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# Kinetic Studies on Intramolecular Excimer Formation in Dinaphthylalkanes

Shinzaburo Ito,* Masahide Yamamoto, and Yasunori Nishijima
*Department of Polymer Chemistry, Kyoto University, Sakyo-ku, Kyoto 606*

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Various dinaphthylalkanes in which two naphthyl groups are separated by three carbon atoms were prepared, and intramolecular excimer formation was investigated. All rate constants in Förster's kinetics were determined by the steady state and time-resolved fluorescence measurements. A large difference in the association rate constant was observed with variation of molecular structure. The results suggest that intramolecular excimer formation is directly controlled by the rotational relaxation processes of the molecules from their neighboring conformations to the excimer conformation. A large formation rate ($7.9\times10^8\ s^{-1}$ at 25 °C) was observed for *meso*-2,4-dinaphthylpentane, the rate for the *racemo* isomer being found to be one tenth of that for the *meso* isomer. This indicates that the isotactic sequence in vinyl aromatic polymers plays an important role in the intramolecular excimer formation.

Excimer is an excited dimer existing only in the excited state by the attractive interaction between an excited chromophore and one in the ground state. It turns unstable in the ground state due to the steric hindrance between chromophores. The formation of intermolecular excimers is thus expected to be controlled by the mutual diffusion of chromophores. Verification of the diffusion controlled process has been carried out mainly using pyrene molecule as a chromophore.[1,2]

The formation of intramolecular excimers is considered to be governed by the micro-structures of molecules to which chromophores are attached. It seems that there are two controlling factors for the intramolecular excimer formation: (a) conformational changes of the molecule which corresponds to the mutual diffusion process in the case of intermolecular excimer formation, and (b) the geometrical arrangement of two chromophores in an excimer state which is determined by the micro-structure of the molecule. Concerning (b), Hirayama proposed the $n=3$ rule for the intramolecular excimer formation.[3] The results indicate that the most favorable arrangement of chromophores is a symmetrical parallel sandwich arrangement which can be formed specifically in a compound having a molecular structure in which two aromatic groups along the alkane chain are separated by three carbon atoms.

This paper deals with (a), the relationship between the micro-structures of molecules and their rotational relaxation processes within the lifetime of a chromophore. A naphthalene chromophore seems to have fairly strict arrangements in the excimer state,[4] its emission properties being favorable for detection in spectroscopic analyses. The photophysical characteristics are useful for investigating the rotational relaxation processes. In order to clarify the problem (a), quantitative study on various model compounds by the time-resolved fluorescence method, is necessary. Advance in the time-resolved technique for photoluminescence measurements enables us to determine the rate constants of the kinetic scheme including the intramolecular excimer formation process.[5—9] We have investigated various dinaphthylalkanes satisfying the $n=3$ rule,[3] under photostationary and transient conditions. The individual rate constant of photophysical processes was determined. From the results, the relationship between the molecular structure and its conformational relaxation is discussed. The compounds examined are regarded as the dimeric model compounds of vinyl polymers. Their photophysical behavior provides useful information on the intramolecular excimers in polymer systems.

## Experimental

*Materials.* 1,3-Di(2-naphthyl)propane (1,3-DNPr) was synthesized by the procedure of Chandross and Dempster.[4] The other sample were prepared by as follows.

1,3-Di(2-naphthyl)butane (1,3-DNBu): 1,3-Di(2-naphthyl)-1-propanone, obtained as an intermediate product in the synthesis of 1,3-DNPr, was reacted with methylmagnesium iodide in ether solution. The oily product was purified by a column chromatography on silica gel. 2,4-Di(2-naphthyl)-2-butanol thus obtained was reduced in acetic acid solution by addition of zinc dust and hydrochloric acid. The product was chromatographed on silica gel with hexane–dichloromethane (4:1): mp 65—66 °C; IR (KBr) 3050, 2950, 2930, 2850, 1630, 1600, 1510, 815, 740, and 475 $cm^{-1}$; NMR ($CS_2$) $\delta=1.35$ (3H, d, $J=6.5$ Hz), 1.90—2.16 (2H, m), 2.52—2.96 (3H, m), and 7.06—7.74 (14H, m). Found: C, 92.69; H, 7.18%. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14%.

