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A KINETIC STUDY OF COUPLED INTERNAL ROTATION IN RACEMIC 2,3-BENZO-9-TRIPTYCYL 2-(DIMETHYLAMINOMETHYL)-9-TRIPTYCYL ETHER BY MEANS OF EXCIPLEX FLUORESCENCE DYNAMICS

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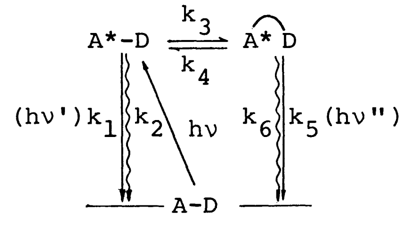
Kinetic parameters for fluorescence dynamics of the title di(9-triptycyl) ether have been obtained by the transient experiments. The temperature dependence of the rate constants gave the activation energy value of 4.2 kcal mol^{-1} for the gear-meshing torsional motion in the di(9-triptycyl) ether.

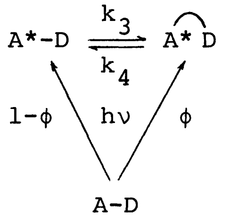
Coupled internal rotation is a concept introduced in dynamic stereochemistry to account for the unexpectedly facile torsional motions of apparently hindered molecular rotors. One of the most dramatic examples is provided by di(9-triptycyl)methanes and di(9-triptycyl) ethers (Tp_2X, $X = CH_2$ and O, respectively) in which two torsional degrees of freedom are highly mobile and yet perfectly coupled in the double rotor molecules.$^{1,2)}$ As a stereochemical consequence, the new stereoisomerism due to the different phase relationship of appropriately labeled benzene rings is generated. Since the two wheels of the molecular gear are tightly meshed, the gear-slipping process is found to require an activation energy of 32 - 33 and 42 - 43 kcal mol^{-1} for Tp_2CH_2 and Tp_2O, respectively. One last remaining question as regards the stereochemistry and dynamics of these molecules is how fast the gear-meshing process takes place and/or how high the barrier to that torsional motion is. A preliminary answer was given recently by a kinetic study under photostationary conditions of the intramolecular exciplex formation in the Tp_2O derivative (**1**) carrying donor (dimethylamino)methyl group on one Tp unit and acceptor naphthalene chromophore on the other.$^{3)}$ Since the method did not allow us to obtain the detailed kinetic information on the dynamic processes, we have now carried out the transient fluorescence measurement of the system under a pulsed excitation.

The intramolecular exciplex formation in **1** dl in solution is most simply described by Scheme 1A, where A-D, A*-D and $\overset{\frown}{A^{*}D}$ are, respectively, **1** dl in the ground state, locally excited state (LE), and exciplex state (EX). Rate constants k_1 and k_5 are for fluorescence, and k_2 and k_6 are for the non-radiative decay, from LE and EX, respectively. Rate constants k_3 and k_4 are for the intramolecular exciplex formation and dissociation processes, respectively, with conformational changes.

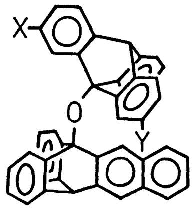
Under photostationary conditions, the fluorescence quantum yields Φ_{LE} and Φ_{EX}



Scheme 1A.



Scheme 1B.



1 meso ($X = CH_2NMe_2$, $Y = H$)

1 dl ($X = H$, $Y = CH_2NMe_2$)

due to the naphthalene chromophore are given by Eqs. 1 and 2.

$$\Phi_{LE} = k_1Y/(XY - k_3k_4) \quad (1) \qquad X = k_1 + k_2 + k_3 \quad (3)$$

$$\Phi_{EX} = k_3k_5/(XY - k_3k_4) \quad (2) \qquad Y = k_4 + k_5 + k_6 \quad (4)$$

