Then a_2 and a_3 values can be calculated from eq 15 and 16 derived from eq 8.

$$a_2 = a_5 = a_2{}^{\mathrm{A}} + (a_2{}^{\mathrm{S}} - a_2{}^{\mathrm{A}})P_{\mathrm{S}}{}^0 = 10.93 - 9.77P_{\mathrm{S}}{}^0 \qquad (15)$$

$$a_3 = a_4 = a_3{}^{\mathrm{A}} + (a_3{}^{\mathrm{S}} - a_3{}^{\mathrm{A}})P_{\mathrm{S}}{}^0 = 4.17 + 3.73P_{\mathrm{S}}{}^0 \qquad (16)$$

The experimental coupling constants, a_α and a_β, are assigned to the respective ring positions so as to give the best fit to the values obtained from eq 15 and 16. The final P_{S} values are determined by the technique of the least squares, so as to minimize $\sum_{i=1}^{5} \{a_i(\mathrm{calcd}) - a_i(\mathrm{obsd})\}^2$, in which a_1 should mean $a_1{}^*$. The equilibrium constants $P_{\mathrm{A}}/P_{\mathrm{S}}$ ($\equiv K$) are then calculated from the final P_{S} values. Different sets of K and P_{S} values are similarly obtained with ρ_i values calculated by the McLachlan method (Table I). These values lead to ΔE and ΔS values listed in Table III.

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Computer Simulation of Intramolecular Electron Transfer in $\alpha N(CH_2)_n\alpha N^{-}\cdot$ System

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Abstract: This paper is concerned with the theoretical treatment of intramolecular electron transfer in $\alpha N(CH_2)_n\alpha N$ radical anions reported by Shimada and Szwarc. By using both static and dynamic models, rate expressions are developed for intramolecular reactions. The equations involve the probability of finding the polymeric chain in favorable conformations for the electron transfer, and we calculate it by the direct enumeration method and the Monte Carlo method. The model considered for a polymethylene chain is that of the g–t rotational isomeric state. In order to determine the stable conformations of the terminal naphthylmethyl group, semiempirical potential functions are applied to *n*-propyl-α-naphthalene. The calculated frequencies of the intramolecular electron transfer divided by those of the corresponding intermolecular electron transfer agree excellently with the experimental values obtained in hexamethylphosphoric triamide and 1,2-dimethoxyethane solutions. The dynamic model is well supported by the fact that the activation energy of electron transfer is substantially higher than that of the calculated probability of the favorable conformations. The average lifetime of conformations favorable for intramolecular electron transfer is independent of the connecting chain length and is equal to the lifetime of the two naphthyl groups being in favorable positions for intermolecular electron transfer. The significance of the calculated results is reported and discussed.

The intramolecular reaction between terminal groups attached to a polymeric chain molecule is a convenient gauge of the flexibility of the connecting chain molecule.[1-11] There have been several authors who examined such a problem. In most of the cases, however, the activation energy of the end-to-end reaction is intrinsically high and the intramolecular reaction takes place after a number of collisions between two terminal groups. Accordingly, the reaction rate is proportional to an equilibrium probability of the polymer chain to find its end-to-end distance r shorter than a critical distance r_0, which depends upon the nature of reaction.[1-6] Several theoretical studies for such reactions have been reported in connection with the conformational properties of polymer chains.[2-4,6] Those may be called a static case.

On the other hand, Shimada and Szwarc[7-11] have reported a series of experimental studies where an intramolecular electron transfer takes place between two α-naphthyl moieties linked by a polymethylene chain in solution, i.e.,

$$\alpha N(CH_2)_n\alpha N^-\cdot \overset{P}{\rightleftharpoons} \alpha N^-\cdot(CH_2)_n\alpha N$$

In this case, the intrinsic activation energy is very low[10] (about 1 kcal/mol) and the reaction virtually occurs at the every encounter of the terminal naphthyl groups. Therefore the frequency of the electron transfer may reflect the dynamics of the polymethylene chain.[7] That may be called a dynamic case. Our concern in this paper is to examine theoretically the diffusion-controlled intramolecular electron transfer and get a more profound insight into the dynamics of chain molecules. Furthermore, we will try to clarify a general understanding of intramolecular reactions that covers both statics and dynamics.