1,3-Di(2-naphthyl)pentadecane (1,3-DNPd) and 1,3-di(2-naphthyl)-5-phenylpentane (1,3-DN-5-PhPe) were synthesized by the same method as that for 1,3-DNBu, 1-bromododecane and 1-bromo-2-phenylethane being used for 1,3-DNPd and 1,3-DN-5-PhPe, respectively, instead of methyl iodide. 1,3-DNPd: IR (KBr) 3050, 2930, 2850, 1630, 1600, 1510, 815, 740, and 475 $cm^{-1}$; NMR ($CS_2$) $\delta=0.75$—0.95 (3H, m), 1.17 (20H, s), 1.54—1.83 (2H, m), 1.92—2.18 (2H, m), 2.50—2.80 (3H, m), and 7.05—7.76 (14H, m). Found: C, 90.67; H, 9.82%. Calcd for: $C_{35}H_{44}$: C, 90.46; H, 9.54%. 1,3-DN-5-PhPe: IR (KBr) 3050, 2930, 2850, 1630, 1600, 1510, 815, 740, 695, and 475 $cm^{-1}$; NMR ($CS_2$) $\delta=1.85$—2.22 (4H, m), 2.30—2.82 (5H, m), and 6.85—7.80 (19H, m). Found: C, 92.87; H, 6.99%; $M^+$, 400. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05%; M, 400.

2,4-Di(2-naphthyl)pentane (2,4-DNPe): 1,3-Di(2-naphthyl)-2-propen-1-one, obtained in the course of the synthesis of 1,3-DNPr, was reacted with methylmagnesium iodide in the presence of a trace amount of cuprous chloride, and the product was extracted with benzene. After benzene had been removed, the residue was recrystallized from carbon tetrachloride to give colorless crystalline 1,3-di(2-naphthyl)-1-butanone: mp 148—150 °C. The ketone was reacted again with methylmagnesium iodide in ether solution. The product, 2,4-dinaphthyl-2-pentanol, was reduced by the same method as that for 1,3-DNBu. The residual oil was purified by a column chromatography on silica gel.

The oily product consists of *meso* and *racemo* isomers (*ca.* 1:2). The isomers were separated by a recycle gel permeation chromatography. After seventy cycles, fractionated samples were used for measurements. The purity of the isomers was found to be 85% for both isomers by the methyl proton resonance in NMR spectra. Emission intensity was corrected by this proportion of isomers. 2,4-DNPe: IR (KBr) 3050, 2950, 2920, 2860, 1630, 1600, 1505, 815, 740, and 475 cm$^{-1}$; NMR ($CS_2$) for *meso* isomer, $\delta = 1.35$ (3H, d, $J = 7$ Hz), 1.7—2.3 (1H, m), 2.5—2.95 (1H, m), and 7.16—7.80 (7H, m), NMR ($CS_2$) for *racemo* isomer, $\delta = 1.24$ (3H, d, $J = 6.8$ Hz), 1.96—2.18 (1H, m), 2.42—2.85 (1H, m), and 7.18—7.80 (7H, m). Found: C, 92.53; H, 7.48%; M$^+$, 324. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46%; M, 324.

*Measurements.* Tetrahydrofuran (THF) was used as a solvent, which was purified by vacuum distillation after preliminary distillation over sodium metal. The concentration of samples was adjusted to *ca.* $10^{-4}$ mol dm$^{-3}$ at which the intermolecular excimer formation is negligible. The sample solutions were deaerated by freeze-thaw cycles at $10^{-5}$ mmHg.† Absorption spectra were obtained with a Shimadzu UV-200S spectrophotometer, and fluorescence spectra with a Shimadzu spectrofluorophotometer model RF-502 in which the spectra were corrected for the instrumental response. The quantum yields of emission were determined relative to that of quinine sulfate in 1 mol dm$^{-3}$ sulfuric acid, whose reported quantum yield is 0.51.[7] The decay curves of fluorescence were directly measured using a pulse fluorometer, TRW instrument model 31B or a single photon counting technique (Ortec Inc., 9200 nanosecond fluorescence spectrometer). The monomer and excimer fluorescence were separated by a suitable combination of filters. A quartz dewar equipped with a thermocouple was used for low temperature measurements.

