

Nanosecond Laser Flash Photolysis Study of 5-Styryl-1,3-dimethyluracil

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The photoisomerization of 5-styryl-1,3-dimethyluracil is studied with nanosecond laser flash photolysis technique at room temperature. The laser flash photolysis of E-isomer produces the transient absorption spectrum regarded as the triplet-triplet absorption, but the transient absorption of Z-isomer does not show the typical decay curve, probably due to the facile photocyclization reaction during the laser flash photolysis. Using the energy transfer method on nanosecond laser spectroscopy, the energy of the lowest triplet state for E isomer is estimated to lie between 41.8 and 47 kcal/mol. The triplet lifetime for E-isomer obtained from the decay curve of the transient absorption is ca. 93 ns. The $S_1 \rightarrow T_1$ intersystem crossing of E-isomer on direct excitation is relatively inefficient at room temperature supporting the singlet mechanism for direct photoisomerization.

Introduction

The photoisomerization mechanism of stilbene and its analogues has been studied with much controversy. Although earlier workers have proposed different mechanisms,¹ Saltiel *et al.*²⁻⁴ concluded on the basis of the azulene quenching experiments that the direct photoisomerization of stilbene proceeds *via* the lowest excited singlet state. The sensitized photoisomerization of stilbene was found to occur through the lowest triplet state.³ In both cases of the direct and sensitized photoisomerization, the phantom states with the twisted double bond are possible intermediates. The laser flash spectroscopy has been employed to investigate the possibility that the lowest triplet state is a reactive intermediate in the direct photoisomerization, not to speak of the sensitized photoisomerization. Several groups have observed the transient absorption in the sensitized laser photolysis of stilbene.⁵⁻⁷ The transient was assigned as the lowest triplet state of stilbene and the triplet lifetime was estimated to be ~ 120 ns in fluid solutions. The triplet state of stilbene was not observed in fluid solutions at room temperature without triplet sensitizer, but was observed by triplet-triplet absorption in glassy frozen solutions at 77°K.⁸⁻¹⁰ Furthermore, a quantum yield for intersystem crossing of 0.2 has been reported recently for stilbene in glycerol at room temperature.¹¹

The heterocyclic compounds containing both (n, π^*) and (π, π^*) excited states behave differently with stilbene because of the participation of (n, π^*) states in the decay and/or reaction processes.¹² In contrast with stilbene, several nitro-substituted stilbenes have strong short-lived transient absorption at room temperature in the laser flash photolysis because nitro groups enhance the intersystem crossing rate.¹³

5-Styryl-1,3-dimethyluracil is a stilbene analogue in which one of the phenyl rings is replaced by 1,3-dimethyluracil. The (n, π^*) excited states introduced by heteroatoms must affect the photochemical and photophysical processes of the compound in comparison with stilbene and we investigated the properties

of the excited triplet states and the mechanism of the $E \rightleftharpoons Z$ photoisomerization of the compound by nanosecond laser flash photolysis.

Experimental

Materials. 5(E)-styryl-1,3-dimethyluracil(5(E)-SDU) was prepared by the reported method¹⁴ using palladium-catalyzed reaction of styrene and 1,3-dimethyluracil and recrystallized from *n*-octanol. 5(Z)-SDU was prepared by photolysis of 5(E)-SDU with benzophenone as a sensitizer and separated by silica gel column chromatography followed by recrystallization from ethanol.

Laser Flash Photolysis. Our nanosecond laser flash photolysis apparatus has been described elsewhere.¹⁵ 5-SDU was irradiated by KrF (248 nm) and a XeF (351 nm) excimer laser (Lambda Physik EMG101E). The monitor light was divided into two beams after passage through the sample cell. One beam was routed through a Nikon P250 monochromator and the other through a Jobin Yvon H20UVL monochromator. With the latter the absorbance at 376 nm was monitored for each laser shot and was used to normalize the spectrum. An analyzing light was monitored by means of a Hamamatsu R758 photomultiplier and the signals were displayed on a Tektronix R7834 oscilloscope with 7A26 and 7B80 plugging units and on a Tektronix R466 oscilloscope. The time resolution of the total system was about 10 ns. A Tektronix 7A13 differential comparator was used for the measurements of triplet-triplet absorption spectrum and of relaxation rates of 5-SDU. The time resolution in this measurement was about 15 ns. Most of the experiments were carried out at 294 ± 0.5 K. The sample was renewed after 3-8 shots. Stationary state differential spectra were obtained on a Cary 17 spectrophotometer. The concentrations ($1.5 \times 10^{-5} \sim 5.9 \times 10^{-5}$ M) of 5(E)- and 5(Z)-SDU were adjusted such that suitable amounts of the laser light was absorbed in the laser system. The lifetimes for decay of the transient of 5(E)-SDU were obtained from oscillograms.