A diffusion-controlled intramolecular reaction was recently studied theoretically by Wilemski and Fixman.[12,13] Their theory is based on the diffusion equation of the end-to-end distance with a sink term. It cannot be applied, however, to the present problem because of the following reasons: (1) The length of the polymethylene chain used in the electron transfer study is too short to be properly expressed by a chain model such as the harmonic spring or the Rouse model. (2) The dynamics of a short polymer chain should be treated in terms of the rate of its conformational changes around C-C bonds, because the movement of even one or a few bonds may play a determinative role, e.g., bonds near terminal groups. (3) The electron transfer in $\alpha N(CH_2)_n\alpha N^-\cdot$ system is reversible and therefore the conformations of polymethylene chains are in equilibrium distribution during the reaction. On the other hand, in the case of intramolecular irreversible reaction such as the intramolecular fluorescence quenching, a reactive group attached to a cyclic conformation disappears quickly during the reaction and this leads to the breakdown of the conformational equilibrium. The theory of Wilemski and Fixman deals with the latter case, although they regarded the conformational equilibrium as the first approximation. Very recently, Brereton and Rusli[14] approached the same problem with the random noise theory. They, however, used the Gaussian chain model, which is not adequate for short polymethylene chains, and did not take item (3) into consideration.

The model considered for the polymethylene chain in this study is the rotational isomeric state model where all C-C bonds of the polymethylene chain are assumed to be one of three rotational isomers, trans, gauche(+), and gauche(−). As reviewed by Flory in his book,[15] this model appears to be a good descripion of long polymeric chains upon reasonable assignment of conformational energies. The feasibility of this model for rather short polymethylene chains has previously been studied in comparison with the other model such as the diamond lattice by one of us (M.S.).[2] Here, we include the contribution of terminal groups to chain conformation and see the applicability of our model to bisnaphthyl alkanes.

Theoretical Section

Let us first consider a chain molecule, $\alpha N(CH_2)_n\alpha N$, which is continuously wiggling in a solution owing to the Brownian motion. The perpetual change of its conformation causes the intramolecular end-to-end collisions. The colliding groups stay together for a short period, then separate from each other, and after some time lag collide again. This is schematically shown in Figure 1. The lifetime of the ith conformational state is denoted by τ_i and the probability of electron transfer during τ_i is p_i.[8] The observed frequency of electron transfer P can then be expressed as

$$P = \sum_{i=1}^{N} p_i \Big/ \sum_{i=1}^{N} \tau_i = \langle p\rangle/\langle\tau\rangle_{N\to\infty} \qquad (1)$$

where $\langle p\rangle = \Sigma p_i/N$ and $\langle\tau\rangle = \Sigma\tau_i/N$. Here, the conformational space average is replaced by the time average. When the intrinsic rate of electron transfer k_i for the ith conformation state is very small, or $k_i\tau_i \ll 1$, then $p_i = k_i\tau_i$. In this case, eq 1 is reduced to

$$P = \langle k\tau\rangle/\langle\tau\rangle \qquad (2)$$

Here, we assume the presence of a critical distance r_0 for electron transfer, i.e.,

$$\begin{aligned} k_i &= k \qquad (r_i \leqslant r_0) \\ &= 0 \qquad (r_i > r_0) \end{aligned} \qquad (3)$$

where r_i is the end-to-end distance of the ith conformation and r_0 is the end-to-end distance within which electron transfer can occur between two ends. Substitution of the above relation into eq 2 gives

$$P = k\sum_{j=1}^{M} \tau_j(r \leqslant r_0) \Big/ \sum_{i=1}^{N}\tau_i = kW(r \leqslant r_0) \qquad \text{(static case)} \quad (4)$$

where M is the number of conformations which fulfill $r_i \leqslant r_0$, and $W(r \leqslant r_0)$ is the equilibrium probability to find the chain ends within $r \leqslant r_0$. In eq 4, the ergodic hypothesis is used. Equation 4 represents the frequency of electron transfer in the static limit.

