

EFFECTS OF THE RING SIZE AND SOLVENT POLARITY ON THE STABILITY OF THE CYCLIC INTRAMOLECULAR EXCIMER OF SATURATED DIAMINES

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The fluorescence of some aliphatic diamines was studied in the gas phase and in some solvents at several temperatures. It was found that *N,N,N',N'*-tetramethylpropane-1,3-diamine (TMPD) and *N,N,N',N'*-tetramethylbutane-1,4-diamine (TMBD) have two emission bands in the gas phase. TMBD also shows two bands in solution. These bands were assigned previously to an excited monomer and an intramolecular excimer. From the temperature dependence of the intensity ratio of the two bands, the enthalpy changes for the excimer formation were evaluated. The stability of the cyclic excimer is discussed in terms of the ring size effect and the solvent effect on the band positions.

INTRODUCTION

Hirayama¹ measured fluorescence spectra for a variety of diphenyl- and triphenylalkanes, and observed the emissions from intramolecular excimers only for compounds in which phenyl groups are separated by exactly three carbon atoms. He called this phenomenon the 'n = 3 rule.' The n = 3 rule generally seems to work well. Intramolecular excimers have been observed for various 1,3-bis-substituted propanes, e.g. phenyl-, α - and β -naphthyl-,² *N*-carbazoyl-³ and dimethylamino.⁴ Zachariasse and Kuhnle⁵ have shown that intramolecular excimer formation occurs in the α,ω -bis(pyrenyl)alkanes, $\text{Py}(\text{CH}_2)_n\text{Py}$, not only for $n = 3$ but also for $n = 4-6, 9-16$ and 22. They pointed out that the larger binding energy of the pyrene excimer relative to the benzene system is one of the mitigating factors in causing the intramolecular excimer formation in alkane chains having $n > 3$. Later, Halpern *et al.*⁶ examined the fluorescence properties of members of the series $(\text{CH}_3)_2\text{N}(\text{CH}_2)_n(\text{CH}_3)_2$ ($n = 1-13, 16, 18$ and 20) and observed emission from both monomer and excimer for $n = 3$ and 4.⁶ Recently, we have studied the cadmium(5^3P_1)-sensitized luminescence of some aliphatic diamines, $\text{R}_2\text{N}(\text{CH}_2)_n\text{NR}_2$ ($\text{R} = \text{H}$ or CH_3 , $n = 1-6$).⁷ It was found that the diamines with $n = 2-5$ have two emission bands, whereas those with $n = 1$ and 6 have only a short-wavelength band. These two bands were assigned to two kinds of 1:1 exciplex (cyclic and acyclic for long- and short-wavelength bands, respectively) between an excited cadmium atom and a diamine

molecule. It was observed that the equilibrium constant ($K = [\text{cyclic exciplex}]/[\text{acyclic exciplex}]$) is largest for a five-membered chelate ring and an increase in the size of the chelate ring leads to a decrease in the stability of the cyclic exciplex. It was concluded that the decrease in K associated with an increase in the ring size is not due to the enthalpy effect, but to the entropy effect.

In this study, the fluorescence of some diamines was investigated in the gas phase and in some solvents and the effect of the ring size of the intramolecular excimers on their stability was examined by comparing the results with those for cadmium-sensitized luminescence of diamines. Since it is known that the emission spectra of some tertiary amines show dramatic red shifts with increase in the solvent polarity,^{8,9} the effect of solvent polarity on the stability of cyclic excimers is of interest. We examined the solvent effects on the band positions for monomer and excimer emission and on the enthalpy change for the formation of the cyclic excimer.

EXPERIMENTAL

Triethylamine (TEA), *N,N,N',N'*-tetramethylmethanedi-amine (TMMD), *N,N,N',N'*-tetramethylethane-1,2-diamine (TMED), *N,N,N',N'*-tetramethylpropane-1,3-diamine (TMPD), *N,N,N',N'*-tetramethylbutane-1,4-diamine (TMBD) and *N,N,N',N'*-tetramethylhexane-1,6-diamine (TMHD) were obtained commercially (G.R. grade). These amines were used after drying with potassium hydroxide and repeated trap-to-trap distillation. The solvents used were of spectroscopic grade and distilled whenever needed.

