(14) In several cases, it was necessary to calculate $[\alpha]_D$ from specific rotations measured at other wavelengths when this quantity could not be measured directly on available instrumentation. These quantities were obtained by extrapolation of the least-squares line fitting the single term Drude equation (λ^2 vs. $1/[\alpha]_\lambda$) to the sodium D wavelength, see: C. Djerassi, "Optical Rotatory Dispersion", McGraw-Hill, New York, N.Y., 1960, p 5.

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Mechanisms of Electron Demotion. Direct Measurement of Internal Conversion and Intersystem Crossing Rates. Mechanistic Organic Photochemistry[1,2]

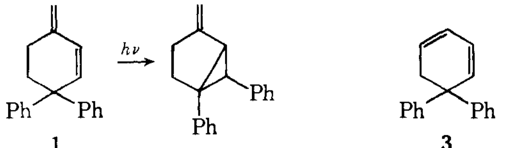
Howard E. Zimmerman,* Kenneth S. Kamm, and Dietrich P. Werthemann

Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706. *Received October 19, 1974*

Abstract: The decay mechanisms of the singlet and triplet excited states of a series of 1-phenylcycloalkenes were investigated. Our previously reported method of computer-assisted single-photon counting was used along with more traditional spectroscopic methods to obtain the total rate of singlet excited-state decay and also that of triplet decay. The singlet decay rate was dissected into rates of fluorescence, of radiationless decay, and of intersystem crossing. Rates were obtained both at 77 K and room temperature. For the triplet excited states, the room-temperature radiationless decay rates increased with ring size and ability of the excited molecule to twist with decrease of the T_1–S_0 energy gap. In the case of the singlet excited states, a similar parallelism was encountered, with one exception, and radiationless decay again correlated with ring size. Here, too, this internal conversion could be related with twisting ability of the excited state, here to minimize the S_1–S_0 energy gap. The implications of these results to organic photochemistry, wherein excited-state reactant most often affords ground-state product, are discussed.

In our previous report,[2b] we described the development of a method for obtaining exceptionally rapid singlet decay-rate constants. This approach utilized the basic technique of single-photon counting[3] along with use of an on-line minicomputer for data collection and processing. The technique allowed direct measurement of singlet decay rates as fast as 10^{10} sec^{-1}. Additionally, a "magic multiplier", based on temperature dependence of fluorescence, allowed amplification of capabilities to deal with rates up to 10^{12} sec^{-1}.

With this method available, we were able to pursue a number of exciting photochemical problems. One fascinating question dealt with the role of molecular flexibility in excited singlet deactivation processes. For example, previously we had postulated,[4] on photochemical grounds (note eq 1), that the presence of a potentially free rotating double bond made available a facile deactivation mechanism for triplets; this was termed the free rotor effect. The question remained regarding the extent to which singlet excited states might also avail themselves of this decay route.



(1)

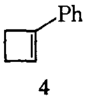
1 2 3

potential free rotor
reaction only from singlet

no free rotor
reaction from singlet
and triplet

These questions were of special interest to us because of their relevance to organic photochemistry. Many years ago we noted[5] that most organic photochemical reactions lead directly from excited state of reactant to ground state of product. For some processes, we suggested "electron demotion",[5] that is, a discrete radiationless decay process. For others, we considered excited state-ground state degeneracies along the reaction coordinate.[6]

Our intention in the present study was an isolation of the decay process in model systems where efficient photochemistry was not to be expected.[7] With the free rotor effect in mind, we selected the series of 1-phenylcycloalkenes **4–8**, beginning with 1-phenylcyclobutene (**4**) and ending with 1-phenylcyclooctene (**8**). This series promised to allow a correlation of decay rates to excited-state twisting.



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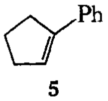

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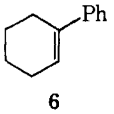

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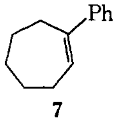

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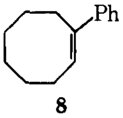

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Results. Fluorescence Decay Times. The first of three types of experimental data required for this study was the total rates of excited singlet decay (i.e., ${}^1k_{dt}$). We were interested in rates both at room temperature and 77 K. These were obtained quite readily using the reiterative convolution—single-photon counting method described in our earlier studies.[2b]

Minor improvements in the apparatus and techniques are detailed in the Experimental Section. The most troublesome pitfall proved to be purification of the phenylcycloalkenes since these were oils at room temperature. The problem was nicely handled by low-temperature recrystallization as described in the Experimental Section. Since even very minor

Table I. Direct Measurement of Singlet Lifetimes

Compd	Temp, K	Lifetime[a] (shifted), nsec	Lifetime (unshifted), nsec	Decay rate ($^1k_{dt}$), sec^{-1}	No. of runs
4	300	15.89 ± 0.58[b]	15.76 ± 0.68[b]	6.29×10^7	9
	77	23.45 ± 0.64	23.25 ± 0.92	4.26×10^7	2
5	300	14.01 ± 0.50	14.25 ± 0.72	7.14×10^7	6
	77	17.38 ± 0.68	17.63 ± 0.54	5.75×10^7	4
6	300	1.44 ± 0,12	1,48 ± 0.15	69.4×10^7	19
	77	15.84 ± 1.86	15,70 ± 1,42	6.31×10^7	5
7	300	0,28 ± 0.04	0.53 ± 0.06	357×10^7	5
	77	9.33 ± 0.68	9,64 ± 0.55	10.7×10^7	5
8	300	11.41 ± 0.55	10.66 ± 0.11	8.76×10^7	5
		and 3.0 ± 0.13[c]	and 2.80 ± 0.37	33×10^7	
	77	12,35 ± 0.21	12.2	8.10×10^7	2
Biphenyl	300	16.87 ± 0.19[d]	17.23 ± 0.13	5.93×10^7	7

[a] All measurements in methylcyclohexane–isopentane 4:1. [b] Standard deviation. [c] This was the only fluorescence decay requiring fitting by a sum of falling exponentials; 3.0-nsec component is 2.8 times more intense than the 11.4-nsec component. [d] Reported as 16.0 nsec in cyclohexane.[3]

Table II. Quantum Yields of Fluorescence

Compd	4	5	6	7	8
ϕ_f^{300}[a]	0.27	0.43	0.03	0.016	0.108[c]
ϕ_f^{77}[b]	0.62	0.72	0.4	0.42	0.46

[a] Measured in methylcyclohexane–isopentane 4:1 using biphenyl ($\phi_f = 0.18$) as a standard; estimated error ±10%, plus any error in the standard. [b] Measured relative to the same sample at 300 K; estimated error ±20%. [c] This ϕ_f is for the combined emission of both decay components. It can be dissected into $\phi_f^{300} = 0.08$ for the 3.0-nsec component and $\phi_f^{300} = 0.03$ for the 11.4-nsec component.

