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Structure–Reactivity Factors in the Quenching of Fluorescence from Naphthalenes by Conjugated Dienes

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Abstract: Fluorescence from naphthalene, a group of its methyl derivatives, and 2-methoxy- and 2,6-dimethoxynaphthalene is quenched by conjugated dienes with variable efficiency. The results are correlated with the ionization potentials of the dienes and the electron affinities of the excited states of the aromatic compounds. A systematic relationship exists, but log k_q is not a good linear function of either parameter. Deviation from linearity may, conceivably, be due to uncontrolled steric factors but probably indicates the importance of other electronic contributions to binding in addition to charge transfer from the diene to the aromatic.

Quenching of fluorescent compounds by molecules which cannot function by classical electronic energy transfer, because of the absence of sufficiently low-lying excited states of the quencher, has been studied in our laboratory for several years.[3–6] We have thought about the process in terms of a rather simple model in which a complex (exciplex) is formed from the excited molecule and the quencher; the exciplex is then believed to undergo fast radiationless decay. We have inferred that the internal conversion step must deliver energy to the quencher as vibrational excitation for two reasons. First, the fact that nonradiative decay must be much faster than in the quenchee by itself implies involvement of the quencher as an active participant in the process. Second, there are cases in which chemical transformation of the quencher indicates that energy in some form must be transferred.[5,6] The simplest formulation of the mechanism is shown in eq 1 and 2.

$$A^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{exciplex}}{(AQ)^*} \qquad (1)$$

$$\begin{tikzcd}(AQ)^* \arrow[r, "k_2"] & A^*(\text{vib}) \arrow[d] & + & Q^*(\text{vib}) \arrow[d] \\ & A & & Q \text{ or other products}\end{tikzcd} \qquad (2)$$

We have regarded two factors as important in determining structure–reactivity relationships: (a) the binding energy of the exciplex, and (b) the rate of reaction 2. Binding in the exciplex could arise from interactions bearing a variety of theoretical labels. In resonance notation we could formulate the exciplex as

$$(A\cdot Q)^* \equiv \underset{\mathbf{1}}{A^*Q} \longleftrightarrow \underset{\mathbf{2}}{AQ^*} \longleftrightarrow \underset{\mathbf{3}}{A^+Q^-} \longleftrightarrow \underset{\mathbf{4}}{A^-Q^+}$$

We anticipate that all of the interactions will contribute to stabilization of weakly bound complexes. We expect that in some cases one interaction will dominate, that in other cases another will be overriding, and that in other, messy situations, all may contribute.

Others[7–9] have taken a hard line and describe quenching as occurring by a "charge-transfer mechanism." We have an uncomfortable feeling as to the significance of such seemingly definitive words. There are at least two ways in which we could account for a dominant influence of charge transfer interaction on quenching activity.

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(1) National Science Foundation Postdoctoral Fellow, 1969–1970.

(2) Air Force Office of Scientific Research Postdoctoral Fellow, 1968–1969.

(3) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968), and references cited therein.

(4) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

(5) R. S. Cooke and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 2739 (1970).

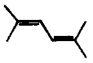
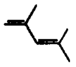
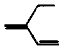
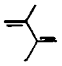
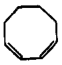
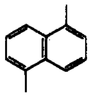
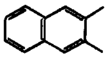
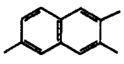
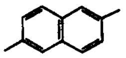
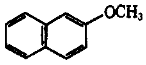
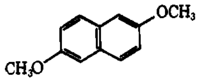
(6) M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *ibid.*, **92**, 6991 (1970).

(7) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).

(8) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

(9) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

Table I. Sensitizer Fluorescence Lifetimes and Kinetic Data for Fluorescence Quenching of Substituted Naphthalenes by Conjugated Dienes

Sensitizer	$\tau_0 \times 10^9$ sec^a	k_q(l. mol^{-1} sec^{-1}) $\times 10^{-7}$ 										
	58.5	170	110	18	12	7.8	7.0	2.8	1.9	1.8	1.4	0.58
	71.0	120	97	11	5.0	6.9	5.9	4.2	0.98	1.0	0.81	0.47
	58.5	84	30	5.1	2.1	4.0	3.3	1.5	0.89	0.56	0.72	0.46
	49.2	96										
	17.4	130						5.7		0.96	2.0	
	11.7	16										

^{a} Average of the lifetimes observed in each experiment.