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The experimental apparatus and procedures for the measurements of the fluorescence in the gas phase were similar to those used previously for the cadmium-sensitized luminescence of amines and diamines,^{7,10} except for a light source. A low-pressure mercury lamp (germicidal lamp) was used. Radiation at 253.7 nm from the lamp excited the substrates in a cylindrical quartz cell placed in a furnace whose temperature was varied from 303 to 458 K. Fluorescence was monitored with a Hitachi Model 135 spectrophotometer. The wavelength dependence of the sensitivity of the detection system was determined using standard fluorescence solutions of phenol,¹¹ quinine sulphate and *N,N*-dimethyl-*m*-nitroaniline.¹² The fluorescence in the liquid phase was measured with a Shimadzu Rf-1500 spectrofluorimeter. Excitation was effected at 250 nm in each case in order to prevent any decomposition of the substrates. The concentrations of the amine and diamines were kept around 10^{-3} M. The temperature of the cell was varied from 285 to 333 K by circulating water around the cell from a thermostat whose temperature was maintained within ± 0.1 K.

RESULTS

Figure 1 shows the corrected fluorescence spectra of TEA, TMMD, TMED and TMHD obtained in the gas phase. These compounds show one emission band and their spectra are independent of temperature. The peak wavelengths for TEA and TMHD are about 295 nm, whereas those for TMMD and TMED are slightly red shifted. Figure 2 shows the emission spectra of TMBD vapour obtained at several temperatures between 303

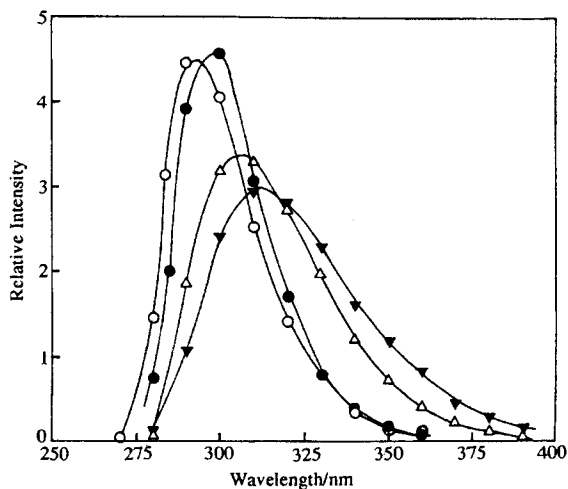


Figure 1. Sensitivity-corrected fluorescence spectra of (○) TEA, (△) TMMD, (▼) TMED and (●) TMHD at 303 K in the gas phase

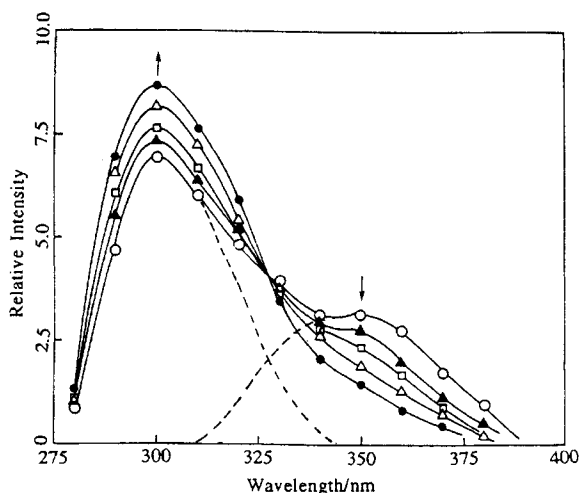


Figure 2. Sensitivity-corrected fluorescence spectra of TMBD at (○) 303, (▲) 333, (□) 363, (△) 393 and (●) 423 K in the gas phase

