minor adduct), 3.25 (s, OMe, major adduct), 7.22–7.40 (m, Ph). Anal. Calcd for $C_{14}H_{20}O$: exact mass 204.1514, found 204.1511.

1-Methoxy-1-phenyl-2-carbomethoxycyclopropanes (6). These isomeric compounds were formed from diazirine **1** and methyl acrylate (containing a trace of hydroquinone monomethyl ether as a stabilizer) by thermolysis at 45 °C in 8.9% yield[45] and a 1:4 isomer distribution. They were purified by Kugelrohr distillation at 40 °C/0.03 mmHg. Their capillary GC retention times were 3.59 and 4.91 (major adduct) min: ^{1}H NMR ($CDCl_3$, 400 MHz) δ major isomer 1.50 (m, 1 H, CH), 1.97 (t, J = 7.5 Hz, 1 H, CH), 2.12 (t, J = 7.5 Hz, CH), 3.20 (s, 3 H, OMe), 3.74 (s, 3 H, COOMe), 7.35 ("s", 5 H, Ph), minor isomer 1.50 (m, CH), 1.79 (t, J = 7.5 Hz, 1 H, CH), 2.33 ("t", J = 7.5 Hz, 1 H, CH), 3.14 (s, 3 H, OMe), 3.43 (s, 3 H, COOMe), 7.30 (m, 5 H, Ph). Anal. Calcd for $C_{12}H_{14}O_3$: exact mass 206.0943, found 206.0931.

1-Methoxy-1-phenyl-2-cyanocyclopropanes (7). These isomeric compounds were formed from diazirine **1** and acrylonitrile (stabilized as for acrylate) by thermolysis at 45 °C in 22% yield[45] and a 1:2.2 isomer distribution. They were purified by Kugelrohr distillation at 40 °C/0.03 mmHg. Their capillary GC retention times were 3.36 and 4.18 (major adduct) min: IR 2230 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.57–2.03 (5 multiplets, CH's, both isomers, 3 H), 3.17 (s, minor adduct), 3.32 (s, major adduct) (total 3 H, OMe's), 7.25–7.50 (m, 5 H, Ph). Anal. Calcd for $C_{11}H_{11}NO$: exact mass 173.0841, found 173.0824.

Competition Experiments. Diazirine **1** (~0.6 mmol in pentane) was added to a weighed, binary mixture of the two alkenes, cooled to −40 °C, and contained in a screw-top Carius tube. The alkenes were each present in at least 9-fold molar excess, relative to **1**. A magnetic stirring bar was added, the tube was sealed and covered with Al foil, and its contents were stirred at 25 °C for ~90 min, at which time the yellow-green color of **1** had bleached and N_2 evolution had ceased. The gross weight of the reaction vessel was checked several times to ensure that leakage of gaseous alkenes had not occurred. After completion of the reaction, the tube was cooled to −25 °C and opened, and the contents were warmed to ambient temperature, stirred for ~2 h, and analyzed by capillary GC using a Varian Model 3700 flame-ionization unit. Injector and detector temperatures were 250 and 300 °C, respectively. Other conditions are given above. The detector was calibrated with authentic samples of the products **2**–**7**. For further methodology, control experiments, and the method of calculating k_{rel}, see the Results section.

Absolute Rate Studies. The laser equipment and methodology are described in the Results section.

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Laser Flash Photolysis Study of Triplet States in Aligned Liquid Crystalline Media

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Abstract: A simple method for the laser flash photolysis study of aligned liquid crystals is reported. The formation of triplets of zinc tetraphenylporphyrin and 2-piperidinoanthraquinone in aligned nematic and isotropic phases of some commercially available cyanobiphenyl liquid crystals was studied. An observed increase in triplet–triplet absorption intensity in the nematic phase compared to the isotropic phase is entirely due to improved alignment and absorption of the polarized laser emission and contradicts a previously reported finding of enhancement of intersystem crossing efficiency. The variation of triplet lifetimes with temperature indicates that the microviscosity unlike the measured macroviscosity does not change drastically at the nematic–isotropic transition temperatures. At high laser intensities local melting of the nematic-to-isotropic phase was observed because of internal conversion–radiationless decay.