Table III. Rate Constants of Fluorescence

Compd	k_f^{300},[a] sec^{-1}	k_f^{77},[b] sec^{-1}	k_f^{calcd},[c] sec^{-1}	k(indirect)/ k(direct)[d]
4	1.70×10^7	2.64×10^7	68×10^7	31
5	3.07×10^7	4.14×10^7	66×10^7	18
6	2.08×10^7	2.52×10^7	59×10^7	26
7	5.71×10^7	4.49×10^7	72×10^7	14
8	2.64×10^7[e]	3.72×10^7	61×10^7	19

[a] Equation 1b; estimated error 25% for **7** and 15% for the rest. [b] Equation 1b; estimated error 25%. [c] Equation 2. [d] Ratio of k_f^{calcd} to the average of k_f^{300} and k_f^{77}. [e] Based on the 3.0-nsec decay compound; the longer lived fluorescence gives $k_f = 0.25 \times 10^7$ sec^{-1}, which does not match the low-temperature result.

impurities can lead to spurious emission, we employed a further test involving preparative VPC followed by repeated low-temperature crystallization. As noted in the Experimental Section, the emission wavelengths and decay rates as well as the less sensitive spectroscopic properties remained invariant. Trace impurities should not survive both VPC separation and fractional recrystallization. Each lifetime measurement was repeated several times, and the reproducibility proved excellent. The results are summarized in Table I.

Results. Fluorescence Quantum Yields and Fluorescence Rate Constants. The second type of data required for our study consisted of the fluorescence rate constants, k_f. We note that the natural fluorescence rate constant is given by the expression in eq 1b. Here ϕ_f is the fluorescence quantum yield, and $^1k_{dt}$ is the total rate of excited singlet decay as obtained in the previous section. Thus, with the $^1k_{dt}$'s already available, it was necessary to determine the ϕ_f's in order to derive the desired k_f's.

$$\phi_f = k_f/{}^1k_{dt} \tag{1a}$$

$$k_f = \phi_f{}^1k_{dt} \tag{1b}$$

For this, biphenyl proved to be an ideal fluorescence standard. The biphenyl fluorescence quantum yield is known to be $\phi_f = 0.18$,[8] and the envelopes of absorption and fluorescence emission were very similar to those of the 1-phenylcycloalkenes (**4**–**8**). Thus the quantum yields were readily obtained from the relative areas under the fluorescence emission curves of the compounds under study.

Since fluorescence quantum yields were desired not only at room temperature but also at 77 K, a number of potential complications had to be considered. These included variation of optical density with temperature, temperature dependence of refractive index leading to potential instrumental sensitivity variation, and temperature dependence of emission polarization. These problems have been discussed in our previous publication[2a] and shown to be unimportant under the present experimental conditions. Also, see ref 16 and the Experimental Section for comment on this aspect.

The measured room-temperature and 77 K fluorescence quantum yields are given in Table II. The derived natural rates of fluorescence are listed in Table III. Also included in Table III are the values for the rates of fluorescence as calculated from the Einstein-Bowen-Wokes[9] expression (note eq 2), where $\bar{\nu}_{max}$ is the wave number of the maximum absorption, and n is the solvent refractive index. It can be seen in Table III (column four) that the k_f's obtained from eq 2 differ from the directly measured rates, and the ratio of the two values is also tabulated. This deviation is discussed below.

$$k_f = 2.88 \times 10^9 \bar{\nu}_{max}{}^2 n^2 \int \epsilon(\nu)\,d\nu \tag{2}$$

Results. Intersystem-Crossing Efficiencies and Rates. The third kind of data needed consisted of the intersystem crossing efficiencies and the derived rates. The requisite quantum yields of intersystem crossing were obtained using the general method of Wilkinson and Dubois[10] and Sandros.[11] Thus, eq 3 gives the biacetyl emission intensity of a mixture of biacetyl and a hydrocarbon triplet-energy donor under conditions sufficiently dilute in biacetyl that no singlet energy transfer occurs, and that only hydrocarbon absorbs.

$$\frac{1}{\phi_p} = \frac{1}{{}^3\phi_p{}^{Bi}}\left[\frac{1}{\phi_{isc}{}^{HC}} + \frac{{}^3k_{dt}{}^{HC}}{\phi_{isc}{}^{HC}k_{ET}[Bi]}\right] \tag{3}$$

Here ϕ_p is the observed phosphorescence emission from the mixture, $^3\phi_p{}^{Bi}$ is the phosphorescence efficiency from the biacetyl triplet, $^3k_{dt}{}^{HC}$ is the decay rate of the hydrocarbon triplet of interest, k_{ET} is the rate of energy transfer from the hydrocarbon triplet to biacetyl, and $\phi_{isc}{}^{HC}$ is the intersystem-crossing efficiency of the hydrocarbon under study.

It is seen that the reciprocal phosphorescence intensity ($1/\phi_p$) is linear with the reciprocal of biacetyl concentration. The intercept has the form given in eq 4a and the slope as given in eq 4b. The constant K is characteristic of biace-

$$\text{intercept} = K(1/\phi_{isc}{}^{HC}) \tag{4a}$$

$$\text{slope} = K({}^3k_{dt}{}^{HC}/\phi_{isc}{}^{HC}k_{ET}) \tag{4b}$$

Table IV. Triplet Parameters

Compd	$^3\tau$,[a] msec	$^3k_{dt}$, sec^{-1}	ϕ_{isc}	k_{isc}, sec^{-1}
4	3.6 ± 2	280	0,004	0.25×10^6
5	0.58	1700	0,11	7.9×10^6
6	0.16	6300	0.0008	0.56×10^6
7	0.035 ± 0.006	30,000	0,0016	5.7×10^6
8	0.007	150,000	0.01	3.3 (0.88)[b] $\times 10^6$
Biphenyl	0.05[c]	20,000	0,81[d]	48×10^6

