Reversible Photochemical Phase Transition Behavior of Alkoxy-Cyano-Substituted Diphenylbutadiene Liquid Crystals[†]

Riju Davis, V. Ajay Mallia, and Suresh Das*

Photosciences and Photonics Division, Regional Research Laboratory (CSIR), Trivandrum 695 019, India

Received July 2, 2002. Revised Manuscript Received October 30, 2002

Reversible photochemical phase transition behavior of some alkoxy-cyano-substituted diphenylbutadiene liquid crystals has been studied. The *EE* isomers of these derivatives were found to undergo photoisomerization to yield thermally stable *EZ* and *ZE* isomers, which could be transformed back to the *EE* isomer using light of a different wavelength. On photolysis, the liquid-crystalline *EE* isomers of these derivatives exhibited isothermal phase transition to the isotropic phase due to the formation of the non-liquid-crystalline *EZ* and *ZE* isomers. The thermal stability of the *EZ* and *ZE* isomers ensures that reverse switching of these materials to the liquid-crystalline phase remains purely a photon-controlled process.

1. Introduction

Liquid crystals (LCs) have been extensively used in display devices due to their large optical anisotropies and ability to undergo electric-field-induced switching.[1−20] Due to the relatively slow switching times of such devices, there has been a growing interest in the development of liquid-crystalline materials wherein the optical properties can be reversibly controlled using light-activated processes.[10,21,22] Since light-induced switching times can be several orders of magnitude faster than electric-field-induced switching, these materials can play an important role in the development of technologies such as high-speed information processing, apart from their use in conventional imaging and display devices. Earlier studies in this area were related to the use of photochromic molecules such as azobenzene[7,8,23] and spiropyrans[24] dissolved in liquid-crystalline matrixes, wherein the photochemical transformations of the guest molecules bring about changes in the phase or alignment of the liquid-crystalline host. Subsequent studies have shown that the switching times for such processes can be much faster when the liquid-crystalline material is inherently photoactive.[8,12,25,26] With a few exceptions, most systems designed for such applications have utilized the trans−cis photoisomerization of azobenzene chromophore since its rod-shaped trans form is known to stabilize the liquid-crystalline phase whereas the cis isomer destabilizes it.[7,8,23] A drawback connected with the use of azobenzene chromophore is that trans−cis photoisomerization is usually thermally reversible and additional measures such as polymerization[8] or formation of glassy liquid crystals[27,28] are required for long-term storage of information. In view of this, development of photoswitchable liquid crystals using alternate chromophores is desirable. Our interest in the study of the photochemical, photophysical, and nonlinear optical properties of some donor−acceptor-substituted butadienes[29,30] led us to explore the use of

---

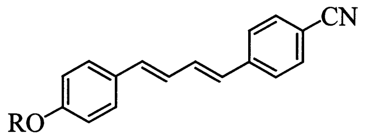
* To whom correspondence should be addressed. Fax: +91 471 2490186. E-mail: sdaas@rediffmail.com.

[†] Dedicated to Professor M.V. George on his 75th birthday.

(1) Eich, M.; Wendorff, J. *J. Opt. Soc. Am. B* **1990**, *7*, 1428.
(2) Anderle, K.; Wendorff, J. H. *Mol. Cryst. Liq. Cryst.* **1994**, *243*, 51.
(3) Gibbons, W. M.; Shannon, P. J.; Sun, S. T. *Mol. Cryst. Liq. Cryst.* **1994**, *251*, 191.
(4) Gibbons, W. M.; Kosa, T.; Palffy-Muhoray, P.; Shannon, P. J.; Sun, S. T.; Swetlin, B. J. *Nature* **1995**, *377*, 43.
(5) Haas, W.; Adams, J.; Wysocki, J. *Mol. Cryst. Liq. Cryst.* **1969**, *7*, 371.
(6) Haas, W. E.; Nelson, K. F.; Adams, J. E.; Dir, G. A. *J. Electrochem. Soc.* **1974**, *121*, 1667.
(7) Ikeda, T.; Kanazawa, A. *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001.
(8) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873.
(9) Ikeda, T.; Sasaki, T.; Ichimura, K. *Nature* **1993**, *361*, 428.
(10) Kurihara, S.; Ikeda, T.; Sasaki, T.; Kim, H.-B.; Tazuke, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1751.
(11) Kurihara, S.; Nomiyama, S.; Nonaka, T. *Chem. Mater.* **2000**, *12*, 9.
(12) Tsutsumi, O.; Shiono, T.; Ikeda, T.; Galli, G. *J. Phys. Chem. B* **1997**, *101*, 1332.
(13) Tamaoki, N.; Moriyama, M.; Matsuda, H. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 509.
(14) Stumpe, J.; Fischer, T.; Menzel, H. *Macromolecules* **1996**, *29*, 2831.
(15) Stumpe, J.; Geue, T.; Fischer, T.; Menzel, H. *Thin Solid Films* **1996**, 606.
(16) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.
(17) Suarez, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 6732.
(18) Janicki, S. Z.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 8524.
(19) Feringa, B. L.; Huck, N. P. M.; Doren, H. A. v. *J. Am. Chem. Soc.* **1995**, *117*, 9929.
(20) Huck, N. P. M.; Jager, W. F.; Lange, B. d.; Feringa, B. L. *Science* **1996**, *273*, 1686.
(21) Ikeda, T.; Sasaki, T.; Kim, H.-B. *J. Phys. Chem.* **1991**, *95*, 509.
(22) Sasaki, T.; Ikeda, T.; Ichimura, K. *Macromolecules* **1992**, *25*, 3807.
(23) Mallia, V. A.; George, M.; Das, S. *Chem. Mater.* **1999**, *11*, 207.
(24) Kobayashi, T.; Degenkolb, E. O.; Rentzepis, P. M. *J. Phys. Chem.* **1979**, *83*, 2431.
(25) Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N. *J. Am. Chem. Soc.* **1997**, *119*, 7791.
(26) Tsutsumi, O.; Demachi, Y.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Nagase, Y. *J. Phys. Chem. B* **1998**, *102*, 2869.
(27) Tamaoki, N.; Song, S.; Moriyama, M.; Matsuda, H. *Adv. Mater.* **2000**, *12*, 94.
(28) Tamaoki, N. *Adv. Mater.* **2001**, *13*, 1135.

