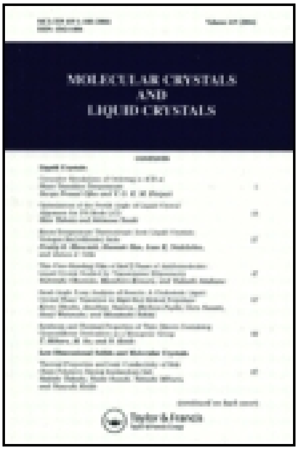

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Liquid-Crystalline Solvents as Mechanistic Probes. 10. Dynamics of Intramolecular Quenching of Pyrenyl Fluorescence in the Liquid-Crystalline and Isotropic Phases of a Cholesteric Solvent[1]

V. C. Anderson [a] , B. B. Craig [b] & R. G. Weiss [a]
[a] Department of Chemistry, Georgetown University, Washington, D.C., 20057
[b] Naval Research Laboratory, Washington, D.C., 20375

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Liquid-Crystalline Solvents as Mechanistic Probes. 10. Dynamics of Intramolecular Quenching of Pyrenyl Fluorescence in the Liquid-Crystalline and Isotropic Phases of a Cholesteric Solvent[1]

V. C. ANDERSON, B. B. CRAIG[§] and R. G. WEISS*
Department of Chemistry, Georgetown University, Washington, D.C. 20057

(Received January 4, 1983)

The effect of cholesteric order in a 59.5/15.6/24.9 (w/w/w) mixture of cholesteryl oleate/cholesteryl nonanoate/cholesteryl chloride (*CM*) on the intramolecular fluorescence quenching of 1,3-bis(1-pyrenyl) propane (*P3P*) has been explored. A comparison with fluorescence quenching of N,N-dimethyl-4-[3-(1-pyrenyl)propyl]aniline (*P3D*) in *CM* is made. From the Arrhenius activation parameters for quenching in the cholesteric and isotropic phases, it is concluded that the motions which take the ground state conformers of *P3P* to their quenching transition state are nearly impervious to macroscopic *CM* mesophase order: in the cholesteric phase, $E_a' = 10.5 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1 \pm 1$ eu; in the isotropic phase, $E_a' = 10.0 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0 \pm 0.5$ eu. An explanation of these results is advanced.

INTRODUCTION

The effects of solvent anisotropy, such as those provided by liquid-crystalline media, upon dynamic and steady-state quenching of electronically excited molecules is an area of increasing interest. Recently, comparing data from the cholesteric and isotropic phases of a 59.5/15.6/24.9 (w/w/w) mixture of cholesteryl oleate/cholesteryl nonanoate/cholesteryl

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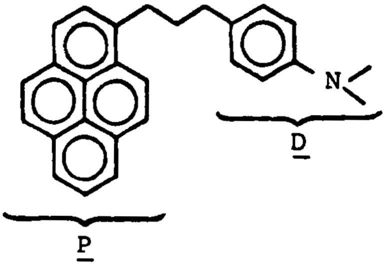
[§] B. B. Craig's present address is Naval Research Laboratory, Washington, D.C. 20375.

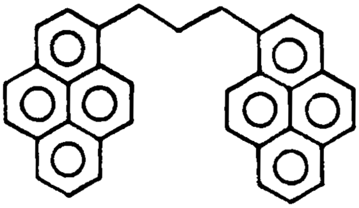
chloride (*CM*), we concluded that phase order does influence the ease with which a pyrene singlet can be quenched intermolecularly by 5α-cholestan-3β-yldimethylamine (*CA*):[2] the attainment of the ^{1}pyrene-*CA* quenching transition state is made more difficult by cholesteric phase order. The influence of the solvent anisotropy is evidenced by the differences measured in the Arrhenius activation parameters for quenching in the cholesteric and isotropic phases of *CM*. The same techniques, when applied to the intermolecular quenching of pyrene singlets by pyrene lead to a completely different conclusion:[3] the mesophase order of *CM* plays a negligible role in the dynamics of the quenching process. Apparently, the ^{1}pyrene-pyrene collisional orientations necessary for quenching are those which are favored in the mesophase.