There have been a few reports on the use of thermotropic liquid crystals as solvents for various photochemical reactions.[1-8] In a laser flash photolytic study,[1] Levanon observed that the triplet absorption yield of zinc tetraphenylporphyrin (ZnTPP) in a magnetically aligned nematic biphenyl showed a marked enhancement below the clearing point of the nematic. This was attributed to the improved alignment of the optical transition and more significantly to an increased intersystem crossing efficiency in the ordered nematic phase. Such an observation could potentially be very important in the use of liquid crystalline solvents to selectively alter the photophysical and/or photochemical behavior of guest molecules. Very recently Leigh[5] investigated the unimolecular triplet decay of a series of alkoxypropiophenones in liquid crystalline phases. They believed that the inhibiting effect of an unaligned nematic liquid crystal solvent on a bond rotation (which is required for intramolecular triplet quenching) was primarily influenced by the microviscosity.

We have been interested in the laser flash photolysis study of various guest molecules in liquid crystalline solvents. One of the major problems involved in this system is the opacity of liquid crystals in the nonaligned state. In the present work, we report a simple method for the laser flash photolysis study of aligned liquid crystals. Using this methodology, we have looked into the temperature and phase dependent triplet formation of ZnTPP in some commercially available nematic liquid crystals in order to evaluate the potential effect of anisotropic and order properties of liquid crystals upon excited state–excited state or excited

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state–ground state interaction. To do this, both the nematic and isotropic phases of several different nematic liquid crystals were examined (as a function of temperature). For similar reasons, we have also looked into the triplet formation of 2-piperidinanthraquinone (2-PAQ), which unlike the disc-shaped ZnTPP has a much better dichroic ratio.

In addition to the foregoing, we wished to evaluate the effect of temperature upon order in the nematic phase and the effect of a phase change on the viscosity (and any accompanying photophysical changes of the guest). Finally, we wished to evaluate the effect of laser intensity and radiationless processes regarding a guest upon properties of a liquid crystal host.

Experimental Section

ZnTPP was used as obtained from Aldrich. 2-PAQ was synthesized by a known procedure involving the refluxing of 2-chloroanthraquinone with a large excess of piperidine for several hours. The crude product was recrystallized from ethanol and chromatographed on an alkaline alumina from carbon tetrachloride and eluting with a 1:1 mixture of acetone and carbon tetrachloride.[9] The liquid crystal solvents, 4-cyano-4′-*n*-hexylbiphenyl (K18), 4-cyano-4′-*n*-pentylbiphenyl (K15), and a eutectic mixture E7, obtained from Merck, were used without any further purification. The transition temperatures from nematic (N) to isotropic (I) for K18, K15, and E7 are 29, 35.3, and 60.5 °C., respectively.

The laser flash experiments were carried out in demountable, variable path length cells with Pyrex windows. The path lengths of these cells could be varied by using Teflon spacers. The path length used in the present work was 0.1 mm. Alignment of the liquid crystal was achieved by using the technique of rubbing the cell plates with 0.1 μm of diamond paste.[10] The efficiency of alignment was checked by measuring the dichroic ratio of the commercially obtained anthraquinone dye, D16 (Merck). An order parameters of 0.61 compared to the 0.65 given by the manufacturers was obtained, indicating that our procedure gave near maximal alignment. ZnTPP was dissolved in the liquid crystal to give optical densities of 0.1–0.2 at 532 nm in a 0.1 mm path length ([ZnTPP] = 1–2 mM) cell and 2-PAQ solutions in liquid crystals were adjusted to have optical densities of 0.45–0.5 at 532 nm ([2-PAQ] = 0.01–0.02 M) in the same cells. Both ZnTPP and 2-PAQ are highly soluble in the liquid crystal solvents used. The concentrations used in the present work are much below the saturation concentration. The clearing point temperatures are not affected (± 0.5 °C) at the concentrations used. The liquid crystals were degassed in a syringe in their isotropic phase prior to injection into the cells. The efficiency of this method of degassing was checked by comparing triplet lifetimes in isotropic solvents in the above setup. Tris(2,2′-bipyridine)ruthenium(II) ion in water gave a lifetime of 0.6 μs which compares well with the literature value of 0.67 μs.[11] The temperature of the cell was controlled to ±0.2 °C by using a water-circulating jacket. The cells were allowed to equilibrate for ≥5 min, at each temperature. Above the clearing point temperature of the various nematics, the melting process was also confirmed visually. Spectra were measured in Hewlett Packard 8450A and Cary spectrophotometers.

