

141.0, 131.5, 129.5, 128.9, 125.0, 123.8, 121.8, 120.8, 116.8.

**3-(Benzoyloxy)-3-benzyl-2-methyl-4-quinolinone, 15.** Anhydrous THF (40 mL) was added to a flame-dried flask charged with NaH (0.144 g, 5.8 mmol) and 3-benzyl-2-methyl-4(1*H*)-quinolinone (1.00 g, 4.0 mmol). After evolution of hydrogen had ceased, the flask and its contents were cooled to  $-78\text{ }^{\circ}\text{C}$ , and a solution of benzoyl peroxide (1.16 g, 4.8 mmol) in 20 mL of THF was slowly added. The flask was kept at  $-78\text{ }^{\circ}\text{C}$  for 12 h and then allowed to warm slowly to room temperature over 3 h. The solvent was removed in vacuo, the residue partitioned between chloroform and water, and the aqueous layer washed with chloroform. The combined organic layers were dried, and the solvent was removed in vacuo, leaving an orange oil, which was chromatographed on silica gel (hexanes/ethyl acetate eluant) to give a yellowish white solid, 0.64 g, 43%. A small amount was purified by HPLC to provide a sample for NMR and EIMS;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.1k (d,  $J = 7.8$ , 2 H), 7.92 (dd,  $J = 7.6$ , 1.5, 1 H), 7.66–7.58 (m, 2 H), 7.52 (t,  $J = 7.6$ , 2 H), 7.43 (d,  $J = 7.6$ , 1 H), 7.32 (dd,  $J = 7.5$ , 1.9, 1 H), 7.22–7.14 (m, 5 H), 3.38 (d,  $J = 13.4$ , 1 H), 3.30 (d,  $J = 13.5$ ,

1 H), 2.10 (s, 3 H);  $^{13}\text{C}$   $\delta$  192.9, 174.3, 165.6, 146.2, 136.0, 133.9, 131.8, 130.3, 130.2, 130.1, 128.6, 128.3, 128.1, 127.8, 127.6, 126.0, 123.4, 83.4, 42.5, 22.0; EIMS,  $m/z$  (rel intensity) 369 ( $\text{M}^+$ , 31), 264 (14), 251 (29), 105 (100), 91 (30), 77 (27), 51 (6), 28 (16); exact mass calcd for  $\text{C}_{24}\text{H}_{19}\text{NO}_3$  369.1364, found 369.1359.

**Registry No.** 1, 5280-06-8; 2, 124443-74-9; 3, 124443-75-0; 12, 124443-77-2; 13, 124443-78-3; 14, 124443-79-4; 15, 124443-80-7; 16, 124443-81-8;  $\text{H}_3\text{CCOCH}(\text{CH}_2\text{Ph})\text{CO}_2\text{Et}$ , 620-79-1;  $\text{H}_3\text{CC}(\text{NHPH})=\text{C}(\text{CH}_2\text{Ph})\text{CO}_2\text{Et}$ , 124443-76-1;  $\text{H}_3\text{CCOCH}(\text{CH}_2\text{Ph})\text{CONHPh}$ , 528-76-7; carbostyryl, 493-62-9.

**Supplementary Material Available:** Low-temperature  $^1\text{H}$  NMR spectrum of 1, room-temperature  $^1\text{H}$  NMR spectrum of carbostyryl with assignments, room-temperature  $^1\text{H}$  NMR spectrum of 14 with assignments, room-temperature  $^1\text{H}$  NMR spectrum of 2 with assignments, COSY  $^1\text{H}$  NMR spectrum of 2 with assignments, and room-temperature  $^1\text{H}$  NMR spectrum of 3 (6 pages). Ordering information is given on any current masthead page.

## Heteroatom Effects on the Photophysical Properties and Conformational Equilibrium of *trans*-1-Phenyl-2-(2-quinoxaliny)ethene

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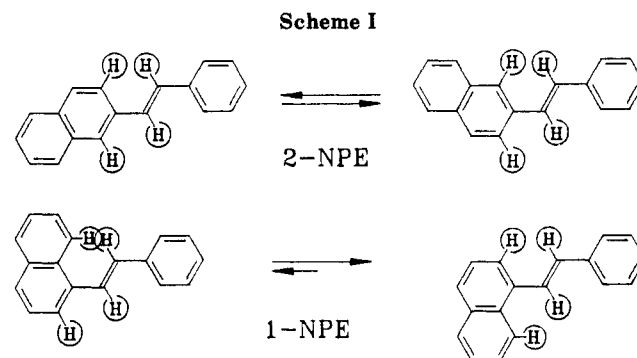
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The absorption and fluorescence spectra of conformationally restricted *trans*-1-phenyl-2-(3-methyl-2-quinoxaliny)ethene (MQxPE) match the long-wavelength spectral component of *trans*-1-phenyl-2-(2-quinoxaliny)ethene (QxPE) which exists in a conformational equilibrium. MM2 calculations predicted four global energy minima for QxPE. One set of enantiomeric geometries with the quinoxaline ring coplanar with the molecular plane has a lower energy (about 0.8 kcal/mol lower) than the other rotamers which have the quinoxaline ring twisted out of the molecular plane ( $-9.2$  or  $+9.2$ ). A large solvent effect on the fluorescence spectra was observed which can be attributed to the proximity effect caused by the vibronic interaction between the lowest ( $\pi, \pi^*$ ) and ( $n, \pi^*$ ) states.