In other dynamic studies, we have investigated the extent to which cholesteric order of *CM* affects *intramolecular* pyrenyl singlet (^1P) fluorescence quenching by an aromatic amino group (*D*) in N,N-dimethyl-4-[3-(1-pyrenyl)propyl]aniline (*P3D*).[1] In contrast to the intermolecular ^{1}pyrene quenching by *CA*, the intramolecular ^{1}P suppression of fluorescence by *D* is only slightly sensitive to the phase of *CM*. As with ^{1}pyrene quenching by pyrene, the slight phase dependence in the Arrhenius parameters seems more compatible with changes in viscosity than in phase order.

In order to test the validity of this conclusion and to determine the extent to which the nature of the chain end-groups influences the efficiency of intramolecular quenching, we have studied the effect of *CM* phase upon the dynamics of 1,3-bis-(1-pyrenyl) propane (*P3P*) fluorescence suppression. The results are reported here.[4]



P3D



P3P

EXPERIMENTAL

Instrumental and general experimental procedures have been described previously.[1-3] 1,3-Bis-(1-pyrenyl) propane, mp 162.5-164.5°C (lit.[5] mp

163.5°C), was obtained from Molecular Probes and used without further purification. HPLC analysis at 254 nm using a Waters Rad-Pak B silica column and 1/10 (v/v) chloroform/*n*-hexane as eluant showed *P3P* to be ca 99% pure. Purifications of cholesteryl oleate, cholesteryl nonanoate, and cholesteryl chloride were performed by previously developed procedures.[2]

RESULTS

Physical characteristics of P3P doped CM. Undoped *CM* exhibits an enantiotropic cholesteric phase from below ambient room temperature to 58°C.[1] Addition of 10^{-4} *M P3P* (the concentration at which all quenching experiments were conducted)[6] depresses the optically-detected transition temperature by less than 1°. Addition of 0.1 *M* (4.4% by weight) results in a 10.5° depression, very similar to the 11.0° depression observed when 4.3% of pyrene is doped into *CM*.[3]

The pitch band of undoped cholesteric *CM* varies slightly with temperature. For example, the reflectance maxima (λ) at 29°C and 48°C are 485 ±5 nm and 520 ±5 nm, respectively.[7] Addition of 0.1 *M P3P* produces small changes in the pitch band: λ = 507 ±5 nm (27°C), 533 ±5 nm (36°C), and 545 ±5 nm (40°C). The changes in the pitch band upon addition of a comparable weight of pyrene (0.22 *M*) are larger (λ = 565 ±5 nm at 29°C and 620 ±5 nm at 44°C), but the sensitivity of the pitch to temperature is very similar with the two dopants.

The polarity of the local environment which the pyrene molecule experiences can be established from its fluorescence spectrum through comparison of the emission intensities of vibronic bands.[8] Although this is a site-averaged measurement, it indicates that a pyrenyl lumophore in *CM* resides primarily in a low-polarity, hydrocarbon-like region ($\varepsilon < 2$).

Emission studies of P3P. The uncorrected steady-state absorption, excitation, and emission spectra of 10^{-4} *M P3P* in cholesteric *CM* and the emission spectrum of 10^{-5} *M P3P* in *n*-hexane[9] are reported in Figure 1. Nearly identical absorption and excitation spectra and emission spectra with a smaller fraction of the red-shifted component are obtained in the isotropic phase of *CM*. The similarity between the absorption and excitation spectra in *CM* is an indication, but not in itself a proof, that ground state association between pyrenyl groups of *P3P* is unimportant in *CM*. This conclusion is affirmed by other experiments (*vide infra*).

The broad, structureless emission which is red-shifted from the structured monomer fluorescence arises from intramolecularly-formed pyrene excimers.[10] The portion of the total emission from the excimer in cholesteric *CM* is significantly less than that found in *n*-hexane. It is reasonable