and 423 K and at constant pressure (133 Pa). These spectra were corrected for the wavelength dependence of the sensitivity of the detection system. As shown in Figure 2, the emission spectra are much broader and two bands are evident (the dashed lines show the separation of the two bands for the spectrum at 303 K). The spectra obtained at 303, 333, 363, 393 and 423 K were adjusted to the same total intensity. The profiles have an isosbestic point at 327 nm. The intensity of the short-wavelength band (band I) increases and that of the long-wavelength band (band II) decreases with increasing temperature. These findings show that the two bands can be ascribed to two different emitters, monomer and intramolecular excimer ascribable to bands I and II,⁴ and that the equilibrium between the monomer and the excimer shifts from the excimer to the monomer with increase in temperature. Similar fluorescence spectra and temperature dependence were observed for TMPD. The shapes of the spectra for TMPD and TMBD were independent of the pressures of the diamines.

Similar fluorescence spectra to those in the gas phase were obtained for TEA, TMMD, TMED and TMHD in several solvents with large shifts of the peak position of the band in THF. Table 1 shows the wavelengths at the peaks of the emission bands obtained in the gas phase and in different solvents. Analogously to the gas phase, two distinct bands were observed for TMBD in all solvents and at all temperatures examined. The emission intensity of the excimer band for TMPD, however, was so high that the monomer band could not be separated in any solvent at the temperatures examined. Table 2 shows the ratio of the intensity of

Table 1. Wavelengths at the peak of the emission bands

Compound	λ_{\max} (nm)					
	Vapour	Hexane	Cyclohexane	DEE ^a	IPE ^a	THF ^a
TEA	293	285	285	308	302	337
TMMD	305	300	300	325	314	354
TMED	312	308	310	327	325	361
TMPD (band I)	310	—	—	—	—	—
TMPD (band II)	350	360	363	377	374	431
TMBD (band I)	300	293	293	310	305	345
TMBD (band II)	350	359	356	379	374	425
TMHD	297	290	291	306	304	339

^a DEE = diethyl ether; IPE = diisopropyl ether; THF = tetrahydrofuran.

Table 2. Intensity ratio of the two bands at 298 K for TMBD and enthalpy change for excimer formation

Solvent	$\frac{I(\text{band II})}{I(\text{band I})}$	ΔH° (kJ mol ⁻¹)
Vapour	0.46 ^a	-9.4
Hexane	1.14	-10.6
Cyclohexane	1.35	-13.4
IPE	1.42	-11.1
THF	0.98	-11.3

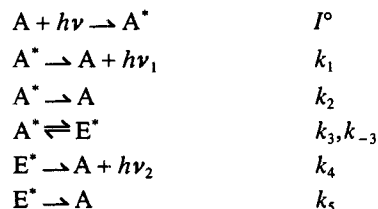
^a At 303 K.

the excimer band to that of the monomer band for TMBD at 303 K in the gas phase and at 298 K in different solvents.

DISCUSSION

Effect of ring size on the stability of the cyclic excimer

The well known reaction scheme for the intramolecular excimer formation is as follows:



where A* and E* are an excited monomer and an intramolecular excimer, respectively. The emission from A* and E* gives bands I and II, respectively. A steady-state treatment based on the assumption that a fast equilibrium between A* and E* is attained leads to the following equations for the intensities of the

monomer and excimer emissions:

$$I(\text{band I}) = \frac{k_1 I^0}{(k_1 + k_2) + K(k_4 + k_5)} \quad (1)$$

$$I(\text{band II}) = \frac{k_4 K I^0}{(k_1 + k_2) + K(k_4 + k_5)} \quad (2)$$

where $I(\text{band I})$ and $I(\text{band II})$ are the integrated intensities of bands I and II and K is the equilibrium constant expressed as $K = [E^*]/[A^*]$. The ratio of the intensities of bands I and II is expressed by