Results and Discussion

Transient Absorption Spectra. The laser irradiation of 5(E)-SDU produces the short-lived transient. Nanosecond time-resolved transient absorption spectra for UV region were obtained with *E* and *Z* isomers of 5-SDU in ethanol at room temperature as shown in Figure 1-3.

The change in absorbance between absorption after the flash and ground state absorption, $\Delta A_{\text{obs}}(t)$, can be represented by the equation (1), and is determined directly by oscillograms on laser flash photolysis.

$$\Delta A_{\text{obs}}(t) = \Delta \epsilon_{\text{obs}}(t) \cdot C_e \cdot l \quad (1)$$

where C_e is the concentration of excited state (equal to the absorbed photon number in Einstein unit/unit volume) and l is the path length of the photolysis cell ($l = 3.8\text{cm}$), and $\Delta \epsilon_{\text{obs}}(t)$ is the difference absorption coefficient between absorption after the flash and ground state absorption.

In order to determine the molar absorption coefficient for triplet-triplet absorption, *trans*-1,2-bispyrazylethylene¹⁶ which

has difference absorption coefficient, $\Delta \epsilon$, of $5600\text{M}^{-1}\text{cm}^{-1}$ at 376 nm is used as a reference compound. The absorption intensity depends on laser output power. The plots of output power vs. absorbance at 376 nm of transient absorption for *trans*-1,2-bispyrazylethylene and 5-SDU shows straight line. From the correlation diagram between absorbance of these two compounds, the ratio of absorbance of *trans*-1,2-bispyrazylethylene ($\text{Abs}_T\text{-BPYE}$) at 376 nm to absorbance of 5(E)-SDU ($\text{Abs}_{5(\text{E})\text{-SDU}}$) at 376 nm was estimated to be 0.38.

$$\begin{aligned} \text{Abs}_{376\text{nm}}^{5(\text{E})\text{-SDU}} &= 0.38 \times \text{Abs}_{376\text{nm}}^{T\text{-BPYE}} \\ (\Phi_{\text{isc}}^{5(\text{E})\text{-SDU}} \epsilon_T^{5(\text{E})\text{-SDU}}) \cdot C_e \cdot l &= 0.38 \times (\Phi_{\text{isc}}^{T\text{-BPYE}} \epsilon_T^{T\text{-BPYE}}) \cdot C_e \cdot l \\ \Delta \epsilon_{376\text{nm}}^{5(\text{E})\text{-SDU}} &= 0.38 \times \Delta \epsilon_{376\text{nm}}^{T\text{-BPYE}} \\ &= 0.38 \times 5600\text{M}^{-1}\text{cm}^{-1} \\ &= 2128\text{M}^{-1}\text{cm}^{-1} \\ &\approx 2130\text{M}^{-1}\text{cm}^{-1} \end{aligned}$$

By the same method, the ratio of absorbance of *trans*-1,2-bispyrazylethylene at 376 nm to absorbance of 5(Z)-SDU at 376 nm was estimated to be 0.39.

$$\begin{aligned} \Delta \epsilon_{376\text{nm}}^{5(\text{Z})\text{-SDU}} &= 0.39 \times \Delta \epsilon_{376\text{nm}}^{T\text{-BPYE}} \\ &= 0.39 \times 5600\text{M}^{-1}\text{cm}^{-1} \\ &= 2184\text{M}^{-1}\text{cm}^{-1} \\ &\approx 2180\text{M}^{-1}\text{cm}^{-1} \end{aligned}$$