In the case of δ excitation, the time dependence of fluorescence intensities is given by Eqs. 5 and 6.[4)]

$$I_{LE}(t) = C_1\exp(-\lambda_1 t) + C_2\exp(-\lambda_2 t) \quad (5)$$

$$I_{EX}(t) = C_3[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \quad (6)$$

$$\lambda_{1,2} = [X + Y \mp \sqrt{(Y - X)^2 + 4\,k_3k_4}]/2 \quad (7)$$

The transient behavior of the fluorescence emission from both LE and EX of 1 dl was analyzed by the nanosecond single photon counting technique.[5)] A dual exponential decay curve of LE emission and a grow-in and decay curve of EX emission were obtained by irradiating the naphthalene chromophore at 290 nm with a flash lamp (Fig. 1). Decay parameters λ_1 and λ_2 were obtained by deconvolution of these transient curves. Rate constants k_1 and k_2 were obtained from the analysis

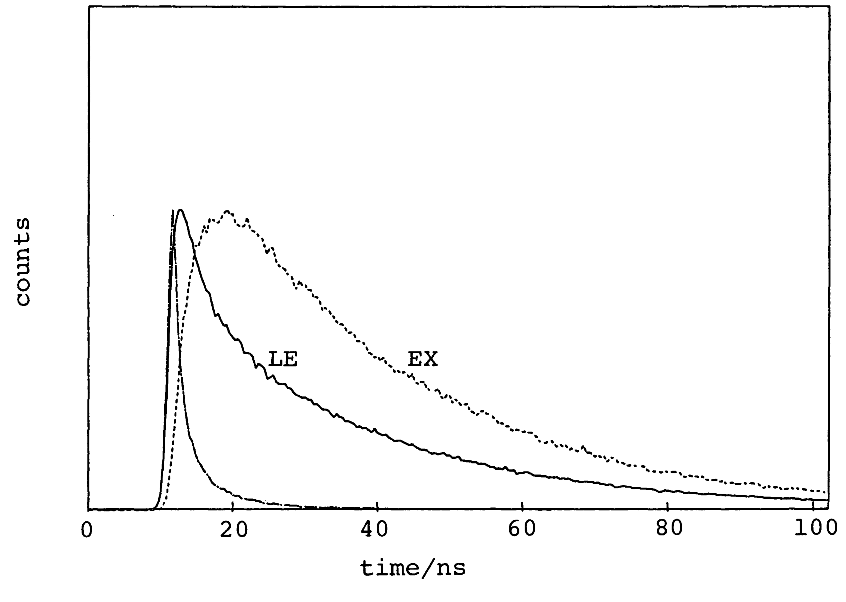


Fig. 1. Single-photon experimental decay curves of fluorescence due to 1 dl in n-butyl ether at 10 °C.

of the emission decay of closely related compound, i.e., **1** meso isomer, which does not contain any conformer capable of showing EX fluorescence.[3] Four rate constants $k_3 - k_6$ were then calculated from Eqs. 1 - 7. Since it was difficult to obtain accurately λ_2 from a small fraction of the fast decay component in the LE emission, the value was taken from the rise time of the EX emission. The data collected in the temperature range 10 - -20 °C allow us to derive the activation energy values as collected in Table 1. The thermodynamic parameters for the exciplex formation are $\Delta H° = -4.2 \pm 0.56$ kcal mol^{-1} and $\Delta S° = -13.6 \pm 2.1$ e.u.

Table 1. Kinetic Parameters for **1** in Bu_2O at 10 °C

	Rate constant/$10^7 s^{-1}$					Quantum yield		Activation energy ±0.4 kcal/mol		
	k_1	k_2	k_3	k_4	k_5+k_6	Φ_{LE}	Φ_{EX}	E_a^3	E_a^4	E_a^{5+6}
1 dl	(0.54)	(2.1)	90.3	45	4.2	0.052	0.077	4.2	8.5	1.0
1 meso	0.54	2.1	–	–	–	0.21	–	–	–	–

Can we equate E_a^3 to the activation energy for the gear-meshing process in **1**? In the picosecond time domain,[6] an unresolvably fast rise of the EX emission (<10 ps) was observed in addition to the slow rise and decay corresponding to those observed in the nanosecond experiments. The fast rise of the EX emission could be explained by the direct exciplex formation from the ground state as shown in Scheme 1B, where ϕ is a fraction of such an instantaneous exciting pathway. On the basis of Scheme 1B, Eq. 6 is converted into Eq. 6':

$$I_{EX}(t) = C_4\exp(-\lambda_1 t) - C_5\exp(-\lambda_2 t) \qquad (6')$$

where

$$\frac{C_5}{C_4} = \frac{\phi(-k_4-X+\lambda_1) + (X-\lambda_1)}{\phi(k_4+X-\lambda_2) + (-X+\lambda_2)} \cdot \frac{(-X+\lambda_2)}{(X-\lambda_1)} \qquad (8)$$