Similarly, in the dynamic case, we assume the presence of a critical distance, i.e.,

$$\begin{aligned} k_i &= \infty \qquad (r_i \leqslant r_0) \\ &= 0 \qquad (r_i > r_0) \end{aligned} \qquad (5)$$

This yields $p_i = {}^1\!/_2$ for $r_i \leqslant r_0$, which is independent of τ_i (see Appendix). Consequently eq 1 is reduced to

$$P = M \Big/ \left(2\sum_{i=1}^{N}\tau_i\right) = W(r \leqslant r_0)/2\langle\tau\rangle_1 \qquad \text{(dynamic case)} \quad (6)$$

where $\langle\tau\rangle_1 = \Sigma_{j=1}^{M}\tau_j/M$ is the mean lifetime of the cyclic conformations. An intermediate case, where $k_i\tau_i \approx 1$, is discussed in the Appendix.

The rates of the corresponding intermolecular electron transfer can be formulated by a similar procedure. The counterparts of eq 4 and 6 are respectively

$$k_{ex} = 4\pi r_0^3 N_a k/3000 \qquad \text{(static case)} \quad (7)$$

$$k_{ex} = 4\pi r_0^3 N_a/6000\langle\tau\rangle_2 \qquad \text{(dynamic case)} \quad (8)$$

where k_{ex} is the second-order rate constant for the intermolecular electron transfer, $\langle\tau\rangle_2$ is the mean lifetime of the two naphthyl groups in such mutual positions as $r \leqslant r_0$, and N_a is Avogadro's number. The ratio of frequencies of intramolecular electron transfer to rate constants of the intermolecular one is therefore given as follows:

$$P/k_{ex} = 3000W(r \leqslant r_0)/4\pi r_0^3 N_a \qquad \text{(static case)} \quad (9)$$

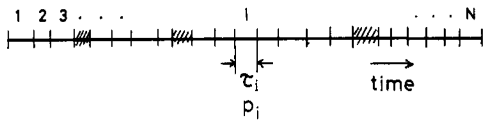

Figure 1. Schematic representation of the perpetual change of the conformation of $\alpha N(CH_2)_n\alpha N$ molecule. The shaded regions represent a favorable conformation for the electron transfer.

$$P/k_{ex} = [3000W(r \leq r_0)/4\pi r_0^3 N_a][\langle\tau\rangle_2/\langle\tau\rangle_1] \quad \text{(dynamic case)} \quad (10)$$

In the next section, we calculate $W(r \leq r_0)$ by the direct enumeration method or the Monte Carlo method, and evaluate P and P/k_{ex} by using eq 4, 6, 9, and 10.

Alternatively, the principle of microscopic reversibility can permit us to derive eq 6 in a more direct manner. Under the thermal equilibrium of a polymer solution, the number of chains which enter into the favorable regions for electron transfer ($r \leq r_0$) per unit time is equal to those which depart from the favorable regions, i.e.

$$\langle k_{\leftarrow}\rangle[1 - W(r \leq r_0)] = \langle k_{\rightarrow}\rangle W(r \leq r_0) \quad (11)$$

and

$$P = \frac{1}{2}\langle k_{\leftarrow}\rangle[1 - W(r \leq r_0)] \quad (12)$$

Here, $\langle k_{\leftarrow}\rangle$ and $\langle k_{\rightarrow}\rangle$ are the mean rate constants of the respective chain motions, $\langle k_{\rightarrow}\rangle$ is equal to $\langle\tau\rangle_1^{-1}$, and $1/2$ is the transfer probability factor.[25] It is clear therefore that eq 12 is equivalent to eq 6. Although this approach is of great value, the previous formulation may be advantageous in the sense that the two limiting cases and also the intermediate case can be treated on the same theoretical ground (see Appendix).