The difference absorption spectrum of 5(E)-SDU and 5(Z)-SDU can be obtained from the normalized difference absorption coefficient at each wavelength using $\Delta \epsilon$ of $2130\text{M}^{-1}\text{cm}^{-1}$ for 5(E)-SDU at 376 nm and $\Delta \epsilon$ of $2180\text{M}^{-1}\text{cm}^{-1}$ for 5(Z)-SDU at 376 nm as a reference, respectively. The plot of ΔA_{obs} (relative optical density) vs. wavelength (nm) shows the difference transient absorption spectra as shown in Figure 1. The plot of the triplet absorption coefficient ϵ_T obtained by assuming Φ_{isc} from equation (2) vs. wavelength also shows the transient absorption spectra as shown in Figure 2-3.

$$\begin{aligned} (\epsilon_T - \epsilon_g) \Phi_{\text{isc}} &= \Delta \epsilon \\ \epsilon_T &= \epsilon_g + \frac{\Delta \epsilon}{\Phi_{\text{isc}}} \quad (2) \end{aligned}$$

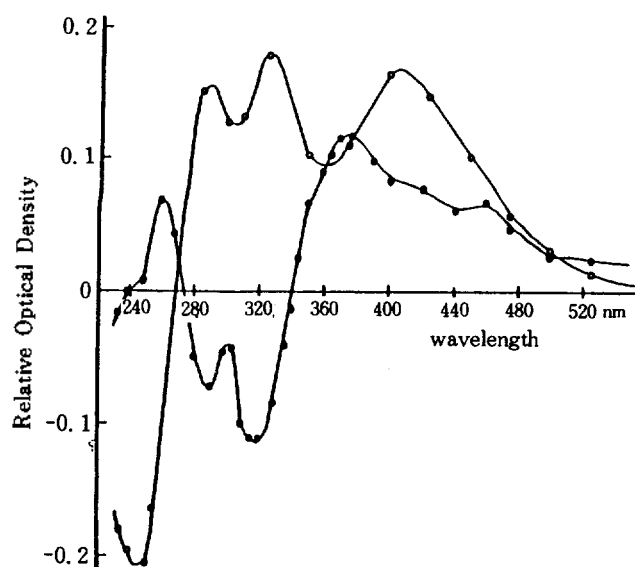


Figure 1. The difference transient absorption spectra at $t=0$ (i.e., immediately after flash photolysis) of 5(E)-SDU (•-•) and 5(Z)-SDU (o-o) in ethanol.

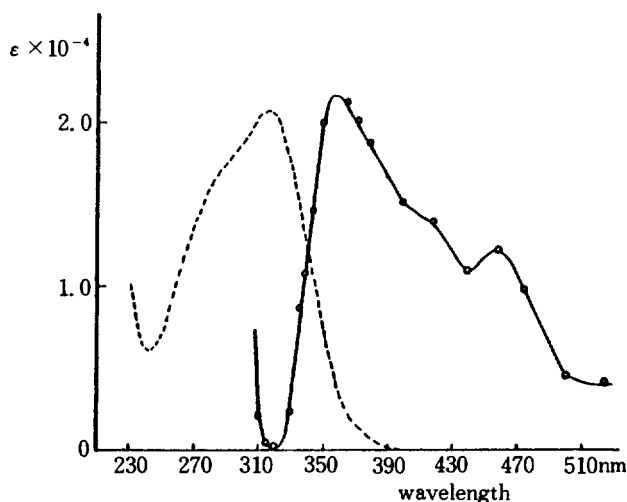


Figure 2. UV absorption (----) and triplet-triplet absorption spectrum (•-•) of 5(E)-SDU in ethanol.

