Intramolecular Excimer Formation in Saturated Amines. A Probe of Linear Chain Alkane Conformational Distribution

Arthur M. Halpern,* Michael W. Legenza, and B. R. Ramachandran

Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115. *Received February 26, 1979*

Abstract: The fluorescence properties of members of the series $(CH_3)_2N[CH_2]_nN(CH_3)_2$ are reported for $n = 1$–13, 16, 18, and 20 in dilute (10^{-4} M) *n*-hexane solution at 23 °C. Based on comparisons with monoamines, emission from diamines n = 1 and 2 is assigned as excimer/monomer fluorescence. For $n = 3$ and 4, emission from both monomer and excimer is distinctly observed. While the emission spectrum of $n = 5$ shows no evidence of an excimer contribution, the decay curve is nonexponential and suggests the involvement of an excimer state. From fluorescence quantum yield and decay curve measurements, the rate constants pertinent to monomer/excimer equilibrium are evaluated for compounds $n = 1$–5. For $n > 6$, fluorescence spectra resemble those of monoamines and, with the exception of $n = 16$ and 20, decay curves show single exponential decay. For diamines $n \geq 4$, intramolecular self-quenching rate constants (k_{isq}) are determined. Between $n = 4$ and $n = 8$, k_{isq} sharply decreases, reaching a minimum at $n = 8$. For $n > 8$, k_{isq} increases, reaching a maximum at ca. $n = 12$; for longer chain lengths, a slight decrease in k_{isq} is indicated. For larger chain sizes, a comparison of k_{isq} with a prediction based on a freely linked model suggests that appreciable chain stiffness is present. In general, the dependence of k_{isq} on chain length (for $n > 5$) is interpreted as a manifestation of changes in the static conformational distribution functions of the diamines. Nonexponential fluorescence decay was observed for $n = 16$ and 20; this might imply that the head-to-head distribution functions are broader for these diamines than for the others.

During the nearly 25 years since the first reported observation of the photoassociation of pyrene in fluid solution by Kasper and Forster,[1] many organic molecules have been shown to undergo excimer formation, both in solution and in the vapor phase. Indeed the general phenomenon of concentration quenching of fluorescence is usually interpreted in terms of intermolecular excimer formation.[2] *Intra*molecular excimer formation was first described by Hirayama, who noticed that the fluorescence spectra of polystyrene solutions exhibited a band near 320 nm in addition to the normal "monomer" band characteristic of alkylbenzene fluorescence.[3] Hirayama subsequently showed that the fluorescence spectra of solutions of 1,3-diphenylpropane also showed monomer and excimer emission, and that the long-wavelength excimer band was absent for those compounds in which the phenyl substituents were separated by any number other than three carbon atoms (up to six carbon atoms).[4]

This phenomenon has been since dubbed the "$n = 3$" rule of intramolecular excimer formation.[5] The rationale for this prediction is that, in order to achieve the parallel sandwich configuration of the two aromatic moieties having the optimum interplanar ring separation of ca. 3.2 Å, the aromatic pendants would have to be attached to the ends of a trimethylene segment. Longer or shorter segments not only affect the pendant ring separation distance, but also begin to involve substantial nonbonded interactions between the alkane chain units themselves.

The $n = 3$ rule generally seems to work well. Intramolecular excimers have indeed been observed for the following 1,3-bis substituted propanes: phenyl, α- and β-naphthyl,[6] *N*-carbazoyl,[7] pyrenyl,[8] and dimethylamino,[9] to name several. Recently, Zachariasse and Kühnle have shown that intramolecular excimer formation occurs in the α,ω-bis(pyrenyl)alkanes, $Py[CH_2]_nPy$, not only for $n = 3$, but also for $n = 4$–6, 9–16, and 22.[10] The larger binding energy of the pyrene excimer (9.4 kcal) relative to the benzene system (5.1 kcal) is one of the mitigating factors in causing the emission of this intramolecular excimer to be observable in alkane chains having $n > 3$. Apparently, the nonbonded interactions which represent much of the barrier to the formation of medium-sized rings can be compensated for by the larger exothermicity of the pyrene excimer vis-à-vis benzene. In addition, of course, there are statistical factors which affect the encounter frequencies of the termini of an alkane chain. Indeed, Zachariasse and Kühnle have compared the chain-length dependence of the intramolecular pyrene excimer fluorescence intensity with various size ring-closure reactions' rates and yields.

This paper reports the results of a study of intramolecular excimer formation in α,ω-bis(dimethylamino)alkanes, $Me_2N(CH_2)_nNMe_2$, for $n = 1$–13, 16, 18, and 20. In the discussion which follows, members of this series are denoted as TM *n*. Since the fluorometric probe, namely, the dimethylamino group (or more simply, the N atom), represents, as a substituent, a small enough perturbation, the kinetics and thermodynamics of the N–N interaction probably closely approximate the intrinsic statics and dynamics of linear chain alkane conformation. Because the N atoms are situated near the termini of the alkane, it is specifically the end-to-end flexibility of the alkane to which these measurements are sensitive.

Results

The fluorescence spectra of dimethylalkylamines, representative monoamines of the series, are characterized by a maximum at 292 nm in *n*-hexane solution. In addition, the maximum and width of these spectra are invariant with concentration (as studied up to ca. 1 M). Thus, there is no evidence of intermolecular excimer formation in these compounds. The fluorescence spectrum of neat *N,N*-dimethylethylamine at low temperature does not deviate significantly from the spectrum obtained in dilute *n*-hexane solution at ambient temperature.

Surprisingly, the "$n = 3$" rule works reasonably well even for saturated amines. To wit, the emission spectrum of TM 3 is dominated by a broad band with λ_{max} at 365 nm; the monomer emission is represented by a weaker shoulder at ca. 290 nm (see Figure 1). From the temperature dependence of the emission spectrum, the binding energy of the TM 3 excimer was estimated to be 2.7 kcal.[9] Both the monomer and excimer fluorescence decay curves were measured using appropriate interference filters. The decay curve of the excimer was adequately analyzed using a convolute-and-compare method based on a single component exponential decay with a lifetime of 26.9 ns. The monomer decay curve, however, was nonexponential showing a very fast decay component which was beyond the resolution of the instrument (<0.3 ns) and an exponential tail (λ 27.0 ns). The amplitude of the long component was approximately twice that of the short one. The very fast compo-

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nent is either caused by scattered light transmitted through the interference filter (the overall quantum yields, Φ_f, of the monomer and excimer are 0.020 and 0.63, respectively), or is due to a very fast decay associated with the excited monomer itself. The latter case probably applies because the inclusion of additional filtering did not result in any significant reduction in the amplitude of the fast component.

Thus, it can be concluded that for TM 3 excimer emission is dominant, and that a substantial fraction of the monomer emission occurs as a consequence of thermal feedback from the excimer. In addition, it can be deduced that the formation rate of the excimer (from excited monomer) is very fast, being on a subnanosecond time scale (i.e., $k_{DM} > 10^{10}\,s^{-1}$).