## Results and Discussion

Structural formulas of dinaphthylalkanes are summarized in Fig. 1. The alignment of aromatic groups favorable for intramolecular excimer formation can be achieved when two adjacent aromatic groups are separated by three carbon atoms of alkane chain. Hence, effective intramolecular excimer formation can be expected in these compounds. Absorption spectra for these samples are nearly the same and similar to those of 2-ethylnaphthalene (MNEt) corresponding to the monomeric unit. This indicates that there is no specific interaction between naphthyl groups in the ground state, each chromophore behaving like an isolated naphthalene unit. Figure 2 shows the fluorescence spectra of three typical compounds at −20 °C. They consist of two emission bands. The structured shorter wavelength band and the broad longer wavelength band are assigned to the monomer fluorescence and intramolecular excimer fluorescence, respectively. Relative fluorescence intensities of these bands differ considerably with sample. Although the molecular structures of these samples are very much alike as a common dimer unit, they show different efficiency in excimer formation. This can be attributed to the conformational relaxation processes after excitation of chromophores, from identity of the absorption and emission bands on the spectra of these samples.

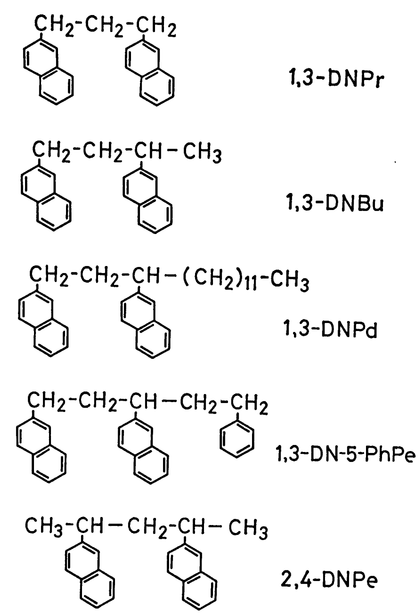

Fig. 1. Structures of dinaphthylalkanes studied in this work.

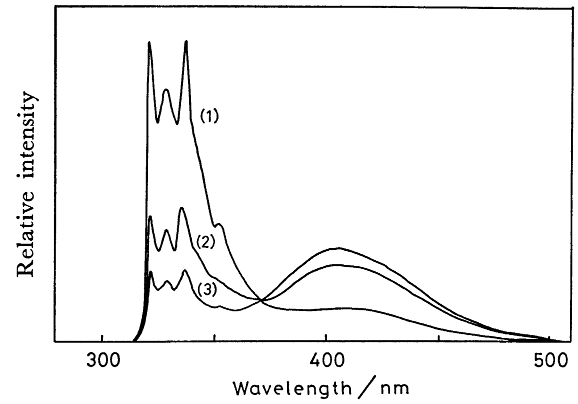

Fig. 2. Fluorescence spectra of the solutions of three typical compounds in THF at −20 °C.
(1): 2,4-DNPe (*rac*), (2): 1,3-DNPr, (3): 2,4-DNPe (*meso*).

The ratios of quantum yield ($\Phi_D$) of excimer fluorescence to that of monomer fluorescence ($\Phi_M$) for all samples at various temperatures are given in Table 1. Figure 3 shows the temperature dependence of $\Phi_M$ and $\Phi_D$ for three typical samples. Below −100 °C, fluorescence spectra of all samples are almost the same as those of MNEt. There is no indication of interaction between the naphthalene groups in the excited state when the molecular motion is suppressed. With rise in temperature, the monomer fluorescence is quenched steadily with increase in the excimer fluorescence. This shows that intramolecular excimer formation is governed by the conformational changes of the molecules. Some remarks are given concerning Table 1. (1) The compounds having alkyl substituents at one side of the dimer unit such as 1,3-DNBu, 1,3-DNPd, and 1,3-DN-5-PhPe, show the same efficiency of excimer formation, the efficiency being independent of the kind of substituent. (2) 1,3-DNPr

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† 1 mmHg = 133.322 Pa.