The viscosity of K15 was measured over the temperature range of 22–50 °C with a "falling ball type" viscosimeter obtained from Gilmont Instruments, Inc. The variation in density of K15 (1.019 at 29 °C) was observed to be less than 0.01 over the temperature range studied.

The Nd:YAG laser setup has been described elsewhere.[12] The 532-nm emission of the laser is greater than 90% polarized. The cells were placed normal to the unpolarized analyzing beam with the nematic alignment vector parallel to the direction of polarization of the exciting laser emission. The incident laser beam enters through the front face of the cell at an angle of ~20° to the analyzing beam. The laser beam diameter was 0.8 cm and had an initial energy of ~90 mJ per pulse. The laser energies were controlled by using wire mesh screens.

No transient absorptions were observed on exciting with the 532 nm laser emission for any of the liquid crystal solvents used in the absence of ZnTPP or 2-PAQ.

Table I. Absorption Spectra and Photophysical Data of ZnTPP and 2-PAQ in Aligned Liquid Crystalline Media as a Function of Temperature

liquid crystal[a]	temp/°C	A^b	ΔOD (λ 470)	β^c	$\tau/\mu s$	η^d/cP
ZnTPP/E7						
N	30	1.44	0.047	1.52	112	
N	40	1.40	0.045	1.45	87	
N	50	1.37	0.043	1.39	65	
N	60	1.30	0.040	1.29	50	
I	67	1.00	0.031	1.00	45	
ZnTPP/K15						
N	26	1.31	0.025	1.38	149	22.8
N	33	1.26	0.023	1.28	123	18.7
I	39	1.00	0.018	1.00	103	19.8
I	39	1.00	0.018	1.00	80	13.2
ZnTPP/K18						
N	26	1.22	0.024	1.25	164	
I	33	1.00	0.019	1.00	134	
2-PAQ/K18						
N	26	1.55	0.012 (λ = 560)	1.50	55	
I	33	1.00	0.008 (λ = 560)	1.00	45	

[a] N → I transition temperature for E7 60.5 °C, K15 35.5 °C, and K18 29 °C. [b] A = OD ZNTPP (2-PAQ) in nematic phase/OD ZnTPP (2-PAQ) in isotropic phase. [c] B = ΔOD in nematic phase/ΔOD in isotropic phase. [d] Macroscopic viscosity (see Experimental Section).

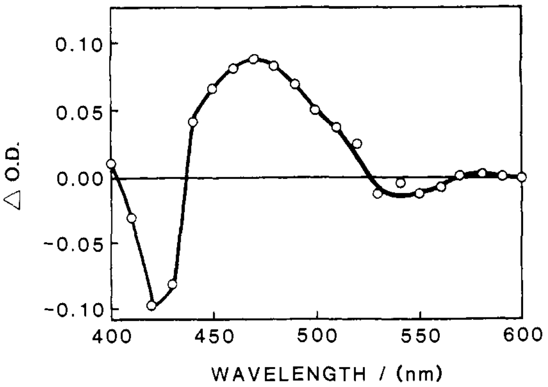

Figure 1. Triplet–Triplet difference absorption spectra of ZnTPP in nitrogen saturated nematic E7, 1 μs after laser pulse.