It should be pointed out that, although eq 6 is derived for intramolecular diffusion-controlled *reversible* reactions, it will also serve as a good approximation for the rate of a diffusion-controlled *irreversible* reaction, after a change of the reaction probability from $1/2$ to 1. This applicability is expected since as demonstrated theoretically by Doi et al.,[16,17] the use of the equilibrium distribution of polymer conformations does not cause a serious error in the rate of the diffusion-controlled *irreversible* reaction.

Procedures for the Computation of $W(r \leq r_0)$. The calculation of the equilibrium probability of the end-to-end distance r to be smaller than r_0 by the direct enumeration method or by the Monte Carlo method for short polymethylene chains has been previously studied and reported by several authors.[2-4] In the present study, we adopt the direct enumeration method for polymethylene chain of $n \leq 12$ and the Monte Carlo method for that of $n = 16$. Special care will be taken so that the contribution of the terminal naphthylmethyl groups can be included. The effect of bulky terminal groups on the conformational properties of a polymeric chain has been studied by Winnik et al.,[4] using a lattice model. In the present study, however, we consider that effect on the basis of the rotational isomeric state model, the stable positions being determined from the semiempirical potential calculation. The calculation for *trans*-1,4-bis(α-naphthylmethyl)cyclohexane will be also made.

Stable Conformations of *n*-Propyl-α-naphthalene and α-Naphthylmethylcyclohexane. Stable rotational states for ultimate and penultimate C–C bonds (ϕ_2, ϕ_3) are determined by the semiempirical potential energy calculation for *n*-propyl-α-naphthalene (Figure 2). Structural parameters for the naphthyl moiety are obtained from x-ray data of naphthalene crystal,[18] and those for the methylene unit are from those used by Abe et al.[19] Semiempirical potential functions for nonbonded atomic pairs and the rotational potential around ϕ_3 are also the same as those used by them. Rotational potential around ϕ_2 has an approximately sixfold symmetry and the potential barrier may be so small as to be neglected. Starting from an all-trans conformation ($\phi_2 = \phi_3 = 0°$), the rotational angles are changed by 5° increments and conformational energy at each state is calculated. The resulting energy map is shown in Figure 3, which reveals a part of nine energy minima with the energy contour lines of 500 cal/mol above each energy minimum. As is expected, the stable conformation of ϕ_2 is considerably shifted from the trans and gauche positions. A detailed inspection of the energy calculation indicates that ϕ_2 in the gauche position (±120°) results in a severe atomic overlap of H_8^N with H_1^1 and H_2^1 and therefore the stable position of ϕ_2 shifts to about ±100°. Similarly, rotational states of $\phi_2 = 0°$ and $\phi_3 = \pm 120°$ lead to severe overlaps of H_2^N with H_1^2 and H_2^2 and a stable position of ϕ_2 deviates from the trans position (0°) to ±20°. These results are in accordance with a study using the CPK atomic model. The area surrounded by

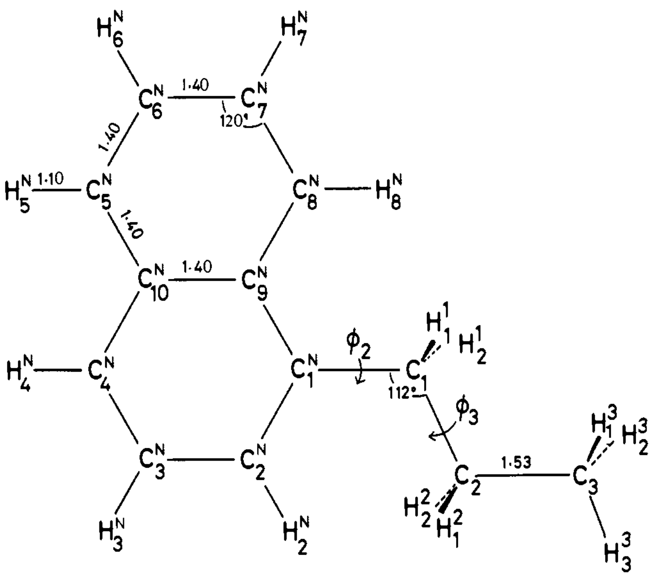

Figure 2. Structural parameters of *n*-propyl-α-naphthalene. The geometry at $\phi_2 = \phi_3 = 0$ is shown.