10.1021/cm020710z CCC: $25.00

Chart 1



BC1, R = CH_3 **BC8,** R = C_8H_{17}
BC4, R = C_4H_9 **BC12,** R = $C_{12}H_{25}$

photoisomerization of the butadiene chromophore for photoswitching in liquid crystals. Although butadiene-based liquid-crystalline materials have been reported,[31,32] the photochemically induced phase transition behavior of these materials have hitherto not been explored. Also, the thermal stability of the photoisomers of donor−acceptor-substituted butadienes is largely dependent on the strength of their donor and acceptor groups.[29,33] Earlier attempts at the isolation and characterization of these isomers have been unsuccessful.[33] Here, we report for the first time the photoinduced isothermal phase transitions in alkoxy-cyano-substituted diphenylbutadiene liquid crystals (Chart 1) along with the isolation and detailed spectral characterization of their photoisomers.

2. Experimental Section

2.1. Instrumentation. HPLC analyses were carried out on a Shimadzu HPLC using the following conditions: Shimadzu System Controller SCL10AVP; Shimadzu LC-6AD pump; Shimadzu SPD-6AV UV−vis spectrophotometric detector set at 317 nm; Rheodyne injection valve with 20-μL (analytical) and 200-μL (preparative) sample loops; Shimadzu CLC-Sil (4.6 mm × 25 cm) analytical column packed with totally porous, spherical silica particles (5-μm particle diameter, 100-Å pore diameter) with chemically modified surfaces; Prep-Sil (20 mm × 25 cm) preparative columns packed with totally porous, irregular-shaped silica particles (15-μm particle diameter, 100-Å pore diameter) with chemically modified surfaces; hexane/ethyl acetate (99:1) as the mobile phase with a flow rate of 2 mL/min for analytical and 20 mL/min for preparative runs.

Phase transitions were observed using a Nikon HFX 35A Optiphot-2 polarized light optical microscope, equipped with a Linkam THMS 600 heating and freezing stage connected to a Linkam TP92 temperature programmer. DSC analyses were preformed under air, using a DuPont DSC 2010 differential scanning calorimeter attached to a Thermal Analyst 2100 data station. Absorption spectra were recorded on a Shimadzu 3101PC UV−vis−NIR spectrophotometer. Steady-state photolysis was carried out using a 200-W high-pressure mercury lamp, in combination with a 360-nm Oriel band-pass filter. The intensity of light was determined using potassium ferrioxalate actinometry.[34] Laser photolysis was carried out using the fourth harmonic (266 nm, 15 mJ/pulse, pulse width 10 ns) of a Quanta Ray GCR-12 Nd:YAG laser.

^1H NMR spectra were measured on Bruker DRX 500-MHz and Bruker DPX 300-MHz spectrometers at 25 °C. $^1H-^1H$ NOESY and $^1H-^1H$ COSY NMR spectra were recorded on the Bruker DRX 500-MHz spectrometer at 25 °C. Tetramethylsilane (TMS) was used as the internal standard and chloroform-d ($CDCl_3$) was used as the solvent.

2.2. Synthesis. The diphenylbutadienes derivatives, **BC1**, **BC4**, and **BC8** were synthesized as reported earlier and their structures were confirmed using NMR, IR, and HRMS analyses.[31,32,35] Purification of the compounds was achieved by column chromatography using silica gel (100−200 mesh) as the stationary phase material and hexane/ethyl acetate (99:1) as the eluent. Recrystallization from hexane/ethyl acetate (99:1) gave pure samples (>99%) of these derivatives as confirmed by HPLC. **BC12** was synthesized and purified using a similar procedure and its detailed spectral data are provided below.

*4-(p-Cyanophenyl)-1-(p-dodecyloxyphenyl)-buta-1E,3E-diene (**BC12**).* Yield: 40%. mp: 171.9 °C (clearing temperature). UV−vis λ_{max} (MeCN): 356 nm ($\epsilon = 4.4 \times 10^4$ M^{-1} cm^{-1}). IR ν_{max} (KBr): 2926, 2857, 2356, 2230, 1735, 1680, 1603, 1511, 1475, 1306, 1258, 1176, 1027, 984, 857, 800 cm^{-1}. HRMS: calcd for $C_{29}H_{37}NO$, 415.2875; found, 415.2887.

^1H NMR (300 MHz, $CDCl_3$) (protons are labeled as shown in Figure 3): δ 0.88 (t, 3H, CH_3), 1.26−1.45 (m, 18H, $(CH_2)_9$), 1.73−1.80 (m, 2H, CH_2), 3.97 (t, 2H, OCH_2), 6.58 (d, 1H, $^3J_{c,d} = 15.4$ Hz, Hd), 6.71 (d, 1H, $^3J_{a,b} = 15.4$ Hz, Ha), 6.78−6.86 (dd, 1H, $^3J_{a,b} = 15.4$ Hz, $^3J_{b,c} = 10.2$ Hz, Hb), 6.87 (d, 2H, $^3J_{1,2} = 8.3$ Hz, H2), 6.99−7.07 (dd, 1H, $^3J_{c,d} = 15.4$, $^3J_{b,c} = 10.2$ Hz, Hc), 7.38 (d, 2H, $^3J_{1,2} = 8.3$ Hz, H1), 7.48 (d, 2H, $^3J_{3,4} = 8.1$ Hz, H3), 7.58 (d, 2H, $^3J_{3,4} = 8.1$ Hz, H4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.08, 22.65, 25.99, 29.20, 29.31, 29.55, 29.60, 31.88, 68.09, 68.25, 104.72, 109.96, 114.78, 115.03, 119.12, 126.11, 126.45, 127.95, 129.21, 129.35, 130.32, 132.38, 133.21, 135.27, 142.12, 159.39 ppm.