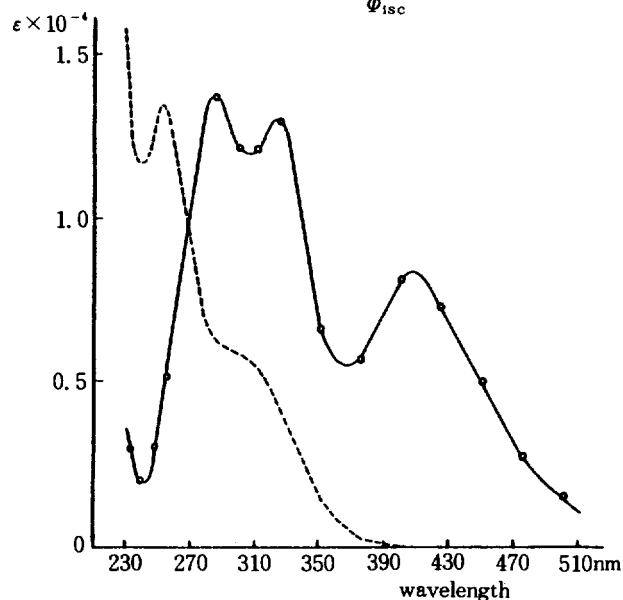


Figure 3. UV absorption (----) and transient absorption spectrum (o-o) of 5(Z)-SDU in ethanol.

where ϵ_g is the ground state absorption coefficient and ϕ_{isc} is the quantum yield of intersystem crossing.

A triplet state of stilbene is not populated in fluid solutions at room temperature consistent with singlet mechanism for the direct photoisomerization of stilbene, but the triplet-triplet absorption of stilbene in glassy frozen solutions at 77 K is observed by nanosecond laser flash photolysis.⁶⁻¹⁰ Recently a quantum yield for intersystem crossing of 0.2 has been reported for stilbene in glycerol at room temperature.¹¹ This raises the question as to whether or not a triplet route participates in the direct $E \rightarrow Z$ photoisomerization of stilbene. By sensitized nanosecond laser photolysis⁵⁻⁷ at room temperature, triplet state of stilbene was observed in fluid solutions with lifetime of ca. 120 ns and the results agree with the well-known triplet mechanism for the sensitized photoisomerization of stilbene. Görner and Schulte-Frohlinde⁷ observed identical triplet-triplet absorption spectra and triplet lifetimes for E - and Z -stilbene as starting material indicating a rapidly established equilibrium between $^1T^*$ and $^3P^*$. In contrast with stilbene, several nitro-substituted stilbenes¹³ have strong short-lived transient absorption at room temperature in the laser flash photolysis. The transients are identified as the triplet states of the nitro-stilbenes. From 4-cyano-4'-dimethoxystilbene, 4,4'-dimethoxystilbene, 4-aminostilbene, and 4,4'-diaminostilbene which is substituted by groups other than nitro group, no transients at room temperature and much weaker triplet-triplet absorption even at low temperature are observed.^{13(b)} Nitro groups enhance the $^1S \rightarrow ^1T$ transition rate without changing the $T \rightarrow ^0S$ transition rate appreciably¹⁷ due to the participation of (n, π^*) state in the decay processes. These enhancement of the intersystem crossing rate leads to the increase of the population of triplet state, thus allowing the transient to appear.

The triplet-triplet absorption of 5(E)-SDU with absorption maxima around 360 nm is observed at room temperature in Figure 2 and is stronger than that of stilbene but very weak in comparison with the nitro-substituted stilbenes. This indicates that the intersystem crossing of 5(E)-SDU is relatively inefficient but detectable. Therefore, it can be suggested that the possibility of the involvement of triplet route for direct photoisomerization of 5(E)-SDU is very small but cannot be completely neglected.

The shape and maxima of transient absorption spectrum of 5(Z)-SDU in Figure 3 differ from that of 5(E)-SDU. It was reported that irradiation of a 1.0 M solution of Z -stilbene in benzene gave only a long-lived absorption centered around 450 nm.^{13(b)} It was formed during the laser flash and is attributed to dihydrophenanthrene. As shown in Figure 4, the flash photolysis of 5(Z)-SDU shows no typical decay curve within 500 ns and only long-lived transient is observed at room temperature probably due to the formation of dihydrophenanthrene derivative during the laser flash just like in the case of Z -stilbene.