Compared with model monoamines (e.g., *N,N*-dimethylalkylamines), the fluorescence spectrum of TM 2 is somewhat broader and red shifted. λ_{max} is 304 nm, relative to 292 nm for monoamines; there is no shoulder or other characteristic of the spectrum which permits the separate assignment of monomer and excimer emission (see Figure 1). The fluorescence decay of TM 2 exhibits exponential decay ($\tau = 26.3$ ns) irrespective of the emission wavelength being analyzed. While the lifetime of TM 2 is similar to that of model monoamines, the quantum yield is considerably smaller (Φ_f is 0.21 compared with 0.69 for dimethylethylamine). Thus the emission of TM 2 represents either pure excimer fluorescence or emission from both monomer and excimer in equilibrium. The relatively slight red shift of the emission spectrum of TM 2 would imply that the excimer is weakly bound and thus the thermal repopulation of monomer from excimer would be expected to be fast (i.e., k_{MD} large). On the basis of the close proximity of the two N atoms in TM 2, it is not unreasonable to assume that the electronically excited molecule could reach a geometry in which both N atoms become coupled on a very short time scale (only a few bond rotations would be involved). Reference 9 also contains a discussion of the photokinetics of TM 2 in the vapor phase.

Similar observations can be made about the emission properties of TM 1. The fluorescence spectrum is slightly red shifted (λ_{max} is 296 nm) and broadened relative to monoamines. The fluorescence decay is exponential ($\tau = 33.0$ ns) irrespective of emission wavelength. As in the case of TM 2, the emission may be taking place from monomeric and excimeric states which are in thermal equilibrium.

It is also possible that in TM 1 and TM 2 the close proximity and favorable orientation of the two N atom lone pairs may result in ground state orbital interaction. The photoelectron spectrum of TM 2 reveals that the first vertical IP is 8.34 eV, which compares with 8.5 eV for trimethylamine. Also, a quantitative comparison of the vapor phase absorption spectra of TM 2 and trimethylamine, both at λ_{max} (the $S_2 \leftarrow S_0$ transition, 195 and 198 nm, respectively) and at 227 nm (a shoulder representing the $S_1 \leftarrow S_0$ transition), provides no indication of ground-state lone pair–lone pair interaction in TM 2. Photoelectron spectral data for TM 1 are not available, but the electronic absorption spectrum suggests that some ground-state coupling may, in fact, be present. To wit, the absorption of TM 1 is somewhat more intense relative to monoamines; for example, ϵ_{max} at 200 nm is 10 000 $M^{-1}\,cm^{-1}$.

In addition to TM 3, the only other diamine in the series which shows definitive monomer and excimer emission is TM 4. For this compound, however, the monomer band is more intense at 25 °C, and the excimer fluorescence appears as a weaker, broad band at ca. 350 nm. The vapor-phase spectrum of TM 4 clearly reveals monomer and excimer components. Vibrational structure is present in the monomer emission and is very similar to that observed in the emission of trimethylamine in the vapor phase. In *n*-hexane solution, the fluorescence bands of the TM 4 monomer and trimethylamine are both structureless, having λ_{max} at 292 nm. The position of the excimer band is the same in both phases. Preliminary studies of the temperature dependence of the TM 4 monomer and excimer fluorescence spectra and decay kinetics reveal that the binding energy of the excimer is about 2.2 kcal. The kinetic analysis of the monomer/excimer system is complicated by the fact that both emission bands are relatively weak ($\Phi_{fM} = 0.0093$ and $\Phi_{fD} = 0.007$ at 25 °C).

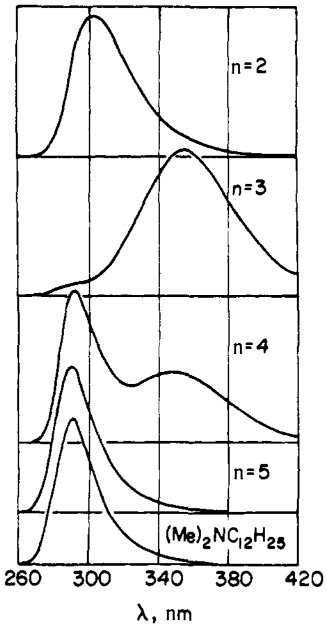

Figure 1. Uncorrected fluorescence spectra of TM 2, TM 3, TM 4, TM 5, and a monoamine, DM 12, in *n*-hexane (1×10^{-4} M). The excitation wavelength is 220 nm.

A more serious problem is that "normal" monomer/excimer decay kinetics are not observed for TM 4 in *n*-hexane solution between 164 and 373 K. For example, at 193 K, the monomer decay curve is represented by the double exponential:

$$I_{fM}(t) = \exp(-t/1.8) + 0.077\exp(-t/10)$$

while the excimer decay curve is

$$I_{fD}(t) = \exp(-t/9.5) + 0.067\exp(-t/27)$$

where t is in nanoseconds. Thus, the excimer decay curve does not show the usual buildup term (a component having a negative amplitude). The failure to observe the buildup feature in the excimer decay curve could be a consequence of the relatively short "monomer" lifetime; alternatively, it may be a reflection of the fact that the excimer is not formed in a strictly "diffusional" mechanism (as in intermolecular systems). Thus there may be a fraction of TM 4 ground state configurations which resembles the actual excimeric structure and this would have the kinetic consequence that excimer formation would not be adequately accounted for by a single time-independent rate constant.

It should be noted that, at all temperatures studied, the value of the short-lived component of the excimer decay curve coincides with that of the long-lived portion of the monomer decay curve. The *long*-lived component of the excimer decay curve, however, was absent in the monomer decay. It is possible to speculate that this component corresponds to the decay of a less emissive TM 4 excimer (D′), which presumably has a different geometry than the species (D) whose feedback term is observed in the monomer decay curve. According to these decay data, and using the two-excimer hypothesis, the general scheme

$$M \rightleftarrows D \rightarrow D'$$

follows, where M, D, and D′ represent the excited monomer

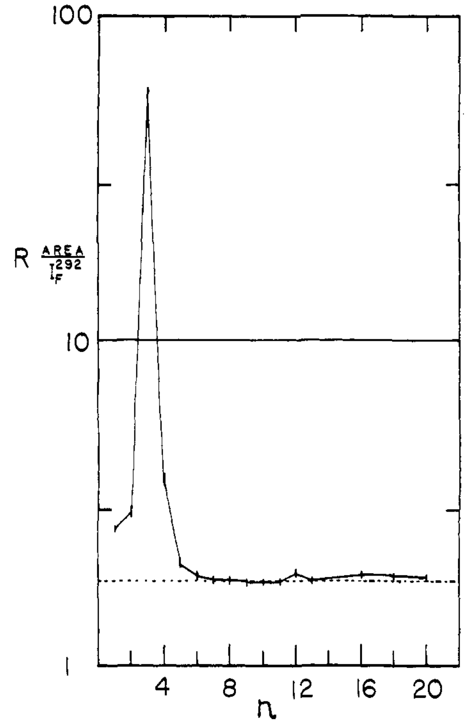

Figure 2. Plot of R, the area under a fluorescence spectrum, divided by I_f (292 nm) vs. n.

and two excimer species. This topic will be reported separately after the completion of more detailed photokinetic studies of TM 4.