In all cases, synthesis yielded purely the *EE* isomer of the compounds, which was confirmed from the trans-^3J coupling constant values of 15 Hz for the olefinic protons in their ^1H NMR spectra.[36]

The NMR data for the photoisomers of **BC1**, isolated from photolyzed solutions, are provided below. The protons are labeled as shown in Figure 3.

*4-(p-Cyanophenyl)-1-(p-methoxyphenyl)-buta-1E,3Z-diene (**BC1-EZ**).* ^1H NMR ($CDCl_3$, 500 MHz): δ 3.84 (s, 3H, OCH_3), 6.43 (d, 1H, $^3J_{c,d} = 11.6$ Hz, Hd), 6.54 (t, 1H, $^3J_{b,c} = 11.6$ Hz, $^3J_{c,d} = 11.6$ Hz, Hc), 6.76 (d, 1H, $^3J_{a,b} = 15.4$ Hz, Ha), 6.89 (d, 2H, $^3J_{1,2} = 8.9$ Hz, H2), 7.09−7.15 (dd, 1H, $^3J_{a,b} = 15.5$ Hz, $^3J_{b,c} = 11.3$ Hz, Hb), 7.37 (d, 2H, $^3J_{1,2} = 8.9$ Hz, H1), 7.49 (d, 2H, $^3J_{3,4} = 8.0$ Hz, H3), 7.68 (d, 2H, $^3J_{3,4} = 8.3$ Hz, H4) ppm.

*4-(p-Cyanophenyl)-1-(p-methoxyphenyl)-buta-1Z,3E-diene (**BC1-ZE**).* ^1H NMR ($CDCl_3$, 500 MHz): δ 3.84 (s, 3H, OCH_3), 6.38 (t, 1H, $^3J_{a,b} = 11.5$ Hz, $^3J_{b,c} = 11.1$ Hz, Hb), 6.62 (d, 1H, $^3J_{a,b} = 11.3$ Hz, Ha), 6.68 (d, 1H, $^3J_{c,d} = 15.2$ Hz, Hd), 6.96 (d, 2H, $^3J_{1,2} = 8.8$ Hz, H2), 7.34 (d, 2H, $^3J_{1,2} = 8.5$ Hz, H1), 7.40−7.45 (dd, 1H, $^3J_{b,c} = 11.1$ Hz, $^3J_{c,d} = 15.5$ Hz, Hc), 7.47 (d, 2H, $^3J_{3,4} = 8.4$ Hz, H3), 7.60 (d, 2H, $^3J_{3,4} = 8.4$ Hz, H4) ppm.

The detailed description of the structural assignments of the photoisomers based on the NMR analyses is provided under the section Results and Discussion.

3. Results and Discussion

3.1. Liquid-Crystalline Property. The liquid-crystalline phases of these diphenylbutadiene derivatives (Chart 1) were characterized using a polarizing optical microscope and the sharp phase transitions observed in the heating and cooling cycles were further confirmed by differential scanning calorimetry. Table 1 summarizes their phase transition temperatures and thermodynamic parameters. **BC1** exhibited Schlieren as well as droplet texture, characteristic of a nematic

---

(29) Davis, R.; Das, S.; George, M.; Druzhinin, S.; Zachariasse, K. *J. Phys. Chem. A* **2001**, *105*, 4790.

(30) Das, S.; George, M.; Mathew, T.; Asokan, C. V. *J. Chem. Soc., Perkin Trans. 2* **1996**, *2*, 731.

(31) Brettle, R.; Dunmur, D. A.; Hindley, N. J.; Marson, C. M. *J. Chem. Soc., Chem. Commun.* **1992**, 411.

(32) Brettle, R.; Dunmur, D. A.; Hindley, N. J.; Marson, C. M. *J. Chem. Soc., Perkin Trans 1* **1993**, 775.

(33) Braatz, H.; Hecht, S.; Seifert, H.; Helm, S.; Bendig, J.; Rettig, W. *J. Photochem. Photobiol., A* **1999**, *123*, 99.

(34) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker Inc.: New York, 1993.

(35) Singh, A. K.; Kanvah, S. *New J. Chem.* **2000**, *24*, 630.

(36) Neuhaus, D.; Williamson, N. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers Inc: New York, 1989.

Table 1. Phase Transition Temperatures and Thermodynamic Parameters of the Diphenylbutadiene Derivatives (Chart 1)

compd	phase transition temperatures[a] (°C)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
BC1	K 175.3 N 213 I	21.1 (K−N)	47.0 (K−N)
BC4	K 141.5 N 209.1 I	25.8, 0.4	85.1, 0.9
BC8	K 105.3 S 159.6 N 186.6 I	36.2, 0.4 (N−I)	95.7, 0.9 (N−I)
BC12	K 96.9 S 171.9 I	46.2, 3.4	124.7, 7.6

[a] K = crystalline, N = nematic, S = smectic A ,and I = isotropic.