[a] Estimated error 60% plus error in $k_{diffusion}$ calculated from viscosity. [b] Value based on the 11,4-nsec fluorescence emission decay is in parentheses. [c] The agreement with literature is acceptable: 0.03 msec[10] and 0.1 msec.[11] [d] Standard; Sandros' value of ϕ_{isc} = 0.81 ± 0.04 was chosen;[11] it will provide upper limits for ϕ_{isc} in the measured compounds. The alternative literature value is ϕ_{isc} = 0.51 ± 0.20.[12]

tyl and common to experiments using different hydrocarbon donors. Thus the ratio of intercepts of such plots for a hydrocarbon of unknown $\phi_{isc}{}^{HC}$ and for a standard such as biphenyl gives the ratio of intersystem-crossing efficiencies. Additionally, for a given hydrocarbon, the ratio of the slope to the intercept is given by eq 5. Since just ratios of phos-

$$(\text{slope})/(\text{intercept}) = {}^3k_{dt}{}^{HC}/k_{ET} \qquad (5)$$

phorescence emission are used, the relative light intensity observed is used in the calculations rather than the absolute quantum yields of phosphorescence.

Using the known value of biphenyl intersystem-crossing efficiency of $\phi_{isc}{}^{biph} = 0.81$[11] and the ratio of intercepts as described above, it was possible to derive the intersystem-crossing efficiencies of the 1-phenylcycloalkenes **4–8.** These values are listed in Table IV.

If one assumes that the rate of energy transfer, k_{ET}, is diffusion controlled and 1.5×10^{10} sec^{-1}, eq 5 along with the slope to intercept ratios then gives the rates of triplet decay (i.e., the $^3k_{dt}{}^{HC}$'s). To the extent that diffusion control is not quite attained but the rate of quenching is constant for the series, the results represent relative decay rates instead. These values are also listed in Table IV and are paraphrased in the convenient form of triplet lifetimes (i.e., $^3\tau$ values).

Finally, with the quantum yields of intersystem crossing known and with the total rates of singlet decay available (note Table I), it is possible to solve eq 6 for the rates of intersystem crossing (i.e., the k_{isc} values). These are gathered

$$\phi_{isc} = k_{isc}/{}^tk_{dt} \qquad (6)$$

in Table IV. Also included in Table IV are the results of measurements for the biphenyl standard. It is seen that the triplet lifetime found, that is $^3\tau$ = 0.05 msec, is in reasonable agreement with the literature values of 0.03 msec[10] and 0.1 msec.[11]

Interpretative Discussion. Temperature Independence of k_f. In our previous publication on excited-state rate measurements,[2] we introduced a useful approach for measuring rates of decay which are too rapid for direct measurement at room temperature but accessible at low temperatures. This was based on the determination of the relative fluorescence quantum yields at the two temperatures. Thus, if we write eq 1a once for 77 K and once for room temperature and divide, we obtain eq 7 and our "magic multiplier" *M.*

$$\phi_f{}^{77}/\phi_f{}^{300} = (k_f{}^{77}/k_f{}^{300})({}^tk_{dt}{}^{300}/{}^tk_{dt}{}^{77}) = {}^tk_{dt}{}^{300}/{}^tk_{dt}{}^{77} = M \qquad (7)$$

However, in eq 7 we have assumed that $k_f{}^{77} = k_f{}^{300}$, that is, that the natural rate of fluorescence k_f is temperature independent. In favor of this assumption, we note that k_f is a property of electronic wave functions which should be temperature independent. Also, some examples of temperature independence of k_f are to be found in the literature.[13] In our own previous study,[2] three cases were available in which k_f was temperature independent within experimental error.

On the other hand, the assumption at this stage that k_f will invariably be temperature independent seemed unsafe. It was known[14] that the Einstein relation (eq 2) may fail where excited-state geometry differs considerably from that of ground state. This derives from the transition probability of singlet emission not being the same as that of absorption due to different well shapes. With this in mind, one can envisage further deviations as different vibrational levels are populated with changes in temperature. Furthermore, in at least one case, the observed k_f proved temperature dependent;[15] this was ascribed to emission from both S_1 and S_2 varying with temperature. Additionally there is the more trivial source of temperature dependence in the expectation that refractive index of the medium, as used in the Einstein relationship, should be temperature dependent. The calculated refractive index[16] at 77 K is only 7% greater than at 300°, giving an expected 14% increase in k_f at the lower temperature.

In the present study, the matter could be investigated directly, and the results in Table III reveal that k_f is indeed temperature independent for the systems under study.[17] Thus, in all the styryl-type systems we have studied, it does appear that the assumption that k_f is temperature independent is safe.

Additionally, this means that the method of magic multipliers, based on this assumption, is supported on a more firm basis.

Interpretative Discussion. Failure of the Einstein Relationship. In one of our earlier studies,[18] we described a method for obtaining rates of singlet decay (i.e., $^1k_{dt}$'s) indirectly by use of the Einstein relationship (eq 2). The method (note eq 8) used eq 1a above together with experi-

$${}^tk_{dt} = k_f{}^{calcd}/\phi_f \qquad (8)$$

mentally determined fluorescence quantum yields and $k_f{}^{calcd}$'s determined from eq 2. However, it is seen in Table III that the $k_f{}^{calcd}$'s (column four) calculated in the present study from the Einstein relation are too large by a factor ranging from 14 to 31. This result is similar to our previous findings of the same effect[2,20] and that the indirect method[18] of eq 8 can give $^1k_{dt}$'s useful as relative values but too large by a factor of ca. 30. Previously we noted[2] that the failure of the Einstein relation (eq 2) may be real or superficial. Thus, as noted above, where excited-state geometry is considerably distorted from ground state, the vibrational levels of the excited state do not mimic those of the ground state, and a mirror image relationship between absorption and emission will not occur. The Einstein relation depends on this mirror image situation and thus does not hold. A more trivial source of failure of eq 2 has been noted[2,20] as deriving from overlap of S_2 with S_1, thus making an estimate of the integral in eq 2 considerably too high.