$$\frac{I(\text{band II})}{I(\text{band I})} = K \frac{k_4}{k_1} \quad (3)$$

In Figure 3, the values of $\ln[I(\text{band II})/I(\text{band I})]$ are plotted against $1/T$ for TMPD and TMBD. Since k_4/k_1 is the ratio of the rate constants for similar radiative processes, it was assumed that the value was independent of the temperature as a first approximation. The values of ΔH° for the equilibrium between A* and E* can be obtained from the slopes of the straight lines in Figure 3, and are listed in Table 2. These values agree with those reported by Halpern and co-workers.^{4,6}

In Figure 4, the intensity ratio of bands I and II is plotted against the ring size on the cyclic excimer. Figure 4 also shows the ratio of the intensity of band B (assigned to a cyclic exciplex) to that of band A (assigned to an acyclic exciplex) in the cadmium-sensitized reaction of diamines for comparison (the values were taken from Ref. 8). As Figure 4 shows, the ratio is a maximum for a five-membered ring. An increase in the size of the ring leads to a decrease in the stability of the cyclic excimer. This tendency is consistent with the result of a decrease in exciplex stability with increase in the size of the chelate ring in the cadmium-sensitized reaction, which was explained in terms of entropy effects associated with the larger connecting links between ligand donor atoms caused by an increase in the chelate ring size.⁷

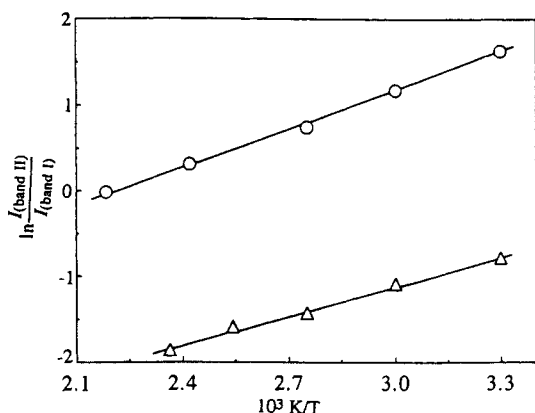


Figure 3. Plots of $\ln[I(\text{band II})/I(\text{band I})]$ against $1/T$ for (o) TMPD and (Δ) TMBD fluorescence in the gas phase

As mentioned above, the stability of the cyclic excimer is largest for a five-membered ring and decreases with an increase in the ring size. In contrast to the cadmium-sensitized luminescence of diamines, no emission from cyclic excimers larger than a seven-membered ring was observed in the fluorescence of diamines. The larger binding energy of the cadmium-sensitized reaction ($31\text{--}41\text{ kJ mol}^{-1}$) compared with the present case ($9.4\text{--}12.2\text{ kJ mol}^{-1}$) seems to be one of the factors resulting in the emission of the cyclic exciplex with ring sizes with $n > 7$. A similar tendency was observed with α,ω -bis(pyrenyl)alkanes and α,ω -bis(phenyl)alkanes. The pyrene excimer has a larger binding energy (39 kJ mol^{-1}) than the benzene system (21 kJ mol^{-1}), and in the former the emission of intramolecular excimers with ring sizes with $n > 6$ was

observed.⁵ The larger exothermicity of the pyrene excimer (and of the cadmium exciplex) can compensate for the non-bonded interactions which represent a large barrier to the formation of medium-sized rings.

A similar tendency of a decrease in complex stability with an increase in ring size was also observed for chelate compounds for metal ions in aqueous solution, which was originally explained¹³ in terms of entropy effects. However, Hancock and Martell¹⁴ pointed out that in complexes involving polyamines with five- or six-membered chelate ring, a decrease in complex stability is associated with an increase in the ring size owing to the greater difficulty of bringing together dipoles and charges on donor atoms as the chelate ring size increases, and also owing to steric strain. They further pointed out that the changes in strain energy calculated with molecular mechanics for the ligand plus metal ion on complex formation correspond very closely to the difference in the enthalpy change of complex formation with an increase in ring size from five- to six-membered. This shows that the decrease in complex stability is largely due to steric strain.