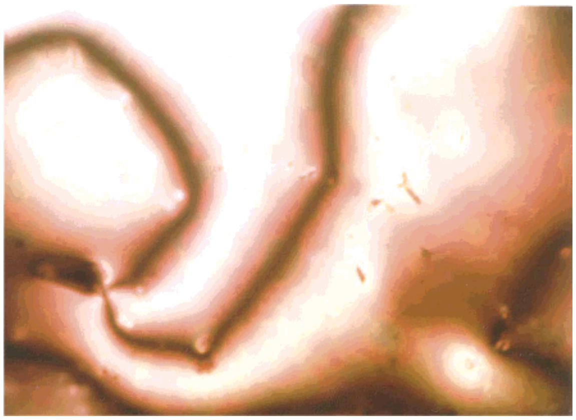


Figure 1. Polarized optical micrograph (400×) showing Schlieren texture of a nematic phase obtained for **BC1** at 194.7 °C.

(N) phase.[37] Figure 1 shows the polarized optical micrograph of **BC1**. The LC phases of **BC4** and **BC8** observed in the present study were identical to those reported by Brettle et al.[31] Whereas **BC4** possessed a nematic LC phase, both nematic and smectic LC phases are observed for **BC8**. The compound **BC12** showed only a smectic A (S_A) phase, which was confirmed by its focal conic texture with homeotropic areas.[37] With increasing length of the alkoxy chain in these derivatives, the isotropization temperature was found to decrease. This observed dependence of phase characteristics and phase transition temperatures on the length of the alkoxy chain conforms with the general behavior of LC molecules.[37]

3.2. Photoisomerization, Isolation, and Characterization of Photoisomers.

Photoisomerization. In solution, the *EE* isomers of the diphenylbutadiene derivatives possess a strong absorption band with a maximum centered on 360-nm. Photolysis with 360-nm light results in a decrease in intensity of this band and formation of a new band centered on 265-nm. These changes are marked by the presence of an isosbestic point at 317-nm (Figure 2A). Donor−acceptor-substituted diphenylbutadiene derivatives are known to undergo photoisomerization,[33,38−42] to yield cis−trans and trans−cis photoisomers. In most of the reported systems the isomers are thermally unstable and undergo transformation to their all-trans isomeric form with lifetimes depending on the nature of the donor and the acceptor, thereby making it difficult to characterize the photoisomers using spectroscopic techniques.[29,33] The structural assignments of the photoisomers of *all-trans*-4-(dimethylamino)-4′-cyano-1,4-diphenylbutadiene, for example, had to be made by quantum-chemical modeling of their absorption spectra.[33] Photolysis of the alkoxycyano-substituted diphenylbutadiene derivatives reported in the present study, however, resulted in the formation of a photostationary state (PSS1) consisting of the *EE* isomer and thermally stable photoisomers (Figure 2A).

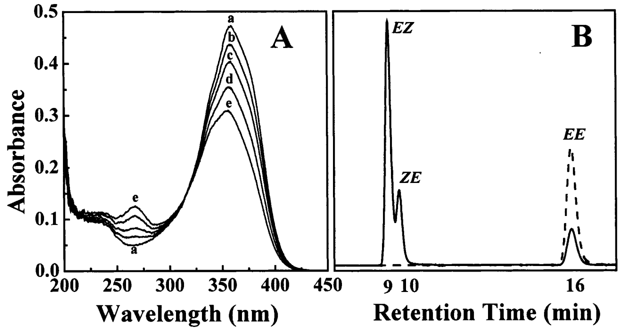


Figure 2. (A) Absorption spectral changes of **BC12** in acetonitrile at different time intervals upon photolysis using 360-nm light. Time of photolysis: (a) 0 s, (b) 30 s, (c) 60 s, (d) 120 s, and (e) 180 s (PSS1). (B) HPLC traces of **BC12** in acetonitrile: (- - -) before photolysis and (—) after attaining the photostationary state, PSS1.

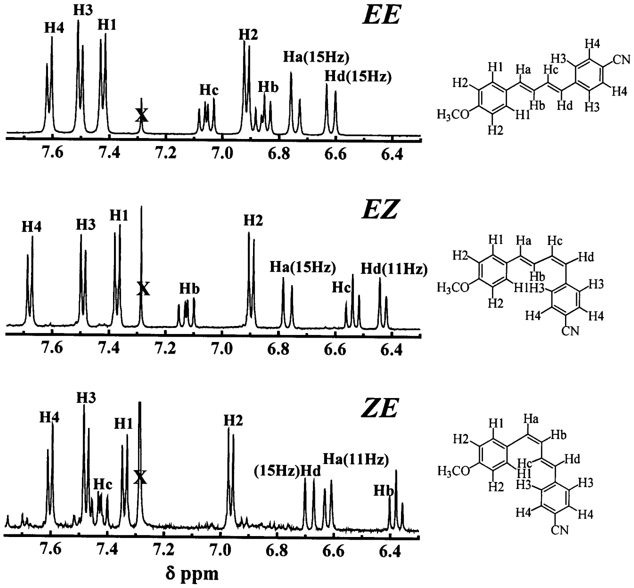


Figure 3. ^{1}H NMR spectra of the isomers of **BC1**.

Isolation and Characterization of the Photoisomers. HPLC analyses of a solution of **BC12** in acetonitrile before and after photolysis (Figure 2B) are clearly indicative of the formation of two photoisomers. Similar observations were made for other derivatives. Isolation and detailed structural characterization of the photoisomers were carried out for **BC1** since the separation between the two photoisomers in HPLC was better than that for the other derivatives. Figure 3 shows the ^{1}H NMR spectra of the *EE* isomer and the two isolated photoisomers of **BC1** in the region showing the olefinic

---

(37) Kelker, H.; Hatz, R. *Handbook of liquid crystals*; Verlag Chemie: Weinheim, 1980.