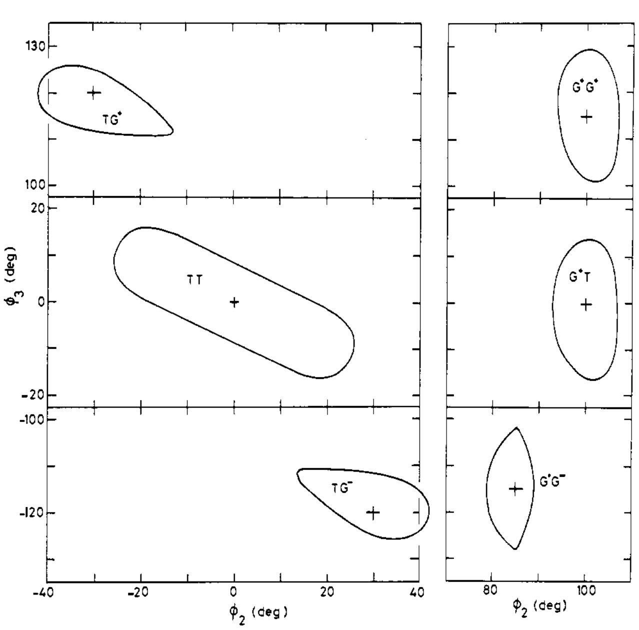

Figure 3. Stable conformations of *n*-propyl-α-naphthalene. The energy minima are indicated by plus signs. The contour lines indicate those of 500 kcal/mol higher than each minimum.

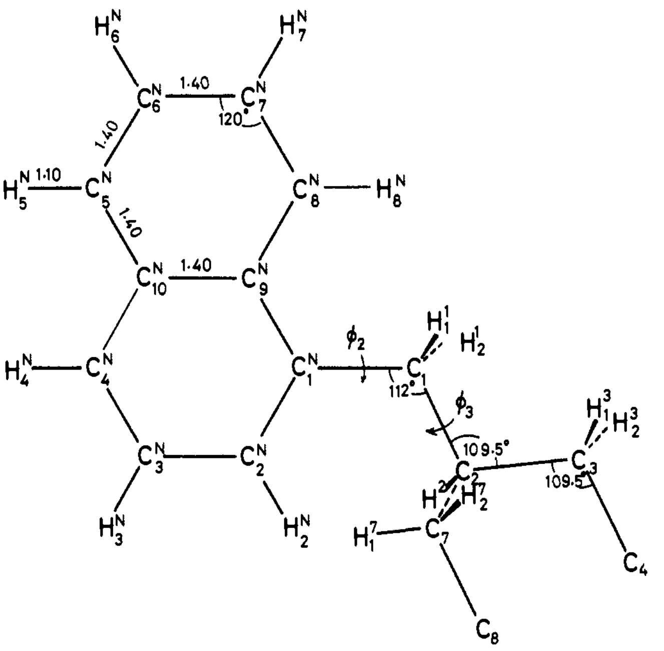

Figure 4. Structural parameters of α-naphthylmethylcyclohexane. The geometry at $\phi_2 = \phi_3 = 0$ is shown.