(1) Within a group of quenchees and quenchers there may be large variations in binding energies of the exciplexes and relatively small variations in k_2, the rate constant for internal conversion. If configurations **1** and **4** are dominant in the structure of the exciplex, reactivity should be simply correlated with the ionization potential of Q and the electron affinity of A*.

(2) The ion pair A^-Q^+ may lie lower in energy than A*, so that complete transfer of an electron is an irreversible decay process. If there is a barrier to be surmounted, formation of the ion pair from A* and Q will be treated as a classical transition state problem.

One can see that cases 1 and 2, although different, can lead to rather similar patterns of reactivity. When he discusses quenching of aromatic compounds by dienes and other hydrocarbons, it is not really clear as to which case Weller has in mind.[7,8] Evans is explicit in formulation of a case 2 mechanism.[9] The encounter complex included in his formulation is not endowed with the kinds of properties which we attribute to exciplexes, so the Evans mechanism is really equivalent to the mechanism formulated above, with reaction 1 being irreversible and (AQ)* being an ion pair. There is ample evidence that quenching of aromatic compounds by tertiary amines[10,11] fits case 1 with the fluorescent exciplexes which are commonly formed having a great deal of A^-Q^+ character. Furthermore, in polar solvents, a common fate of the exciplexes is dissociation to ion radicals, so formation of an ion pair is undoubtedly a decay process. However, phenomena such as solvent effects on the wavelength of the exciplex emission show that the emitting species itself is not an ion pair. Since joining the Bell Telephone Laboratories, Taylor has found that fluorescent exciplexes are formed from 1-cyanonaphthalene and a number of electron-rich monoolefins.[12] The variation of the wavelength of the new emission with solvent polarity indicates that the exciplexes, although having a large amount of polar character, are less polar than the exciplex from naphthalene and triethylamine.[11,13]

In this paper and those immediately following,[14] we will examine a number of data for the quenching of fluorescence of naphthalene and its derivatives by conjugated dienes. The results will be discussed in relation to the proposed mechanistic models.

Results

Quenching data were treated by the usual Stern–Volmer relationship expressed in eq 3. Table I summarizes the data obtained from study of a number of naphthalene derivatives in quenching by several conjugated dienes. Duplicate and triplicate series of measurements were made in a number of cases indicating that the nonsystematic error in τ_0 and k_q is in the range ±5–10%.

$$\frac{\phi_f^0}{\phi_f} = \frac{\tau^0}{\tau} = 1 + k_q\tau_0[Q] \qquad (3)$$

Discussion

The general mechanism proposed in the introduction would give the experimental rate constant, k_q, the significance shown in eq 4.

$$k_q = k_1k_2/(k_{-1} + k_2) \qquad (4)$$

If the Evans mechanism[9] is correct, $k_q \approx k_1$ and we could logically try the assumption that the potential barrier opposing the irreversible step is proportional to the potential energy of formation of an ion pair by charge transfer, as Evans has done

$$RT \ln k_q = \alpha({}^1E_S - IP_Q + EA_A + C) = \alpha\beta \quad (5)$$

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[10] A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968), and references cited therein.

[11] S. P. Van, Ph.D. Dissertation, California Institute of Technology, Pasadena, Calif., 1969.

[12] G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

[13] M. G. Kuzmin and L. N. Guseva, *ibid.*, **3**, 71 (1969).