(38) Spaletti, A.; Bartocci, G.; Galiazzo, G.; Macchioni, A.; Mazzucato, U. *J. Phys. Chem. A* **1999**, *103*, 8994.

(39) Allen, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691.

(40) Liu, R. S. H. *Acc. Chem. Res.* **2001**, *34*, 555.

(41) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23.

(42) Singh, A. K.; Krishna, T. S. R. *J. Photosci.* **1998**, *5*, 47.

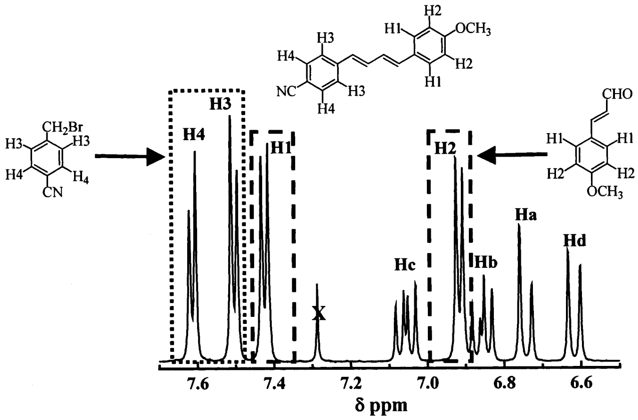


Figure 4. Classification of the aromatic protons, H1,H2 (- - -) and H3,H4 (···) in the ^{1}H NMR spectra of the isomers of **BC1**, based on comparison with the ^{1}H NMR spectra of the model compounds.

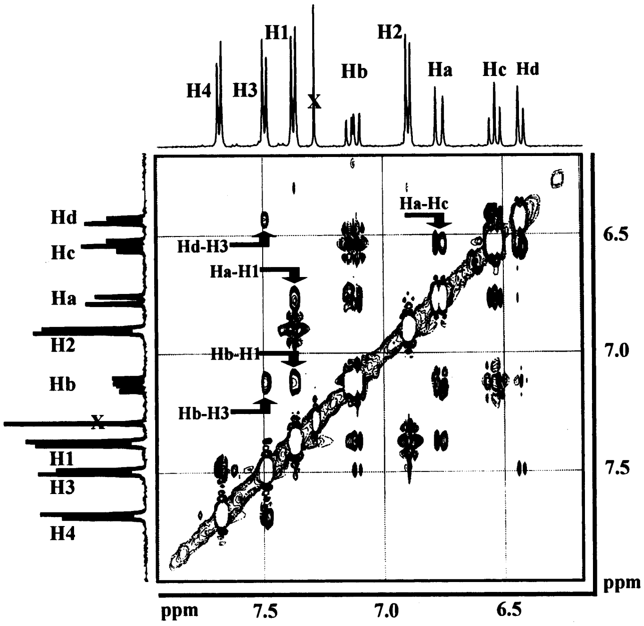


Figure 5. ^{1}H−^{1}H NOESY spectrum of **BC1-*EZ***.

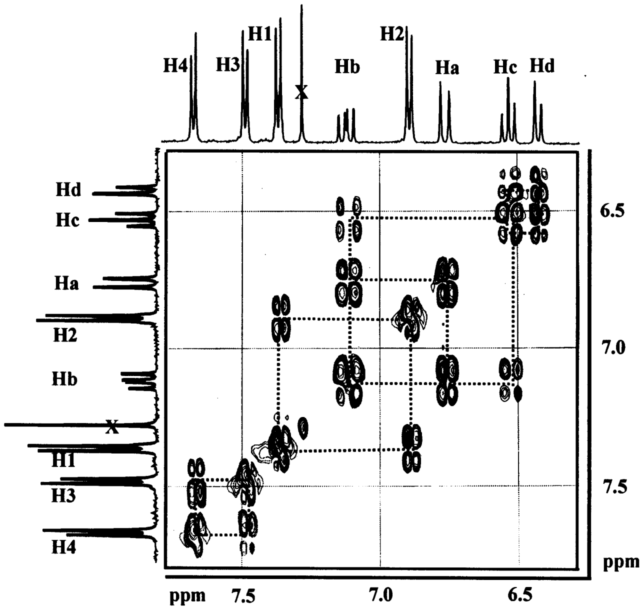


Figure 6. ^{1}H−^{1}H COSY spectrum of **BC1-*EZ***.

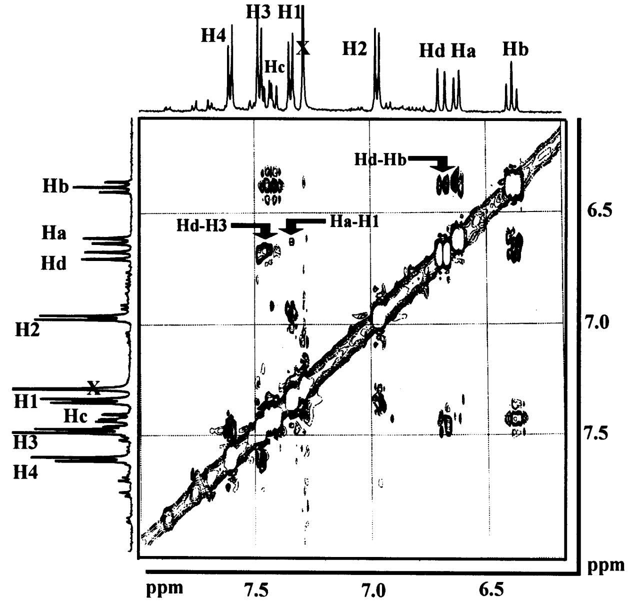


Figure 7. ^{1}H−^{1}H NOESY spectrum of **BC1-*ZE***.

and aromatic protons. The detailed ^{1}H NMR data of the photoisomers are provided in the Experimental Section.

