Conformational Analysis of Intramolecular Fluorescence Quenching of α-(9-Carbazolyl)-ω-[*p*-(methoxycarbonyl)benzoyloxy]alkanes

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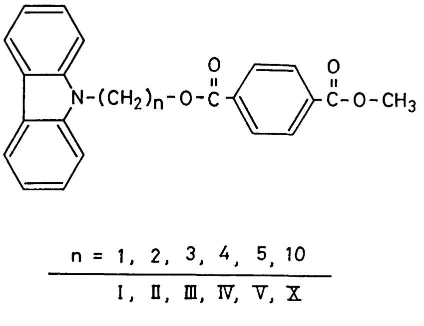
Equilibrium distribution of conformations of the series of compounds, α-(9-carbazolyl)-ω-[*p*-(methoxycarbonyl)benzoyloxy]alkanes in the ground state was calculated to explain the intramolecular fluorescence quenching of these compounds in a rigid medium. It was found that when the radius of active sphere R_0 for the intramolecular fluorescence quenching is taken to be 8.8—9.0 Å, the experimentally observed chain length dependence of the fluorescence quenching can be well simulated by this calculation. The active sphere for the dynamic intermolecular fluorescence quenching in solution was also discussed to compare with that of the intramolecular fluorescence quenching.

Since Leonhardt and Weller[1] first reported the intermolecular exciplex formation between perylene in its excited singlet state and *N*,*N*-dimethylaniline in the ground state, extensive studies have been carried out on the intermolecular exciplex formation. Recently, intramolecular exciplexes have been studied to investigate the geometry of exciplexes and their electronic structures for various exciplex systems, *e.g.*, $(CH_3)_2N$-$(CH_2)_n$-(naphthyl) (n=2—4),[2] *p*-$(CH_3)_2N$-C_6H_4-$(CH_2)_n$-(9-anthryl) (n=0—3),[3] *p*-$(CH_3)_2N$-C_6H_4-$(CH_2)_n$-(1-pyrenyl) (n=1—3),[3] (9,10-dicyanoanthryl)-$(CH_2)_3$-(naphthyl).[4] In the previous reports,[5] we have studied the intramolecular fluorescence quenching and exciplex formation for a series of α-(9-carbazolyl)-ω-[*p*-(methoxycarbonyl)benzoyloxy]alkanes (Fig. 1). It was found in these investigations that intramolecular fluorescence quenching of the system can be separated into "static quenching" and "dynamic quenching," and only the static quenching is observed in a rigid medium where the Brownian motion of the methylene chain is frozen.

The present investigation was undertaken to see if the experimentally observed chain length dependence of the static fluorescence quenching[5] can be simulated by the calculation of the equilibrium conformations of the intramolecular exciplex system. Equilibrium distribution of conformations for individual compounds in the ground state was determined by the calculation of potential energy of each conformation[6] and the degree of intramolecular static fluorescence quenching was estimated by the calculation of the probability of end-to-end encounter in all the conformations.



n = 1, 2, 3, 4, 5, 10
I, II, III, IV, V, X

Fig. 1.

Procedures for Calculation

Structural parameters used in this calculation are shown in Figs. 2(a) and 2(b). In this calculation we assume that the ester groups are coplaner with the benzene ring and the trans conformation is predominant over the cis. This assumption has been taken routinely in conformational calculations.[7,8] Generally, conformations of methylene chain are treated by the trans(t)-gauche(g) rotational isomer model, where the statistical weight for two gauche states (g^+ and g^-) is estimated by $\exp(-500/RT)$, since the energy difference between g and t is about 500 cal/mol. However, for relatively short methylene chain having large