As shown in Table 2, the value of ΔH° for TMPD is smaller (more negative) than that for TMBD. This increase in ΔH° for TMBD compared with TMPD can partly explain the decrease in the excimer stability.

From equation (3), the following equation can be obtained:

$$\frac{R_1}{R_2} = \frac{K_1 (k_1/k_4)_2}{K_2 (k_1/k_4)_1} \quad (4)$$

where R denotes the $I(\text{band II})/I(\text{band I})$ ratio and subscripts 1 and 2 represent TMPD and TMBD, respectively. If we employ the values of k_1 and k_4 for TMPD and TMBD obtained by Halpern *et al.*⁶ ($k_1/k_4 = 1$ for

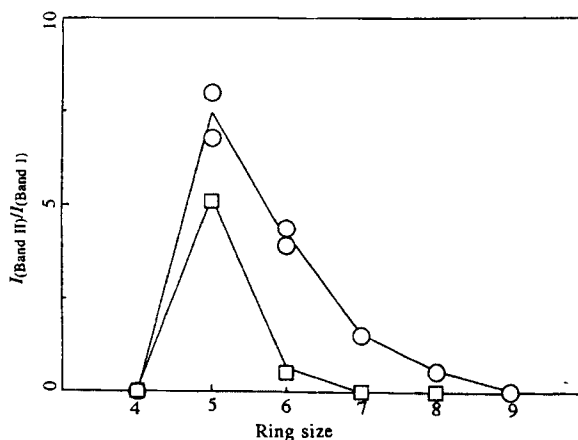


Figure 4. Effect of ring size of excimer on intensity ratios of two bands for (\square) diamine fluorescence and (\circ) cadmium-sensitized luminescence of diamines. The value for a ring size of 7 for diamine fluorescence was taken from Ref. 6

TMPD and 0.08 for TMPD), the following relationship can be obtained:

$$\begin{aligned} \frac{R_1}{R_2} &= 0.08 \frac{K_1}{K_2} \\ &= 0.08 \exp(-\Delta\Delta H/RT) \exp(\Delta\Delta S/R) \end{aligned} \quad (5)$$

By using the values of 10.9 for R_1/R_2 obtained at 303 K and $\Delta\Delta H = \Delta H_1^\circ - \Delta H_2^\circ = -2800 \text{ J mol}^{-1}$, we estimated a value of $\Delta\Delta S$ (the difference in the entropy changes for the equilibrium between A^* and E^* for TMPD and TMBD) of $32 \text{ J K}^{-1} \text{ mol}^{-1}$. This value seems to be too large. Here, we used a small value of $(k_1/k_4)_2/(k_1/k_4)_1$, resulting in overestimation of $\Delta\Delta S$. However, it must be true that the decrease in entropy from the monomer to the excimer is larger for TMBD than for TMPD. This is consistent with the general tendency.

In conclusion, the decrease in the equilibrium constant from TMPD to TMBD is partly due to the enthalpy effect and mostly due to the entropy effect.

Solvent effects on the fluorescence spectra of diamines and on the enthalpy changes for the equilibrium between A^ and E^**

Muto *et al.*⁸ observed a large solvent shift of the fluorescence spectra of some aliphatic amines and explained this in terms of the large solvation energy for the Rydberg excited state of the amines. Halpern⁹ also observed a large red shift of the fluorescence of some saturated amines. It was pointed out that since the shift in the fluorescence spectrum occurs continuously as the amount of THF in THF-hexane mixed solvent is increased and an intramolecular exciplex by N^*-O association is not formed in dimethyl aminoalkyl ethers, the large shift from hexane to THF is due to the universal interaction between the excited amine and the solvent, and this universal interaction is accounted for by the original view presented by Muto *et al.*⁸ The shift for diamines shown in Table 1 is explained in the same manner.