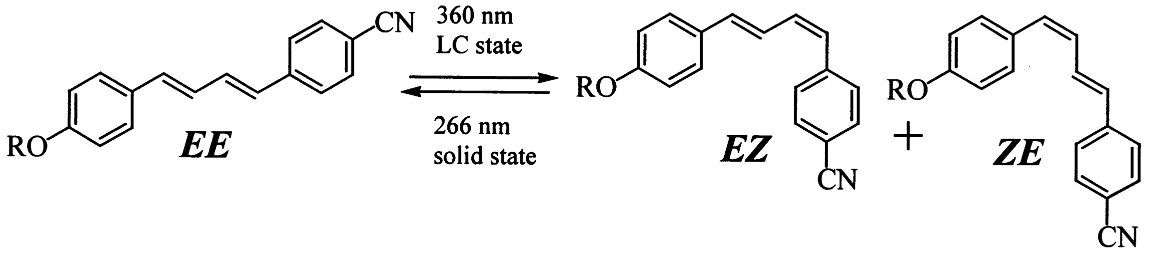
^{1}H NMR spectra of the photoisomers suggest that one of the double bonds has undergone isomerization since in both cases the two olefinic doublets (Ha and Hd) possess different ^3J-coupling constant values with one corresponding to an *E* coupling (~15 Hz) and the other to a *Z* coupling (~11 Hz).[36] ^{1}H−^{1}H NOESY and ^{1}H−^{1}H COSY NMR analyses were carried out to identify which of the double bonds had undergone isomerization in each of the isomers.

The two sets of aromatic protons in the ^{1}H NMR spectra of the isomers could be classified as those appearing on the methoxyphenyl and cyanophenyl by comparison with model compounds such as 4-methoxycinnamaldehyde and 4-cyanobenzyl bromide, respectively, as shown in Figure 4. Whereas H1 and H2 belong to the methoxyphenyl moiety, H3 and H4 appear on the cyanophenyl ring.

The structures of the two possible photoisomers (*EZ* and *ZE*) are shown in Figure 3. ^{1}H−^{1}H NOESY NMR spectrum (Figure 5), which shows a spatial interaction of the *E*-olefinic doublet proton (Ha, δ 6.76) with one of the protons (H1, δ 7.37) appearing on the methoxyphenyl group, suggests that the isomer may be assigned an *EZ* configuration. Further confirmation on the assignment was obtained by observing a spatial interaction between the *Z*-olefinic doublet (Hd, δ 6.4) and one of the protons on the cyanophenyl ring (H3, δ 7.5).

In the ^{1}H−^{1}H COSY NMR spectrum (Figure 6) of the *EZ* isomer, Ha was found to couple with the double doublet olefinic proton (Hb, δ 7.15) and similarly Hd coupled with the triplet olefinic proton (Hc, δ 6.53). In the *EZ* isomer, Hc couples with Hb and Hd with identical ^3J-coupling constant values and hence appears as a triplet, unlike in the *EE* isomer. The ^{1}H−^{1}H COSY NMR spectrum also showed that the double doublet olefinic proton (Hb, δ 7.15) coupled with the triplet olefinic proton (Hc, δ 6.53). The couplings between the two types of protons on each aromatic ring was also observed in the ^{1}H−^{1}H COSY NMR spectrum (H1 with

Scheme 1. Photoisomerization of the Diphenylbutadiene Derivatives



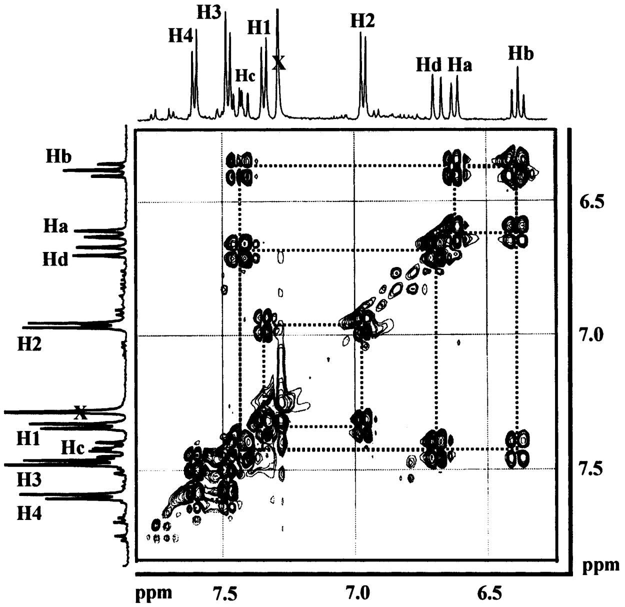


Figure 8. $^{1}H-^{1}H$ COSY spectrum of **BC1-*ZE***.

Table 2. Quantum Yield of Photoisomerization of the Diphenylbutadiene Derivatives in Toluene and Acetonitrile

solvent	BC1	BC4	BC8	BC12
toluene	0.19	0.15	0.13	0.13
acetonitrile	0.16	0.10	0.19	0.15

H2 and H3 with H4). The observation of these couplings formed the basis for labeling the protons in the ^{1}H NMR spectrum of the *EZ* isomer.

