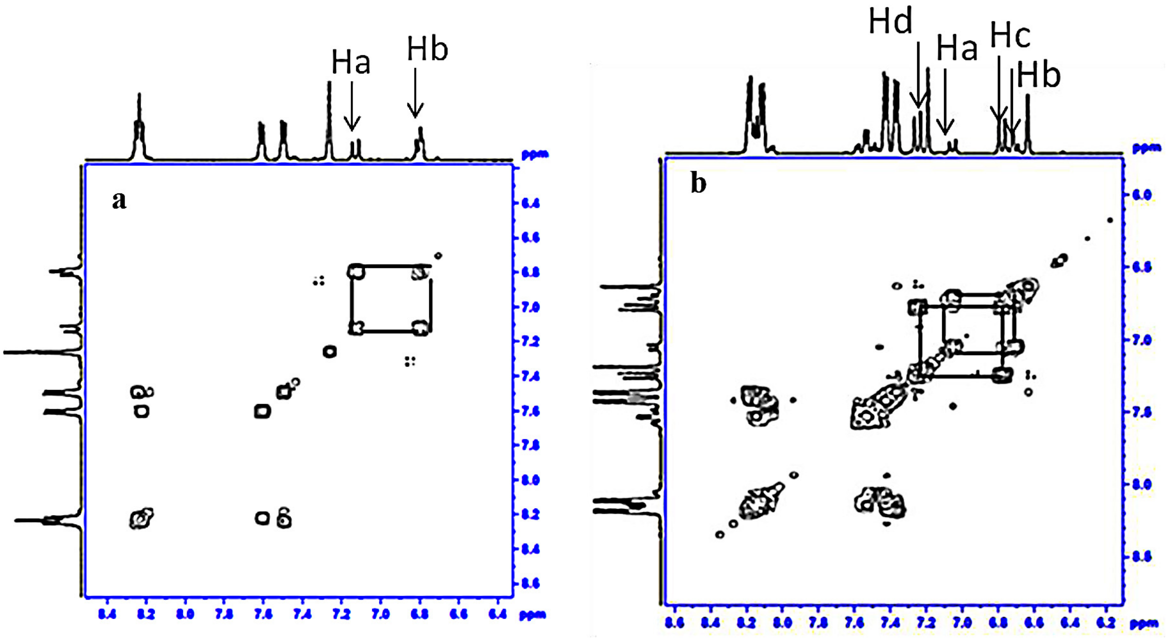


Fig. 8. COSY spectra of diene (**5**) (a) pure *trans* isomer before irradiation (b) after irradiation.

4. Conclusions

Photoisomerization of nitro substituted diphenylbutadienes lacking methyl group results in loss of absorbed energy as vibrational, rotational or thermal channels and therefore leads to non-detectable or extremely inefficient photoisomerization. However, a methyl group on the conjugated double bond that is either proximal or distal to the nitro group enables facile isomerization. In the case of dienes (**1**) and (**2**) electron withdrawing effect of the nitro group dominates and in the case of dienes (**3**)–(**5**) steric encumbrance of methyl has a significant influence. Presence of an angular methyl group twists the structure out of plane reducing the conjugation and minimizing the strong electron withdrawing effects of the nitro group. This reduction in conjugation allows facile *trans*–*cis* isomerization and the molecule exists in an isomerization facilitating twisted-conformation owing to lowering of excited state torsional barrier. Moreover, by changing the position of the methyl group the site of isomerization is completely controlled.

Acknowledgements

Financial grant from Council of Scientific and Industrial Research (01(2487)/11/EMR-II) and Department of Science and Technology, India (SR/S1/PC-024/2010) and support from IIT Gandhinagar is greatly appreciated. We also thank reviewers for helpful suggestions.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2014.07.019.

References

[1] G. Wald, The molecular basis of visual excitation, Nature 219 (1968) 800–807.

[2] K. Palczewski, Chemistry and biology of vision, J. Biol. Chem. 287 (2012) 1612–1619.

[3] A. Wand, I. Gdor, J. Zhu, M. Sheves, S. Ruhman, Shedding new light on retinal protein photochemistry, Ann. Rev. Phys. Chem. 64 (2013) 437–458.

[4] M.T. Allen, D.G. Whitten, The photophysics and photochemistry of α,ω-diphenylpolyene singlet states, Chem. Rev. 89 (1989) 1691–1702.