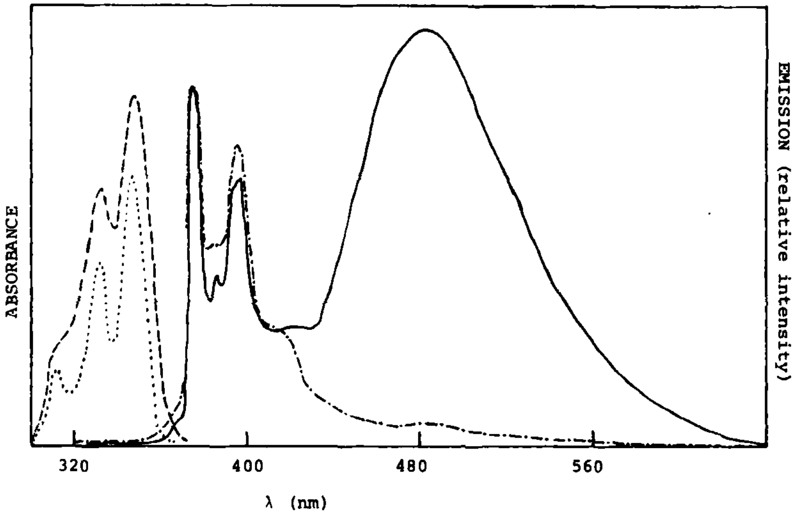


FIGURE 1 Uncorrected emission (λ_{excit} 310 nm;–·–·–), excitation (λ_{emis} 400 nm;– – –), and absorption (λ >300 nm;·····) spectra of 10^{-4} *M P3P* in deaerated *CM* (ambient room temperature) and emission spectrum (λ_{excit} 310 nm;———) of 10^{-5} *M P3P* in nitrogen-saturated *n*-hexane at 30°C.

to ascribe at least a part of this difference to the disparity in viscosity of the two media.[11]

Excitation spectra of *P3P* recorded at various cholesteric temperatures and employing several monitoring wavelengths in the monomer and excimer emission regions ($\lambda_{emission}$ 375, 385, 460, and 480 nm) are indistinguishable. This suggests that several distinct ground state conformers of *P3P* are not precursors to the emissive states. Possibly, one family of (rapidly equilibrating) conformers exists. With other bichromophoric systems dissolved in isotropic solvents, evidence for more than one discrete ground state conformer (each of which forms the same excited state complex but at a different rate) has been gathered.[12]

Further evidence for the presence of no more than one family of ground state *P3P* conformers *and* for the irreversibility of excimer formation is found in dynamic measurements of emission intensity. The monoexponentiality of ^1P fluorescence decays in both cholesteric and isotropic *CM* suggests that all ground state conformations, upon vertical excitation, have an equal probability of forming the equilibrated excimer geometry. This monoexponentiality and the lack of an instantaneous *P3P* excimer emission (*vide infra*) also preclude a conformation in which the pyrenyl groups are associated with one another prior to excitation.

Plots of ln τ' (where τ' is the ^1P lifetime) versus the inverse of temperature for 10^{-4} *M P3P* and *P3D* in *CM* are presented in Figure 2. The *P3P* data can be fit reasonably to two straight lines which intersect ca 3° from the optically-detected phase transition temperature. No discernible slope change occurs with *P3D* as the solvent changes from cholesteric to isotropic.

Kinetic treatment of the rate data for P3P. A standard mechanism for intramolecular quenching of *P3P* (and *P3D*) in a nonpolar solvent is