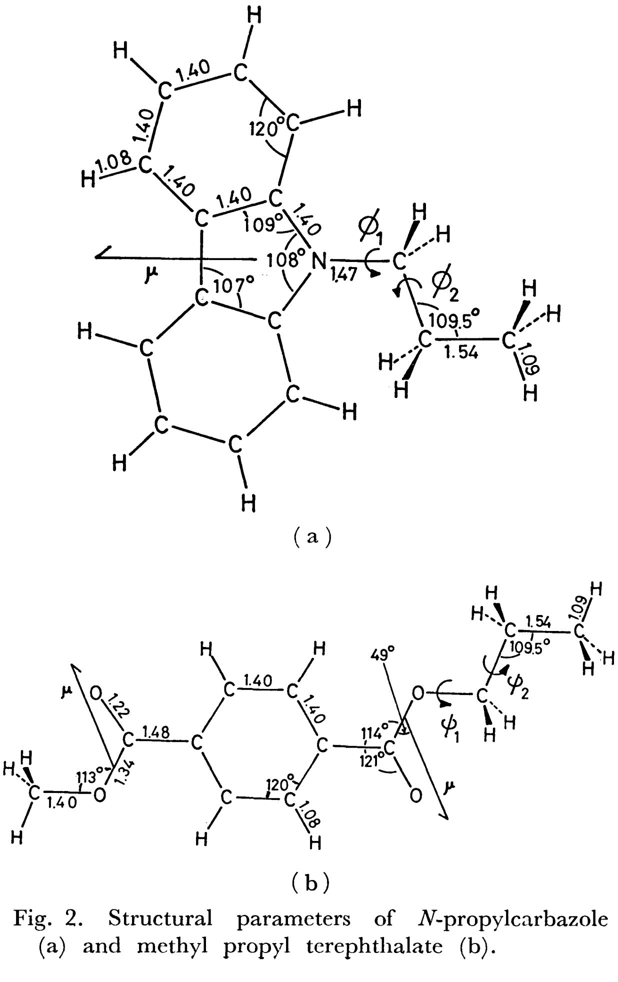


Fig. 2. Structural parameters of *N*-propylcarbazole (a) and methyl propyl terephthalate (b).

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end groups, rotations about each C–C bond is related so strongly to one another that the statistical weight for gauche states may differ from $\exp(-500/RT)$. Hence, we calculated the conformational energy, considering that the rotations about all bonds are correlated, though we employed the t-g rotational isomer model in these calculations.

Potential energies due to the van der Waals interactions between nonbonded atoms and due to the electrostatic dipole-dipole interaction between polar end groups were calculated for all of $2\times 3^{n+1}$ conformations where n denotes the number of methylene units. For the compound having $n=10$, we adopted the Monte Carlo method, since the number of possible conformation of this compound is too large. In this method we selected randomly 14500 conformations out of $2\times 3^{n+1}$ conformations and calculated the potential energy of each one.

Calculation of the Potential Energy due to the Van der Waals Interaction. We adopted a potential function of the Lennard-Jones type. The potential energy P_{ij} between ith and jth nonbonded atoms is given as follows

$$P_{ij} = B_{ij}/r_{ij}^{12} - A_{ij}/r_{ij}^{6}, \tag{1}$$

where, r_{ij} is the distance of separation between ith and jth nonbonded atoms, A_{ij} and B_{ij} are parameters. The parameters A_{ij} have been estimated, using the Slater-Kirkwood equation modified by Scott and Scheraga,[9]

$$A_{ij} = \frac{(3/2)(e\hbar/m^{1/2})\alpha_i\alpha_j}{(\alpha_i/N_{\mathrm{eff}}^{(i)})^{1/2}+(\alpha_j/N_{\mathrm{eff}}^{(j)})^{1/2}}, \tag{2}$$

where, e is the charge of an electron, m is the mass of an electron, $\hbar$ is equal to $h/2\pi$ where h is the Planck's constant, α_i and $N_{\mathrm{eff}}^{(i)}$ are the polarizability and the effective number of electrons of ith atom, respectively. The values of $N_{\mathrm{eff}}^{(i)}$ were graphically determined using Pitzer's data[10] according to Scott and Scheraga.[9] The parameter B_{ij} is obtained by requiring P_{ij} to be minimum at a distance $r_{ij}=r_{ij}^{\circ}$, which is the sum of the van der Waals radii of the interacting atoms. Values of the van der Waals radius r_{w}, the polarizability α, and the effective number of electrons N_{eff} are summarized in Table 1.