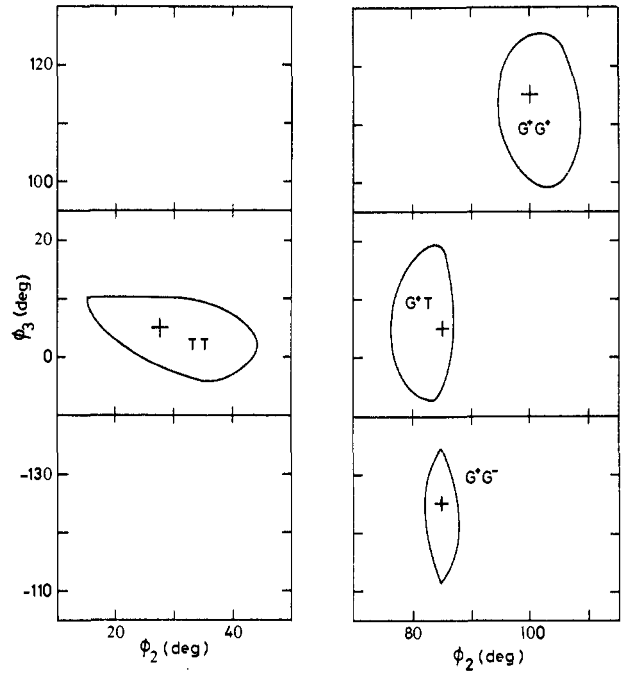

Figure 5. Stable conformations of α-naphthylmethylcyclohexane. Notations are the same as Figure 3.

Table I. Stable Rotational States for C_1^N-C_1 Bond (ϕ_2) and C_1-C_2 Bond (ϕ_3) in $\alpha NCH_2CH_2CH_3$

	ϕ_2, deg	ϕ_3, deg	E,[a] kcal/mol	W[b]
tt	0	0	2.25	2.30
$tg^{\pm}$	∓30	±120	3.76	0.800
$g^{\pm}t$	±100	0	0.075	0.996
$g^{\pm}g^{\pm}$	±100	±115	0.0	0.823
$g^{\pm}g^{\mp}$	±85	∓115	1.86	0.533

[a] Conformational energy at the potential minimum. [b] Statistical weight for the minimum.

Table II. Stable Rotational States for C_1^N-C_1 Bond (ϕ_2) and C_1-C_2 Bond (ϕ_3) in $\alpha NCH_2C_6H_{11}$

	ϕ_2, deg	ϕ_3, deg	E,[a] kcal/mol	W[b]
tt	27.5	5	3.93	0.789
tg^+	−27.5	115	3.93	0.789
g^+t	85	5	2.39	0.615
g^+g^+	100	115	0.0	0.762
g^+g^-	85	−125	3.70	0.255
g^-t	−100	5	0.0	0.762
g^-g^+	−85	115	2.39	0.615
g^-g^-	−85	−115	3.70	0.255

[a] Conformational energy at the potential minimum. [b] Statistical weight for the minimum.

the contour for each energy minimum considerably differs from one to another. This difference is included in the calculation by assigning to each minimum a weighting factor which is proportional to the area. The rotational angle, energy, and statistical weight for each energy minimum are collected in Table I.

A similar calculation is performed on a naphthylmethyl group attached to the equatorial position of cyclohexane, the structural parameters of which are shown in Figure 4. Bond angles in a cyclohexane ring are assumed to be tetrahedral. Calculated results of conformational energy are listed in Table II and plotted in Figure 5. The rotational angle ϕ_3 is measured from the "trans" position as is shown in Figure 4, which leads to the presence of a symmetry center at $\phi_2 = 0°$, $\phi_3 = 60°$ on the energy map.

Generation of All Possible Conformations of $\alpha H(CH_2)_n\alpha N$ and *trans*-1,4-Bis(α-naphthylmethyl)cyclohexane. All C-C bonds in a polymethylene chain, except the ultimate and penultimate bonds located at both ends, are assumed to take trans (t, 0°), gauche(+) (g^+, 120°), and gauche(−) (g^-, −120°) rotational states. Conformational energies are allotted as 0 cal/mol for t and 500 cal/mol for $g^{\pm}$, respectively. For $g^{\pm}g^{\mp}$ sequence, 2000 cal/mol is added. Calculations are carried out by generating all non-self-intersecting conformations in 3^{n+1} possible conformations for the chain molecules with n methylene units.[2] Intrachain atomic overlap is excluded by means of assigning an atomic radius of 1.5 Å to all carbon atoms including those in naphthyl groups. Namely, conformations with any carbon-carbon atom pairs closer than 3.0 Å are rejected. For each non-self-intersecting conformation, the conformational energy E, the statistical weight for the rotational states of terminal C-C bonds $w = w_{\text{right}}w_{\text{left}}$, and the end-to-end distance r are calculated. The end-to-end distance is measured from the center of one naphthyl group to the center of the other. For the molecule having $n = 16$, the direct enumeration method is impractically time consuming and therefore the Monte Carlo method is used instead. In the latter method, 4000 non-self-intersecting conformations are generated at random and the average quantities are obtained. This procedure is repeated four times and the total average of 16 000 non-self-intersecting conformations is calculated. In Table III are summarized the total number of conformations, the number of non-self-intersecting conformations, and the mean square end-to-end distances for molecules of $n = 3$–16. For $n = 12$, calculations are made by the direct enumeration method as well as by the Monte Carlo method. Results obtained by both procedures agree very well within the statistical error of the Monte Carlo calculation.