Table 1. Ratios of the quantum yield of excimer fluorescence to that of monomer fluorescence

| Temp/°C | 1,3-DNPr | 1,3-DNBu | 1,3-DNPd | 1,3-DN-5-PhPe | 2,4-DNPe | |
|---|---|---|---|---|---|---|
| | | | | | (*meso*) | (*rac*) |
| 0 | 2.6 | 3.2 | 3.6 | 3.6 | 5.2 | 0.59 |
| −20 | 1.4 | 1.7 | 2.0 | 2.0 | 3.3 | 0.27 |
| −40 | 0.61 | 0.83 | 0.89 | 0.98 | 1.9 | 0.10 |
| −60 | 0.22 | 0.33 | 0.35 | 0.38 | 0.87 | 0.05 |

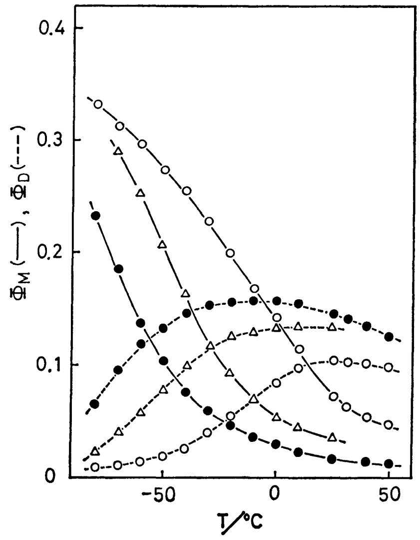

Fig. 3. Temperature dependence of quantum yields, $\Phi_M$ and $\Phi_D$.
○: 2,4-DNPe (*rac*), △: 1,3-DNPr, ●: 2,4-DNPe (*meso*).

shows lower efficiency than that of 1,3-DNBu. (3) The highest efficiency of excimer formation is observed for 2,4-DNPe(*meso*), but its isomer 2,4-DNPe(*rac*) gives the lowest efficiency among the measured compounds. The effect of molecular configuration for intramolecular excimer formation appears typically in these isomers. This large difference in excimer formation for 2,4-DNPe between (*meso*) and (*rac*) is similar to the result of the steady state observation for diphenylpentanes.[10)]

The activation energy, $E_a$, for the excimer formation process can be obtained in the low temperature region by the equation

$$\Phi_D/\Phi_M = K\exp(-E_a/RT),$$

where $K$ is a constant. The plots are shown in Fig. 4. In all samples except for 2,4-DNPe(*rac*), $E_a$ was found to be 4.8—5.3 kcal/mol.[††] 2,4-DNPe(*rac*) gives a somewhat larger value of $E_a$, 5.5 kcal/mol. The activation energy required for intermolecular excimer formation of MNEt in THF was found to be 3.2—3.4 kcal/mol.[11)] The larger activation energies of intramolecular excimers indicate methylene chain restriction in the conformational changes. Somewhat larger activation energy for 2,4-DNPe(*rac*) suggests that some other conformational restraints in the excimer formation process are imposed on this compound. Although the activation energies for *meso*- and *rac*-diphenylpentanes were reported by Bokobza *et al.*[10)] to be 2.0 and 4.6 kcal/mol, respectively, no such large difference was found for the two isomers of 2,4-DNPe in the present investigation.

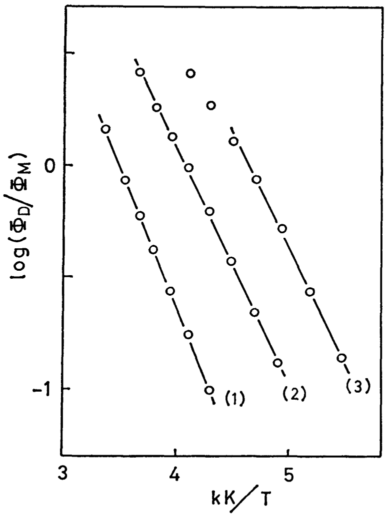

Fig. 4. Arrhenius plots of the ratio, $\Phi_D/\Phi_M$.
(1): 2,4-DNPe (*rac*), (2): 1,3-DNPr, (3): 2,4-DNPe (*meso*).