Interpretative Discussion. Dissection of the $^1k_{dt}$'s to Obtain Rates of Internal Conversion. One of the ultimate aims in organic photochemistry of singlets is the determination of all fates of a potentially reacting excited-state molecule. Most difficult often is determination of the different modes of radiationless decay; and, as noted earlier, this was one of the major goals of the present effort.

Thus, with the $^1k_{dt}$'s for the present molecules determined (note Table I), with the k_f's (Table III) and k_{isc}'s measured (Table IV), and with the knowledge that the molecules under study were relatively unreactive (i.e., any k_r's were neglectable), it was only necessary to subtract k_f and k_{isc} in each case from $^1k_{dt}$ to obtain the rates of singlet in-

Table V. Radiationless Decay of Singlets

Compd	ϕ_{ic}^{300}	$\phi_{ic}^{77\,a}$	k_{ic}^{300}, sec^{-1}	k_{ic}^{77}, sec$^{-1\,a}$	k_{ic}^{300}/k_{ic}^{77}
4	0.73	0.38	4.6×10^7	1.6×10^7	2.9
5	0.46	0.17 (0.28)	3.3×10^7	$0.98\ (1.77) \times 10^7$	3.4 (2.1)
6	0.97	0.6	67×10^7	3.8×10^7	18
7	0.98	0.58	349×10^7	6.2×10^7	56
8	0.88	0.53 (0.54)	$32 \times 10^{7\,b}$	$4.3\ (4.4) \times 10^7$	7.5

[a] Based on the room-temperature value of k_{isc}, i.e., assuming little temperature dependence of k_{isc}. In the worst case, k_{isc} might decrease to zero. Where this affects the results, the values based on $k_{isc}^{77} = 0$ are given in parentheses. [b] Based on the 3.0-nsec decay component.

Table VI. Calculation of Fluorescence Rate Constant (k_f)

Compd	λ_{max}, nm	$\bar{\nu}_{max}$, kK[a]	FWHM,[b] kK	ϵ_{max},[c] M^{-1} cm^{-1}	k_f, sec^{-1}
4	253	39.7	5.3	14,200	6.8×10^8
5	256	39.1	5.7	13,200	6.6×10^8
6	246	40.7	4.9	12,600	5.9×10^8
7	246	40.7	6.6	11,500	7.2×10^8
8	246	40.7	5.5	11,700	6.1×10^8

[a] kK = 1000 cm^{-1}. [b] FWHM = full width at half-maximum. [c] Refractive index of MCIP 4:1 ~1.4.

ternal conversion to ground state, i.e., the k_{ic}'s. This results from

$$^{t}k_{dt} = k_f + k_{isc} + k_{ic}$$

The resultant k_{ic}'s are summarized in Table V. Alternatively, instead of partitioning the different modes of excited singlet decay in terms of rate constants, one might use quantum yields for the different processes. Thus Table V also includes the quantum efficiencies for internal conversion.

We note that the corresponding rates of triplet radiationless decay are already available without dissection (note Table IV).

Interpretative Discussion. Understanding of the Rates of Singlet Internal Conversion. Referring to column four of Table V, we turn first to the room-temperature rates of internal conversion. Here we note a striking increase in rate of this radiationless decay as the ring size is increased from the four-ring phenylcycloalkene **4** to the seven-ring phenylcycloalkene **7**, with a ca. 100-fold enhancement being observed in the seven-ring compound compared with the four-ring one. The case of 1-phenylcyclooctene (**8**) is unique in corresponding to a lower rate than the six- or seven-ring compounds. One might be tempted to try to correlate the rates of internal conversion to molecular flexibility as available in the NMR literature of cycloalkanes and cycloalkenes.[21] However, the NMR data deal with all molecular motions, and one has to consider the extent to which such distant vibrations are important to radiationless decay relative to the effect of local twisting about the excited π bond.

In attempting to understand the observed trend in internal conversion, we explored the ground-state and excited-state potential-energy surfaces using configuration interaction calculations along with the approximation of σ–π separation. The energetics were obtained as a function of angle of twist about the styrene-like π bond (note Figure 1a). In simulating the twist, the approximation was made that only the π-bond resonance integral and repulsion integral are affected. Additionally, it was of interest to consider the effect of constraining the twist by virtue of differently sized rings. Accordingly, a Hooke's law potential energy was superimposed on the electronic energy, and Figures 1b, 1c, and 1d show the results of increasing ring constraint. Further details of the calculations are included in the Experimental Section under Calculations.

Although the calculations are assumed to be of only qualitative significance, we do take the general form to be valid. It is interesting to note that the ground-state surface is similar to that described for ethylene (note Figure 2)[22] with a minimum at 0° and a maximum at ±90°. Both T_1 and S_1 have minima at ±90°, paralleling ethylene; however, there are additional minima at 0° in contrast to the ethylene situation.[23] For this comparison, one should refer to Figures 1a and 2 since both of these lack ring constraint.

If one were dealing just with the ethylene surface, the results would be understandable on the basis of the ring incorporating the styryl moiety inhibiting attainment of the 90° conformation of S_1. As the 90° conformation is reached, the S_1 and S_0 surfaces approach one another, and one would expect an increasing probability of radiationless transition.[24]

In the present instance, however, we find that ring size affects the population of the (90°) "twisted well" which is situated near the S_0 maximum, and which provides a pathway for efficient internal conversion.[25] Here the energy separation between the twisted well and the S_0 maximum remains constant with varying ring size. Nevertheless, in the extreme (see Figure 1d), the twisted well has been lost, and one is left with decay from the 0° S_1 state, and this will have an exceedingly small Franck-Condon factor and thus slow decay.

There are several experimental observations which support the general picture of the situation for S_1 as presented above and in Figure 1. First, the observation of fluorescence typical[2a,8,18] of the styryl chromophore provides support for existence of an S_1 minimum at 0° since fluorescence emission for a rather varied series of compounds with this chromophore appears at a relatively constant wavelength which would be unlikely if emission were from different conformations.

Secondly, our picture of efficient decay requiring attainment of the twisted conformation accords nicely with the finding (note Table VI) that radiationless decay is dramatically inhibited at 77 K in a matrix where twisting may be prevented both by the matrix rigidity and by the low thermal energy available. Strikingly, all of the k_{ic}^{77} values are seen to converge and approach the limiting value of ca. 3.6 $\times$ 10^7 sec^{-1} (average of k_{ic}^{77} for the five 1-phenylcycloalkenes). This limit is quite similar to the room-temperature value of 4.6 $\times$ 10^7 sec^{-1} observed for k_{ic}^{300} in the case of the 1-phenylcyclobutene which is rigid because of molecular geometry.