[5] M. Natali, S. Giordani, Molecular switches as photocontrollable smart receptors, Chem. Soc. Rev. 41 (2012) 4010–4029.

[6] G.M. Spinks, Deforming materials with light: photoresponsive materials muscle in on the action, Angew. Chem. Int. Ed. 51 (2012) 2285–2287.

[7] R.D. Kaiser, E. London, Location of diphenylhexatriene (DPH) and its derivatives within membranes: comparison of different fluorescence quenching analyses of membrane depth, Biochemistry 37 (1998) 8180–8190.

[8] A. Simeonov, M. Matsushita, E.A. Juban, E.H.Z. Thompson, T.Z. Hoffman, A.E. Beuscher Iv, M.J. Taylor, P. Wirsching, W. Rettig, J.K. McCusker, R.C. Stevens, D.P. Millar, P.G. Schultz, R.A. Lerner, K.D. Janda, Blue-fluorescent antibodies, Science 290 (2000) 307–313.

[9] X.X. Zhou, M.Z. Lin, Photoswitchable fluorescent proteins: ten years of colorful chemistry and exciting applications, Curr. Opin. Chem. Biol. 17 (2013) 682–690.

[10] Y. Zhang, J. Sun, G. Bian, Y. Chen, M. Ouyang, B. Hu, C. Zhang, Cyanostilben-based derivatives: mechanical stimuli-responsive luminophors with aggregation-induced emission enhancement, Photochem. Photobiol. Sci. 11 (2012) 1414–1421.

[11] R. Davis, V.A. Mallia, S. Das, Reversible photochemical phase transition behavior of alkoxy-cyano-substituted diphenylbutadiene liquid crystals, Chem. Mater. 15 (2003) 1057–1063.

[12] R.K. Vijayaraghavan, S. Abraham, D.S.S. Rao, S.K. Prasad, S. Das, Light induced generation of stable blue phase in photoresponsive diphenylbutadiene based mesogen, Chem. Commun. 46 (2010) 2796–2798.

[13] W.A. Yee, S.J. Hug, D.S. Kliger, Direct and sensitized photoisomerization of 1,4-diphenylbutadienes, J. Am. Chem. Soc. 110 (1988) 2164–2169.

[14] W. Fuß, Hula-twist *cis*–*trans* isomerization: the role of internal forces and the origin of regioselectivity, J. Photochem. Photobiol. A: Chem. 237 (2012) 53–63.

[15] J. Saltiel, T.S.R. Krishna, R.J. Clark, Photoisomerization of *cis*,*cis*-1,4-diphenyl-1,3-butadiene in the solid state: the bicycle-pedal mechanism, J. Phys. Chem. A 110 (2006) 1694–1697.

[16] J. Saltiel, T.S.R. Krishna, S. Laohhasurayotin, K. Fort, R.J. Clark, Photoisomerization of *cis*,*cis*-to *trans*,*trans*-1,4-diaryl-1,3-butadienes in the solid state: the bicycle-pedal mechanism, J. Phys. Chem. A 112 (2007) 199–209.

[17] L.-Y. Yang, M. Harigai, Y. Imamoto, M. Kataoka, T.-I. Ho, E. Andrioukhina, O. Federova, S. Shevyakov, R.S.H. Liu, Stilbene analogs in Hula-twist photoisomerization, Photochem. Photobiol. Sci. 5 (2006) 874–882.

[18] L.-y. Yang, R.S.H. Liu, K.J. Boarman, N.L. Wendt, J. Liu, New aspects of diphenylbutadiene photochemistry. Regiospecific hula-twist photoisomerization, J. Am. Chem. Soc. 127 (2005) 2404–2405.

[19] L.-y. Yang, R.S.H. Liu, N.L. Wendt, J. Liu, Steric effects in hula-twist photoisomerization. 1,4-Dimethyl- and 2,3-dimethyl-1,4-diphenylbutadienes, J. Am. Chem. Soc. 127 (2005) 9378–9379.

[20] R.S.H. Liu, D.T. Browne, A bioorganic view of the chemistry of vision: H.T.-n and B.P.-m,n mechanisms for reactions of confined, anchored polyenes, Acc. Chem. Res. 19 (1986) 42–48.