### Introduction

The emission spectroscopy of *trans*-1,2-diarylethenes in solution has been the subject of great interest in the past few years since these molecules exist in equilibria between the relatively unhindered (quasi-planar) conformers around the quasi-single bond connecting the aromatic group and ethylenic carbon.<sup>1</sup> Dramatic changes in the emission properties (spectral shape, quantum yield, and lifetime) of the *trans*-1,2-diarylethenes upon variation of excitation wavelength were observed and attributed to these conformational equilibria.<sup>1b-d</sup>

The detection of ground-state rotational conformers by emission spectroscopy is based on the hypothesis that the excited-state conformers do not interconvert during their lifetimes, in accord with the so-called "principle of nonequilibration of excited rotamers (NEER)", first proposed by Havinga and co-workers<sup>2</sup> in order to rationalize the photochemical behavior of conjugated trienes. The bond order of the quasi-single bond between the aromatic ring and ethylenic carbon in *trans*-1,2-diarylethenes is re-



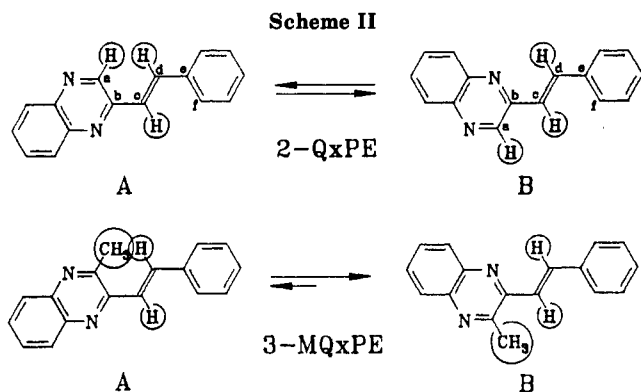
markably enhanced upon excitation, such that conformational changes which occur freely in the ground state are rendered very difficult, leading to noninterconverting excited molecules. Since each of the ground-state conformers in equilibrium has its own distinctive absorption characteristics, different excitation wavelengths can lead to different compositions of conformers in the excited state and consequently to wavelength-dependent emission behavior.<sup>1</sup>

Calculations of the ground-state potential curves for internal rotation about the quasi-single bonds<sup>3</sup> have dem-

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(2) Vroegop, P. J.; Lugtenburg, J.; Havinga, E. *Tetrahedron* 1973, 29, 1393.

(3) (a) Momicchioli, F.; Baraldi, I.; Fischer, E. *J. Photochem. Photobiol. (A) Chem.* 1989, 48, 95. (b) Balradi, I.; Momicchioli, F.; Ponterni, F. *J. Mol. Struct. (Theochem)* 1984, 110, 187.



onstrated that the conformation of the *trans*-1,2-diarylethenes is determined by (a) the tendency toward planarity of the delocalized system including the double bond and aromatic ring and (b) the steric repulsion between aromatic ring hydrogens and ethylenic hydrogens. The potential minimum can be assigned to the quasi-planar conformations (e.g., *trans*-1-phenyl-2-(2-naphthyl)ethene, 2-NPE) or predominantly one conformer (1-phenyl-2-(1-naphthyl)ethene, 1-NPE),<sup>4,5</sup> depending on this competition (see Scheme I).

There are two quasi-planar conformers in 2-NPE with similar steric interactions but slight differences in UV absorption which lead to different spectral shapes, quantum yields and lifetimes of fluorescence on variation of excitation wavelength. The photophysical parameters of two stable rotamers of 2-NPE were evaluated by analyzing the fluorescence spectra.<sup>2,3</sup> When the energy differences between different conformers is large, as in 1-NPE, fluorescence spectra are independent of the excitation wavelength because the most stable conformer dominates.<sup>4,5</sup> The fluorescence spectra of 2-NPE with a methyl group in the ortho-position were insensitive to changes in excitation wavelengths, as the molecule is conformationally restricted and exists only as the most sterically stable conformer. Saltiel and co-workers obtained fluorescence spectra of a pure conformational component through application of principle component analysis and a comparative study of 2-NPE and 1,2-dinaphthylethene with the corresponding *o*-methyl derivatives.<sup>6-8</sup>

We recently reported our results suggesting a conformational equilibrium, as well as a great solvent dependence of the photophysical properties of *trans*-1-phenyl-2-(2-quinoxaliny)ethene (QxPE) based on a fluorimetric analyses.<sup>9</sup> By incorporating two nitrogen atoms into the naphthalene ring of 2-NPE, ( $n, \pi^*$ ) states are introduced into the excited manifold of QxPE, and the planarity in one conformer is increased as a result of decreased steric crowding.<sup>9-11</sup> The bonding interactions between the ethylenic hydrogen atom and the nonbonding electrons of a nitrogen atom in the quinoxaline ring also tend to increase the planarity of the molecule (see Scheme II). The conformational equilibrium as well as the photophysical

properties will, therefore, be different from those of 2-NPE.