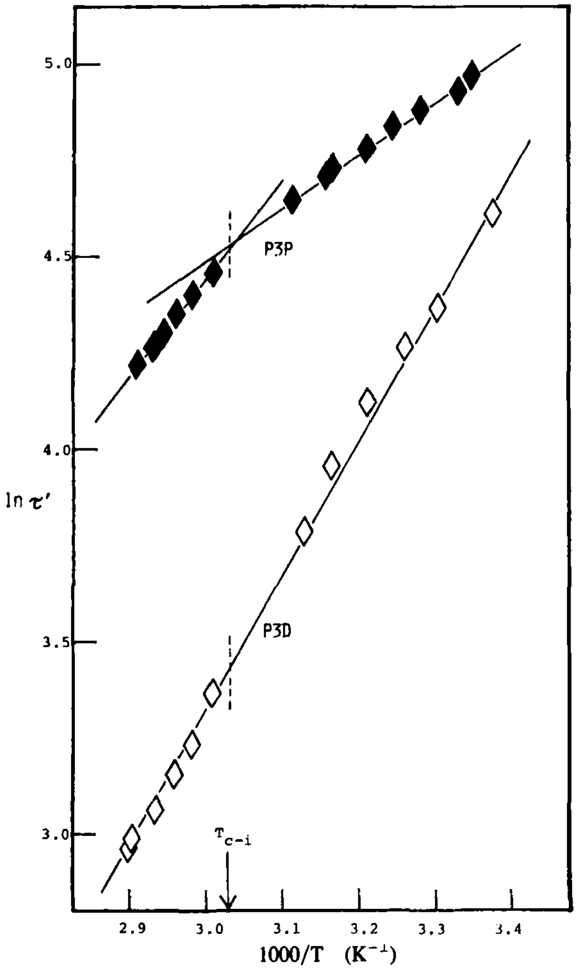
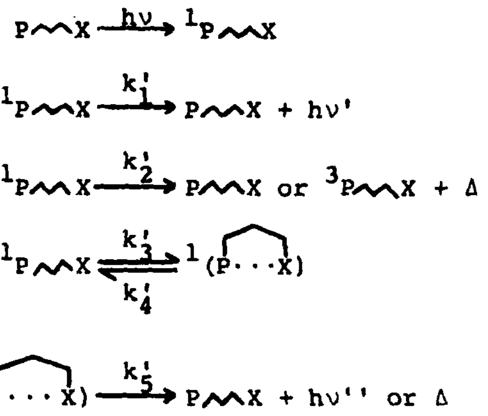


FIGURE 2 Natural logarithm of decay constants vs the inverse of temperature for 10^{-4} *M P3P* (◆) and *P3D* (◇) in *CM*.

presented in Scheme 1. The sum of the monolumophoric deactivation rate constants, $k_1' + k_2'$, is taken to be the inverse of the lifetime of 1-ethylpyrene.[1] Zachariasse *et al.*[14] have shown that *P3P* excimer formation in methylcyclohexane is irreversible, such that $k_3'/k_4' \cong 50$ at 20°C. In a more viscous, nonpolar solvent like *CM*, k_3'/k_4' will be at least as large. This is corroborated by the previously mentioned single exponential ^{1}P decays observed in *CM*. Thus, τ' is given by Eq. 6 and τ_E', the excimer lifetime, by Eq. 7.



(1)

(2)

(3)

(4)

(5)

$$1/\tau' = k_1' + k_2' + k_3' \qquad (6)$$

$$1/\tau_E' = k_4' + k_5' \approx k_5' \qquad (7)$$

$$k_3' = A'\exp(-E_a'/RT) \qquad (8)$$

Scheme 1. Standard Mechanism for Intramolecular Quenching of *P*⁀*X* (X = *P*, *D*) Singlets in Nonpolar Media

Determination of excited state complex lifetimes. The intensity of time-dependent excimer/exciplex emission exhibits a delayed maximum relative to the ^1P emission. Depending upon the value of the magnitudes of the ^1P and excited state complex lifetimes, the rise of the excited state complex emission can reflect either the formation or destruction of the excimer/exciplex state. In *P3D*, the time constant for the rise of the exciplex waveform (τ_R) was determined by standard mathematical techniques[15] to be

TABLE I

Decay Constants for 10^{-4} *M P3P* and *P3D* in *CM*[13]

	P3P	
T(°C)[a]	42.9[b]	63.0[c]
τ'(ns)	113.1 ±2	80.0 ±2
τ_R(ns)	48.3 ±4	50.4 ±4
τ_D(ns)	122.2 ±6	84.4 ±4
	P3D	
T(°C)[a]	46.8[b]	71.5[c]
τ'(ns)	44.3 ±2	20.2 ±2
τ_R(ns)	48.1 ±4	23.4 ±4
τ_D(ns)	87.8 ±4	89.8 ±4

[a] Temperature ±0.5 °C
[b] Cholesteric
[c] Isotropic

within experimental error of the ^1P decay time in both phases of *CM* (Table I). The lifetime of the exciplex is reflected in the decay constant (τ_D) of the exciplex emission waveform. In contrast, τ_D of the *P3P* system is within experimental error of the ^1P lifetime. Then, τ' is given by τ_R. Although τ' of *P3P* is very temperature dependent over the range of this investigation, the value of τ'_E (ca. 50 ns) remains nearly invariant.[16]