In the case of TM 5, the fluorescence spectrum closely resembles that of a monoamine. However, although λ_{max} is still at 292 nm, there is a slight broadening of the spectrum relative to representative monoamines. This observation, when taken alone, is only very weakly suggestive of the existence of an intramolecular excimer. In order to cast a diamine's spectral appearance into sharper perspective, the area to intensity (taken at 292 nm) ratio, R, was measured for the diamines in the series. $R = 292$ nm was chosen because it corresponds to the λ_{max} position of model monoamines; hence, this ratio provides an indication of the extent to which a diamine's fluorescence spectrum deviates from that of a monoamine prototype. Figure 2 portrays these data. It is immediately clear that the $n = 3$ rule is generally borne out. The dashed line corresponds to the R value for model monoamines, and thus represents the case of no excimer emission. Even for $n = 4$ in which excimer emission is definitive (see Figure 1), R is some 16 times smaller relative to the $n = 3$ diamine. For $n = 1$ and 2, the overall red shifts in the respective fluorescence were noted as being possibly indicative of an unresolved, monomer/excimer emission system. Now, it can be seen that, for $n = 5$, R is slightly above the base line, suggesting the presence of a very weak excimer spectral component. It is interesting that, for $n = 12$, 16, and 20, R values are somewhat larger as compared with monoamines; this can be viewed as suggestive of excimer emission in these compounds. It is noteworthy that Zachariasse and Kühnle[10] have observed the emission of the intramolecular excimer of 1,13-diphenyltridecane.

Additional evidence for very weak excimer emission in $n = 5$ is provided by the fluorescence decay curve (at 292 nm), which is

$$I_{FM}(t) = 1.00 \exp(-t/0.7) + 0.031 \exp(-t/19)$$

where t is in nanoseconds. The first component represents highly (intramolecularly) quenched monomer emission, and the second component is presumably due to weak excimer feedback.

The emission spectra of the other members of the series (i.e., $n > 6$) appear to be typical of *N,N*-dimethylalkylamines; i.e., λ_{max} is 292 nm and the R values are all (with perhaps the exception of TM 6) very close to the base-line value (see Figure 2). With the exception of TM 16 and TM 20, the decay curves of these longer chain diamines can be adequately represented by single exponential functions.

Discussion

The spectral data for the diamines studied quite clearly show that the Hirayama $n = 3$ rule is generally followed. This is the case notwithstanding the fact that the structures of the excimers of saturated amines and aromatic molecules are fundamentally different. In the former case, it has been suggested that the lone pairs of the two N atoms face each other in forming an intermolecular excimer.[11] The excimers of aromatic molecules, on the other hand, have a sandwich configuration in which the interplanar separation is ca. 3.2 Å. An examination of molecular models suggests that, for $n = 3$, in the absence of severe bond angle distortions, the close proximity of the two N atoms makes excimer stabilization via a coaxial lone pair approach seem unlikely. It would seem reasonable to assume that the maximal stability would be achieved by a noncoaxial encounter of the lone pairs at some larger N atom separation.

Because of the considerable restrictions which are imposed on the interaction geometry of the lone pairs in the α,ω-diamines by the intervening methylene units, and because the formation enthalpies of these excimers are relatively small (i.e., −2.7 kcal for TM 3[9] and −2.2 kcal for TM 4),[12] it is perhaps unlikely that the intramolecular excimers which are observed in the series conform to a single structure. To wit, the λ_{max} values of the excimer bands of TM 3 and TM 4 are different (365 and 350 nm).

It is interesting that evidence of an emissive *inter*molecular excimer could not be obtained for *N,N*-dimethylethylamine, even in the neat liquid and in highly concentrated *n*-hexane solutions at low temperature. Thus it can be concluded that the structure(s) of the intramolecular excimers must be quite specific and are presumably selected out of a very large number of configurational possibilities by the fortuitous intervention of the hydrocarbon chain which links the two pendants.

The fluorescence spectra of all diamines for which $n > 5$ appear to be typical of monoamines (see Figure 2). For most of these longer chain diamines, the fluorescence decay curves are exponential. The lifetimes, however, are all shorter than prototype monoamines and thus signify the presence of intramolecular dynamic quenching which we refer to as internal self-quenching. This is a process which is obviously sensitive to the intramolecular dynamic interactions between the dimethylamino pendants of the alkane backbone. Accordingly, the determination of the internal self-quenching rate constants of the diamines can lead to quantitative information about the head-to-tail interaction frequencies or probabilities in these compounds. Methodologically, the diamines seem to be attractive for this purpose. The end-group probes (the dimethylamino moieties) are not involved in associative ground-state interactions, and therefore should not perturb the "innate" configurational distribution of the linear chain alkane backbone itself. Moreover, shape and size of the probes are both very alkane-like and would thus not impose significant drag on the termini of the alkane chain. Also, the solvent—itself an *n*-alkane (*n*-hexane)—would not be expected to cause solute-solvent-induced changes in the solute configuration.

Intramolecular Excimer Formation. Table I contains a summary of the fluorescence lifetime and quantum-yield data for the diamines studied. In addition, it shows these data for three prototype monoamines: *N,N*-dimethylethylamine (DM 2), *N,N*-dimethyl-*n*-octylamine (DM 8), and *N,N*-dimethyl-

Table I. Rate Parameters for Diamines TM 1 to TM 5 at 23 °C

amine	τ_f,[a] ns	Φ_f	k_{fM}, 10^7 s^{-1}	k_{isq}, 10^7 s^{-1}
		Monoamines		
DM 2	26.2	0.69	2.65	
DM 8	25.0	0.80	3.20	
DM 12	24.5	0.78	3.18	
		Diamines		
TM 1	23.0	0.12 (M)	2.5	
		0.12 (D)		
		0.21 (M)	3.4	
TM 2	26.3	0.19 (D)		
	c [1]	0.021 (M)		
TM 3	26.9 [1.9]	0.63 (D)	~3	
	~0.3 [1]	0.0093 (M)	2	~3.3×10^2
TM 4	2.6 [0.1]	0.007 (D)		
TM 5	0.7 [1]	0.020 (M)	>2	1.4×10^2
	19.0 [0.031]	0.002 (D)		
TM 6	3.15	0.097	3.08	28
TM 7	18.6	0.57	3.06	1.4
TM 8	23.7	0.68	2.87	0.2
TM 9	21.6	0.61	2.82	0.6
TM 10	18.2	0.54	2.97	1.5
TM 11	17.2	0.53	3.08	1.8
TM 12	12.2	0.36	2.95	4.2
TM 13	12.0	0.35	2.92	4.3
TM 16	*d*	0.39	*d*	*d*
TM 18	17.2	0.58	3.37	1.8
TM 20	*d*	0.33	*d*	*d*