Results and Discussion

The absorption spectra of ZnTPP and 2-PAQ were measured at different temperatures with use of polarized light with the direction of polarization parallel to the alignment of the crystal. The absorption spectra of ZnTPP and 2-PAQ are similar to the reported spectra of these compounds in isotropic solvents.[13,14] The λ_{max} of the long wavelength absorption of 2-PAQ which is solvent dependent was 468 nm in the liquid crystal solvents. Table I lists the ratio, *A*, for the absorption measured at various temperatures in the nematic phase to that measured in the isotropic phase (N → I temperature; K18 = 33 °C, K15 = 39 °C, and E7 = 67 °C). It can be observed that the ratio decreases significantly in the temperature region where the nematic to isotropic transition occurs. It can also be seen that within the nematic phase, this ratio decreases with increasing temperature. This is especially evident in E7 which has a much wider nematic temperature range (−10 to 60.5 °C). These results suggest that the liquid crystal becomes less ordered as the temperature nears the N → I transition temperature.

Laser flash photolysis of ZnTPP in E7 gave rise to a transient absorption. The absorption spectrum of the transient, shown in Figure 1, is identical with the triplet–triplet (T–T) absorption obtained in isotropic solvents[13] and by Levanon in K18[1] and is attributed to triplet formation. Table I also includes the ΔOD measured at 470 nm immediately after the flash (~200 ns) at various temperatures. The ratio, *B*, of ΔOD due to T–T absorption

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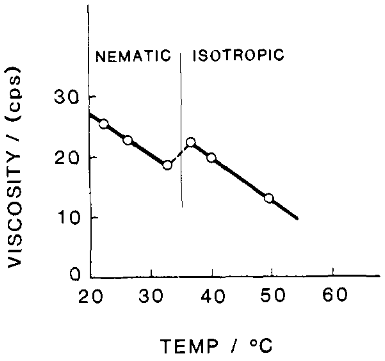

Figure 2. Viscosity of K15 measured as a function of temperature.

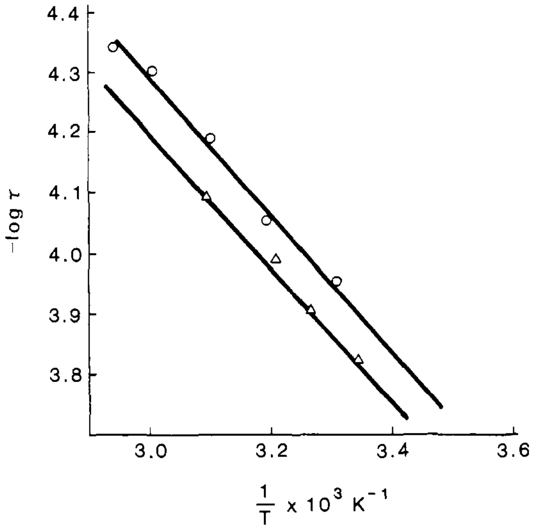

Figure 3. Arrhenius plot ($-\log \tau$ vs. $1/T$) for triplet decay of ZnTPP in (△) K15 and (○) E7.

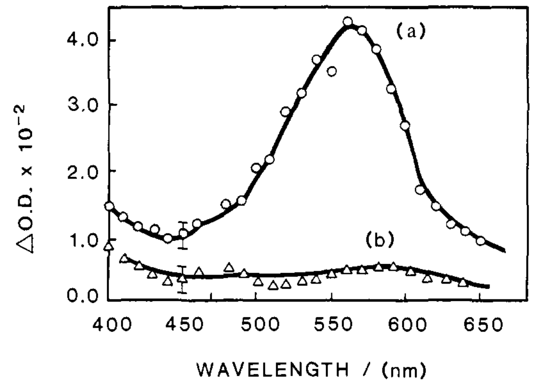

Figure 4. Transient absorption measured at (a) 1 μs and (b) 120 μs after laser pulse (5.7 mJ/pulse) for 2-PAQ in nitrogen-satured nematic K18.