Formation of the Triplet State and Quantum Yield of the Intersystem Crossing. If a very dilute solution is exposed to a flash of high intensity from a flash lamp, all of the ground state molecules are excited to their upper singlet state. As shown in Scheme 1, after a time τ corresponding to the lifetime of the

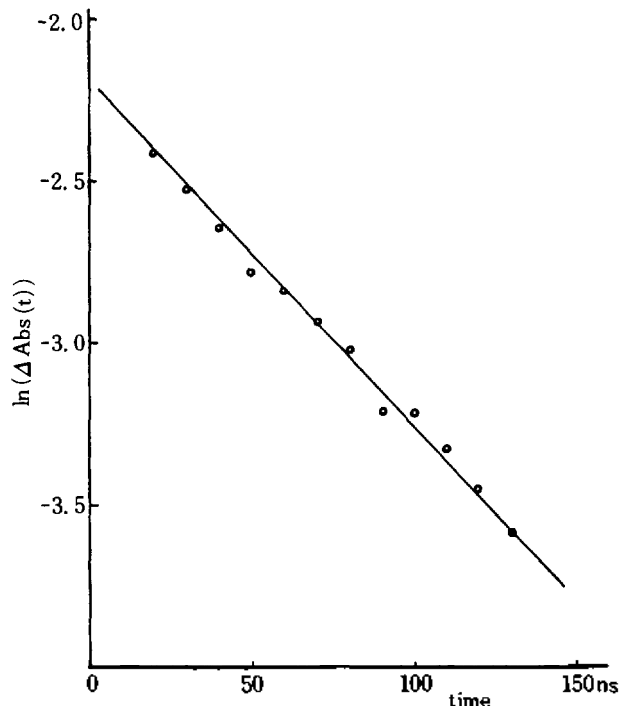
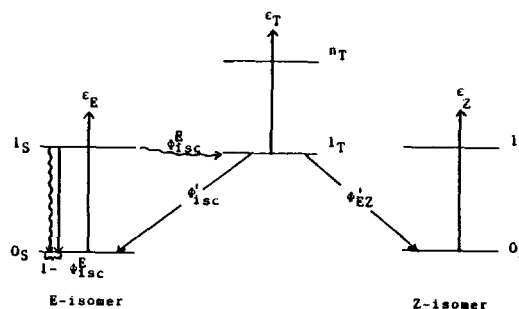


Figure 4. A plot of $\ln(\Delta Abs(t))$ vs. time t after the photolysis flash from the decay curve of triplet-triplet absorption of 5(E)-SDU at 375 nm in ethanol.



Scheme 1. Radiative and nonradiative processes on $E \rightarrow Z$ Photoisomerization in laser flash photolysis.

lowest excited singlet state, some of the molecules will have returned to the ground state via fluorescence and internal conversion processes. Others, however, will be in the lowest triplet state through intersystem crossing.

Since all the triplet states formed decay through intersystem crossing to the ground state, the following equation is established from Scheme 1.

$$\phi_{isc}^E + \phi_{EZ}^E = 1.0 \quad (3)$$

$$\phi_{isc}^{obs} = \phi_{EZ}^E \times \phi_{isc}^E \quad (4)$$

where ϕ_{isc}^{obs} is the observed quantum yield for $E \rightarrow Z$ isomerization, ϕ_{isc}^E is the fraction of molecules in the triplet state that decay to ground state E -isomer, and ϕ_{EZ}^E is the fraction of molecules in the triplet state that decay to ground state Z -isomer, and ϕ_{isc}^E is the quantum yield of intersystem crossing for E -isomer.