[a] Values at 23 °C; for compounds having two-component decay, the numbers in brackets indicate the relative amplitudes of the components. [b] Based on a value of 0.17 for toluene; (M) and (D) refer to monomer and excimer quantum yields, respectively. [c] The short component of TM 3 falls beyond the resolution of the instrument (0.3 ns). [d] The decay curves for TM 16 and TM 20 are nonexponential; see discussion in text.

n-dodecylamine (DM 12). As noted above both TM 1 and TM 2 exhibit single exponential decay, and the suggestion has been made that emission from these molecules takes place from a monomer/excimer system which is in thermal equilibrium. If this is the case, then the observed decay constant, λ, is equal to a weighted sum of monomer and excimer decay parameters, k_M and k_D, respectively[13]

$$\lambda = 1/\tau = mk_M + dk_D$$

where $m = (1 + k_{DM}/k_{MD})$ and $d = 1 - m$. k_{DM} and k_{MD} are the (unimolecular) excimer formation and dissociation rate constants, respectively.

While one cannot use the fluorescence lifetime and quantum-yield data for TM 1 and TM 2 to obtain values for k_{DM} and k_{MD} individually, the ratio of these rate constants, i.e., the equilibrium constant, $(K_e)_0$, can be determined as follows.

The monomer fluorescence quantum yield is given by the following expression:[14]

$$\Phi_{fm} = \frac{q_{fM}}{1 + [k_D/k_M][k_{DM}/(k_D + k_{MD})]} \tag{1}$$

where q_{fM} is the intrinsic monomer fluorescence quantum efficiency. Under conditions in which the monomer and excimer are in thermal equilibrium (i.e., the "high-temperature limit" so that $k_{MD} > k_D$ and $k_{DM} > k_M$), the exponential decay constant, λ, can be represented by the expression

$$\lambda = \frac{k_M + k_D(k_{DM}/k_{MD})}{1 + k_{DM}/k_{MD}}$$

Using the two above expressions for Φ_{fM} and λ, the *apparent* radiative rate constant of the monomer becomes

$$\Phi_{fM}\lambda = \frac{k_{fM}}{1 + k_{DM}/k_{MD}} = \frac{k_{fM}}{1 + (K_e)_0}$$

where k_{fM} is the monomer radiative rate constant. Thus

$$(K_e)_0 = \frac{k_{fM}}{\Phi_{fM}\lambda} - 1$$

Finally, k_D can be approximated (assuming that $k_{MD} > k_D$):

$$k_D \simeq k_M \frac{[q_{fM}/\Phi_{fM} - 1]}{[k_{fM}/\Phi_{fM}\lambda - 1]}$$

For TM 1 and TM 2, Φ_{fM} was determined by estimating the extent to which a monomeric fluorescence spectrum (e.g., as obtained from the shape of the *N,N*-dimethylethylamine fluorescence spectrum) contributed to the observed fluorescence spectrum of the diamine. Using this approach, the fluorescence quantum yield data listed in Table I for TM 1 and TM 2 are broken down into Φ_{fM} and Φ_{fD}. Values of k_D and $(K_e)_0$ for these diamines, determined from these data, and the fluorescence decay parameters are listed in Table II. In this analysis, the value of k_M was assumed to be the same for all diamines, namely, 4.00×10^7 s^{-1}. This is taken from the $1/\tau_f$ value for prototype monoamines (see Table I). This presumes that the intrinsic radiative *and* nonradiative decay rates of the dimethylamino fluorophore in the diamine are identical with those of an isolated dimethylalkylamine.

As noted above, the monomer decay curves for TM 3, 4, and 5 exhibit two exponential components. This indicates that the monomer and excimer of these diamines are not in equilibrium, and the nonexponentiality accordingly reflects the feedback between excimer and monomer. For TM 3, an estimate of the value of $(K_e)_0$ may be made as follows. Because the fast component observed in the monomer decay falls below the resolution of the instrument, it can be presumed that $k_{DM} > 3 \times 10^9$ s^{-1}. From the value of the TM 3 monomer quantum yield, 0.021, and the expression for Φ_{fM} (see eq 1), one obtains

$$q_{fM}/\Phi_{fM} = 1 + (k_{DM}/k_M)[k_D/(k_D + k_{MD})]$$

The data require that $k_{MD} > 5 \times 10^7$ s^{-1}, assuming that $k_D \simeq \lambda_1^{-1} = 3.7 \times 10^7$ s^{-1} and thus $(K_e)_0 > 34$.

For the discussion which follows, the nonexponential decay observed for monomer (and, when observed, excimer) fluorescence under δ-pulse excitation is represented as

$$I_{fM}(t) = A \exp(-\lambda_1 t) + \exp(-\lambda_2 t)$$

and the excimer as

$$I_{fD}(t) = \exp(-\lambda_1 t) - \exp(-\lambda_2 t)$$

where $2\lambda_{1,2} = X + Y \mp [(X - Y)^2 + 4k_{MD}k_{DM}],^{1/2}$ $X = k_M + k_{DM}$, $Y = k_D + k_{MD}$, and $A = (X - \lambda_2)/(\lambda_2 - X)$.

For TM 4 and TM 5, the two exponential decay parameters obtained from the monomer fluorescence decay curves (i.e., λ_1, λ_2, and A) were used to obtain values of the individual monomer/excimer rate parameters using an approach described in ref 11. Estimates of these rate constants are contained in Table II. The uncertainties in the decay curve data (that is, the very fast short component in TM 4 and the very small amplitude associated with the long component in TM 5) resulted in fairly large uncertainties in one or more of the rate parameters (e.g., k_{MD} for TM 4 and k_{MD} and k_D for TM 5).

These data show that the excimer formation rate constant, k_{DM}, decreases in going from TM 3 to TM 5, a probable consequence, simply, of the increasing chain size. The equilibrium constants for these diamines, on the other hand, show no clear trend. This may be, in part, because of the uncertainties in the $(K_e)_0$ values of TM 3 and TM 5. It is also possible that the structures of the excimers are sufficiently different in each case

Table II. Fluorescence Lifetimes, Quantum Yields, Radiative Rate Constants, and Intramolecular Self-Quenching Constants (Where Appropriate) for Monoamines and Diamines at 23 °C

	k_M[a]	k_D	k_{DM}	k_{MD}	$(K_e)_0$	k_{fD}	k_{fM}
TM 1	4×10^7	3×10^7			7	7×10^5	2.5×10^7
TM 2	4×10^7	4×10^7			40	2×10^5	3.4×10^7
TM 3	4×10^7	4×10^7	$>3 \times 10^9$	$>5 \times 10^7$	>34	$\sim 8 \times 10^5$	$\sim 3 \times 10^7$
TM 4	4×10^7	5×10^8	3×10^9	2×10^8	15	7×10^4	2×10^7
TM 5	4×10^7	$\sim 6 \times 10^7$	1.4×10^9	$<6 \times 10^7$	<23	$<7 \times 10^3$	$>2 \times 10^7$

[a] All rate constants are in units of s^{-1}.