Then, the potential function is modified in consideration of molecule-solvent interaction following Flory *et al.*[11] For a molecule in a solvent, intramolecular contact through alternation of conformation must occur at the expense of intermolecular interaction with the solvent. Since these latter interactions are necessarily attractive, the effect would suppress the attractive term P_{ij} occurring at the greater distance r_{ij} between the ith and the jth atoms. Thus the minimum in this function would be eliminated. Calculations have, therefore, been carried out using the potential function modified as follows

$$\begin{aligned} P_{ij}^{*} &= P_{ij} - P_{ij}^{\circ} \quad (r_{ij} < r_{ij}^{\circ}) \\ P_{ij}^{*} &= 0 \qquad\qquad (r_{ij} \geq r_{ij}^{\circ}), \end{aligned} \tag{3}$$

where P_{ij}° is the value of P_{ij} at $r_{ij}=r_{ij}^{\circ}$. We obtained the total potential energy due to the van der Waals interaction as the sum over all pairs of nonbonded atoms.

$$V_n = \sum_{i<j}\sum P_{ij}^{*} \tag{4}$$

TABLE 1. ATOMIC PARAMETERS FOR THE CALCULATION
The van der Waals radius r_{w}, the polarizability α, and the effective number of electrons N_{eff}.

Atom	r_{w}/Å a)	α/Å^3 b)	N_{eff}
H (arom.)	1.01	0.42	0.9
H (aliph.)	1.20	0.42	0.9
C (sp^2)	1.75	1.20	4.9
C (sp^3)	1.70	1.30	4.9
O (sp^2)	1.52	0.64	6.8
O (sp)	1.50	0.84	6.8
N (sp^2)	1.55	1.15	5.9

a) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964). b) J. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York (1958), p. 91.

Calculation of the Potential Energy due to the Electrostatic Dipole-Dipole Interaction. The mutual potential energy D_{ij} of two point dipoles $\vec{\mu}_i$ and $\vec{\mu}_j$ separated by the vector $\vec{r}_{ij}$ is given by

$$D_{ij} = (1/\varepsilon)[(\vec{\mu}_i\cdot\vec{\mu}_j)/r_{ij}^{3} - 3(\vec{\mu}_i\cdot\vec{r}_{ij})(\vec{\mu}_j\cdot\vec{r}_{ij})/r_{ij}^{5}], \tag{5}$$

where ε is the dielectric constant of the solvent and r_{ij} is the scalar magnitude of $\vec{r}_{ij}$. The total potential energy V_{e} due to the dipole-dipole interaction is given by the sum over all pairs of dipoles as follows.

$$V_{\mathrm{e}} = \sum_{i<j}\sum D_{ij} \tag{6}$$

In the present calculation, the dipole moments of CZ residue and ester group were taken to be 2.09 D[12] and 1.83 D, respectively; the latter value is taken from the value for the dipole moment of methyl benzoate.[13] The angle between the dipole moment (indicated by μ in Fig. 2) and the O–CO bond was taken to be 49°.

Conformations of Methylene Chain in the Neighborhood of Carbazole (CZ) and Terephthalic Acid Methyl Ester (TPM) Residues. We calculated the conformational energy applying the t-g rotational isomer model to the methylene chain. However, the location of the potential minima in the neighborhood of the large end groups might somewhat deviate from that in the t-g rotational isomer model. Hence, we have calculated the potential energies of *N*-propylcarbazole and methyl propyl terephthalate, whose structures are shown in Fig. 2, at intervals of 5° for each rotation angle, starting from conformations shown in Fig. 2 ($\phi_1=\phi_2=0$, $\psi_1=\psi_2=0$).

The potential energy, $V(\theta_i)$, associated with rotation θ_i about ith bond is given by

$$V(\theta_i) = V_{\mathrm{r}}(\theta_i) + \sum_{i<j}\sum P_{ij}, \tag{7}$$

where $V_{\mathrm{r}}(\theta_i)$ is the intrinsic torsional potential attributable to the bond itself, P_{ij} is the potential energy between nonbonded atoms given by Eq. 1 and the sum is over all pairs, i,j of atoms. For threefold rotation, V_{r} is given by

$$V_{\mathrm{r}}(\theta_i) = (V_0/2)(1-\cos 3\theta_i), \tag{8}$$

where V_0 is the torsional barrier height. In this calculation the internal rotation having a sixfold