From Scheme 1, the difference absorption coefficient (the difference between absorption after decay and ground state absorption (initial absorption) on laser flash photolysis), $\Delta \epsilon_{obs}(t)$, is represented as follows:

$$\Delta \epsilon_{obs}(t) \approx -\epsilon_E + \phi_{isc}^E \epsilon_T e^{-t/\tau_T} + \phi_{isc}^E \phi_{EZ}^E \epsilon_Z (1 - e^{-t/\tau_T}) + \epsilon_E \phi_{isc}^E (1 - \phi_{EZ}^E) (1 - e^{-t/\tau_T}) + (1 - \phi_{isc}^E) \epsilon_E \quad (5)$$

$$- \phi_{isc}^E (\epsilon_T - \epsilon_E) e^{-t/\tau_T} + \phi_z^{obs} \Delta \epsilon_{ZE} (1 - e^{-t/\tau_T}) \quad (6)$$

where, ϵ_T is the absorption coefficient of triplet-triplet absorption of E-isomer, ϵ_E and ϵ_Z are the absorption coefficient of ground state absorption of E- and Z-isomer, respectively, t is the scanning time of oscillogram for transient absorption, τ_T is the lifetime of the triplet state for E isomer, and $\Delta \epsilon_{ZE}$ is the difference in absorption coefficient between ground state Z- and E-isomer (i.e., $\Delta \epsilon_{ZE} = \epsilon_Z - \epsilon_E$).

In equation (5), the first term is the initial absorption from ground state E-isomer to the excited singlet state after the flash photolysis, the second term is triplet-triplet absorption of E-isomer after intersystem crossing from excited singlet state, the third term is the ground state absorption of Z-isomer formed by isomerization via triplet state, the fourth term is the ground state absorption of E-isomer formed by decay of the triplet state, and the fifth term is the ground state absorption of E-isomer formed by decay of the excited singlet state.

At $t=0$ (i.e., immediately after flash photolysis), equation (6) can be replaced by equation (7).

$$\Delta \epsilon_{obs}(t=0) = \phi_{isc}^E (\epsilon_T^E - \epsilon_E) \quad (7)$$

Since it is observed that $\Delta \epsilon_{obs}$ at $t=0$ is equal to zero at 340 nm in ethanol for 5(E)-SDU, ϵ_T^E is equal to ϵ_E at 340 nm. Because the rate of intersystem crossing is very fast compared to our time resolution (ca. 15 nsec), triplet-triplet absorption just after intersystem crossing is observed practically at $t=0$.

At $t=\infty$ (i.e., at the point of complete decay of the triplet-triplet absorption) and at wavelengths where ϵ_T^E is equal to ϵ_E , equation (6) is represented as the following equation (8).

$$\Delta \epsilon_{obs}(t=\infty) = \phi_z^{obs} \Delta \epsilon_{ZE} \quad (8)$$

For 5(E)-SDU, $\Delta \epsilon_{obs}(t=\infty)$ is $-270 M^{-1}cm^{-1}$ at 340 nm in ethanol from the calculation using equation (1). Since ϵ_E is $13140 M^{-1}cm^{-1}$ and ϵ_Z is $2627 M^{-1}cm^{-1}$ at 340 nm in ethanol, $\Delta \epsilon_{ZE}$ is $-10513 M^{-1}cm^{-1}$. Therefore, the observed quantum yield of E→Z isomerization via the triplet surface at this wavelength is 0.026 from equation (8). Using ϕ_z^{obs} value of 0.026 and equation (4), the quantum yield of intersystem crossing for 5(E)-SDU can be calculated. Assuming that ϕ_{zz} is 0.5, the quantum yield of intersystem crossing, ϕ_{isc} , is 0.052 in ethanol for 5(E)-SDU. This result agrees with the results of our previous report¹⁴ for benzophenone sensitized photoisomerization, azulene quenching, etc. Both cases indicate that the quantum yield of intersystem crossing is very inefficient at room temperature in fluid solutions.

In the case of 5(Z)-SDU, the quantum yield of Z→E isomerization and intersystem crossing cannot be calculated by the same method as above because transient absorption spectrum of 5(Z)-SDU does not show the typical decay curve, probably due to the facile photocyclization reaction during the laser flash photolysis.