In this study, fluorescence analyses on QxPE and conformationally restricted *trans*-1-phenyl-2-(3-methyl-2-quinoxaliny)ethene (MQxPE) have been carried out under varying conditions in order to clarify the effect of the nitrogen atoms on both the photophysical properties and conformational equilibrium of QxPE.

## Experimental Section

**Methods.** Infrared spectra were measured on a Perkin-Elmer 267 spectrophotometer. Nuclear magnetic resonance spectra were measured on a Varian FT-80A spectrometer. Mass spectra were obtained with a Hewlett-Packard 5985A GC/MS system by the electron-impact method and are reported as  $m/z$  (intensity in percent). High-performance liquid chromatography was accomplished on a Waters Associate Model 244 liquid chromatograph. Gas chromatography was performed on a Varian Model 3700 gas chromatograph (column OV-17). UV absorption spectra were recorded on a Cary 17 spectrophotometer and/or a Hitachi 330 spectrophotometer. The fluorescence spectra were measured on an Aminco-Bowman spectrofluorometer and/or a Hitachi MPF 4 spectrofluorometer. For the corrected fluorescence spectra, a JASCO FP 770 spectrofluorometer with rhodamine B as a quantum counter was used. The fluorescence quantum yields were determined by three or four independent measurements using quinine sulfate ( $\Phi_f(298\text{ K}) = 0.55$  in 0.1 N  $\text{H}_2\text{SO}_4$ ) and/or 9,10-diphenylanthracene ( $\Phi_f(298\text{ K}) = 1.0$  in cyclohexane) as standards.<sup>12</sup> The maximum absorbance of the solution used for determination of the fluorescence quantum yields and excitation spectra was less than 0.05, and all the quantum yields were corrected for the different refractive indices of the solvents. Fluorescence lifetime measurements were performed with a nanosecond time-resolved single photon counter (Horiba NAES 1100, pulse width 2 ns).

**Materials.** *trans*-1-Phenyl-2-(2-quinoxaliny)ethene (QxPE). QxPE was prepared by condensation of 2-methylquinoxaline with benzaldehyde and was recrystallized several times from petroleum ether (bp 30–70 °C) and ethanol, mp 109–110 °C (lit.<sup>13</sup> mp 105 °C); MS 232 ( $M^+$ , 59.8), 231 (100.0), 204 (5.0), 102 (65.6), 76 (74.1), 63 (16.4), 50 (62.5); IR (KBr pellet) 970  $\text{cm}^{-1}$  ( $=\text{C}-\text{H}$  out-of-plane bending vibration of *trans*-olefin);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) 9.05 (s, 1 H), 7.20–8.10 (m, 11 H).

*trans*-1-Phenyl-2-(3-methyl-2-quinoxaliny)ethene (MQxPE). MQxPE was prepared by the condensation reaction of 2,3-dimethylquinoxaline with benzaldehyde as described for the preparation of QxPE. The MQxPE was isolated by column chromatography on silica gel (70–230 mesh, *n*-hexane–ethyl ether (1:2 by volume)) and was recrystallized several times from petroleum ether (bp 30–70 °C) and ethanol, mp 101–103 °C; MS 246 ( $M^+$ , 70.5), 245 (100.0), 231 (64.1), 169 (33.7), 102 (43.1), 76 (45.6), 63 (9.7), 50 (16.3); IR (KBr pellet) 970  $\text{cm}^{-1}$  ( $=\text{C}-\text{H}$  out-of-plane bending vibration of *trans*-olefin);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) 2.83 (s, 3 H), 7.20–8.10 (m, 11 H).

The purities of QxPE and MQxPE were checked by gas chromatography (GC) and high-performance liquid chromatography (HPLC). 2-Methylquinoxaline (Aldrich), 2,3-dimethylquinoxaline (Aldrich), benzaldehyde (Sigma), and methyl iodide (Aldrich) were used as received. Quinine bisulfate (Aldrich) was recrystallized several times from water. 9,10-Diphenylanthracene (Aldrich) was purified by recrystallization from ethanol. The solvents for fluorimetric analyses were of spectral quality.

**Molecular Mechanics Calculation.** Molecular mechanics calculations were performed with VAX/VMS using the Macro-Model Package version 2.0 which is incorporated with the MM2(85) force field of Allinger<sup>14</sup> and BDNR method as a minimum algorithm.<sup>15</sup> In order to find global energy minima, the dihedral angles C(a)–C(b)–C(c)–C(d) and C(c)–C(d)–C(e)–C(f) in QxPE and MQxPE were systematically changed in 10 ° steps