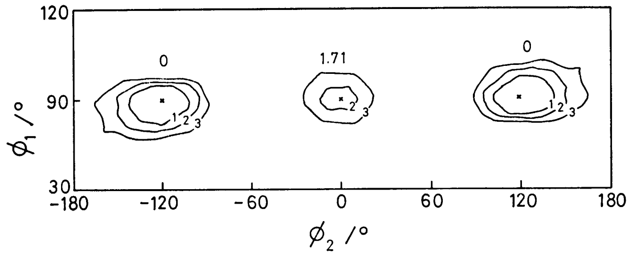

Fig. 3. Conformational energy map of *N*-propylcarbazole. Energy contours are given at interval of 1.0 kcal/mol. Numerals in the figure are the values of potential energy at its minimum position marked by X.

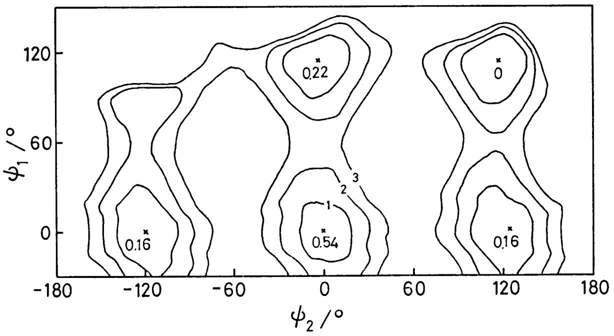

Fig. 4. Conformational energy map of methyl propyl terephthalate. Notations are the same as Fig. 3.

periodicity was neglected. Values of 2.8 kcal/mol and 1.8 kcal/mol were assigned to V_0 for C–C bond and C–O bond, respectively.[14]

Results are shown in Figs. 3 and 4. For *N*-propylcarbazole, the potential mimima are situated at rotations $\phi_1=90°$, $\phi_2=0°$, $\pm120°$ and $\phi_1=-90°$, $\phi_2=0°$, $\pm120°$. The potential mimima for methyl propyl terephthalate are found to be about at $\phi_1=0°$, $\phi_2=0°$, $\pm120°$, $\phi_1=120°$, $\phi_2=0°$, $+120°$, and $\phi_1=-120°$, $\phi_2=0°$, $-120°$. For these two compounds, the locations of potential mimima are not so deviated from that in the t-g rotational isomer model, hence the use of the t-g rotational isomer model in the neighborhood of CZ and TPM residues appears to be justified.

Results and Discussion

The total potential energy, *E*, is given by the sum of the potential energy due to the van der Waals interaction and that due to the dipole-dipole interaction. Assuming that the distribution of conformations obeys the Boltzmann distribution, the fraction of *i*th conformation, W_i, is given by

$$W_i = \exp(-E_i/RT)/\sum_j \exp(-E_j/RT),$$

where E_i is the potential energy for *i*th conformation.

Distribution of End-to-end Distance. Distribution of the end-to-end distance, *r*, for each compound at 298 K is shown in Fig. 5, where *r* was defined as the distance between the center of five membered ring of CZ and the center of the benzene ring of TPM.

For the compounds having shorter methylene chains, I, II, III, the appearing conformations are so few that the distribution of end-to-end distance is very sharp. There is no conformation whose end-to-end distance is less than 5 Å since the two end groups are large.

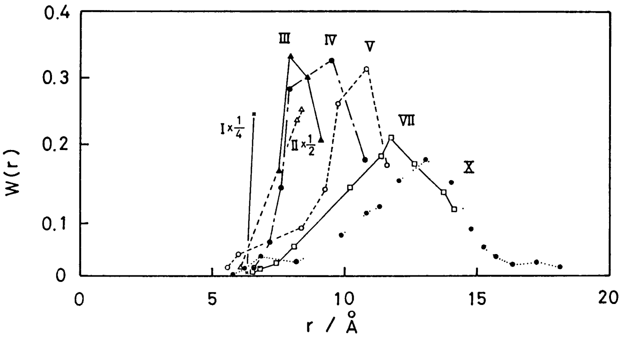

Fig. 5. Distribution of the end-to-end distance *r* of samples, I, II, III, IV, V, VII, and X at 298 K.