The case of the eight-ring compound is of interest since two emissions are observed, and since its rate of decay is surprisingly slow. The emissions seem likely to be from cis and trans isomers.[26] The slow rate of radiationless decay seems to suggest that attainment of the 90° conformation is difficult.[27]

Thus, for the 1-phenylcycloalkenes **4–8**, the rates of internal conversion to ground state seem controlled by the energy required to reach the twisted conformation from which decay is rapid because of close approach of ground and excited states.

Interpretative Discussion. Rates of Decay of T_1. The rates of triplet decay to ground state are given in Table IV. These are seen to follow a trend quite similar to that for S_1 to S_0

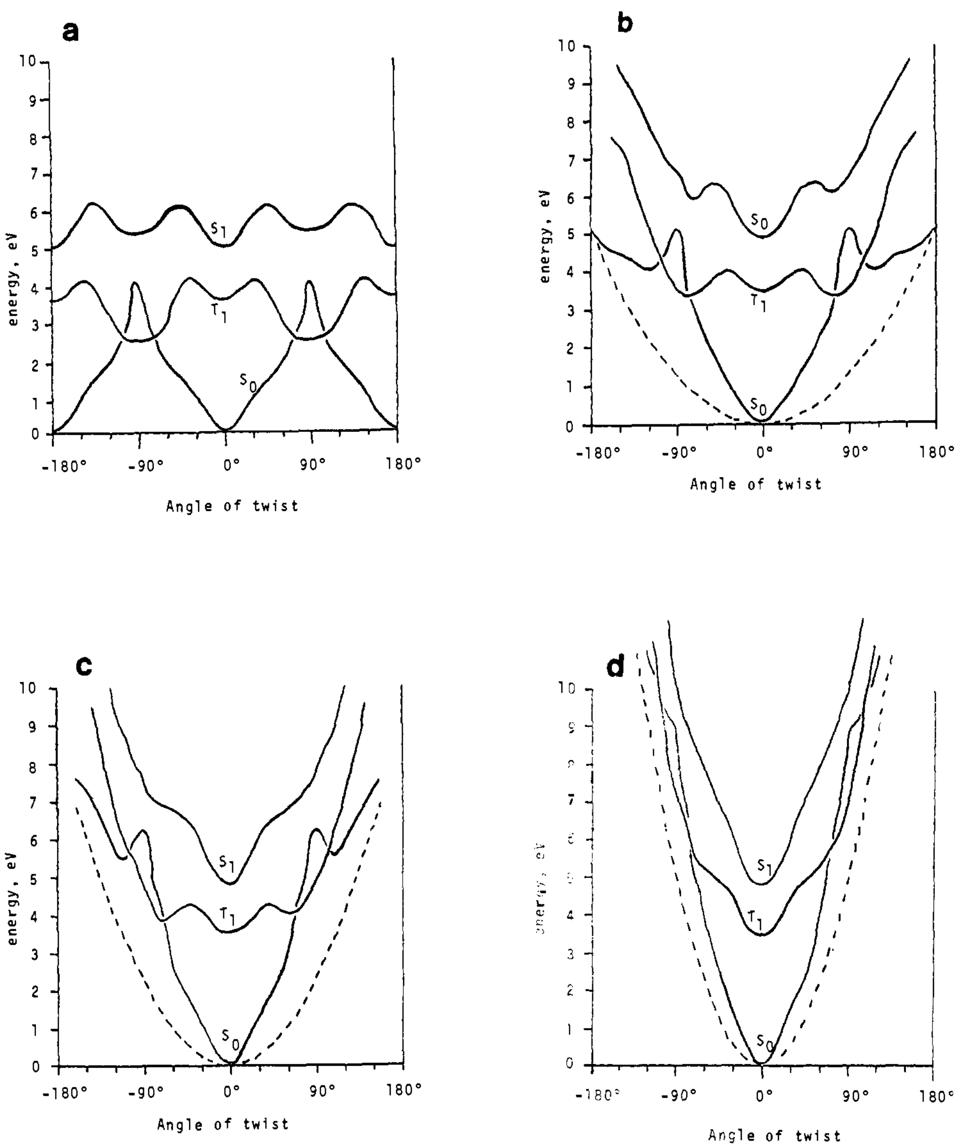

Figure 1. (a) Styrene electronic energy curves for twisting of the ethylenic bond. No added constraint. (b) Styrene electronic energy with small amount of added ring constraint. (c) Styrene electronic energy curves with moderate amount of added constraint. (d) Styrene electronic energy curves with large amount of added ring constraint.

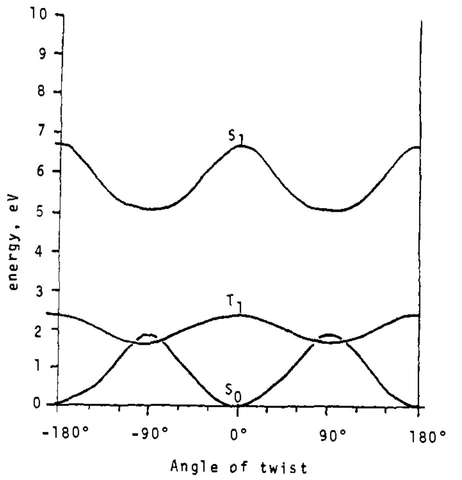

Figure 2. Ethylene electronic energy curves for twisting.[22a]

decay with the rate increasing with ring size. Inspection of Figures 1a through 1d shows that the T_1 potential-energy surface intersects ground state. The energy required for T_1 to reach the point of intersection is seen to increase with increasing ring constraint (i.e., decreasing ring size). Thus, the rates of decay are understood as deriving from the activation energies needed for reaching the potential-energy surface crossing.

In general the triplet rates are seen to be 10^4 to 10^5 times slower in decay to ground state than the corresponding singlet excited states. However, the dependence on ring size is essentially the same. Note that the decay of T_1 requires a multiplicity change, and thus this difference, while intriguing, is not inconsistent. In Siebrand's theory,[24b] triplet decay rates for a given energy gap are expected to be roughly 10^8 times slower than singlet decay rates for that gap. The presently observed greater rate of triplet decay may derive from the existence of crossings in the potential-energy surface.