Triplet State of 5(E)-SDU. Energy transfer method in nanosecond laser spectroscopy was utilized to determine the energy of the triplet state of 5(E)-SDU. Addition of trans-stilbene ($E_T = 50$ kcal/mole) does not affect the transient absorption curve of 5(E)-SDU at 375 nm. With added 9,10-diphenylanthracene ($E_T = 41.8$ kcal/mole), strong triplet-triplet absorptions of 9,10-diphenylanthracene at 425 nm and 480 nm are

observed. As benzantracene ($E_T = 47.2$ kcal/mole) is added, strong triplet-triplet absorption of benzantracene at 475 nm is detected with and without 5(E)-SDU. *trans*-1,3,5-Hexatriene ($E_T = 47.0$ kcal/mole) gave no effect on the transient absorption curve of 5(E)-SDU. From these results, the triplet energy of 5(E)-SDU is estimated to lie between 41.8 and 47 kcal/mol.

When the decay of the triplet species is first order with respect to the triplet concentration, the following equations are applicable.

$$-d[T]/dt = k_T [T]$$

$$\ln([T]_0/[T]) = k_T t$$

Since the absorbance for the triplet absorption depends on the concentration of the triplet species,

$$\ln(\Delta Abs(t)) \propto k_T t$$

where [T] is the concentration of the triplet species and k_T is the sum of all first order processes leading to deactivation of the triplet state. The plot of $\ln(\Delta Abs(t))$ from decay curve vs. time t after the flash photolysis shows the straight line following first-order kinetics with the slope equal to k_T as shown in Figure 4. From the decay curve of triplet-triplet absorption at 375 nm, the triplet lifetime of 5(E)-SDU is estimated to be ca. 93 ns. This value is consistent with the triplet lifetime calculated by azulene quenching studies¹⁴ for the sensitized photoisomerization, assuming the diffusion controlled quenching ($k_q = 1.2 \times 10^{10}$ l/mol·sec at 20°C in chloroform) of the triplet state by azulene.

Acknowledgement. This investigation was supported by the Korea Science and Engineering Foundation. Authors thank Professor K. Yoshihara and N. Nakashima of the Institute for Molecular Science, Okazaki, Japan for their help and advice in flash photolysis experiments.

References

- (1) (a) Th. Förster, *Z. Electrochem.*, **56**, 716 (1952); (b) H. Dycck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).
- (2) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *J. Am. Chem. Soc.*, **88**, 2386 (1966).
- (3) J. Saltiel, J.D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O.C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973).
- (4) J. Saltiel and J. L. Charlton, "Rearrangements in Ground and Excited States", P. de Mayo, Ed., Vol. 3, p. 25, Academic Press, New York (1980).
- (5) M. Sumitani, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **51**, 2503 (1978).
- (6) F. S. Dainton, E.A. Robinson, and G.A. Salmon, *J. Phys. Chem.*, **76**, 3897 (1972).
- (7) H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, **85**, 1835 (1981).
- (8) G. Heinrich, H. Blume and D. Schulte-Frohlinde, *Tet. Lett.*, 4693 (1967).
- (9) W. G. Herkstroeter and D. S. McClure, *J. Am. Chem. Soc.*, **90**, 4522 (1968).
- (10) H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, **83**, 3107 (1979).
- (11) L. A. Brey, G. B. Schuster, and H. G. Drickamer, *J. Am. Chem.*

- Soc., **101**, 129 (1979)
- (12) U. Mazucato, *Pure Appl. Chem.*, **54**, 1705 (1982).
- (13) (a) D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66**, 2486 (1962); (b) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 446 (1974); (c) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 451 (1974); (d) H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, **82**, 2653 (1978).
- (14) E. J. Shin, B. S. An, and S. C. Shim, to be published.
- (15) N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, **77**, 6040 (1982).
- (16) P.-H. Bong, K.H. Chae, S.C. Shim, N. Nakashima, and K. Yoshihara, *J. Photochem.* in press.
- (17) S. P. McGlynn, R. Ajumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., p. 251-256, 1969

Platinum(II) Complexes of 6,6'-Dimethyl-2,2' diaminobiphenyl

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Carbonato and diammine platinum(II) complexes of resolved 6,6'-dimethyl-2,2'-diaminobiphenyl have been prepared. The absolute configuration of the square planar platinum(II) complexes is determined on the basis of stereospecificity of the 6,6'-dimethyl-2,2'-diaminobiphenyl ligand, circular dichroism spectra of the complexes, and nonempirical circular dichroism method.