Static Fluorescence Quenching. We have shown[5] that the normal fluorescence of the series of compounds, I—X, is quenched by both the "static quenching" and the "dynamic quenching." The static quenching is caused by an electron transfer from CZ moiety to TPM moiety immediately after the excitation of CZ moiety regardless of the thermal motion of the methylene chain, when CZ moiety exists in the vicinity of TPM moiety. On the other hand, the dynamic quenching is diffusion controlled and reflects the frequency of intramolecular encounters between TPM moiety and the excited CZ moiety within its lifetime. We have estimated the magnitude of the static quenching from the measurement of the quantum yield of the normal fluorescence emission of CZ moiety at 77 K in a rigid 2-methyltetrahydrofuran (MTHF) matrix.

Now, the static quenching will be considered in terms of the active sphere model, in which fluorescence quenching occurs with the probability of one when the TPM moiety exists within the radius of the active sphere of CZ moiety and there is no interaction between CZ moiety and TPM moiety outside the active sphere (hard core approximation). According to this model, the static quenching occurs in the molecules having the conformation in which TPM moiety exists in the radius of the active sphere of CZ moiety immediately after the excitation of CZ moiety. In a rigid medium we observe only the static quenching, since no conformational change of molecules occurs. Therefore, the degree of the static quenching in a rigid medium reflects the distribution of conformations of these compounds immediately after the excitation of CZ moiety. In a rigid medium, it is valid to assume that the conformational distribution of these compounds in the excited state is equal to that in the ground state. Then, the magnitude of the static quenching for each compound corresponds to the fraction of conformation with the end-to-end distance, *r*, being shorter than the radius of the active sphere, R_0, in the conformational distribution in the ground state. So, the fraction of conformations with the end-to-end distance, *r*, shorter than the radius of the active sphere, R_0, for various values of R_0 was calculated for each compound. The results at 77 K and 136 K are shown in Figs. 6 and 7, respectively. At both temperatures, the best fit with experimental results was given when the value of the radius of active sphere is equal

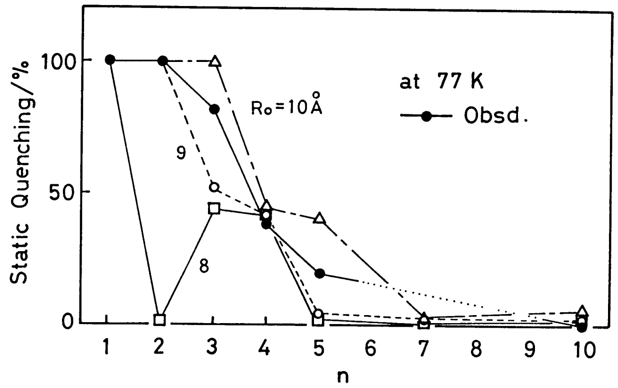

Fig. 6. Comparison of calculated fraction of the static quenching for 77 K with the observed fraction in MTHF at 77 K. (—●—): Observed value, (—△—): calculated value for $R_0=10$ Å, (--○--): calculated value for $R_0=9$ Å, (—□—): calculated value for $R_0=8$ Å.

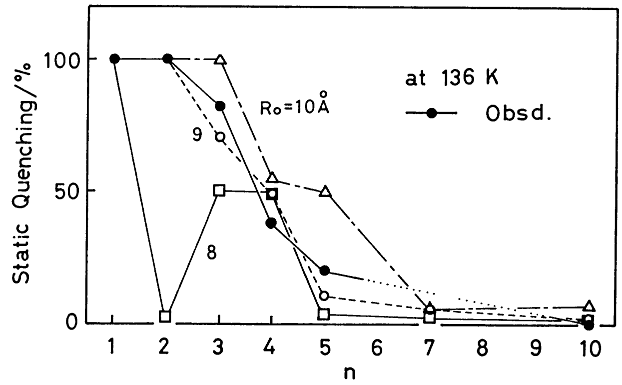

Fig. 7. Comparison of calculated fraction of the static quenching for 136 K with the observed fraction in MTHF at 77 K. Notations are the same as Fig. 6.

to 8.8—9.0 Å. The agreement between the calculated and experimental values is better at 136 K than at 77 K. This result might indicate that the equilibrium distribution of conformations at 136 K is conserved below 136 K, since the freezing point of MTHF is 136 K.