Activation parameters for intramolecular quenching in CM. The rate constant for intramolecular quenching (and excimer formation), k'_3, at one temperature was calculated as $1/\tau' - 1/\tau_{EtP}$ (where τ_{EtP} is the lifetime of $10^{-4}M$ 1-ethylpyrene in *CM*). Expressing k'_3 in an Arrhenius form (Eq. 8) and plotting ln k'_3 versus $1/T$ (Figure 3) allow calculations of A' and E'_a in each phase of *CM* (Table 2). The corresponding *P3D* data are included for purposes of comparison.

Use of another model compound, 1-dodecylpyrene, (which allows k'_3 to be extracted in an analogous fashion) leads to slightly different activation parameters for ^1P quenching in *P3X* (*X* = *P* or *D*). In fact, with this model, $\Delta E'_a$ [= E'_a(cholesteraic) − E'_a(isotropic)] and $\Delta\Delta S^\ddagger$ [= $\Delta S^\ddagger$ (cholesteric) − $\Delta S^\ddagger$(isotropic)] of *P3P* are within experimental error of $\Delta E'_a$ and near to $\Delta\Delta S^\ddagger$ of *P3D*: for *P3P*, $E'_a = 15.1 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = +9 \pm 2$ eu in cholesteric *CM* and $E'_a = 11.4 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = +4 \pm 1$ eu in isotropic *CM*; for *P3D*, $E'_a = 11.8 \pm 0.4$ kcal mol^{-1} and $\Delta S^\ddagger = +9 \pm 1$ eu in cholesteric *CM* and $E'_a = 8.1 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = -2 \pm 2$ eu in isotropic *CM*. Thus, although the choice of model is important with respect to the absolute magnitudes of the activation

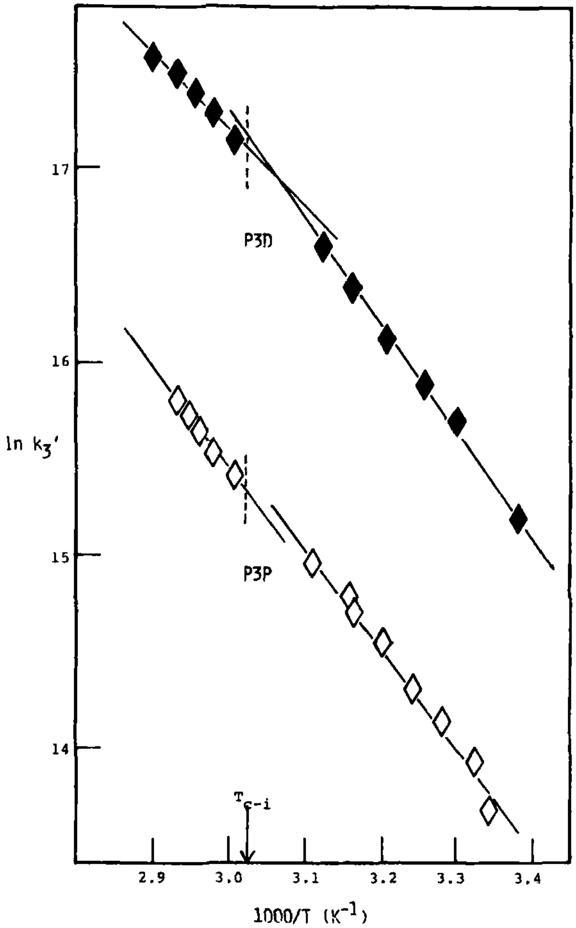


FIGURE 3 Arrhenius plots of 10^{-4} *M* *P3P* (◇) nd *P3D* (◆) in *CM*.

parameters, it does not appreciably affect the conclusions derived from comparisons of those parameters.

While the *EtP* model results in the conclusion that the activation parameters for *P3P* are virtually *CM* phase independent, the 1-dodecylpyrene model predicts that they are slightly phase dependent (in a fashion similar to *P3D*'s dependence). We believe at this time that *EtP* is the more appropriate model for *P3X* compounds and have emphasized data from it throughout. However, we recognize that a better understanding of which model is most appropriate to a given substrate is necessary. Studies to obtain this information are in progress.