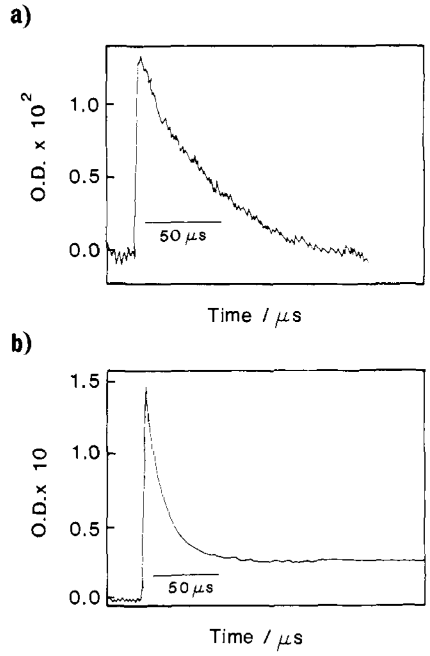

Figure 5. Transient decay in the flash photolysis of 2-PAQ in nitrogen-saturated nematic K18 at laser intensities of (a) 3.7 mJ/pulse and (b) 26.1 mJ/pulse.

at various temperatures to that at the isotropic temperature is also shown in Table I. It can be observed that the ratios, B, measured at temperatures just below the nematic to isotropic transition temperatures for the different liquid crystals correlate well with the corresponding A values, within a ±10% error range. Good correlation is also found for A and B at the other temperatures studied. This strongly implies that the enhancement of T–T absorption in the nematic phase can be entirely attributed to improved absorption of the polarized laser emission in the aligned nematic phase as compared to the unaligned isotropic phase. These results are not in agreement with those of Levanon.[1] We have no evidence for the enhancement of intersystem crossing efficiency for ZnTPP in the nematic phase as compared to that in the isotropic phase in any of the liquid crystal solvents studied.

Table I shows the triplet lifetime of ZnTPP in the different liquid crystal solvents studied. These lifetimes are substantially lower than the natural lifetimes measured in isotropic solvents[13] and are attributed to the difficulty of completely removing oxygen from the solutions in the present setup. The main path of ZnTPP triplet decay in the present experiments is attributed to oxygen quenching. As this is a diffusion-controlled process, the decay lifetimes are expected to be a function of viscosity of the solvent whereby they increase with an increase in viscosity. It is observed in K15 that although the viscosity decreases with increasing temperature within the nematic phase, near the nematic to isotropic transition temperature there is an abrupt increase in viscosity (Figure 2). This phenomenon has been reported earlier[15,16] for some different liquid crystals. The triplet lifetime in K15, however, generally decreases with increasing temperature even at temperatures close to the nematic-to-isotropic transition and smoothly continues through the phase transition. These results suggest that the triplet lifetimes is not dependent on the measured macroviscosity of the liquid crystal. Figure 3 shows the Arrhenius plot for triplet decay of ZnTPP in K15 and E7. The activation energies are 5.0 ± 0.1 kcal in K15 and E7. The smooth continuity in triplet lifetimes going from the nematic to the isotropic phase indicates that unlike the macroviscosity, the microviscosity imposed on ZnTPP and oxygen molecules by K15 decreases uniformly through the phase transition. The triplet lifetimes also decreased uniformly with increasing temperature for all of the other liquid crystal solvents as for K15.

Figure 4 shows the transient absorption spectrum obtained in the flash photolysis of nitrogen saturated solution of 2-PAQ in K18 in the nematic phase. The absorption spectrum is identical with the T–T absorption of 2-PAQ obtained in isotropic solvents.[17] The rate of transient decay is also enhanced by oxygen. The intensity of T–T absorption of 2-PAQ in the nematic phase is greater than that in the isotropic phase by a factor of 1.5 (Table I). This corresponds very closely to the ratio of 1.55 obtained for the ground-state absorption of polarized light by 2-PAQ in the aligned nematic (with the alignment vector parallel to the plane of polarization) and to that by 2-PAQ in the isotropic phase (Table

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I). As in the ZnTPP case no enhancement of intersystem crossing efficiency was observed in the aligned nematic. Thus the results regarding 2-PAQ compared to ZnTPP show more clearly that the enhancement of the T–T absorption intensity in the nematic phase is the result of increased absorption of the polarized laser light.