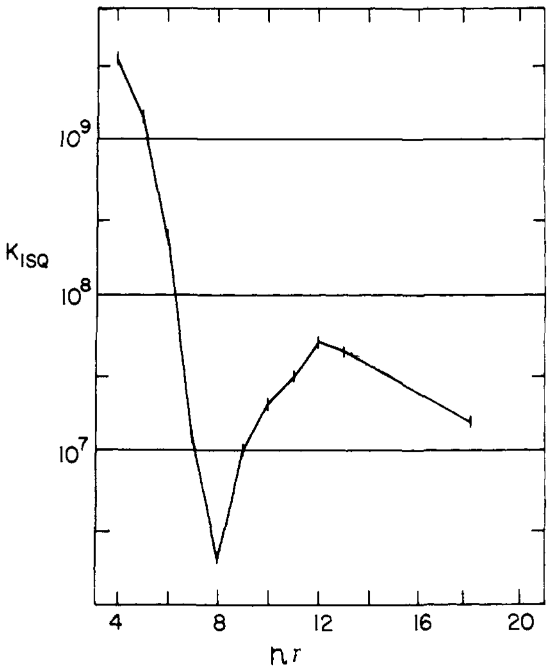

Figure 3. Plot of k_{isq}, the internal self-quenching rate constant for a diamine, vs. n.

so that no trend in $(K_e)_0$ exists with respect simply to chain size. Indeed, the "allowable" excimer geometry (or geometries) imposed by an amine-coupling chain would be expected to depend on the size of the chain.

As an internal check of the monomer excimer rate constants, values of the radiative rate constant for monomer fluorescence, k_{fM}, were computed. Rearranging eq 1, one obtains

$$q_{fM}k_M = k_{fM} = \frac{\Phi_{fM}k_{DM}k_D}{k_D + k_{MD}}$$

The rate constants shown in Table II and the quantum yields listed in Table I were used to compute k_{fM} values for the five diamines. The results are quite consistent with the value of k_{fM} of 2.65×10^7 s^{-1} for DM 2 (see Table I).

In a similar manner, the radiative rate constant for excimer fluorescence, k_{fD}, was determined from the following expression:

$$q_{fD}k_D = k_{FD} = \frac{\Phi_{fD}k_M(k_{MD} + k_D)}{k_{DM}}$$

These results are shown in Table II; it can be seen that in this case there is no consistency in k_{fD} values for the diamines. This gives further credence to the supposition that the excimer geometries differ considerably in these compounds.

Thus the weak emissivity of the TM 4 and TM 5 excimers is mainly due to a low radiative transition probability, although in TM 4 radiationless deactivation seems somewhat more important than in the other excimers.

As has been noted above, the fluorescence decay curves for diamines TM 6 through TM 13 are exponential, as measured for about three orders of magnitude. The lifetime of these diamines are all shorter than that of a prototype monoamine, e.g., DM 2, DM 8, or DM 12. Because the diamines are comparable to prototype monoamines with respect to (1) the quantitative absorption spectra and (2) the position and shape of the fluorescence spectra, it can be presumed that the decrease in the fluorescence lifetime and quantum efficiency of a diamine is due to dynamic intramolecular self-quenching. Thus, assuming that the total intrinsic radiative and nonradiative decay rates of the dimethylamino fluorophore in a diamine are identical with those of the monoamine (irrespective of intramolecular self-quenching in the diamine), the reciprocal lifetime of a diamine, Tm n, can be written as

$$(1/\tau)_n = 1/\tau_0 + (k_{isq})_n$$

where τ_0 is the fluorescence lifetime of a monoamine and $(k_{isq})_n$ is the intramolecular self-quenching rate constant for the diamine. In this work, $1/\tau_0$ is taken as 4.00×10^7 s^{-1}.

Values of k_{isq} for the diamines are listed in Table I and are also displayed in Figure 3 as log k_{isq} vs. n for $4 \leq n \leq 20$. These data reveal three obvious trends in k_{isq} with respect to the chain size: (1) the sharp decrease in k_{isq} for $4 \leq n \leq 8$, (2) an increase in k_{isq} for $8 \leq n \leq 12$, and (3) an apparent tapering off for $n > 12$. The behavior of k_{isq} with respect to n is strikingly similar to a plot of the excimer-to-monomer fluorescence intensity ratio for bis(pyrenyl)alkanes reported by Zachariasse and Kühnle.[10] They observe a drop in this ratio between $n = 3$ and $n = 7$–8, followed by an increase for $n = 8$ to $n = 11$. For larger values of n (up to 22) the ratio seems to reach a plateau. Zachariasse and Kühnle also report the interesting observation that for $n = 13$ there is an abrupt increase in the excimer/monomer emission. As noted above, one sees a similar, but much weaker, effect for TM 12 (see Figure 2).

The trend in the rates of certain other intramolecular reactions which depend on the approach of pendant groups attached to the termini of linear chain alkanes also bears remarkable resemblance to the k_{isq} data described here. For example, Illuminati et al.[15] have reported a thorough investigation of the intramolecular lactonization of ω-bromoalkanoic acids, $Br(CH_2)_nCO_2H$. Their data show a precipitous drop in this rate constant between $n = 3$ (corresponding to the formation of a five-membered ring) and $n = 6$–7. The decrease in the lactonization rate constant over this range in n spans more than six orders of magnitude. Between $n = 7$ and $n = 21$, the rate constant increases somewhat, reaching a plateau at ca. $n = 13$. These data are analyzed by Illuminati et al. in terms of the dependence of the activation enthalpy and entropy for ring formation on the ring size.

Szwarc et al.[16,17] have reported a fascinating study dealing with intramolecular electron transfer rates in radical (mono)-anions of the type $X(CH_2)_nX$ where X = the naphthyl or N-phthalimide residue. For the bis(naphthyl)alkanes the intramolecular electron transfer rate constant, as measured using ESR techniques, shows a monotonic decrease from $n = 3$ to $n = 20$, while for the bis(N-phthalimide) substituted alkanes a more complex behavior is observed. For the latter compounds, the rate of exchange decreases for $n = 3$ to $n = 5$–6, then increases to a broad maximum for $n = 9$–10, and then decreases for $n > 10$. The authors suggest that this difference in behavior may be a result of the fact that in the bis(naphthyl)alkanes electron transfer can take place when the naphthyl moieties are as far as 9 Å apart and, therefore, alkane ring formation is not a necessary concomitant process in electron transfer. For the bis(phthalimide) system, however, electron exchange is weaker, and would presumably require a more intimate approach of the phthalimide groups. In other words, the critical reaction distance, r_0, is smaller for the bis(phthalimide) alkanes relative to the bis(naphthyl) system. Indeed, theoretical statistical calculations of cyclization probabilities performed by Sisido[18] reveal that the nature of the chain-length dependence of the intramolecular reaction rates of $X(CH_2)_nY$ type compounds (for $n > 6$) is very sensitive to the value of r_0.