[14] G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3684, 3687 (1972).

where ${}^1E_S$ and EA_A are the singlet excitation energy and electron affinity of the quenchee, IP_Q is the ionization potential of the quencher, and C is everything else, such as the Coulombic stabilization of the complex and all free-energy changes associated with interaction of the complex with the solvent. An extreme opposite point of view arrives at a very similar formulation. If k_{-1} is much larger than k_2, k_q then takes the form of eq 6.

$$k_q = (k_1/k_{-1})k_2 = K_1k_2 \qquad (6)$$

The binding energy of the complex might then be estimated by writing down exactly the expression within the parentheses in eq 5 and then adding $RT \ln k_2$ as another, unknown term to the expression for $\ln k_q$.

$$RT \ln k_q = \beta + RT \ln k_2 \qquad (7)$$

If one were to use the formulation of eq 7 and introduce the view that charge transfer from quencher to quenchee is only one of several binding interactions in the complex, the quenching rate constant would then take the form of eq 8. The term γ would then take

$$RT \ln k_q = \alpha'\beta + \gamma + RT \ln k_2 \qquad (8)$$

account of other interactions, such as charge transfer from quenchee to quencher and excitation resonance.

Establishment of correlations between rates and appropriate ionization potentials and electron affinities can lead to useful predictions concerning structure–reactivity relationships but will not provide unequivocal indication as to the number of steps in the quenching mechanism or their relative rates. That kind of information can only be obtained directly in cases such as those reported by Taylor[12] in which an exciplex can be observed directly by some kind of spectroscopy.

If, for a series of quenchers and quenchees, a relationship of the form of eq 8 is appropriate, and k_2 does not vary a great deal, one may find excellent linear relationships between $\ln k_q$ and the ionization potential of the quencher or the electron affinity of the quenchee. This does not *prove* that charge transfer is the only significant interaction involved in quenching. On the other hand,[11] irregularities, where they are encountered, do not *disprove* the importance or even the uniqueness of charge transfer as either a binding mechanism or an irreversible relaxation process. We are inclined to believe that the noncorrelation between unsaturated compounds and strained hydrocarbons[12] is due to variation in k_2 but cannot give more than intuitive support to this view.

Table II lists available data for the ionization potentials of dienes used in this study. Both vertical and adiabatic potentials are included. Taylor[12] has shown that correlations are better if adiabatic values are used. This is reasonable if the physical basis for correlation lies in heats of formation of exciplexes in which quencher and quenchee have achieved equilibrium configurations.

Figure 1 shows a plot of the adiabatic ionization potentials against $\log k_q$ for two dimethylnaphthalenes and 2,3,6-trimethylnaphthalene. A plot of the quenching data against vertical ionization potentials is shown in Figure 2 for comparison, but no correlation lines are included because of the relatively random distribution of the data points. If the data for 1,3-cyclohexadiene are excluded, there is a remarkably good set of linear relationships between the quenching data and adiabatic ionization potentials.

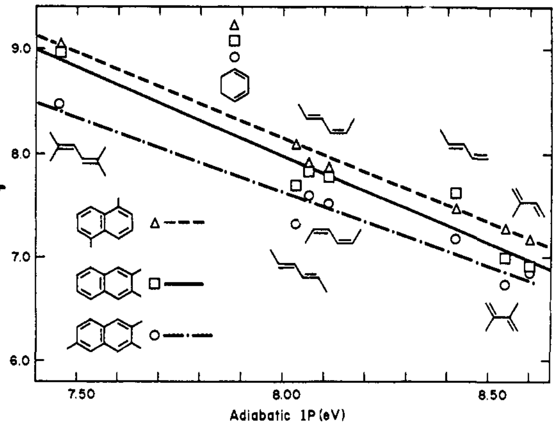

Figure 1. Correlation of quenching rate constants for methylated naphthalenes with diene adiabatic ionization potentials.

Table II. Diene Ionization Potentials

Diene	IP, eV[a] Adiabatic	IP, eV[a] Vertical
2,5-Dimethyl-2,4-hexadiene	7.46	7.84
1,3-Cyclohexadiene	7.88	8.30
trans,trans-2,4-Hexadiene	8.03	8.17
cis,trans-2,4-Hexadiene	8.06	8.22
cis,cis-2,4-Hexadiene	8.11	8.25
Cyclopentadiene	8.20	8.55
trans-1,3-Pentadiene (*trans*-piperylene)	8.42	8.59
cis-1,3-Pentadiene (*cis*-piperylene)	8.45	8.65
2,3-Dimethyl-1,3-butadiene	8.54	8.72
2-Methyl-1,3-butadiene (isoprene)	8.60	8.85

[a] G. N. Taylor, N. A. Kuebler, and C. R. Brundle, unpublished results. Determined by photoelectron spectroscopy using a 127° electrostatic analyzer. Adiabatic potentials were taken as the onset of the first vibrational band.