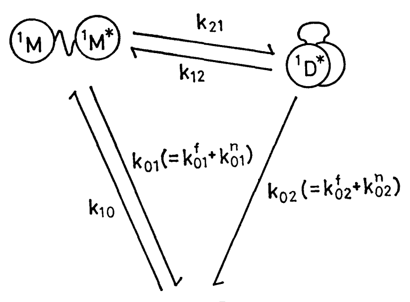

Fig. 5. Photophysical kinetic scheme of the energy dissipation processes. $^1M$, $^1M^*$, and $^1D^*$ represent the ground state of monomer, the excited singlet state of monomer, and the intramolecular excimer, respectively.

The scheme of photophysical kinetics including the intramolecular excimer formation process is given in Fig. 5. However, it is not clear which process causes the difference in the efficiency of excimer formation for these compounds. For the sake of clarification, all the rate constants in the kinetic scheme should be determined by the time-resolved measurements. Rise and decay curves of the excimer emission after excitation by a pulse with a half-width of about 2.5 ns, are

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[††] 1 cal=4.184 J.

Table 2. Intramolecular excimer formation rate constants and their activation energies

| Temp/°C | $k_{21}/10^7\ \mathrm{s}^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | 1,3-DNPr | 1,3-DNBu | 1,3-DNPd | 1,3-DN-5-PhPe | 2,4-DNPe | |
| | | | | | (*meso*) | (*rac*) |
| 50 | | | | | | 17 |
| 25 | 21 | 28 | 29 | 29 | 79 | 8.7 |
| 0 | 12 | 17 | 17 | 17 | 41 | 3.6 |
| −20 | 4.8 | 7.0 | 7.0 | 7.1 | 17 | |
| −40 | 1.9 | 2.6 | 2.8 | 2.9 | 7.8 | |
| −60 | 0.7 | 1.0 | 1.0 | 1.0 | 3.3 | |
| $E_a$/kcal mol$^{-1}$ | 5.1 | 5.2 | 5.3 | 5.3 | 4.8 | 5.5 |

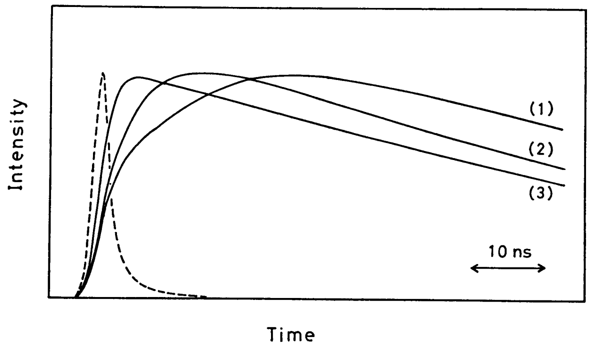

Fig. 6. Rise and decay curves of the intramolecular excimer fluorescence in THF at 25 °C.
(1): 2,4-DNPe (*rac*), (2): 1,3-DNPr, (3): 2,4-DNPe (*meso*). The broken line is the excitation light pulse.

shown in Fig. 6 for three typical samples at 25 °C. On the assumption that the actual lifetime of the monomer emission in the absence of the excimer formation process is equal to the lifetime of MNEt under the same conditions, all the rate constants given in Fig. 5 can be determined by analysis of the transient curves and the quantum yields, $\Phi_M$ and $\Phi_D$.