It should be noted that there really is a singlet free rotor effect, in addition to the established triplet one.[4] In both singlet and triplet decay, there is an approximately 100-fold rate increase in going from **4** to **7**. This indicates that there is no inherent reason why the singlet free rotor effect should be less real than its triplet counterpart. However, most singlet reactions are much faster than the present free rotor decay process; in such situations, the more rapid k_r would mask the free-rotor effect.

If it is correct that the decay of S_1 occurs from the twisted conformation, and that decay of T_1 occurs near the intersection of T_1 and S_0, then it can be seen from Figures 1a–d that less twist is required of the triplets for decay. This may account for the eight-ring excited triplet decay being the fastest of the series and conforming to an increasing sequence with increasing ring size since a slight twist incurs less of the nonbonded repulsion of 90° twisted S_1 1-phenylcyclooctene (**8**).

Decay Mechanisms in Organic Photochemistry. Interpretative Discussion. It is a truism to note that, in all of photochemistry at some point along the reaction coordinate, the excited-state molecule must lose its excitation and become ground-state product. Any excited-state molecules decaying to ground-state reactant account for reaction quantum efficiencies which are usually less than unity. Some years ago we noted[28] that one can envisage two types of photochemical reactions not leading to excited state of product.[29] It was pointed out, for example, that a number of n-π reactions can lead directly to ground-state product by dissociative processes,[29,30] while other reactions required an "electron demotion" step along the reaction coordinate.[28] Subsequently,[6a] we commented that ground state-forbidden processes have a ground state-excited state degeneracy in the one-electron approximation, and that this, along with Jahn–Teller effects, will afford a point along the reaction coordinate where the probability of an excited state reaching the ground-state configuration will be high. Similarly, Dauben[31] has noted that sufficient energy is often not available to reach excited state of product in electrocyclic closures, and that electronic demotion then occurs from an intermediate geometry. Also, these modes of loss of electronic excitation have been dealt with in considerable detail by Michl recently.[32,33]

Most recently there has been a tendency in organic photochemistry to look for excited state-ground state degeneracies, of the type discussed above, with a view toward predicting photochemical reactivity. While we, ourselves, have noted the *requirement* for the loss of electronic excitation energy, often via such a degeneracy, somewhere along the reaction coordinate, nevertheless it seems wise at this point to comment that more generally it is not the mere existence of a degeneracy which controls the direction of most photochemical reactions but rather the question is *which degeneracy* will be utilized.

Early in our photochemical investigations, we pointed out that excited-state molecules tend to transform themselves in such a way as to minimize their energies, much as in the reactions of ground-state species. Minimum energy barriers are traversed and energy maxima are avoided. Indeed, often there are activation energies encountered along excited-state hypersurfaces,[34] and excited-state molecules seem to utilize the lowest energy possible processes. In predicting such preferred pathways, we have suggested using excited-state bond orders,[28,35] excited-state electron densities,[36] calculated potential-energy surfaces,[37] and simple MO estimates of half-reaction excited-state energy.[38]

Finally, supporting this view, we note that, in the present study where no reaction occurs, the decay rates are considerably slower than those measured in our previous paper on decay rates in the di-π-methane rearrangement.[2a] The main difference seems to be that, in the di-π-methane systems, decay was facilitated by occurrence of decay pathways along the reaction coordinate. Also, the extent of twisting available in the acyclic systems was greater than in the present cycloalkenes with less activation energy needed to reach the points of near degeneracy.

Experimental Section

Sample Preparation. Methylcyclohexane–isopentane (4:1) was used for emission experiments. Reagent grade solvents were purified by shaking 2 l. of solvent with successive 25-ml portions of 15% fuming sulfuric acid until the acid remained colorless, then stirring at reflux with 400 ml of 10% sulfuric acid, saturated with potassium permanganate. Every hour, an additional 3 g of permanganate was added. After 6 hr, the solvent was washed with water, dried over phosphorus pentoxide, and passed through a 2.5 × 40 cm column of alumina bearing 10% (wt) silver nitrate as described by Murray and Keller.[39] Solvent prepared in this manner was transparent in the ultraviolet (OD 0.1 at 226 nm, 1-cm path) and gave no detectable emission either at room temperature or as an outgassed glass at 77 K. 1-Phenylcyclobutene[40] (**4**), 1-phenylcyclopentene[41] (**5**), 1-phenylcycloheptene[41] (**7**), and 1-phenylcyclooctene[42] (**8**) were prepared as described[40-42] from the corresponding cycloalkanones by Grignard reaction followed by treatment with sulfuric or *p*-toluenesulfonic acid. Phenylcyclobutene was also prepared via the Bamford–Stevens reaction from cyclopropyl phenyl ketone.[40c] 1-Phenylcyclohexene (**6**) was purchased from Aldrich Chemical Co. All the phenylcycloalkenes were liquids at room temperature. They were purified by fractional spinning-band distillation. Just prior to use, all except the phenylcyclooctene were recrystallized several times from methylcyclohexane and from anhydrous methanol, using a Dry Ice-cooled air bath for gradual cooling and centrifugation for removal of the mother liquors. Melting points are: **4**, 0–1°; **5**, 23–24°; **6**, 5.5–6.0°; **7**, −12 to −11°. The phenylcyclooctene could not be crystallized, even at −78°. Its elemental analysis was satisfactory. Preparative gas chromatography of the distilled material (6 ft × 1 in., 15% Carbowax 20M on Chrom W, 170°) gave no changes in the uv, NMR, ir, and singlet lifetime as determined by single-photon counting.

Biphenyl was sublimed twice, recrystallized from ethanol and resublimed. Biacetyl was purified by fractional freezing, followed by fractional distillation, and was stored in the dark.

All samples were degassed with freeze–pump–thaw cycles on a vacuum line using liquid nitrogen for freezing. Five cycles were sufficient for singlet work, but ten cycles with warming to near reflux and with vigorous agitation were required in triplet work for the emission intensity to approach its asymptotic value. All low-temperature spectra were run at 77 K. Room temperature varied between 18 and 30°, and ambient temperature measurements are thus superscripted 300 K.