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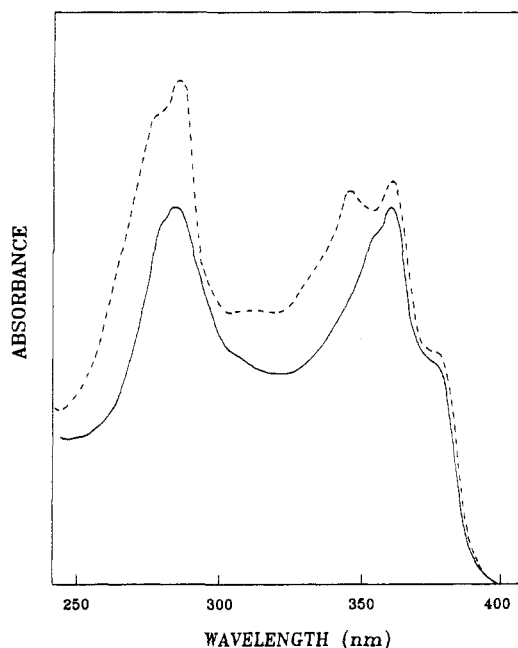
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**Table I. Fluorescence Maxima,  $\lambda_{\text{max}}^{\text{a}}$ , Fluorescence Quantum Yields,  $\Phi_{\text{f}}$ , and Photoisomerization Quantum Yields,  $\Phi_{\text{c}}$ , of QxPE and MQxPE in Various Solvents**

solvent	$\lambda_{\text{max}}^{\text{a}}$ , nm			$\Phi_{\text{f}}$			$\Phi_{\text{c}}$ QxPE	
	QxPE		MQxPE <sup>b</sup>	QxPE		MQxPE <sup>b</sup>	320 <sup>a</sup>	380 <sup>a</sup>
	320 <sup>a</sup>	390 <sup>a</sup>		320 <sup>a</sup>	390 <sup>a</sup>		320 <sup>a</sup>	380 <sup>a</sup>
methanol	434	445	444	0.24	0.15	0.10	0.058	0.091
ethanol	428	442	442	0.16	0.12	0.08	0.033	0.075
2-butanol	420	434	434					
acetonitrile	413	425						
chloroform	414	423	425	0.06	0.06	0.03		
dichloromethane	415	422	423	0.019	0.025	0.02	0.026	0.083
cyclohexane	417	417						
<i>n</i> -hexane	417	417	419	0.002	0.003	0.003	0.051	0.054

<sup>a</sup>  $\lambda_{\text{ex}}$ , nm. <sup>b</sup> For excitations at 320–390 nm.



**Figure 1.** UV absorption spectra of QxPE (---) and MQxPE (—) in *n*-hexane.

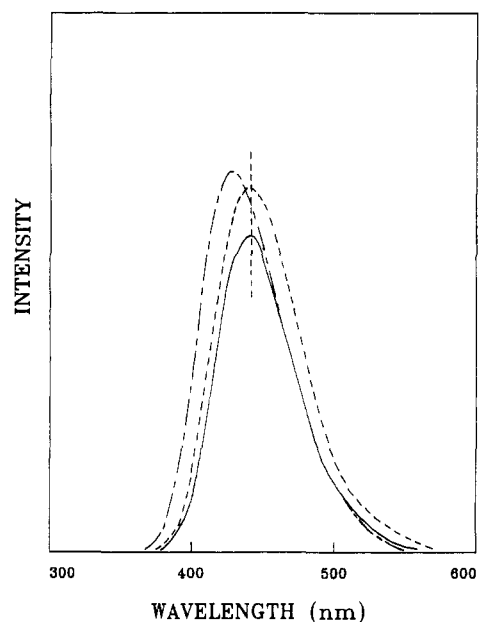
to cover all possible combinations. This provided a  $36 \times 36$  data matrix of initial geometries for energy minimization. The input geometries were allowed to fully relax using a BDNR minimization scheme.

## Results and Discussion

**Conformational Equilibrium.** The absorption spectra of QxPE and MQxPE in *n*-hexane at room temperature are shown in Figure 1. The conformationally restricted MQxPE shows only the long-wavelength absorption bands at 362 nm (max) and 376 nm (shoulder) which match closely the 362-nm absorption component of QxPE. The absorption spectra of QxPE with two maxima (347 and 362 nm) may, therefore, be considered to be the sum of the spectra of conformers in equilibrium, and the long-wavelength absorbing conformer of QxPE is very similar to MQxPE (Scheme II).<sup>9</sup>

The fluorescence spectra of QxPE in various solvents varied greatly upon changing the excitation wavelength, especially in polar solvents which also give high fluorescence quantum yields.<sup>9</sup> The fluorescence spectra of MQxPE, on the other hand, were insensitive to excitation wavelengths, and the fluorescence maxima matched identically that of the long-wavelength component of QxPE which is excited at 390 nm (see Figure 2 and Table I).