For *trans*-1,4-bis(α-naphthylmethyl)cyclohexane, the calculation was carried out by the direct enumeration method. In this case, a naphthylmethyl moiety may take eight rotational states and 64 conformations are possible for a total molecule. The calculated results are also listed in Table III. The structure

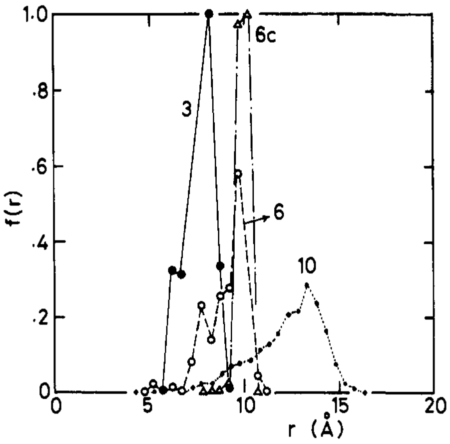

Figure 6. Distribution of the end-to-end distance r of $\alpha N(CH_2)_n\alpha N$. Numbers in the figure indicate the number of methylene units n. 6c = *trans*-1,4-bis(α-naphthylmethyl)cyclohexane.

Table III. Results of Direct Enumeration and Monte Carlo Calculation* for Conformations of $\alpha N(CH_2)_n\alpha N$

n	N_t[a]	N_a[b]	N_a/N_t	$\langle r^2 \rangle$[c]
3	81	53	0.654	50.1
4	243	131	0.539	54.7
5	729	329	0.451	71.6
6	2 187	917	0.419	84.7
8	19 683	6 551	0.333	116.5
10	177 143	47 901	0.270	150.2
12	1 594 323	348 076	0.218	184.1
12*	73 970	16 000	0.216	191 ± 10
16*	114 242	16 000	0.140	264 ± 15
6c[d]	64	64	1.0	99.9

[a] Total number of possible conformations for the direct enumeration (= 3^{n+1}) or the number of total trials for the Monte Carlo calculation. [b] Number of allowed conformations in N_t possible conformations. [c] Mean square end-to-end distance. [d] *trans*-1,4-Bis(α-naphthylmethyl)cyclohexane.

of this molecule is analogous to that of the linear molecule of $n = 6$, when the latter takes the t-g$^-$-t conformation as its middle part. Hence, it will be referred to as n = 6c in the following discussion.

Results and Discussion

Distribution of End-to-End Distance. The distribution of end-to-end distance at 15 °C is computed with 0.5 Å increment and the result is plotted in Figure 6. It clearly reveals that virtually no conformation leads to the end-to-end distance of $r < 5$ Å for molecules with n = 3-16. Obviously, this arises from the bulkiness of terminal naphthyl groups. If we ignore the bulkiness of terminal groups,[2] a similar calculation yields many conformations having $r < 5$ Å. For $n = 3$, the end-to-end distance lies mostly between 6 and 8 Å. In Figure 6 also is shown the distribution for *trans*-1,4-bis(α-naphthylmethyl)cyclohexane. For this molecule, the distribution is very sharp and the end-to-end distance lies between 9 and 10 Å.