As mentioned above, two distinct bands were observed for TMBD in some solvents at temperatures between 283 and 323 K. In Figure 5, the value of $\ln[I(\text{band II})/I(\text{band I})]$ is plotted against $1/T$. In hexane and cyclohexane straight-line plots were obtained, and the ΔH° values can be estimated from the slopes of the lines. In IPE and THF, however, the points at the lowest temperatures deviate downwards from the straight lines. This abnormal behaviour was also observed by Halpern and Chan⁴ for TMPD in methylcyclohexane-2-methylbutane mixture at low temperatures. They offered the explanation that at low temperatures the excimer-monomer equilibrium is not attained within their lifetimes. The values of ΔH° in IPE and THF were estimated roughly from the slopes

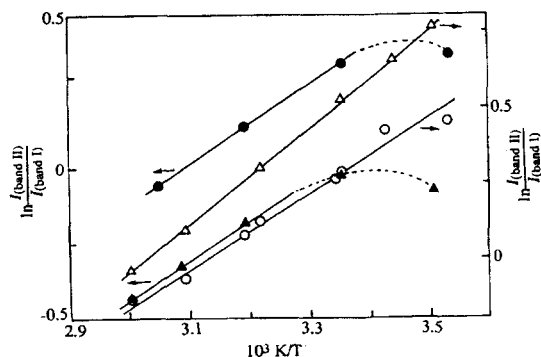


Figure 5. Plots of $\ln[I(\text{band II})/I(\text{band I})]$ against $1/T$ for TMBD fluorescence in (o) hexane, (Δ) cyclohexane, (\blacktriangle) IPE and (\bullet) THF

of the lines obtained at high temperatures. The values of ΔH° in different solvents are listed in Table 2.

Although bands I and II show large red shifts on going from hexane to THF (Table 1), the value of ΔH° in hexane is very similar to that in THF. Figure 6 shows the relationship between the wavenumbers of the peaks of bands I and II and the solvent polarity (E_T). These bands show large red shifts, but these shifts are parallel to each other. Figure 6 also shows the solvent effects on the difference in the wavenumbers of two bands and the value of ΔH° . If the energies of the ground-state monomer and excimer configurations do not depend on the solvent polarity, the solvent effect of the difference

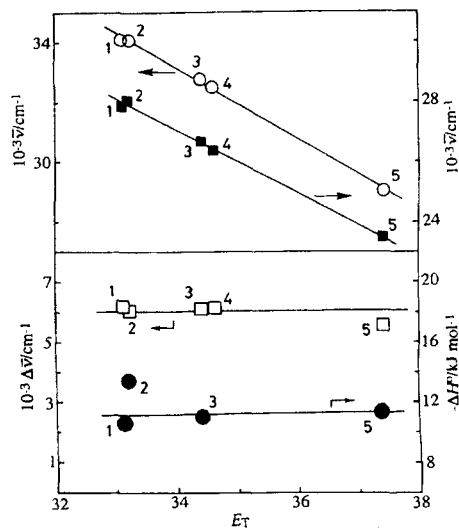


Figure 6. Relationships between wavenumbers at peak of (o) band I and (\blacksquare) band II, (\square) their difference and (\bullet) ΔH° and solvent polarity (E_T). Solvent: (1) hexane; (2) cyclohexane; (3) IPE; (4) diethyl ether; (5) THF

in the wavenumbers is a measure of the difference in the stability energies induced by the solvent between A^* and E^* . As can be seen in Figure 6, the difference in the wavenumbers is almost independent of the solvent polarity, which is consistent with the fact that the value of ΔH° is also independent of the solvent polarity.

From the parallel solvent shifts of the monomer and excimer bands, it is concluded that the monomer and the excimer are stabilized almost equally by polar solvents and both the ΔH° value and the equilibrium constant are independent of solvent polarity.

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