It is interesting to consider intramolecular self-quenching as a pseudo-first-order *inter*molecular process. For example, one can calculate the "effective" concentration of quencher C_{eff}, based on the known intermolecular self-quenching rate constant (k_q), which would be necessary to result in the observed intramolecular self-quenching rate constant, k_{isq}, i.e.

$$C_{\text{eff}} = k_{\text{isq}}/k_q \text{ (M)}$$

For DM 8, k_q is 3.90×10^9 M^{-1} s^{-1}, which is approximately a factor of 5 smaller than diffusion controlled in *n*-hexane at 25 °C. Thus, using TM 12 as an example, $C_{\text{eff}} = 0.011$ M.

Using a very naive approach, it can be reasoned that the minimum "concentration" of quencher, C_{min}, which could interact intramolecularly with a reaction center located at one end of a linear chain, when the quencher itself is fixed at the other end point of the chain, could be calculated as

$$C_{\text{min}} \text{ (M)} = \frac{1000}{(\frac{4}{3}\pi r_{\text{ex}}^2)N_{\text{Av}}}$$

where r_{ex} is the length of the *extended* chain (cm) and N_{Av} is Avogadro's number. r_{ex} is simply obtained from the C–C bond length of the chain segment and the C–C–C bond angle; for a diamine, TM *n*, there will be $(n + 1)$ chain segments. This approach assumes that, except for the fixed C–C–C bond angles, the chain is freely linked and thus ignores differences in conformational energies. It also presumes that the overall chain length is much larger than the segment length.

Using a bond length of 1.54 Å and a C–C–C bond angle of 112°, C_{min} for TM 12 is found to be 0.867 M. This is about eight times larger than C_{eff}, and in effect means that the attachment of the amino groups to the ends of the chain actually retards the (quenching) reactivity relative to having free intermolecular diffusional mobility. This can be viewed as a manifestation of the "stiffness" of the chain which is not taken into account in the freely linked chain model.

Cuniberti and Perico[19] studied the intramolecular quenching of pyrene monomer fluorescence in end-labeled poly(ethylene oxide) polymers (molecular weights on the order of 10^4). When analyzed according to the freely linked chain model, their results show that, for the lower molecular weight chains, intramolecular quenching appears to be relatively inhibited relative to the longer chains. Kirsh et al.[20] have observed a reduction of 4 in the intramolecular quenching of anthracene fluorescence by pyridinium groups in a poly(4-vinylpyridine) polymer relative to analogous intermolecular quenching. Similar trends have been reported by Szwarc et al. for intramolecular electron transfer reactions.[16,17]

Looking at the trend of the k_{isq} data in Figure 3, it is obvious that the discrepancy between C_{eff} and C_{min} worsens for longer chain diamines. This is because, as *n* increases, r_{ex} increases, causing C_{min} to decrease, while the k_{isq} data show a leveling off or at best a slight decrease for longer chains. A more sophisticated calculation of C_{min} based on linear chain configurational statistics would be expected to provide even larger values than the treatment used above. Morawetz[21] has pointed out that the application of configurational statistics to linear chains in order to calculate C_{eff} (through the use of a second-order rate constant) assumes that the rate of the intramolecular process is *not* governed by the conformational dynamics of the chain. Thus this approach would seem invalid for reactions which are (bimolecularly) diffusion controlled or which have very low activation energies.

Another factor which would detract from the validity of the C_{eff} calculation is the relative shortness of the chains studied in this work. In the example cited above, $n = 12$, and there is some doubt as to whether this type of statistical treatment is valid for chains of this size.

Szwarc et al. have tried to use their data of intramolecular electron transfer in α,ω-bis(naphthyl)- (and *N*-phthalimide) alkanes to distinguish between two models of intramolecular interactions: dynamic and static. In the former case, the rate (of end-to-end interaction) is governed by the actual dynamics of the chain conformation transitions. In the latter model, the rate is determined by the static distribution of chain conformations in which each configuration (having a probability p_i) has an intrinsic reaction rate constant, k_i. The overall reaction rate, then, is governed by the weighted average:

$$k_{\text{stat}} = p_i k_i$$

p_i, in turn, is expressed using the partition functions:

$$p_i = \frac{\exp(-E_i/RT)}{\exp(-E_j/RT)}$$

where the *i* in the summation in the numerator refers to all configurations in which the end-to-end separation, r_i, is less than some reactive distance, r_0, and the *j* in the lower summation denotes *all* configurations.

The fact that the longer chain diamines ($n > 5$) show exponential fluorescence decay is significant. It indicates that the rates of interconversion between different chain conformers are larger than the rate of fluorescence decay. Thus the rate constants for chain conformational transitions are $>4 \times 10^7$ s^{-1}. In this context, then, the value of k_{isq} would reflect the weighted average of intramolecular encounter rates, i.e., k_{stat} (see above). The dependence of k_{isq}, therefore, on the chain length is a manifestation of changes in the (static) conformation distribution functions of the diamines.

Presumably, then, as the conformational distribution functions becomes broader (i.e., as the chain length increases), the intramolecular head-to-head encounter rates of certain conformers would no longer be larger than 4×10^7 s^{-1}, and the fluorescence decay observed for the diamine would no longer appear exponential.

In this context, it may be significant to note that, as mentioned above, the decay curves of TM 16 and TM 20 are nonexponential and can be represented (with good precision) as

$$I_f(t) = 0.947 \exp(-t/9.2) + 0.0558 \exp(-t/25.0)$$

for TM 16 and

$$I_f(t) = 0.872 \exp(-t/11.5) + 0.128 \exp(-t/26.0)$$

for TM 20 (*t* is in nanoseconds). Figure 4 shows the decay curve for TM 16. Even though the fit to the double exponential form is very good, the value of the short-lived component cannot be easily interpreted. It is not to be correlated with values of k_{isq} because the latter refer presumably to the weighted averages of intramolecular self-quenching rate constants. The long-lived component, 25–26 ns, would be assigned to those diamines having conformations for which the intramolecular self-quenching rate constant is much less than