Figure 3 shows the same kind of plot for the data for quenching of naphthalene reported by Stephenson[3] and Taylor[12] along with the data for 2-methoxynaphthalene gathered in the present study. The best slope for any correlation of the data for the naphthyl ether is clearly different from the common slope of the two, separated, correlation lines established by Taylor[12] for different classes of quenchers.

A relationship including at least as many degrees of freedom as eq 8 would be needed to effect an analytic fit of the data. The relatively high reactivity of 1,3-cyclohexadiene could be interpreted as indicating that the s-cis configuration gives the diene a high value of α', $\ln k_2$, or both. Some, but not all, of the small deviations from perfect linear correlation among the data for acyclic dienes, shown in Figure 1, *could* be attributed to variations in the relative amounts of s-cis and s-trans forms. The details of such partial rationalization do not appear worthy of elaboration. Figure 3 can be interpreted by the view that the α' is different for naphthalene and 2-methoxynaphthalene.

Table III shows data needed to estimate the electron affinities of the first-excited singlet states of some of the aromatic compounds. Polarographic reduction po-

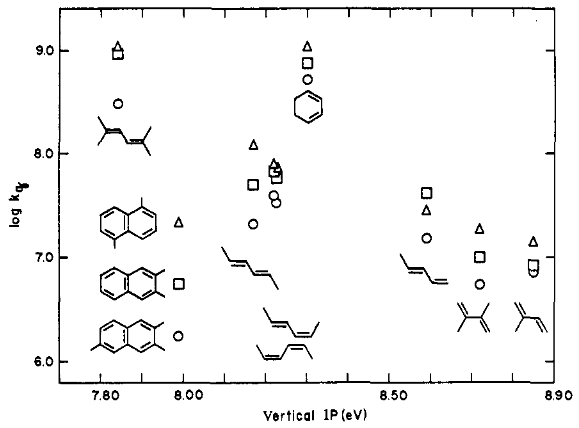

Figure 2. Correlation of quenching rate constants for methylated naphthalenes with diene vertical ionization potentials.

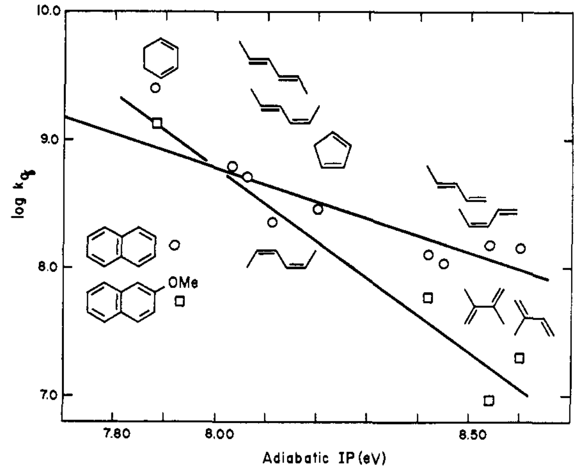

Figure 3. Correlation of quenching rate constants for naphthalene and 2-methoxynaphthalene with diene adiabatic ionization potentials.

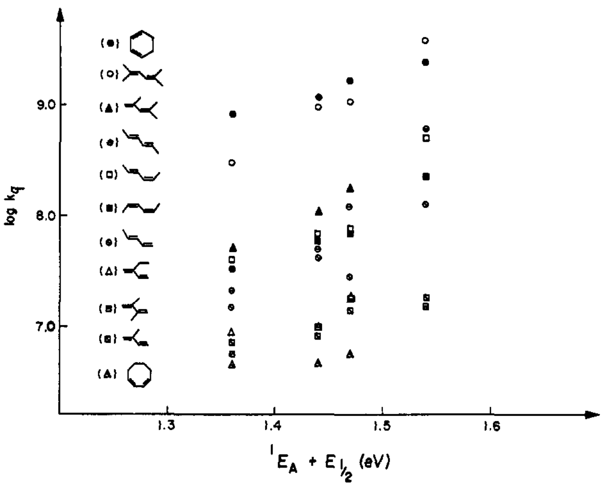

Figure 4. Correlation of quenching rate constants with electron affinities of excited naphthalenes.