Magic Multipliers and Fluorescence Quantum Yields. These were measured as described previously,[2b] exciting at 250 nm. The room-temperature concentrations were adjusted to provide an optical density (OD) of 0.80 at 250 nm. Fluorescence is maximized in the present geometry at 0.87 OD. The intensity error caused by matrix contraction is minimized since the room-temperature OD and the 77 K OD are on opposite sides of the intensity maximum at 0.87 OD, but near it. The fluorescence standard was biphenyl, $\phi_f = 0.18$,[3] selected because of the close similarity between its absorption and emission and those of the phenylcycloalkenes. The emission monochromator slits were set wide enough that the structured biphenyl emission merged into a smooth envelope nearly identical with the phenylcycloalkene fluorescence. Rates of fluorescence were calculated from the Einstein relationship as modified by Bowen and Wokes[9] by the method of Zimmerman and Baum[18] (see Table VI). Absorption spectra were measured on a Beckman DK-2A or a Cary 11MS recording ultraviolet spectrometer; 1 × 1 cm Suprasil cells with fused joints, grease traps, and stopcocks above were used.

Single-Photon Counting. The apparatus and procedure have been described previously.[2b] The lamp was modified to allow the center (negative) electrode to be moved in and out, by external adjustment, thus adjusting the gap. This was accomplished with O-ring seals. The lamp is now run at 80 psi of N_2 (6.5 atm) to provide more intensity below 300 nm. A highly reproducible flash of 3.5 nsec full width at half-maximum is obtained at a repetition rate of 20–30 kHz. The high brightness and frequency of the lamp (combined with relatively large ϕ_f's) result in short data collection times. Only 5 min is needed to collect 2000 counts in the highest channel (about 300,000 counts total in 512 channels), when collecting at 5% of the 20-kHz lamp frequency. The 5% factor assures that few double photons are collected.[43]

Table VII. Calculation of Triplet Parameters

Compd	[Bi] range, mol l.$^{-1}$		Slope, mol l.$^{-1}$	Intercept	[Intercept/slope] l. mol^{-1}	$^3\tau$,[b] sec	$\frac{1}{\text{intercept}}$	ϕ_{isc}[c]
4[a]	1×10^{-7}	2×10^{-8}	6×10^{-9}	0.52	8.7×10^7	5.8×10^{-3}	1.92	0.0031
			1.4×10^{-8}	0.30	2.1×10^7	1.4×10^{-3}	3.3	0.053
5	1×10^{-7}	2×10^{-8}	1.6×10^{-9}	0.014	8.7×10^6	5.8×10^{-4}	71	0.11
6	2×10^{-6}	1×10^{-7}	8.34×10^{-7}	2	2.4×10^6	$1{,}6 \times 10^{-4}$	0.5	0.0008
7[a]	1×10^{-4}	2×10^{-6}	1.75×10^{-6}	1.06	6.1×10^5	4.1×10^{-5}	0.945	0.0015
			2.3×10^{-6}	0.96	4.2×10^5	2.8×10^{-5}	1.08	0,0017
8	1×10^{-4}	1×10^{-5}	1.5×10^{-6}	0.15	1×10^5	7×10^{-6}	6.7	0.011
Biphenyl	1×10^{-5}	2×10^{-8}	3×10^{-10}	0.002	7×10^6	5×10^{-4}	500	0.81

[a] Calculations for **4** and **7** carried out for lines at boundary of the plot to demonstrate error limits; other calculations for best visual fit. [b] Based on $k_{\text{diffusion}} = 1.5 \times 10^{10}$ (see text);[45] error estimated at ±60% + error in $k_{\text{diffusion}}$. [c] Based on ϕ_{isc} of biphenyl; error estimated at ±60%.

A second Bausch and Lomb high intensity monochromator has replaced the interference filters used earlier to isolate the emission. Excitation was generally at 250 nm, and emission was monitored by the RCA 8850 photomultiplier at 310 nm. Different choices of excitation and emission wavelength produced no significant change in the observed decay rate of all compounds investigated.

Mathematical Treatment of Data. The versatile computer programs described earlier[2b] were modified only by the inclusion of a new criterion for goodness of fit, the "*A*-value" in place of the ratio of SSQR to SSQP,[2b,44] which was found to be overly sensitive to small deviations in the low-intensity extremities of the decay. Formerly, a high, poor ratio of SSQR to SSQP was usually due to two or three bad points out of the 512 composing a full curve, which was otherwise fit very closely. A more practical criterion is the *A* value, defined as the sum of the absolute value of the point by point difference between the experiment and the computer best-fit curve, divided by the sum of all experimental points (eq 9). This

$$A = \sum_{t=1}^{512} |\Delta E_t| \Big/ \sum_{t=1}^{512} E_t \qquad (9)$$

can be visualized as the ratio of the area of mismatch to the area under the experimental curve. For experiments with ca. 2000 photon counts in the highest channel, the computer-fitted curve shows no visual mismatch with the experimental curve when the *A* value is below 3%.

Measurement of Triplet Parameters. The general method of Wilkinson and Dubois[10] and Sandros[11] was used. A triplet-yield standard (biphenyl, ϕ_{isc} 0.51 ± 0.2[12] or 0.81 ± 0.04[11]) was included as an additional sample in each series. The higher value of ϕ_{isc} was used.

For each hydrocarbon, a series of samples was prepared, in which the concentration of hydrocarbon was fixed at about 10^{-4} *M* to provide an optical density of ca. 0.87 at 250 nm, and the concentration of biacetyl was varied from 10^{-4} to 10^{-8} *M*. Sensitized biacetyl phosphorescence at 510 nm was monitored in an Aminco spectrofluorimeter by an RCA 4818 photomultiplier, through a plate of Corning 3-75 filter glass which excluded the second order of the 250-nm excitation light. No biacetyl fluorescence was observed as long as the biacetyl concentration was below 1×10^{-4} *M*. Plots of the reciprocal of the observed phosphorescence intensity vs. $[\text{Bi}]^{-1}$ were linear in the region of [Bi] low enough to prevent singlet transfer. The reciprocal of the intercept gives the extrapolated fluorescence intensity that would be produced in the experimentally unrealizable situation of perfect triplet transfer to biacetyl, with no singlet transfer. The biphenyl intercept provides a standard so that yield of intersystem crossing of a given hydrocarbon HC can be calculated using eq 10. Additionally for an unknown hydrocarbon, the ratio of the slope to the intercept is given by eq 11. The diffusion-controlled rate was calculated from the solvent viscosity η by use of eq 12.[45] The data used in calculating the triplet parameters are shown in Table VII.