The population of excited conformers is determined by the population and the molar absorption coefficient of the ground-state conformers at given excitation wavelengths



**Figure 2.** Fluorescence spectra of QxPE ( $\lambda_{\text{ex}} = 320$  nm (---) and  $\lambda_{\text{ex}} = 390$  nm (-.-)) and MQxPE ( $\lambda_{\text{ex}} = 320$ – $390$  nm (—)) in ethanol.

in accord with the NEER principle. The emission spectral change is also dependent on the absorption of ground-state conformers varying with the excitation wavelength. If the number of photons absorbed at various excitation wavelengths is the same, the fluorescence spectra of the mixture should depend only on the relative absorption of each conformer at the excitation wavelength. Figure 3 shows the fluorescence spectra of QxPE in ethanol at various excitation wavelengths, which has been normalized to the intensity of the exciting light and absorbance of sample at each wavelength. The fluorescence of QxPE changes dramatically with  $\lambda_{\text{ex}}$  (428 and 442 nm at  $\lambda_{\text{ex}} = 320$  nm and  $\lambda_{\text{ex}} = 390$  nm, respectively) even though the spectrum of QxPE is broad and featureless, and a distinct isoemissive point is observed at 435 nm. This result strongly indicates that only two conformers (not three or more conformers) with finite lifetimes exist in the conformational equilibrium of QxPE in ethanol. A simple correlation between the excitation wavelength and observed emission properties (maxima and quantum yields) is shown in Figure 4. The correlation indicates that the conformer which absorbs at shorter wavelength gives short-wavelength fluorescence with slightly higher fluorescence quantum yield, and the long wavelength absorbing conformer displays long-wavelength fluorescence with lower quantum yield in ethanol. The differences in the absorption and emission spectra of the two conformers may be attributed to the difference in planarity between the two conformers.

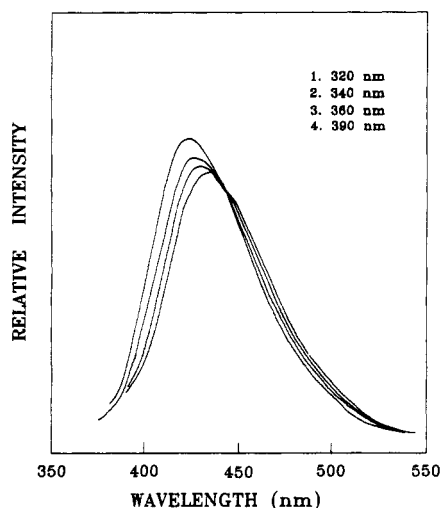


Figure 3. Fluorescence spectra of QxPE in ethanol at various excitation wavelengths.

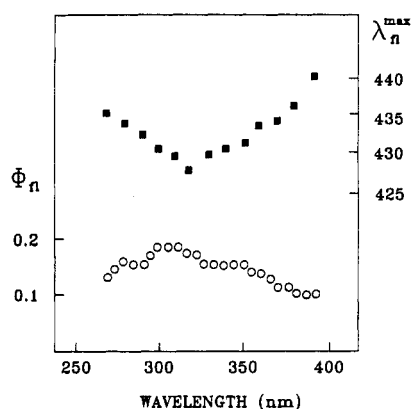
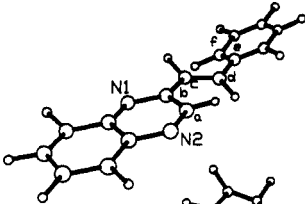
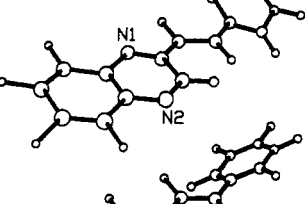
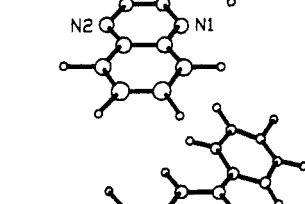
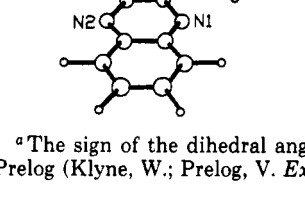


Figure 4. Correlation diagram of fluorescence quantum yields (O) and maxima (■) of QxPE with excitation wavelengths.

The fluorescence of QxPE in ethanol at room temperature decays monoexponentially with lifetimes of 0.5 ns (at both  $\lambda_{\text{ex}} = 320$  nm and  $\lambda_{\text{ex}} = 390$  nm) in spite of the fact that there is a relatively large difference between the fluorescence maxima of the two conformers. MQxPE shows a similar monoexponential fluorescence decay with a lifetime of 0.5 ns. The lifetime of QxPE decreases with decreasing solvent polarity and reaches the time resolution limit of our instrument (0.2 ns), making it impossible to determine the lifetime in nonpolar solvents. In some cases in which emission spectra vary with  $\lambda_{\text{ex}}$ , none of the expected biexponential decay was observed.<sup>1b,16</sup> This monoexponential decay could be explained either by (a) very similar lifetimes of the two conformers or (b) a very short lifetime ( $\tau_f < 0.2$  ns) of one conformer compared to that of the other. Fluorescence quenching experiments with methyl iodide at each excitation wavelength (320 and 390 nm) allowed us to distinguish between the two possibilities. The equal quenching efficiency achieved at different excitation wavelengths ( $\lambda_{\text{ex}} = 320$  nm,  $k_q\tau = 17.3$  and  $\lambda_{\text{ex}} = 390$  nm,  $k_q\tau = 17.4$ ) confirms that the excited singlet states of the two conformers have very similar lifetimes in ethanol.