It was observed in the 2-PAQ/K18 system that upon flashing at high laser intensities at the same macroscopic temperature, the triplet lifetime decreased considerably. At 26 °C, the lifetime decreased from 55 μs for a 4.1% laser screen (~3.7 mJ/pulse) to 13 μs for a 29% laser screen (26.1 mJ/pulse). The decay process, however, remained first order (Figure 5a,b); hence, the decreased lifetime cannot be attributed to increased triplet–triplet annihilation. The transient absorption also does not return to the original base line at higher input intensities, leaving a positive optical density change at long time scales (>100 μs), Figure 5b. The optical density changes at these longer times were relatively constant in the wavelength region studied (Figure 4b). Similar experiments were carried out in the isotropic phase of K18, where it was observed that the triplet lifetime also decreases with increasing dose. At the highest laser dose used (~68 mJ/pulse) the lifetime was 10 μs compared to 45 μs observed at low dose (~4 mJ/pulse). Also at the higher doses considerable second-order contribution was observed in the decay kinetics. However, the transient absorption always decayed to the base line in contrast to the results in the nematic phase.

These results are interpreted as follows. At high laser energies, the total electronic energy degraded by the radiationless transitions of 2-PAQ is sufficient to locally melt the liquid crystal. The subsequent cooling of the isotropic phase to the nematic phase leads to a permanently scattering nonaligned texture as indicated by the decreased optical transmission at longer times. The decay of the transient absorption to the base line in the isotropic phase even at laser energies much higher than those used in the nematic phase study confirms the fact that the positive ΔOD changes observed in the nematic phase are due to a scattering texture and not due to a permanent product formation. Results similar to those in K18 were observed for K15. The shape of the curve of ΔOD vs. time will vary as a function of the relative values of the rates for triplet decay and cooling of the isotropic phase to the scattering phase. If the rates were comparable, a multiexponential decay would be observed. Our results in Figure 5 show that the triplet decays by a clean first-order process to a scattering phase, suggesting that the rate of cooling is at least an order of magnitude faster than that for triplet decay.

A laser dose dependence of the decay rate of the 2-PAQ triplet was observed in the nematic and isotropic phase. A similar dependence on excitation dose was also observed in benzene in an earlier pulse radiolysis study.[17] Therefore it is apparent that the excitation energy dependency of the triplet decay rate (shortening of the lifetime as the excitation energy increases) is inherent to the photophysics of 2-PAQ and does not depend specifically on a liquid crystalline phase.

We may note that the reversible melting/cooling by laser excitation of a dye/liquid crystal mixture, leaving behind a scattering texture, has important applications in the field of display devices.[18]

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Dynamics of Atropisomerization of 1,1′-Binaphthyl in Several Nematic Solvents. Rate Enhancement by a Solid Phase[1]

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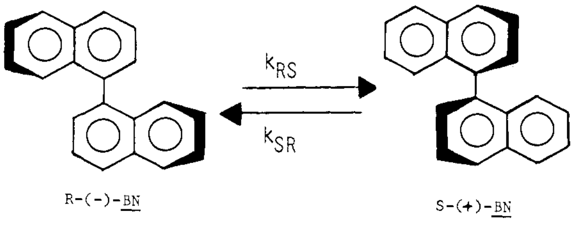
Abstract: The rates of atropisomerization of (*S*)-(+)-1,1′-binaphthyl (BN) are compared in six nematic phases and in the solid phase of *p*-methoxybenzylidene-*p*-*n*-butylaniline. The influence of each phase on the activation parameters for atropisomerization are correlated with the solvent molecular structures. The results in the nematic and solid phases are interpreted in terms of the degree to which the solvent matrices flatten the angle between the naphthyl rings of BN.

Since its spontaneous optical resolution by Wilson and Pincock,[2] 1,1′-binaphthyl (BN) has been employed extensively to investigate the factors which affect hindered rotation about σ-bonds.[3,4] Its low enthalpy of activation ($\Delta H^{\ddagger}$) for atropisomerization, ca. 22 kcal/mol in a wide variety of isotropic solvents,[5] allows the kinetics of naphthyl ring rotations in BN to be followed conveniently near room temperature (eq 1).



(1)

In a previous study, we suggested that rate enhancements observed for atropisomerization of BN in cholesteric mesophase solvents can be attributed to solvent-induced compression of the angle (θ) between the two naphthyl rings.[3] In principle, the same factors should be operative in nematic mesophases; also, in many respects, cholesteric phases are only twisted nematics.[6]

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