[21] Y.O. Jung, J.H. Lee, J. Kim, M. Schmidt, K. Moffat, V. Srajer, H. Ihee, Volume-conserving *trans*–*cis* isomerization pathways in photoactive yellow protein visualized by picosecond X-ray crystallography, Nat. Chem. 5 (2013) 212–220.

[22] H. Braatz, S. Hecht, H. Seifert, S. Helm, J. Bendig, W. Rettig, Photochemistry and photophysics of donor–acceptor-polyenes. I: all-*trans*-4-dimethylamino-4′-cyano-1,4-diphenylbutadiene (DCB), J. Photochem. Photobiol., A 123 (1999) 99–108.

[23] A.K. Singh, G.R. Mahalaxmi, Excited state properties of α,ω-diphenylpolyenes: photophysical and photochemical studies of donor-acceptor diarylbutadienes, Photochem. Photobiol. 71 (2000) 387–396.

[24] B.H. Baretz, A.K. Singh, R.S.H. Liu, Photochemical *cis*, *trans* isomerization of three cyano-substituted diphenyl-1,3-butadienes and a diphenyl-1,3,5-hexatriene. The dipolar character and the torsional potential surfaces of the S1 state, Nouv. J. Chim. 5 (1981) 297–303.

[25] Y. Sonoda, S. Tsuzuki, M. Goto, N. Tohnai, M. Yoshida, Fluorescence spectroscopic properties of nitro-substituted diphenylpolyenes: effects of intramolecular planarization and intermolecular interactions in crystals, J. Phys. Chem. A 114 (2009) 172–182.

[26] A.K. Singh, M. Darshi, S. Kanvah, α,ω-Diphenylpolyenes cabable of exhibiting twisted intramolecular charge transfer fluorescence: a fluorescence and fluorescence probe study of nitro- and nitrocyano-substituted 1,4-diphenylbutadienes, J. Phys. Chem. A 104 (1999) 464–471.

[27] A.K. Singh, T.S.R. Krishna, Fluorescence and photodimerization studies of cyano-substituted diphenylbutadienes, J. Phys. Chem. A 101 (1997) 3066–3069.

[28] H. El-Gezawy, W. Rettig, R. Lapouyade, Solvatochromic behavior of donor–acceptor-polyenes: dimethylamino-cyano-diphenylbutadiene, J. Phys. Chem. A 110 (2005) 67–75.

[29] S. Abraham, V.A. Mallia, K.V. Ratheesh, N. Tamaoki, S. Das, Reversible thermal and photochemical switching of liquid crystalline phases and luminescence in diphenylbutadiene-based mesogenic dimers, J. Am. Chem. Soc. 128 (2006) 7692–7698.

[30] S. Abraham, R.K. Vijayaraghavan, S. Das, Tuning microstructures in organogels: gelation and spectroscopic properties of mono- and bis-cholesterol-linked diphenylbutadiene derivatives, Langmuir 25 (2009) 8507–8513.

[31] I.D. Johnson, E.W. Thomas, R.B. Cundall, Fluorescence solvatochromism of nitrodiphenylhexatrienes, J. Chem. Soc., Faraday Trans.—2: Mol. Chem. Phys. 81 (1985) 1303–1315.

[32] J. Liu, K.J. Boarman, N.L. Wendt, L.M. Cardenas, Regiospecific photoisomerization of fluorinated (*E*,*E*)-1,4-diphenyl-1,3-butadienes, Tetrahedron Lett. 46 (2005) 4953–4956.

[33] Y. Sonoda, Y. Kawanishi, Solvent-dependent *cis*–*trans* photoisomerization of *p*-methoxy-*p*′-nitro-substituted *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene, Chem. Lett. 32 (2003) 978–979.

[34] I. Škorić, I. Kikaš, M. Kovács, L. Fodor, Ž. Marinić, K. Molčanov, B. Kojić-Prodić, O. Horváth, Synthesis, photochemistry, and photophysics of butadiene derivatives: influence of the methyl group on the molecular structure and photoinduced behavior, J. Org. Chem. 76 (2011) 8641–8657.

[35] D. Vuk, D. Potroško, M. Šindler-Kulyk, Ž. Marinić, K. Molčanov, B. Kojić-Prodić, I. Škorić, Synthesis and photochemical transformations of new butadiene chromophores: the influence of the nature and position of chlorine substituent on the photoinduced behaviour, J. Mol. Struct. 1051 (2013) 1–14.