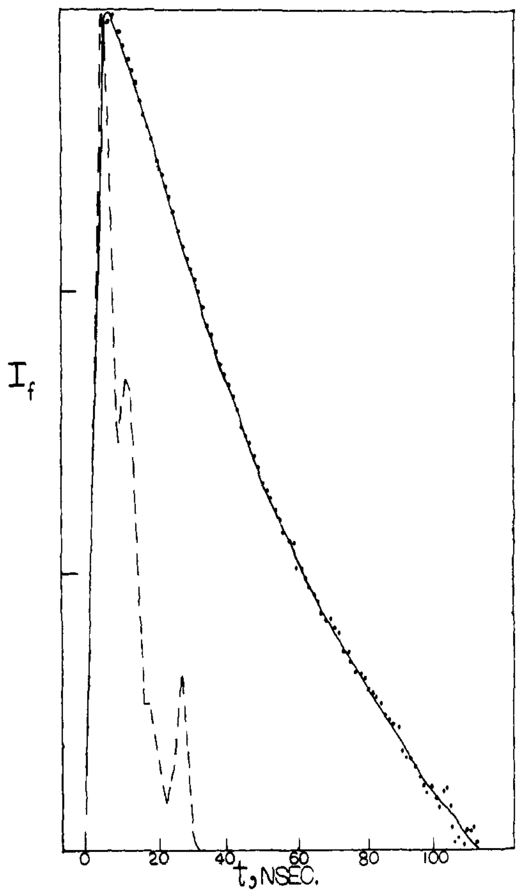

Figure 4. Fluorescence decay curve for TM 16 (1×10^{-4} M), λ_{exc} 220 nm. The decay curve is resolved into the components indicated in the text.

4×10^7 s^{-1} (the intrinsic fluorescence rate of the fluorophore).

Another possible explanation for the nonexponentiality of the TM 16 and TM 20 fluorescence decay curves is that some tertiary monoamine is present as an impurity. These molecules would superimpose their 25-ns lifetime on the decay curve of the diamine species. The total concentration is low enough so that *inter*molecular quenching ($C = 1.0 \times 10^{-4}$ M) can be ignored. If this were true, the relative amplitudes of the long and short components in the nonexponential decay curve would reflect the relative concentrations of monoamine and diamine, respectively. Assuming that at λ_{exc} (220 nm) ϵ(diamine) = 2ϵ(monoamine), this would require the fraction of tertiary monoamine present in TM 16 and TM 20 to be 0.11 and 0.23, respectively. The syntheses of these compounds are described in the Experimental Section. It seems inconceivable that, of all diamines studied, only these two compounds would contain levels of tertiary monoamine to this extent. Thus we interpret the nonexponentiality as being intrinsic to TM 16 and TM 20.

One would have to proceed with the interpretation of the nonexponentiality of TM 16 and TM 20 mentioned above with caution because TM 18, quite surprisingly, does *not* exhibit nonexponential decay. To wit, TM 18 conforms to a single exponential decay component for over three orders of magnitude ($\tau = 17.2$ ns). This would tend to imply that the conformational distribution function for TM 18 is narrower than that for TM 16 and TM 20. While this does not seem to be logical a priori, there is no compelling evidence to cause one to deviate from the interpretation that the decay curve reported for TM 16, TM 18, and TM 20 represents the intrinsic fluorescence decay of those molecules. Some of the questions posed by these data may be resolved by examining the properties of longer chain diamines. Such studies, along with the temperature dependence of the photokinetics of the diamines, are being pursued.

Experimental Section

Materials. TM 1, TM 2, TM 3, TM 4, and TM 6 were obtained from Aldrich Chemical Co., and were distilled at ambient pressure under N_2 or at reduced pressure, depending upon the boiling point of the amine. TM 5, TM 7, TM 8, TM 10, and TM 12 were synthesized from the corresponding bis primary amines (obtained either from Aldrich or Columbia Organics, Columbia, S.C.) via a modified Leuckart methylation.[22] The resulting pale yellow oils were distilled under reduced pressure. NMR and IR spectra were consistent with the molecular structures. TM 9, TM 16, and TM 20 were obtained by reacting the respective α,ω-dibromides with freshly distilled dimethylamine in a methanol medium. Purification and structure validation of these compounds were performed as stated above. TM 11 was prepared by reacting 1,9-dibromononane with KCN in an ethanol medium.[23] The resulting dinitrile was reduced to the bis primary amine using diborane in THF.[24] The solid primary amine was then methylated as described above[22] and purified in the same manner. The same procedure was used to obtain TM 18.

All solutions of the amine were prepared in *n*-hexane (Baker spectral grade) which was passed through an activated silica gel column. The purity of the solvent was checked periodically using fluorescence as a criterion. With λ_{exc} 220 nm, fluorescence at $\lambda > 250$ nm was negligible.

Quantum-Yield Measurements. These measurements were performed on dilute solutions of the amines (ca. 10^{-4} M). The amount of light absorbed at λ_{exc} (220 nm) was determined using either a Cary 14 spectrophotometer or a monitor situated in the fluorometer cavity. Fluorescence was detected at right angles using a conventional dc fluorometer excitation and emission band-pass values were 3.2 and 2.0 nm, respectively). Toluene in *n*-hexane (5.0×10^{-3} M) was used as the absolute standard (Φ_f was taken to be 0.17).[25] The lifetime of the toluene solution was measured to be 39.3 ns. Deaeration was accomplished by bubbling with "oxygen-free" nitrogen gas (Matheson); results were found to be identical with freeze-thaw-pump prepared samples. The yields reported are the averages of three or four separate measurements for each compound. Lifetimes were measured using the time-correlated single photon counting method; the instrument was described elsewhere.[26] Fluorescence decay curves were analyzed using the convolute-and-compare method. The criterion for best fit was the weighted sum of the squared deviations (WSSD) between the experimental decay curve and the convoluted function, which were each normalized to a maximum value of 10. Typically, an excellent fit corresponded to a WSSD value of 0.05, and using between 100 and 110 data points (channels). The nonexponential decay curve shown in Figure 4 for TM 16 was fit to the two components cited in the text and had a WSSD value of 0.0678 (summing over 85 channels). Fluorescence excitation had a band-pass of 1.6 nm, and emission was viewed through an interference filter (10-nm band-pass).

Acknowledgment. The authors are grateful to the National Science Foundation (CHE-74-08883) and to the National Institutes of Health, General Medical Sciences (GM-20921), for support of this research. It is a pleasure to acknowledge many helpful discussions with Professor Mitchell Winnik.

References and Notes

(1) T. Forster and K. Kasper, *Z. Elektrochem.*, **59**, 977 (1955); (b) *Z. Phys. Chem.* (*Frankfurt am Main*), **1**, 275 (1954).

(2) W. R. Ware, *Pure Appl. Chem.*, **41**, 635 (1975).

(3) F. Hirayama, Ph.D. Thesis, University of Michigan, 1963.

(4) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).

(5) W. Klopffer in "Organic Molecular Photophysics", Vol. 1, J. B. Birks, Ed., Wiley-Interscience, New York, 1973, Chapter 7.

(6) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970).

(7) W. Klopffer, *Chem. Phys. Lett.*, **4**, 193 (1969); *J. Chem. Phys.*, **50**, 2337 (1969).