**Molecular Mechanics Calculation.** In order to provide some insight into the comparative analysis of the two conformers, molecular mechanics calculations were per-

Table II. Calculated Geometries of the Lowest Energy Minima in QxPE<sup>a</sup>

geometry	dihedral angle, deg	
	a-b-c-d	c-d-e-f
	+9.2	-29.4
	-9.2	+29.4
	180.0	-29.4
	180.0	+29.4

<sup>a</sup> The sign of the dihedral angle follows the rules of Klyne and Prelog (Klyne, W.; Prelog, V. *Experientia* 1960, 12, 521).

formed using the MM2(85) force field.<sup>14</sup> The calculation predicted four global energy minima (two sets of two enantiomeric conformers) for QxPE (Table II). One set of enantiomeric geometries (conformer B) which have lower energy (about 0.8 kcal/mol lower) when compared to the others, are planar in the quinoxaliny group and ethylenic double bond but have twisted phenyl rings (+29.4° or -29.4°). The other set of enantiomeric geometries (conformer A) are twisted out of the molecular plane, both in the quinoxaline ring (-9.2° or +9.2°) and the benzene ring (+29.4° or -29.4°). It seems that the lower energy associated with one set of conformers arises out of an increase in conjugative interactions due to good planarity which is achieved in the absence of repulsive steric interactions between the ethylenic hydrogen and ortho-hydrogen of the quinoxaliny group (present in the second set of conformers). The calculated energy difference between the two conformers of QxPE can be reduced to 0.8 kcal/mol, and hence the relative mole fractions of the two conformers at equilibrium are predicted to be about 0.2 (conformer A) and 0.8 (conformer B), respectively.<sup>17</sup> However, different values may be obtained in solution because of the different solvation stabilizations of each conformer.

Energy minima for MQxPE were predicted as only one set of enantiomers which exist in almost the same geometry as that of the stable planar conformer of QxPE. As expected from the absorption and fluorescence spectra described above, it appears that methyl substitution in the

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(17) The shallow valleys in the energy surface or ring rotation suggest a very flexible molecule, indicating that entropy will be important for the free energy of the particular conformation. On the other hand, we are dealing with relative energies, thus, eliminating the entropy term.

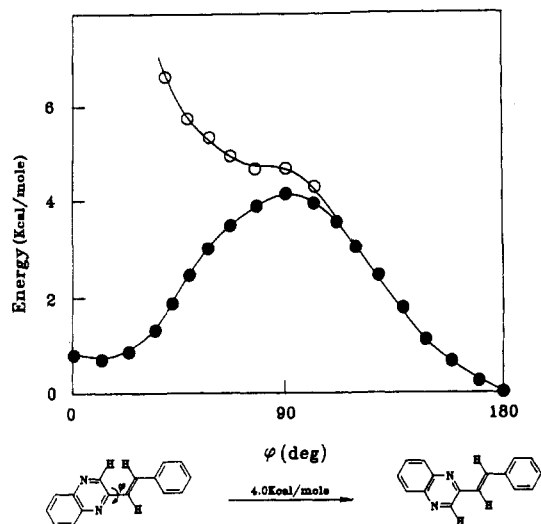


Figure 5. Rotational energy profile of QxPE (●) and MQxPE (○).

ortho-position of MQxPE produces significant steric repulsion, shifting the equilibrium to a more planar conformer similar to that of QxPE conformer B. These planarity relationships obtained from the calculations are in good agreement with the spectroscopic observations (absorption and fluorescence) of QxPE and MQxPE, suggesting that the principal source of the different spectral properties for the QxPE conformers is the difference in planarity described above.

The rotational energy barrier of the quinoxaliny ring was also derived from dihedral angle driver calculations by changing the angle C(a)–C(b)–C(c)–C(d) when the angle C(c)–C(d)–C(e)–C(f) is fixed at 29.4°, and the resulting profile of rotation is represented in Figure 5. The minima of rotation are relatively shallow, and the energy barrier of rotation is about 4.0 kcal/mol, indicating that the rotation can be neither entirely free nor entirely hindered at room temperature. As for MQxPE, it is important to note that a large interval of the conformational coordinate ( $0^\circ < \rho < 90^\circ$ ) is completely hindered because of exceedingly high steric interactions between the ethylenic and methyl hydrogens. It was also found that MQxPE exists in only one conformer, which may actually be the same geometry as that found in the stable QxPE conformer B.

**Solvent Effect on the Fluorescence of QxPE Conformers.** While the absorption spectra of QxPE are not greatly affected by solvent polarity,<sup>9</sup> the fluorescence of QxPE at room temperature is greatly influenced by solvent polarity as shown in Table I. The fluorescence quantum yields of QxPE and MQxPE in nonpolar solvents are significantly lower than those of the corresponding hydrocarbon, 2-NPE.<sup>15</sup> This effect is probably due to efficient internal conversion by extensive vibronic mixing between close-lying ( $n, \pi^*$ ) and ( $\pi, \pi^*$ ) states.<sup>22</sup> With increasing solvent polarity the fluorescence quantum yields of QxPE and MQxPE increase dramatically while the photoisomerization quantum yields,  $\Phi_c$ , do not change significantly as shown in Table I. The results indicate that the trans-cis photoisomerization of QxPE and MQxPE proceeds