The ratio of the EX emission intensity of the slower rising component to that of the decay component was 0.52 when the data of the picosecond transient study was extrapolated to $t = 0$. The ϕ value is found to be 0.32 at 23 °C from Eq. 8, and agrees nicely with the unbiased population of the conformer in which the fluorescent state of the naphthalene chromophore is born right next to the tert-amino group in the gear-meshing conformational circuit (Fig. 2). Here conformers a and b are less stable in the ground state, but are considered to show exciplex emission at 412 nm in Bu_2O at 23 °C. As the temperature is lowered, contribution of the direct path to the EX state decreases. In the temperature range 10 - -20 °C where the E_a values were determined, the decay parameter λ_1 of the EX emission agreed within the experimental error (<5%) with the one obtained from the slow component of the decay in the LE emission. The ratio of the preexponential factors of the rise and decay components showed deviation not higher than 8% from unity.

The E_a^3 value of 4.2 kcal mol^{-1} and k_3 of 9.0×10^8 s^{-1} at 10 °C are concluded

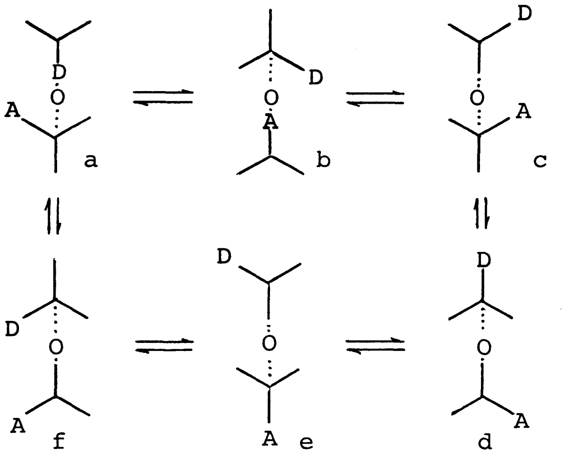


Fig. 2. A conformational gearing circuit. Conformers a and b are considered to show exciplex emission.

to be the activation energy and rate constant, respectively, of the process in which two chromophores A and D approach each other over at least one benzene ring, i.e., a tooth of the molecular gear, to form the exciplex within the lifetime of the naphthalene chromophore in the excited state. In reference to Fig. 2, k_3 corresponds to the average rate constants for the formation of conformers a and b from c - f. Since the non-bonded interaction in the gear framework of the molecule in the electronically excited state should not be very much different from that in the ground state, the E_a^3 value is regarded to be a good measure of the barrier height to the gear-meshing process of **1**.7)

References

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3) N. Koga and H. Iwamura, J. Am. Chem. Soc., 107, 1426 (1985).

4) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York (1970).

5) Decay measurements were executed with the single-photon technique with a Horiba NAES-1100 time-resolved spectrofluorometer. Excitation occurred at 290 nm. The LE and EX emissions were collected through Hoya glass filters U340-UV 30 and a combination of a glass filter L42 and a 1 M Cu_2SO_4 solution, respectively.

6) Decay measurements were carried out on a synchronously pumped, cavity dumped Rhodamine 6G dye laser system (I. Yamazaki, N. Tamai, H. Kume, H. Tsuchiya, and K. Oba, Rev. Sci. Instrum., 56, 1187 (1985)). We thank Prof. I. Yamazaki and Mr. N. Tamai of the Institute for these measurements.

7) The Me_2NCH_2- group is considered to have additional modes of freedom, torsion around the CH_2-NMe_2 bond and nitrogen inversion, which might be attributed to the observed activation energy. According to DNMR experimental data, the barriers to these motions in appropriately substituted amines are in the range 6 - 8 kcal mol^{-1}. Our value is slightly too low to be assigned to such processes.

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