[36] Y. Miura, A. Momotake, Y. Kanna, Y. Nishimura, T. Arai, Extremely efficient photoisomerization of water-soluble diphenylbutadiene dendrimers, Dyes Pigm. 92 (2012) 802–806.

[37] Y. Miura, A. Momotake, Y. Kanna, Y. Nishimura, T. Arai, Unusually efficient *trans*-to-*cis* photoisomerization of diphenylbutadiene dendrimers in water, Photochem. Photobiol. Sci. 10 (2011) 1524–1526.

[38] S.F. Russo, Two fluorescence experiments, J. Chem. Educ. 46 (1969) 374.

[39] D. Phillips, A quantitative photochemical experiment for undergraduates, J. Chem. Educ. 48 (1971) 198.

[40] H. Chen, H. Jiang, C. Cai, J. Dong, W. Fu, Facile synthesis of (*E*)-alkenyl aldehydes from allyl arenes or alkenes via Pd(II)-catalyzed direct oxygenation of allylic C—H bond, Org. Lett. 13 (2011) 992–994.

[41] A. Sandoval, L. Zechmeister, Some spectroscopic changes connected with the stereoisomerization of diphenylbutadiene, J. Am. Chem. Soc. 69 (1947) 553–557.

[42] A.K. Singh, M. Darshi, S. Kanvah, Twisted intramolecular charge transfer fluorescence in nitro-substituted α,ω-diphenylpolyene compounds, New J. Chem. 23 (1999) 1075–1078.

[43] J.-S. Yang, C.-K. Lin, A.M. Lahoti, C.-K. Tseng, Y.-H. Liu, G.-H. Lee, S.-M. Peng, Effect of ground-state twisting on the *trans* → *cis* photoisomerization and TICT state formation of aminostilbenes, J. Phys. Chem. A 113 (2009) 4868–4877.

[44] C.T. Lin, H.W. Guan, R.K. McCoy, C.W. Spangler, Dual fluorescence of *p*,*p*′-disubstituted 1,6-diphenyl-1,3,5-hexatrienes: evidence of a twisted

intramolecular charge-transfer state, J. Phys. Chem. 93 (1989) 39–43.

[45] H. Gruen, H. Goerner, *Trans–cis* photoisomerization, fluorescence, and relaxation phenomena of *trans*-4-nitro-4′-(dialkylamino)stilbenes and analogues with a nonrotatable amino group, J. Phys. Chem. 93 (1989) 7144–7152.

[46] A.K. Singh, S. Kanvah, A fluorescence emission study of nitro- and nitromethyl-substituted 1,4-diarylbutadiene in solid state, Ind. J. Chem. 40B (2001) 965–973.

[47] J.H. Pinckard, B. Wille, L. Zechmeister, Comparative study of the three stereoisomeric 1,4-diphenylbutadienes, J. Am. Chem. Soc. 70 (1948) 1938–1944.

[48] A. Barbon, M. Bortolus, M. Brustolon, A.L. Maniero, R. Zanrè, Photoexcited triplets of nitrodiphenylpolyenes hosted in channel cavities. A time resolved EPR study, Phys. Chem. Chem. Phys. 6 (2004) 2396–2402.

[49] H.J. Kuhn, R. Straatmann, D. Schulte-Frohlinde, Chemical evidence of a triplet mechanism in the photoisomerization of nitrostibenes. Formation of singlet oxygen from triplet states of nitrostilbenes, J. Chem. Soc., Chem. Commun. (1976) 824–825.

[50] H. Görner, D. Schulte-Frohlinde, *Cis–trans* photoisomerization of 4-nitrostilbenes, Pure Appl. Chem. 51 (1979) 279–297.

[51] R. Hurley, A.C. Testa, Triplet-state yield of aromatic nitro compounds, J. Am. Chem. Soc. 90 (1968) 1949–1952.

[52] C.-K. Lin, Y.-F. Wang, Y.-C. Cheng, J.-S. Yang, Multisite constrained model of *trans*-4-(*N*,*N*-dimethylamino)-4′-nitrostilbene for structural elucidation of radiative and nonradiative excited states, J. Phys. Chem. A 117 (2013) 3158–3164.