The theoretical response functions $I_M(t)$ and $I_D(t)$, for the monomer and excimer fluorescence, are derived by

$$I_M(t) = C_M(e^{-\lambda_1 t} + Ae^{-\lambda_2 t}),$$
$$I_D(t) = C_D(e^{-\lambda_1 t} - e^{-\lambda_2 t}),$$

where $C_M$, $C_D$, $A$, $\lambda_1$, and $\lambda_2$ are given as functions of the rate constants,[1] and

$$\lambda_{1,2} = [k_{01}+k_{21}+k_{02}+k_{12} \mp \{(k_{01}+k_{21}-k_{02}-k_{12})^2 + 4k_{21}k_{12}\}^{1/2}]/2,$$
$$A = (k_{01}+k_{21}-\lambda_1)/(\lambda_2-k_{01}-k_{21}).$$

The value of $A$ is too large to be estimated accurately from the monomer fluorescence decay curve in the intramolecular excimer systems. On the assumption mentioned above, the rate constants, $k_{01}^f$ and $k_{01}^n$ are determined by measurement of the quantum yield and lifetime of MNEt. The other rate constants, $k_{21}$, $k_{12}$, $k_{02}^f$, and $k_{02}^n$ are then obtained from the observed values, $\lambda_1$, $\lambda_2$, $\Phi_M$, and $\Phi_D$, by using the following relations,

$$\Phi_M = k_{01}^f(k_{02}+k_{12})/\lambda_1\lambda_2,$$
$$\Phi_D = k_{02}^f k_{21}/\lambda_1\lambda_2,$$

Table 3. Kinetic rate constants at 25 °C

| | |
|---|---|
| $k_{01}^f/10^7\ \mathrm{s}^{-1}$ | 0.49 |
| $k_{01}^n/10^7\ \mathrm{s}^{-1}$ | 1.3 |
| $k_{02}^f/10^7\ \mathrm{s}^{-1}$ | 0.16—0.22 |
| $k_{02}^n/10^7\ \mathrm{s}^{-1}$ | 0.8 —1.2 |
| $k_{12}/10^7\ \mathrm{s}^{-1}$ | 2.6 —0.8 |

$$\lambda_1 + \lambda_2 = k_{01} + k_{21} + k_{02} + k_{12},$$
$$\lambda_1\lambda_2 = (k_{01}+k_{21})(k_{02}+k_{12}) - k_{21}k_{12}.$$

The rate constant $k_{21}$ values measured at various temperatures are given in Table 2, other rate constants at 25 °C for all the samples being summarized in Table 3. There is an appreciable difference in the pseudo-1st order rate constant $k_{21}$ values of the association process among these compounds, although little change is seen in the other rate constants. It is apparent that the marked increase of the excimer formation efficiency observed in the steady state measurements is due to the large values of the association rate constant $k_{21}$.

The observed compounds seem to have the same geometrical alignment of the naphthyl groups in the excimer state. We might conclude that the rate constant $k_{02}$ does not vary so much with sample. There is no considerable change in the dissociation rate constant $k_{12}$, although somewhat a larger value is obtained for 2,4-DNPe(*meso*). The value of $k_{12}$ for the intermolecular excimers in concentrated solution of MNEt in THF is given by

$$k_{12} = A \exp(-E_d/RT),$$

where $A$, $E_d$, and $R$ are the Arrhenius factor, the activation energy of the dissociation process, and the gas constant, respectively. The values for $A$ and $E_d$ were found to be $4.4 \times 10^{15}\ \mathrm{s}^{-1}$ and 7.7 kcal/mol, respectively. A much smaller value is obtained for $k_{12}$ in the case of the intramolecular excimer than in the case of the intermolecular excimer. This is due to the binding effect of the methylene chain. The binding energy of the excimer state seems to be the same in the compounds we studied because of a similar molecular structure in the dimer unit. Therefore, it is understandable that there is no appreciable difference in the value of $k_{12}$. The methyl group of 2,4-DNPe(*rac*) should be situated in an unstable gauche position in the excimer conformation. However, the unstable energy is too small to affect the dissociation rate constant.