TABLE II

Activation Parameters for Intramolecular Quenching of Pyrenyl Singlets of *P3X* (X = *P*, *D*) in *CM* at 10^{-4} *M*

		Cholesteric	
	E'_a, kcal mol^{-1}	A', s^{-1}	$\Delta S^{\ddagger}$,[a] eu
P3P	10.5 ±0.4	$(3.8 \pm 2.6) \times 10^{13}$	1 ±1
P3D	10.8 ±0.3	$(3.5 \pm 1.8) \times 10^{14}$	6 ±1
		Isotropic	
	E'_a, kcal mol^{-1}	A', s^{-1}	$\Delta S^{\ddagger}$,[a] eu
P3P	10.1 ±0.2	$(2.1 \pm 0.5) \times 10^{13}$	0 ±0.5
P3D	7.9 ±0.5	$(4.3 \pm 3.3) \times 10^{12}$	−3 ±1

[a] Calculated from the intercept of a standard Eyring plot

DISCUSSION

Theoretical studies predict that the most likely structure for the *P3P* excimer involves a superposition of the two aromatic systems in a "sandwich-like" geometry.[10a,17] In principle, the stability of the complex is determined by the extent to which the two pi systems overlap. In practice, a stability of <10 kcal mol^{-1} has been calculated from the energies of the ^1P and excimer emissions.[15,18] Since the degree to which the pyrenyl ring systems overlap is of critical importance, conformational (rotational) constraints imposed by the trimethylene chain of *P3P* should strongly influence the quenching process, *perhaps* more strongly than externally applied constraints as manifested by the order of a cholesteric solvent phase.

The lowest energy ground state conformer of *P3P* is believed to include an extended trimethylene chain in which the bulky end groups are spatially removed from one another.[10,19] Space-filling (CPK) models indicate that this conformation or one very similar to it should be favored in cholesteric *CM*, also. If correct, formation of the quenching complex requires *at least* one C–C bond rotation within the trimethylene chain. Such a motion should be sensitive both to the drag of nearby solvent molecules (viscosity) and to local solvent order (anisotropy).

Although the microscopic fluidity of a solute in *CM* is unknown, bulk viscosity measurements on other mesophases[20] indicate that the mobility of *P3P* in the isotropic phase of *CM* is much greater than in its cholesteric phase. It is clear from other studies that pyrene is aligned in a cholesteric phase with its long molecular axis parallel to the long axis of the solvent molecules.[21] Thus, the orientations of individual pyrenyl groups within a *P3P* may be changed when *CM*, as solvent, undergoes a phase change.

Furthermore, the shape changes which occur upon taking the preferred ground state (cylindrical) conformer of *P3P* to its (globular) quenching transition state should be resisted much more by the cholesteric phase of *CM* than by its isotropic phase since a more globular dopant disrupts phase order more than a cylindrical one.[22] These considerations suggest that excimer formation would be less efficient in the cholesteric phase. *However, all of the solvent influences on P3P conformational lability presuppose that the solute can be incorporated into the mesophase matrix without greatly disrupting it.* It remains to be established whether this condition obtains.

Effect of CM on intramolecular excited state complex formation in P3P and P3D. The data presented here demonstrate that the activation parameters for intramolecular *P3P* fluorescence quenching in *CM* are nearly unaffected by solvent order and viscosity differences. At least three explanations for these results are possible: (I) The preferred ground state conformer of *P3P* in both phases of *CM* resembles very closely the quenching geometry (*e.g.*, the lowest energy conformer of *P3P* may have a kinked trimethylene chain which places the pyrenyl end groups in proximity of one another); (II) The rate-controlling step in the quenching process is C—C bond rotation in the trimethylene chain; (III) The presence of a foreign species, *P3P*, disrupts the *local* cholesteric environment to such an extent that it is only weakly anisotropic.