$$\frac{\phi_{isc}{}^{HC}}{(\text{intercept}^{HC})^{-1}} = \frac{\phi_{isc}(\text{standard})}{(\text{intercept}^{std})^{-1}} \qquad (10)$$

$$(\text{slope})/(\text{intercept}) = {}^3k_{dt}{}^{HC}/k_{ET} \qquad (11)$$

$$k_{diff} = 8RT/2000\eta \qquad (12)$$

Polarization. A set of Glan prisms was inserted in the excitation and emission beams of the Aminco-Kiers spectrofluorometer. The degree of polarization (*P*) was measured at room temperature and at 77 K by the method of Azumi and McGlynn[46] which includes a correction for instrumental factors (eq 13). The symbol I_{EB}, for example, stands for the intensity of fluorescence observed when the exciting light is polarized vertically (E), with the emitted light observed through a horizontal polarizer (B). The prisms did not transmit 250-nm light so the samples were irradiated at 260 nm and observed at 310 nm.

$$P = \frac{I_{EE} - I_{EB}(I_{BE}/I_{BB})}{I_{EE} + I_{EB}(I_{BE}/I_{BB})} \qquad (13)$$

The largest polarization among the phenylcycloalkenes was 0.05 (the limits of *P* for stationary emitters are 0.5 to −0.33).[47] The low polarization means that there will be less than 0.1% polarization-caused error in the fluorescence intensity measurements.[48]

Calculations. The program CONFIG-P, written in this laboratory,[50] was used to calculate energies and bond orders in styrene as a function of the angle of twist about the ethylenic bond. From the input values for Coulomb integrals, resonance integrals, and repulsion integrals, the program first calculates the Hückel energies and wave functions. The Hückel wave functions served as the basis set for 16 singly excited configurations which were then allowed to mix with the ground configuration and with each other to provide final configuration interaction electronic states.

Coulomb integrals, resonance integrals, and repulsion integrals were set up as in the earlier work.[50] The angle of twist was increased from 0° in 10° increments by setting the ethylenic resonance integral $\beta = \beta° \cos \theta$. The ethylene repulsion integral was similarly reduced: $G = G°(1 - 0.05 \sin \theta)$. The repulsion integral between adjacent sp^2 hybridized carbons is reduced only 5% at full 90° twist, by analogy with repulsion integrals for the carbonyl group (π_C–π_O *vs.* π_C–n_O).[35b] The resulting configuration interaction ground state and lowest excited triplet and singlet states are plotted as a function of twist angle in Figure 1a. To simulate the effects of ring constraint, three successively tighter parabolic[51] wells centered at 0° were added to the electronic curves. The approximate force constant of the well in Figure 1b is 1.6×10^{-4} eV deg^{-2}; in Figure 1c, 2.8×10^{-4} eV deg^{-2}; in Figure 1d, 3.6×10^{-4} eV deg^{-2}.

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(17) In comparing $k_f{}^{77}$ and $k_f{}^{300}$ for each compound, the largest change is 36% (compound **4**), which is within experimental error considering the individual errors in Table III. Note that, in all cases except 7, there is a tendency for a decrease in k_f at the higher temperature. This may reflect the expected ca. 14% decrease in the n^2 term of the Einstein relationship at higher temperature.

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(21) (a) Cycloalkanes (e.g., 4, 5, 7, and 8 rings) tend to be rather flexible[21b–d] and undergo rapid pseudorotation. Flexibility data for cycloalkenes are sparser. Cyclohexene undergoes an extremely rapid inversion,[21e] cyclooctene pseudorotates,[21c] but cycloheptene is relatively rigid.[21f] (b) J. E. Anderson, *Q. Rev., Chem. Soc.*, **19**, 426 (1965); (c) G. Chiurdoglu, Ed., "Conformational Analysis", Academic Press, New York, N.Y., 1971; (d) M. Hanack, "Conformational Theory", Academic Press, New York, N.Y., 1965; (e) F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, **87**, 3147 (1965); (f) S. Kabuss, H. Friebolin, and H. Schmid, *Tetrahedron Lett.*, 469 (1965).

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(24) (a) A recent chapter by Henry and Siebrand[24b] provides an entry into the several theories of radiationless transitions. The present treatment is based on Siebrand's theory, which shows that the rate of a radiationless transition is proportional to $\exp(-\Delta E)$, where ΔE is the energy difference between the states involved in the transition. (b) B. R. Henry and W. Siebrand in "Organic Molecular Photophysics", J. B. Birks, Ed., Wiley, London, 1973. (c) The interestingly long lifetime of compound 4 has precedent in the 40 sec^{-1} $^3k_{dt}$ value for anthracene in THF at room temperature reported by H. Linschitz, C. Steel, and J. A. Bell, *J. Phys. Chem.*, **66**, 2574 (1962).

(25) (a) The calculations are not expected to have quantitative significance, especially for twisted conformations. Thus, the barrier height between the "planar well" and the "twisted well" seems to be exaggerated in the present calculations. (b) It should be recognized that presently we focus attention on one mode of decay which seems dominant, namely twisting. However, other molecular vibrations may interact in the decay process. Thus, for example, the slightly inverted order of k_{ic} for **4** and **5** may result from more ready phenyl twisting in the four-ring case.

(26) (a) The relative stability of ground-state trans and cis cyclooctenes is shown by the heat of hydrogenation, which is 9 kcal more exothermic for trans.[26b] At low temperature, only one emission is seen from the 1-phenylcyclooctene. Both matrix rigidity and low thermal energy prevent population of trans excited singlets. It is tempting to assign the 3.0-nsec fluorescence decay component to *cis*-**8** since its $k_f{}^{300}$ is much closer to the value of $k_f{}^{77}$ than is the $k_f{}^{300}$ derived from the 11.4-nsec decay component. The single falling exponential emission decay at 77 K is almost certainly due to cisoid excited states since the ground state is cis, and the rigid matrix would prevent isomerization of excited states. It would be most unusual, however, for the room-temperature trans excited singlet to have a longer lifetime than the cis. The trans excited singlet has additional strain energy to be released on twisting to the "twisted well" from which decay is facile. (b) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).

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