For the association rate constant $k_{21}$, the compounds 1,3-DNBu, 1,3-DNPd, and 1,3-DN-5-PhPe show the same value. This indicates that the association rates are determined only by the configuration of the common dimer units, and the conformations in the dimer units are not much influenced by the substituent groups of the 3-position for these model compounds. This indicates that the rate of conformational relaxation in the terminal dimer units is not strongly affected by the increase of mass or chain length of these substituent groups. The effect of molecular weight on the rotational relaxation times was reported, *e.g.*, by the measurement of fluorescence depolarization,[12,13) $^{13}$C NMR,[14) and ESR.[15) The results indicate that the relaxation time of molecular motions increases with increasing molecular weight. However, no such changes were observed in the case of intramolecular excimer systems. The observed rate constants of intramolecular excimer formation reflect the local segment motions of the end group of the molecule with respect to the molecular coordinate system. It seems that the molecular size of the alkane chain such as pentadecane, is too small to cause changes in the local segment motion and the local environment around the end groups.

Large differences in the association rate constants for 1,3-DNPr, 1,3-DNBu, and 2,4-DNPe(*meso*) and (*rac*) are observed (Table 2). First, let us discuss the results for 2,4-DNPe(*rac*) which gives the smallest value of $k_{21}$. The rate of intramolecular excimer formation is controlled by the internal rotational motion of the molecule from the equilibrium conformation in the ground state to the excimer one. From the analysis of NMR spectra,[16–18) we know that the preferred conformation for *racemo* dimers is situated at tt, indicating a planar conformation for the alkane chain. In order to reach the excimer conformation from the tt conformation, it is necessary to carry out an unfavorable conformational cange, $g^+ \rightleftarrows g^-$ with respect to the naphthyl groups. This seems to be the cause of the small values of $k_{21}$ and the somewhat larger value of $E_a$ for 2,4-DNPe(*rac*). Secondly, there are considerable differences in 1,3-DNPr, 1,3-DNBu, and 2,4-DNPe(*meso*). These differences are due to the equilibrium distribution of conformations at the ground state, whose distribution determines the initial positions of the naphthalene chromophores immediately after their excitation. Particularly, the population of the neighboring conformation to the excimer conformation seems to play an important role in the excimer formation rate (Fig. 7). The results are interpreted as follows: In 1,3-DNPr where $R_1=R_2=H$, the planar conformation with respect to the naphthyl groups (a) is most stable, the fraction of the neighboring conformation such as (b) not being large. In 1,3-DNBu where $R_1=H$ and $R_2=CH_3$, the neighboring conformation (b) becomes favorable owing to the steric hindrance of the methyl group. In 2,4-DNPe(*meso*) where $R_1=R_2=CH_3$, the conformational distribution seems to be predominantly in the neighboring conformation (b). According to the analysis of NMR spectra for *meso*-diphenylpentane,[16–18) all other conformations have no appreciable fractions. The observed $k_{21}$ values of the three compounds increase in this order. Thus, the association rate constants reflect the population of the neighboring conformation to the excimer state (c), and the rotational motion from this neighboring one to the excimer state.

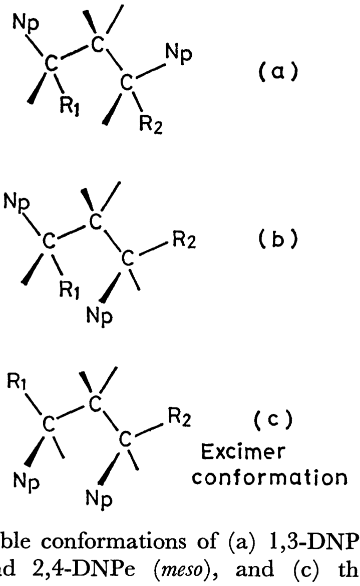

Fig. 7. Stable conformations of (a) 1,3-DNPr, (b) 1,3-DNBu and 2,4-DNPe (*meso*), and (c) the excimer conformation. Np: 2-naphthyl.

The compounds we studied can be regarded as model compounds of poly(2-vinylnaphthalene) (PVN), which shows efficient intramolecular excimer formation.[7) 2,4-DNPe(*meso*) is considered to be a model compound of the isotactic sequence in PVN, the large value of $k_{21}$ indicating the important role of isotactic sequence in the intramolecular excimer formation in vinyl aromatic polymers.

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