Active Sphere of the Dynamic Fluorescence Quenching in Solution. In this study, the active sphere model is used for the static fluorescence quenching of the intramolecular exciplex system. This model was first introduced by Perrin[15] for the static fluorescence quenching of the molecularly dispersed system. Smoluchowski's solution of diffusion-controlled reactions[16] are derived under the boundary condition of the hard core in the active sphere model: $c(r,0)=c_0$, $c(\infty,t)=c_0$, $c(R,t)=0$, where R is the sum of the collision radii and c_0 is the initial concentration of the diffusion species, and they have been applied to dynamic diffusion-controlled fluorescence quenching.[17]

Now, the active sphere of the dynamic fluorescence quenching of the intermolecular system: *N*-ethylcarbazole-dimethyl terephthalate will be compared with that of the static fluorescence quenching of the intramolecular exciplex system in a rigid medium. Radius of the active sphere of the dynamic fluorescence quenching of the intermolecular system was estimated in various solvents at 25 °C by the method B of Ware and Novros,[18] *i.e.*, the Stern-Volmer plots were analyzed by the theory of diffusion-controlled fluorescence quenching including a transient term. An example of the analysis is as follows. Stern-Volmer plots of both steady-state fluorescence quantum yield Φ and fluorescence lifetime τ in THF solvent at 25 °C is shown in Fig. 8. The Stern-Volmer plot of τ gives $K_q=202$ dm^3 mol^{-1} and the lifetime in the absence of electron acceptors τ_0 was measured to be 15.8 ns, then $4\pi R'DN'=1.28\times10^{10}$ dm^3 mol^{-1} s^{-1} is obtained and furthermore, $4\sqrt{\pi D}R'^2N'=1.1\times10^5$ dm^3 mol^{-1} s$^{1/2}$ is estimated from the Stern-Volmer plot of Φ. Then the combination of these values gives $R'=7.3$ Å and $D=2.32\times10^{-5}$ cm^2 s^{-1}. The values obtained for other solvents are also shown in Table 2. As described in the previous section, the radius of active sphere $R_0=8.8$—9.0 Å was obtained for the intramolecular fluorescence quenching from the chain length dependence of the fluorescence quantum yield of CZ moiety in a rigid medium. The values of R' are slightly smaller than the intramolecular one R_0, but the agreement between the radius of active sphere for the intramolecular fluorescence quenching and the intermolecular one is fairly good.

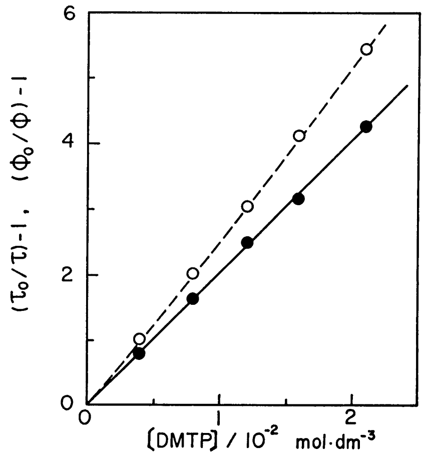

Fig. 8. Stern-Volmer plots of Φ (○) and τ (●) for the fluorescence of ECZ quenched by dimethyl terephthalate (DMTP) in THF solvent at 25 °C.

TABLE 2. RADIUS OF ACTIVE SPHERE (R') AND DIFFUSION CONSTANT (D) IN VARIOUS SOLVENTS

Solvent	Dielectric constant ε	R'/Å	$D/10^{-5}$ cm^2 s^{-1}
Toluene	2.4	5.6	2.83
Dibutyl ether	3.1	5.3	2.72
Diethyl ether	4.3	6.8	5.01
Tetrahydropyran	5.6	6.0	2.11
Tetrahydrofuran	7.6	7.3	2.32
Acetonitrile	36.7	6.4	3.34

Though we employed the hard core approximation ($c(R_0, t)=0$) for the active sphere at the present stage, neglecting the effect of the mutual orientation between CZ and TMP moieties, experimentally observed fractions of the static quenching were well simulated with appropriate parameters of the radius of active sphere and the temperature of the system.

The calculations reported in this paper were carried out on the FACOM 230-75 computer at the Computer Center of Kyoto University.

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