The $^{1}H-^{1}H$ NOESY NMR spectrum (Figure 7) of the second photoisomer shows a spatial interaction of the *Z*-olefinic doublet proton (Ha, δ 6.62) with one of the protons on the methoxyphenyl ring (H1, δ 7.34) and that of the *E*-olefinic doublet proton (Hd, δ 6.68) with one of the protons on the cyanophenyl ring (H3, δ 7.47), both confirming the *ZE* configuration of the photoisomer. $^{1}H-^{1}H$ COSY NMR spectrum (Figure 8) of the *ZE* isomer showed that Ha coupled with the triplet olefinic proton (Hb, δ 6.38) and Hd coupled with the double doublet olefinic proton (Hc, δ 7.43). The triplet olefinic proton (Hb, δ 6.38) was also found to couple with the double doublet olefinic proton (Hc, δ 7.43). The couplings between the two types of protons on each aromatic ring was also observed (H1 with H2 and H3 with H4).

Photoisomerization of the EZ and ZE Isomers. HPLC analyses of the photolyzed solutions were carried out with the UV spectrophotometer detector set at 317-nm, which corresponds to the isosbestic point observed in the absorption spectral changes upon photolysis of the *EE* isomer. At this wavelength the extinction coefficients of the isomers are the same and hence the HPLC peak areas will be proportional to the relative concentrations of the isomers. The composition of the photostationary state (PSS1) of **BC12**, in acetonitrile upon photolysis with 360-nm light at 27 °C, was found to be *EZ* (50%), *ZE* (15%), and *EE* (35%) isomers. The quantum yield of (*EE*-PSS1) photoisomerization of these diphenylbutadiene derivatives ranged from 0.1 to 0.2 (Table 2). Although the photoisomers were thermally irreversible, they could be photochemically reverted back to their initial *EE* form by excitation with 266-nm light. Excitation of PSS1 with 266-nm light results in an increase in intensity of the 360-nm band and a decrease in that of the 265-nm band, until a new photostationary state (PSS2), rich in the *EE* isomer (*EZ* (20%) *ZE* (10%) *EE* (70%)), is reached. Complete reversibility could be observed between these two photostationary states. The photoisomerization process of these diphenylbutadiene derivatives may be represented as in Scheme 1.

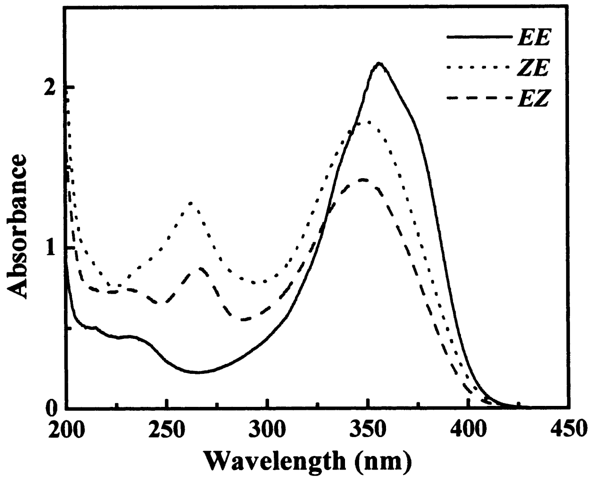


Figure 9. Absorption spectra of the isomers of **BC1** in acetonitrile.

Figure 9 shows the absorption spectra of all the isomers of **BC1**. Absorption changes observed upon photolysis of pure solutions of *EZ* and *ZE* isomers using 266-nm light clearly showed their transformation to the *EE* isomer (Figure 10).

3.3. Photochemical Phase Transitions. None of the photoisomers were found to possess liquid-crystalline phases. For example, the *EZ* isomer of **BC12** shows a sharp crystal to isotropic transformation at 67 °C. Perturbations in molecular structure from linear to a bent shape is known to disrupt long-range ordering, leading to breakdown of the liquid-crystalline phases.[8] The drastic difference in the phase transition characteristics between the all-trans isomer and the photoisomers make these materials highly suitable for study-

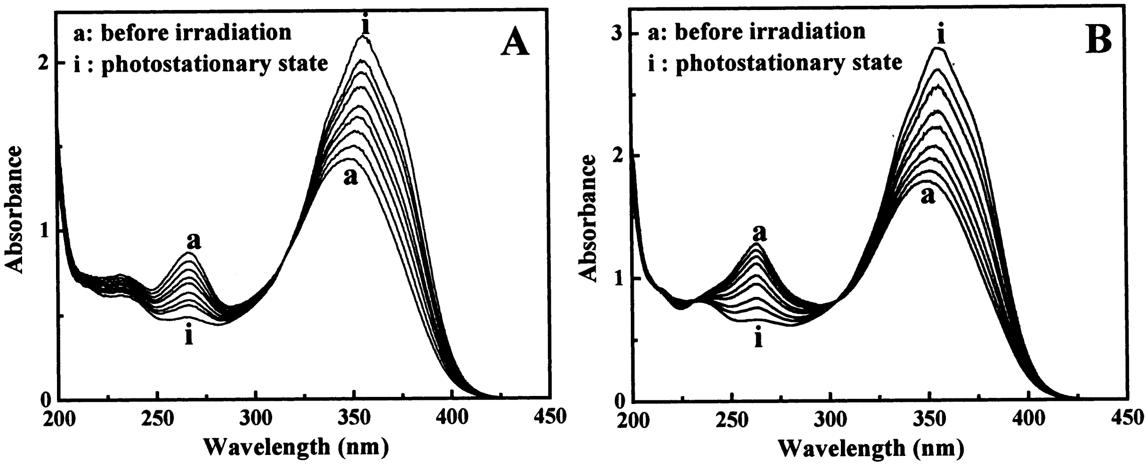


Figure 10. Absorption changes upon photolysis using 266-nm light: (A) acetonitrile solution of **BC1-*EZ*** and (B) acetonitrile solution of **BC1-*ZE***.