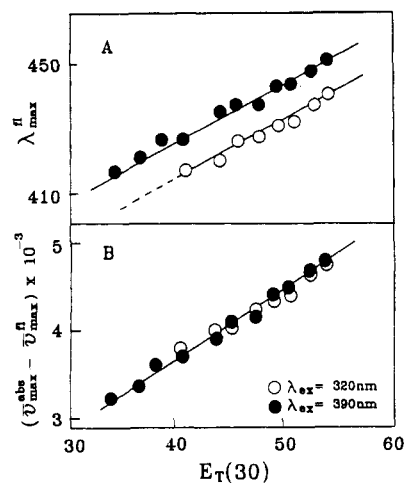
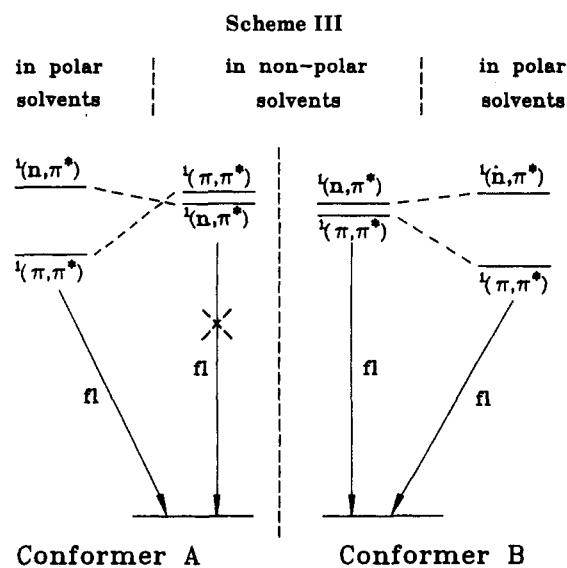


Figure 6. Stokes shift of QxPE with empirical Dimroth polarity,  $E_T(30)$ .



through an excited state distinct from the fluorescing state. Azulene quenching and laser flash photolysis studies also strongly indicated that the photoisomerization of QxPE and MQxPE proceeds mainly via a triplet excited state at room temperature.<sup>23</sup> The dramatic increase in the fluorescence quantum yield with increasing solvent polarity is, therefore, probably due to a decrease in the nonradiative decay processes caused by a decrease of the vibronic coupling between the lowest  ${}^1(\pi, \pi^*)$  state and  ${}^1(n, \pi^*)$  states in these conformers.

The fluorescence quantum yields at  $\lambda_{ex} = 320$  nm, however, increase more than 100-fold on changing the solvent from *n*-hexane to methanol while they increase only 50-fold at  $\lambda_{ex} = 390$  nm, as shown in Table I. The fluorescence quantum yields of MQxPE increase 30-fold, rather small compared to those of QxPE, indicating the similarity with that of QxPE at  $\lambda_{ex} = 390$  nm. The results suggest that the extent of the vibronic coupling between the lowest  ${}^1(\pi, \pi^*)$  state and the  ${}^1(n, \pi^*)$  state in the QxPE conformers is not the same.

In general, the fluorescence maxima ( $\lambda_{max}^{fl}$ ) of trans-1,2-diarylethenes are not markedly affected by the nature of the solvents.<sup>18</sup> However, the fluorescence maxima of QxPE and MQxPE shift to significantly longer wavelengths with increasing solvent polarity (Table I). The

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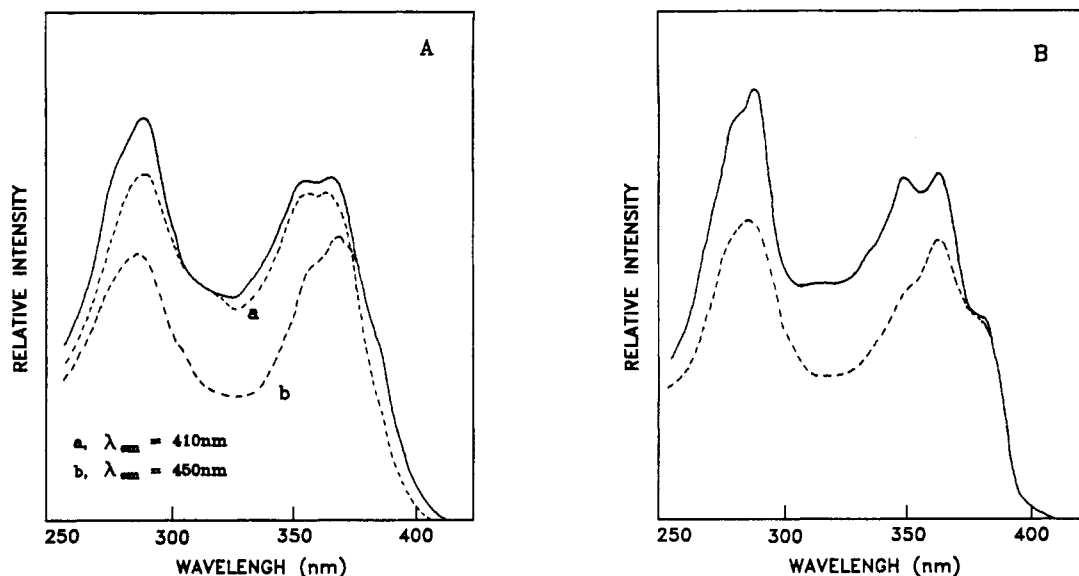
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**Figure 7.** Absorption (—) and excitation (---) spectra QxPE in ethanol (A) and *n*-hexane (B). The excitation spectra are normalized to the intensity at 310 nm (for curve A-a) and 390 nm (for curve A-b and B).