tentials are used to estimate electron affinities of the molecules in their ground states. There are many problems in making such an estimate, since the medium used in polarography is different from those used in the quenching studies and the polarographic reduction observed is an unresolved, two-electron step leading ultimately to irreversible formation of dihydronaphthalenes.[15] Somewhat conflicting rationalizations of these concerns have been offered by Streitwieser,[16] and we are in the position of using what we have to seek correlations that may be suggestive, if not definitive. Figure 4 shows graphically the results of plotting values of ($^1E_A + E_{1/2}$) against log k_q for several quenchers with various dienes used as quenchers. We have not drawn correlation lines, because they would create an unreadably confused figure. The fact that any such lines would cross is clear from the fact that there are inversions of reactivity order with the various quenchers. There is, however, an overall tendency for the sensitivity to quenching to increase as the electron affinity of the quenchee is made more favorable.

Table III. Sensitizer Singlet Excitation Energies and Polarographic Reduction Potentials

Sensitizer	^1E_A,[a] eV	$E_{1/2}$ (*vs.* sce),[b] eV	$^1E_A + E_{1/2}$, eV
Naphthalene	3.98	−2.437	1.54
1,5-Dimethylnaphthalene	3.94	−2.475	1.47
2,3-Dimethylnaphthalene	3.94	−2.50	1.44
2,6-Dimethylnaphthalene	3.86	−2.476	1.38
2,3,6-Trimethylnaphthalene	3.88	−2.523	1.36

[a] Taken from the estimated onset of fluorescence in *n*-hexane
[b] Halfwave reduction potentials in 75% dioxane–water, ref 15.

We believe that the deviations from simple, linear correlations are experimentally valid. Their significance is hard to assess, but they certainly imply that structure–reactivity relationships are rather more complicated than has been implied by previous discussions[8–10] based upon fewer data. Factors other than ionization potentials and electron affinities are of importance. For example, steric inhibition of interaction has been shown to be of obvious importance in decreasing the reactivity of highly hindered naphthalene derivatives.[3] This might be a factor in influencing the reactivity pattern of the various methylated derivatives of naphthalene. As a matter of fact, the desire to find a significant pattern of reactivity which could define the topology of the exciplex was part of the motivation for carrying out this study. We can only observe that, if steric hindrance by methyl groups attached to the naphthalene nucleus is important, the magnitude of the effect must vary as the structure of the diene is varied. Since methylation of naphthalene both changes the electron affinity and increases steric hindrance to close approach of a quencher we do not now believe that unequivocal sorting of these effects can be accomplished.

Probably the greatest inhibition to forcing a simple charge-transfer correlation on these data arises, not from the considerations discussed above, but from the discovery of a group of quenching reactions in which dominant charge-transfer interactions, if they are im-

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(15) L. H. Klemm and A. J. Kohlik, *J. Org. Chem.*, 28, 2044 (1963).

(16) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 175–185.

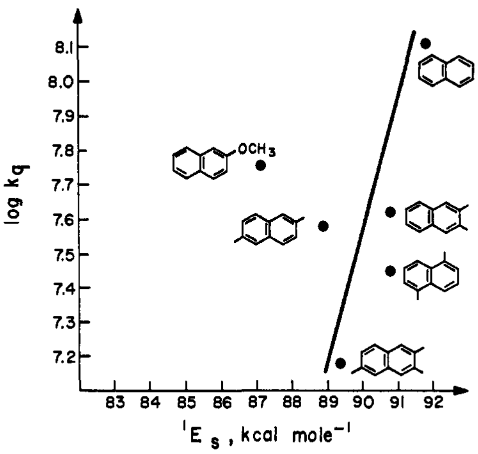

Figure 5. Correlation of quenching rate constants with sensitizer singlet energies for energy transfer to *trans*-piperylene.