Given the magnitude of the activation energy for quenching, $E_a' \cong 10$ kcal mol^{-1}, it seems implausible that (I) be correct. A slithering motion of the pyrenyl groups with respect to one another would require much less than 10 kcal mol^{-1}, regardless of the phase type.[23] A similar argument can be applied against (II). In "normal" fluid solutions, the energy barriers for rotation about a C–C bond in a hydrocarbon chain are ca 3–5 kcal mol^{-1}.[24] Although it may be argued that the barrier must increase (to 10 kcal mol^{-1}, perhaps) in a viscous, ordered phase like cholesteric *CM*, a completely different reason must be advanced to explain the equally large E_a' in the less-viscous, isotropic phase of *CM*.

Surprisingly, the activation entropies and activation energies for *P3P* fluorescence quenching in CM are nearly phase independent. Were there a significant change in the degree of solvent interaction with ground state *P3P* upon changing the phase, then a quenching transition state common to both phases requires that E_a' and $\Delta S^{\ddagger}$ be phase dependent.[25] The similarity between the activation parameters in the two phases is an indication that excited *P3P* "sees" a local environment which does not depend strongly upon solvent phase. In other unimolecular processes, where this is not the case, we have observed very large, phase dependent differences in the kinetics for product formation.[26] Thus, (III) appears to be the most probable explanation. Of course, II may be operative as well as III. However, II cannot hold independent of III.

There are two factors which complicate comparisons between results with *P3P* and *P3D* in *CM*: the electronic requirements for intramolecular quenching differ in the two cases and the shapes of the dimethylanilino and pyrenyl groups are different. Yet, the two molecules are sufficiently similar to allow some conclusions to be drawn.

From Table 2, it is seen that the activation parameters for *P3D* quenching *are* slightly phase dependent. The changes in E_a' can be ascribed to viscosity differences and the changes in $\Delta S^\ddagger$ to a greater solvent disruption in the cholesteric phase as *P3D* proceeds from its preferred ground state conformation(s) to a bulkier quenching transition state. If the motions which take the preferred ground state conformers of *P3P* in cholesteric *CM* to its quenching transition state involve no large shape changes and/or the *P3P* shape "seen" by nearly solvent molecules is quite different from their own, then the lack of phase dependence in E_a' and $\Delta S^\ddagger$ may be reasonable.

With pyrenyl groups on its chain termini, the *P3P* molecule can be considered "two-headed." The dimethylanilino group, however, when attached to a trimethylene chain, approaches the dimensions of a branched hydrocarbon chain. As such, it and the pyrenyl head combine to make *P3D* more like the constituents of *CM* than is *P3P*. Thus, although the effect of *CM* order on the quenching of *P3D* fluorescence is expected to be small, it very well may be larger than that exerted on *P3P*.[27]

Balanced against these arguments is other data which make us question the validity of explanation (III). On a percent doping basis, the depression in the cholesteric-isotropic transition temperature by *P3P* is approximately the same as that induced by pyrene. Since pyrene is known to be ordered within a cholesteric phase, the degree of transition temperature depression by *P3P* does not support its being unoriented within the mesophase of *CM* (as a result of the disorder of nearby solvent molecules).[27] Furthermore, at equal dopant weight percentages of either pyrene or *P3P*, the variations in the *CM* pitch band with temperature are very similar while the absolute change in pitch induced by pyrene is larger. Only if the presence of *P3P* molecules creates local pools of isotropic-like *CM* constituents can the pitch data be reconciled with explanation (III).

Thus, although we are not totally satisfied with this hypothesis, it appears to be the one which is most consistent with the data in hand. We are presently extending this work to determine the degree to which the dynamics of fluorescence quenching from bichromophorics with longer methylene chains are affected by the order of cholesteric *CM* and other mesophases.

CONCLUSIONS

Studies of the dynamic and steady-state emission properties of *P3P* indicate that the quenching of ^1P in the cholesteric and isotropic phases of *CM* can result in the formation of an intramolecular excimer. Excimer formation in *CM* proceeds with a much lower efficiency than in "normal", less-viscous, isotropic solvents. The activation parameters for intramolecular ^1P-P quenching in *CM* are nearly insensitive to solvent order. The analogous parameters for *P3D* are slightly dependent upon the *CM* phase. We conclude that the local environment of *P3P* in cholesteric *CM* resembles that in the isotropic phase.

Acknowledgment

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