solvent-induced shifts of the emission spectra can be attributed to a large change in dipole moment ( $\mu_e$ ) in the excited state compared with that of the ground state ( $\mu_g$ ).<sup>20</sup> It is suspected that the electronegative nitrogen atoms in QxPE and MQxPE lead to extensive charge transfer character in the excited  $^1(\pi, \pi^*)$  states of the compounds, and consequently, large dipole moments which are easily stabilized by polar solvents. The solvent induced Stokes shift ( $\bar{\nu}_{abs}^{max} - \bar{\nu}_f^{max}$ ) and fluorescence maxima of QxPE were correlated with the empirical Dimroth polarity parameter  $E_T(30)$ <sup>19</sup> as shown in Figure 6. The fluorescence maxima show a good linear relationship with  $E_T(30)$  at each excitation wavelength (320 and 390 nm), although they show linearity from some higher  $E_T(30)$  in the case of 320-nm excitation (Figure 6, part a). Figure 6, part b, shows the correlation of the Stokes shift with  $E_T(30)$  when short- and long-wavelength absorption maxima are assigned to absorption maxima of the conformers A and B. The similar results obtained on 320- and 390-nm excitations indicate that the magnitudes of solvent relaxation in the lowest  $^1(\pi, \pi^*)$  states of the two conformers are nearly the same.

The fluorescence spectra of conformationally restricted MQxPE conformers are independent of excitation wavelength in all solvents. For QxPE, no significant fluorescence dependence on excitation wavelength was observed in nonpolar hydrocarbon solvents such as *n*-hexane and benzene, while remarkable solvent dependence was observed in other solvents. These anomalous solvent effects are more apparent in the excitation spectra with different emission wavelengths (Figure 7). In ethanol, there is a huge difference between the excitation spectrum obtained when the emission wavelength is fixed at  $\lambda_{em} = 410\text{ nm}$  and when it is fixed at  $\lambda_{em} = 450\text{ nm}$ . The former shows excitation maxima at 290 and 355 nm (curve a) like the absorption spectrum, while the latter exhibits maxima at 290 and 364 nm (curve b). However, in *n*-hexane solution, only the long-wavelength band was observed at both emission wavelengths (410 and 450 nm), and no further change was detected in the spectrum even at other emission wavelengths (410–470 nm). A comparison of the absorption spectra with the excitation spectra in nonpolar and polar solvents strongly suggests that the two conformers are both fluorescent in polar solvents but only one conformer (conformer B) is fluorescent in aprotic nonpolar

solvents. This result suggests that the lowest excited state in conformer A is a nonfluorescent  $^1(n, \pi^*)$  state. The fluorescence emission spectra obtained with varying excitation wavelengths also strongly support this scheme, i.e., in polar solvents the fluorescence spectra of QxPE varied with excitation wavelengths while in nonpolar solvents emission was independent of the excitation wavelengths.

The solvent dependence of QxPE fluorescence excitation and emission spectra can be schematized as in Scheme III. In nonpolar hydrocarbon solvents, conformer A gives no fluorescence because its lowest excited state is  $^1(n, \pi^*)$ . Conformer B, on the other hand, which has good planarity and long-wavelength emission, has a  $^1(\pi, \pi^*)$  state as its lowest excited state and exhibits weak fluorescence due to a strong proximity effect with a close-lying  $^1(n, \pi^*)$  state. With increasing solvent polarity, however, the stabilization of the  $(\pi, \pi^*)$  state reverses the energy levels of the  $^1(\pi, \pi^*)$  and  $(n, \pi^*)$  states in conformer A, and thus both conformers become fluorescent in polar solvents.

### Conclusions

The absorption and fluorescence spectra of QxPE indicate that two QxPE conformers exist in equilibrium. The spectra of the conformationally restricted MQxPE match the long-wavelength spectral component of QxPE. Results of MM2 calculations were in good agreement with spectroscopic observations (absorption and fluorescence spectra). The geometries wherein the quinoxaline ring is coplanar with the ethylenic plane are at lower energies (about 0.8 kcal/mol lower) than those in which the quinoxaline ring is twisted out of the molecular plane ( $-9.2$  or  $+9.2$ ). Remarkable solvent effects on the fluorescence spectra were observed which are attributed to the proximity effect between the lowest  $^1(\pi, \pi^*)$  and  $^1(n, \pi^*)$  states of QxPE conformers. It can be concluded that the difference in planarity between the QxPE conformers causes the large differences observed in the photophysical properties between the two conformers.

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