portant at all, must be quenchee to quencher, rather than the reverse.[6]

We suggested some years ago that excitation resonance might contribute to binding in exciplexes and to the electronic interactions required for internal conversion using the quencher as a vibronic sink.[3] This would imply that there should be a correlation with singlet excitation energies, with reactivity increasing with increasing excitation energy of the quenchee and with decreasing excitation energy of the quencher. Sensitivity to steric hindrance does in fact suggest that the partners do approach each other very closely so that orbital overlap *may* become significant. Figures 5 and 6 show a plot of log k_q for *trans*-piperylene and 1,3-cyclohexadiene against ^1E_S for several quenchees. The correlation is not very good but is surely not inferior to those based upon charge-transfer models.

The authors of this paper vacillate in their own views and do not always agree with each other as to what is important in nonclassical quenching. A reasonable case can be made for the view that in a weakly bound complex a number of electronic configurations can contribute to binding.

$$\Psi_{(AQ)*} = a\Psi_{A*Q} + b\Psi_{AQ*} + c\Psi_{A^{-}Q^{-}} + d\Psi_{A^{-}Q^{+}} \quad (9)$$

If all the terms in the expansion are potentially significant, tests of reactivity covering a limited series of related compounds may tend to show the importance of a particular interaction. Other tests will show other interactions if, in fact, "everything counts a little." Obviously there will be cases in which one interaction becomes dominant.

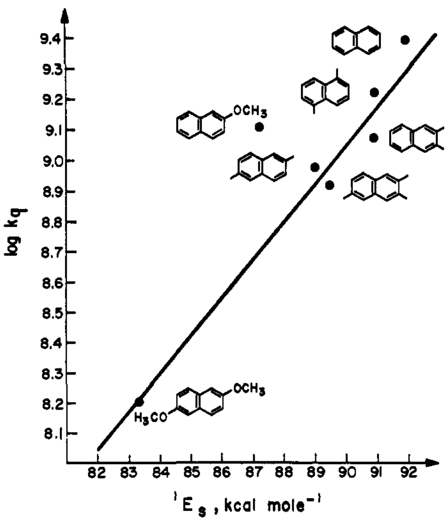

Figure 6. Correlation of quenching rate constants with sensitizer singlet energies for energy transfer to 1,3-cyclohexadiene.

Experimental Section

Materials. Hexane (Phillips Pure Grade) was purified as described by Taylor and Hammond.[14] Naphthalene (Eastman) was recrystallized from methanol and sublimed. 2,6-Dimethylnaphthalene (Calbiochem), 2-methoxynaphthalene (Matheson Coleman and Bell), and 2,6-dimethoxynaphthalene (Aldrich) were recrystallized from 95% ethanol and sublimed. The remaining methylated naphthalenes (Aldrich) were recrystallized from ethanol and sublimed. 2,5-Dimethyl-2,4-hexadiene (Matheson Coleman and Bell), isoprene (Aldrich, Phillips), the three isomers of 2,4-hexadiene (Columbia, Aldrich, K & K), and all other dienes (Aldrich) were purified by distillation from lithium aluminum hydride.

Measurements. Relative fluorescence intensities were determined with an Aminco-Bowman spectrophotofluorometer. Fluorescence lifetimes were measured with a TRW Model 31A nanosecond spectral source coupled to a Tektronix Type 556 dual-beam oscilloscope, employing a deuterium lamp and a 340-nm interference filter to filter emitted light.

Samples were prepared in duplicate in 13 × 100-mm Pyrex test tubes, using 3-ml solutions of *ca.* 0.01 *M* sensitizer and varying concentrations of diene, and were degassed by three freeze-pump-thaw cycles at $<5 \times 10^{-4}$ Torr. The concentration of 2,6-dimethoxynaphthalene was *ca.* 0.001 *M* because of the poor solubility of this material in hexane. Eight readings were taken for the lifetimes, and the average values of τ_0 and τ were used. Fluorescence intensities for each sample were determined at least twice.

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