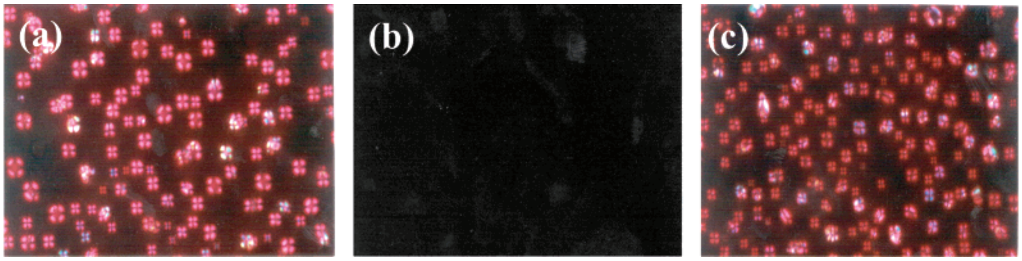


Figure 11. Polarized optical micrographs (400×) depicting the photoinduced isothermal phase transition of **BC12**: (a) S_A phase at 120 °C before photolysis; (b) isotropic state at 120 °C obtained upon photolysis using 360-nm light; (c) S_A phase at 120 °C regenerated upon photolysis of the same film at room temperature (27 °C) using a 266-nm laser.

ing photoinduced phase transitions. Photoinduced phase transitions in these materials were investigated in thin liquid-crystalline films prepared by slow cooling from their isotropic state between quartz disks. Photolysis of the S_A phase of **BC12** at 120 °C (Figure 11a), using 360-nm light, results in a destruction of the LC texture and isothermal formation of the isotropic phase (Figure 11b). HPLC analysis of the photolyzed film (isotropic state) indicated that the isomer composition was similar to that at PSS1 obtained in the corresponding solution phase experiment. The photolyzed mixture transforms sharply from its crystalline to isotropic phase at 80 °C and does not possess an LC phase. Similarly, photoinduced isothermal phase transitions were observed for the *EE* isomers of other derivatives also. The photochemically induced isotropic phase was found to be thermally irreversible in all cases.

Photolysis of the isotropic phase held at 120 °C did not lead to recovery of the S_A phase. However, photolysis of the isotropic mixture at room temperature (RT, 27 °C), where it exists in its crystalline form, using a 266-nm laser (fourth harmonic of Nd:YAG, pulse width of 10 ns, 15 mJ), for 20 s results in the formation of a material which possesses a clear S_A phase with phase transition temperatures matching that of the *EE* isomer of **BC12** (Figure 11c). Steady-state photolysis using low-intensity 265-nm light did not result in recovery of the S_A phase. Due to the lowered efficiency of photoconversion in the solid state, high-intensity light is required for the regeneration of the S_A phase.

HPLC analysis of a laser-photolyzed sample of the isotropic mixture in the solid state showed a near complete conversion (>95%) to the *EE* form upon photolysis with a 266-nm laser, in contrast to that observed in the solution phase experiment (Figure 12). This can be understood on the basis of the dependence of photoisomerization on the viscosity of the medium. Whereas trans−cis isomerization is prevented in a frozen medium, cis−trans isomerization remains feasible, resulting in stereospecific isomerization. This aspect of photoisomerization of polyenes is well-documented.[40,43−45] For example, the photoisomerization of trans-stilbene decreases rapidly upon an increase in solvent viscosity and is stopped upon freezing of the sample.[43,44] The photoisomerization of the cis isomer of stilbene on the other hand remains observable, even in the frozen

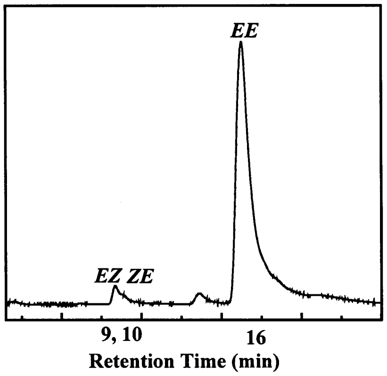


Figure 12. HPLC trace of the regenerated LC state (*EE* form >95%) of **BC12** obtained upon 266-nm laser photolysis of the isotropic state.

---

(43) Dellinger, B.; Kasha, M. *Chem. Phys. Lett.* **1976**, *38*, 9.

(44) Sun, Y.-P.; Saltiel, J.; Hoburg, E. A.; Waldeck, D. *J. Phys. Chem.* **1991**, *95*, 10336.

media. A similar effect of the viscosity of the medium on the stereoselectivity of photoismerization of polyenes has been reported.[45]

Photoswitching of the LC phase was further confirmed using the pure *EZ* photoisomer of **BC12**, which does not possess a liquid-crystalline phase. Photolysis, using a 266-nm laser, of the crystalline state of the *EZ* isomer, results in the formation of a material that shows an S_A phase with phase transition temperatures similar to that of the *EE* isomer of **BC12**.

4. Conclusion

In summary, we have demonstrated, for the first time, photochemically induced isothermal phase transitions in alkoxy-cyano-substituted diphenylbutadiene derivatives. Since the phototransformations are thermally irreversible, switching between the mesogenic and isotropic phases remains purely photon-controlled in these materials. These properties of the alkoxy-cyano-substituted diphenylbutadienes make them uniquely suited for the design of a wide variety of photoactive liquid crystals, including chiral nematic and ferroelectric liquid crystals. Studies on these aspects as well as on enhancing the range of the phase transition temperatures of these materials are in progress.

Acknowledgment. The authors wish to thank CSIR and DST for financial assistance. The NMR facility provided at SIF, IISc Bangalore, is also gratefully acknowledged. This is contribution No. RRLT-PPD(PRU)-148 from the Regional Research Laboratory, Trivandrum, India.

CM020710Z

---

(45) Liu, R. S. H.; Asato, A. E.; Denny, M. *J. Am. Chem. Soc.* **1983**, *105*, 4829.