(8) W. Kühnle and K. Zachariasse, *Ber. Bunsenges. Phys. Chem.*, **78**, 1254 (1974).

(9) A. M. Halpern and P. P. Chan, *J. Am. Chem. Soc.*, **97**, 2971 (1975).

(10) K. Zachariasse and W. Kühnle, *Z. Phys. Chem.* (*Frankfurt am Main*), **101**, 267 (1976).

(11) A. M. Halpern, P. Ravinet, and R. J. Sternfels, *J. Am. Chem. Soc.*, **99**, 169 (1977).

(12) A. M. Halpern and D. K. Wong, unpublished results.

(13) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1970, Chapter 7, p 313.
(14) Reference 13, Chapter 7, contains many of the expressions. The nomenclature and expressions can be found in ref 13, Chapter 7.
(15) C. Galli, G. Illuminati, L. Mandolini, and P. Tamborra, *J. Am. Chem. Soc.*, **99**, 2591 (1977).
(16) K. Shimada and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 3313 (1975).
(17) K. Shimada, Y. Shimazato, and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 5834 (1975).
(18) M. Sisido, *Macromolecules*, **4**, 737 (1971).
(19) C. Cuniberti and A. Perico, *Eur. Polym. J.*, **13**, 369 (1977).
(20) Y. E. Kirsh, N. R. Pavlova, and V. A. Kabanov, *Eur. Polym. J.*, **11**, 495 (1975).
(21) H. Morawttz, *Pure Appl. Chem.*, **33**, 267 (1974).
(22) R. N. Icke, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1954, p 723.
(23) H. Krimm, "Preparative Organic Syntheses", Vol. VI, Wiley, New York and London, 1963, p 536.
(24) H. C. Brown, *J. Am. Chem. Soc.*, **86**, 3566 (1964).
(25) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed., Academic Press, New York, 1971, p 113.
(26) A. M. Halpern, *J. Am. Chem. Soc.*, **96**, 7655 (1974).

Studies Dealing with the Intramolecular Hydrogen Atom Transfer Reaction of Tetrasubstituted Cyclopropenes[1a]

Albert Padwa,*[1b] Thomas J. Blacklock, Chuen S. Chou, and Naoto Hatanaka

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received March 9, 1979*

Abstract: The photochemical behavior of a number of 3-alkyl substituted cyclopropenes which contain a hydrogen atom in the γ position of the side chain has been studied in mechanistic detail. The results obtained indicate that the products of the direct and triplet sensitized photolysis are completely different. The singlet state of these systems reacts by σ-bond cleavage of the ring to give products which are explicable in terms of the chemistry of vinyl carbenes. The triplet state, generated by sensitization techniques, undergoes hydrogen-atom abstraction by a mechanism analogous to the well-known Norrish type II process of carbonyl compounds. Rate constants for hydrogen abstraction were obtained by plotting Φ_0/Φ_q vs. *trans*-stilbene at a constant quencher to cyclopropene ratio. The rate constants for hydrogen abstraction were found to be two orders of magnitude less than that for related phenyl alkyl ketones and increased as the strength of the C–H bond in the γ position decreased. Measurements of Arrhenius activation parameters were carried out at different temperatures. The entropy of activation was typical of a reaction proceeding via a strain-free six-center transition state. The activation energy associated with hydrogen abstraction was found to be dependent on the γ C–H bond strength. In contrast to the symmetrically substituted 1,2-diphenyl substituted cyclopropenes, the quantum efficiency of hydrogen abstraction of the 1,3 isomers was found to depend on the concentration of starting material. This dependence was rationalized in terms of an electron-transfer reaction to give a radical cation which reacts further with starting material. This interpretation is supported by the observation that the quantum yield for reaction exceeds unity at high concentrations of cyclopropene.

Alkene photochemistry is an unusually complex and versatile field of study.[2-4] The principal photochemical processes which have been observed for simple alkenes are cis $\rightleftarrows$ trans[5] isomerization and [2 + 2] cycloaddition.[6] Numerous studies have established that transfer of triplet energy to acyclic or macrocyclic olefins from suitable photosensitizers results in cis–trans isomerization of the double bond, undoubtedly as a consequence of the preferred orthogonal conformation of triplet olefins.[7] A 90° twist places the unpaired electrons in noninteracting orthogonal orbitals. The triplet state behavior of cyclohexenes, -heptenes, and -octenes has been studied in some detail by Kropp[8] and Marshall.[9] The reactions observed have been attributed to an initial cis $\rightleftarrows$ trans isomerization of the olefin followed by protonation of the resulting highly strained trans isomer. The divergent behavior exhibited by cyclopentene and other highly constrained olefins, on the other hand, is thought to be associated with the inability of these olefins to undergo cis $\rightarrow$ trans isomerization.[10] The radical-type behavior exhibited by these systems originates by intermolecular hydrogen abstraction by the π–π^* excited state itself. In fact, a number of reports have appeared in the literature which show that the excited π–π^* state of certain olefins has the ability to abstract hydrogen.[11-28] Thus, both intermolecular photoreduction and intramolecular hydrogen transfer reactions have recently been reported for alkenes. Intramolecular hydrogen abstractions by carbon have also been observed in the photochemistry of α,β-unsaturated enones.[29]

It was the purpose of the present study to investigate the triplet-induced hydrogen-abstraction reaction of a number of tetrasubstituted cyclopropenes. Formation of an orthogonal oriented triplet with these systems is inconceivable as a result of structural constraints. The photochemistry of cyclopropene derivatives has attracted considerable interest over the past several years.[30] The photochemical behavior of this highly strained ring system has been shown to be remarkably dependent on the multiplicity of the excited state involved.[31,32] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes[33] while triplet states, generated by sensitization techniques, usually give high yields of cyclopropene dimers.[34-38] Some earlier observations by DeBoer indicate that there are severe steric constraints associated with the triplet dimerization reaction.[31] Thus, 1,2-diphenylcyclopropenes, where both 3 positions are substituted with alkyl groups, do not dimerize.[31] Instead, the triplet states of tetrasubstituted cyclopropenes which possess γ hydrogen have been found to undergo an intramolecular hydrogen transfer reaction[39] by a mechanism analogous to the well-known Norrish type II photoreaction of carbonyl compounds.[40] In this paper we wish to describe some of the salient features associated with this reaction.

Results

Synthesis of Diphenylmethyl-3-alkyl Substituted Cyclopropenes. 1,2-Diphenyl-3-methyl-3-alkyl substituted cyclopropenes were prepared by treating diphenylmethylcyclopropenyl cation with Grignard reagents according to the general procedure of Breslow and co-workers.[41] In all the cases studied, nucleophilic attack by the Grignard reagent on the cyclopropenyl cation afforded the 1,2-diphenyl-3,3-disubstituted cyclopropene as the major product. This is consistent with

0002-7863/79/1501-5743$01.00/0