6,6'-Dimethyl-2,2'-diaminobiphenyl (dmdabp) belongs to the skewed biaryl group. The two phenyl rings of R- or S-dmdabp have been found to be puckered by more than 70 degrees in angle¹ and thus provide a good source of dissymmetry owing to such nonplanarity of the chelate rings when coordinated to a metal ion. Investigations involving dmdabp have been with cobalt (III) complexes^{2,3} and more recently with dichloro and 2,3-diaminobutane platinum(II) complexes.⁴ The present work has been undertaken to prepare carbonato and diammine platinum(II) complexes of resolved dmdabp and to determine the absolute configuration of those complexes based on the nonempirical CD method.

The nonempirical determination of absolute configuration has been applied to the metal complexes of particular ligands containing two non-coplanar chromophores.⁴⁻⁹ This method has been successful in predicting the absolute configuration of metal complexes of 1,10'-phenanthroline,^{10,11} 2,2'-bipyridine¹¹, acetylacetonate,¹² and catecholate.¹³ The sterically hindered dmdabp has the electric dipole π - π^* transitions in the near ultraviolet region and should provide an ideal background material for the application of nonempirical CD determination of absolute configuration.

Experimental

Preparation and resolution of 6,6'-dimethyl-2,2'-diaminobiphenyl. This has been reported elsewhere.^{1,2}

[Pt-(R-dmdabp)Cl₂] and [Pt-(S-dmdabp)Cl₂]. The preparation of these complexes is similar to that used for [Pt(en)Cl₂]⁴.

[Pt(R-dmdabp)CO₃]. 0.48g of [Pt-(R-dmdabp)Cl₂] and 0.14 g K₂CO₃ were suspended in 300 ml of water in 500-ml three-neck round bottom flask equipped with a mechanical stirrer, thermometer and water cooled condenser. The mixture was stirred and heated at a temperature of 65-75°C for 7 hours.

The gradually the suspension dissolved. The solution was cooled and filtered. The filtrate was concentrated on a rotary evaporator until crystallization. The mixture was placed in an ice bath. The white crystals were collected on a sintered glass funnel, washed with ethanol and ether. The product was recrystallized once from warm water to which a few drops of 1M HCl were added. *Anal.* Calcd for Pt(C₁₄H₁₆N₂)CO₃: C, 38.54; H, 3.43; N, 6.00 Found: C, 38.57; H, 3.40; N, 5.95.

[Pt(NH₃)₂Cl₂]. This was prepared by the method of Johnson.¹⁴

[Pt(R-dmdabp)(NH₃)₂]Cl₂. 1.12 g of Pt(NH₃)₂Cl₂ and 0.80 g of R-dmdabp were suspended in 300 ml of water in a 500-ml three-neck round bottom flask equipped with a mechanical stirrer, thermometer, and water cooled condenser. The mixture was stirred and heated at a temperature of 60-70°C for 8 hours. Gradually the suspension dissolved and the solution changed from yellow to almost colorless. The solution was cooled and filtered to remove any unreacted materials. The filtrate was concentrated on a rotary evaporator until crystallization. The mixture was placed in an ice bath. The product was collected on a sintered glass funnel, washed with ethanol and ether, air dried. It was recrystallized from warm water (Yield 0.84 g (46%)). *Anal.* Calcd for [Pt(C₁₄H₁₆N₂)]Cl₂·H₂O: C, 32.20; H, 4.60; N, 10.72; Cl, 13.60 Found: C, 31.18; H, 4.63; N, 10.68; Cl, 13.66

[Pt(S-dmdabp)(NH₃)₂]Cl₂. This was prepared in the same way as that used for [Pt(S-dmdabp)(NH₃)₂]Cl₂ using S-dmdabp in place of R-dmdabp. (Yield 0.47 g (48%)). The infrared spectra of the two compounds were identical. Physical measurements. The electronic absorption spectra were obtained using a Cary 17 UV-Visible Spectrophotometer. The infrared spectra were recorded using Shimadzu IR-435 Spectrophotometer. The circular dichroism spectra were measured using a Jasco-20 CD Spectrophotometer.