Evaluation of Fraction of Favorable Conformations, $W(r \leqslant r_0)$. As mentioned in the previous section, the end-to-end distance is about 7 Å for $n = 3$ and about 10 Å for n = 6c. On the other hand, the observed frequency of electron transfer is 6.7×10^9 s^{-1} for $n = 3$ and 0.9×10^7 s^{-1} for n = 6c at 15 °C in HMPA (hexamethylphosphoric triamide) solution.[7,11] These results indicate that the critical distance r_0 defined in eq 3 or 5 may be between 7 and 10 Å for an electron transfer in HMPA solution and that the frequency of electron transfer decreases by a factor of about 10^{-3} when the separation of two naphthyl groups increases from 7 to 10 Å. Using the distribution of r, we calculate the equilibrium probabilities to find a conformation with $r \leqslant r_0$, $W(r \leqslant r_0)$ for r_0 = 6, 8, and 10 Å, and also the right-hand side of eq 9 for the respective r_0. The P/k_{ex} calculated from eq 9 is plotted in Figure 7 with those observed in HMPA and DME (1,2-dimethoxyethane) solutions. The inspection of the figure shows that the calculated values for r_0 = 8 Å are in excellent agreement with the observed ones in their dependence on the chain length as well as in their absolute values. The calculated values for r_0 = 10 Å also show an acceptable agreement for $n \geqslant 5$. Their disagreement for n = 3 and 4 may not necessarily indicate the failure of this value of r_0 (see below). On the other hand, for r_0 = 6 Å, the agreements of the tendency and of the absolute values are extremely poor. In the same figure are also plotted the calculated and observed results for n = 6c. The observed value lies between the calculated values for r_0 = 10 and 8 Å. Consequently, we can safely conclude that eq 9 holds in the present system and r_0 is 8-10 Å.

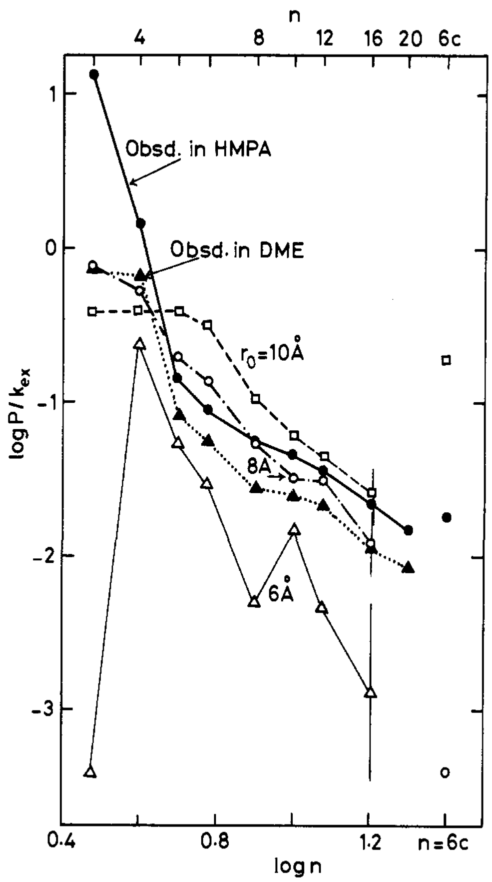

Figure 7. Comparison of the observed values of P/k_{ex} with the calculated ones at 15 °C: (—●—), observed value in HMPA; (···▲···), observed value in DME; (- -□- -), calculated value for r_0 = 10 Å; (--○-), calculated value for r_0 = 8 Å; (—△—), calculated value for r_0 = 6 Å. The vertical bars for the calculated values at n = 16 indicate the range of the scattering of the Monte Carlo data with 4000 samples.

The result calculated for small r_0 indicates a different chain length dependence from the others. Namely, in Figure 7, the equilibrium probability of $n = 3$ is found to be much smaller than that of $n = 4$ when r_0 = 6 Å. When $r_0 < 6$ Å, that of n = 3 becomes negligibly small. This is contrary to the experimental findings of intramolecular excimer formation, where the r_0 value may probably be shorter than 6 Å. In intramolecular excimer formation, it is well known as the "n = 3 rule"[20-22] that the association between two chromophores linked by a polymethylene chain is most efficient when they are separated by three methylene units. The following expla-

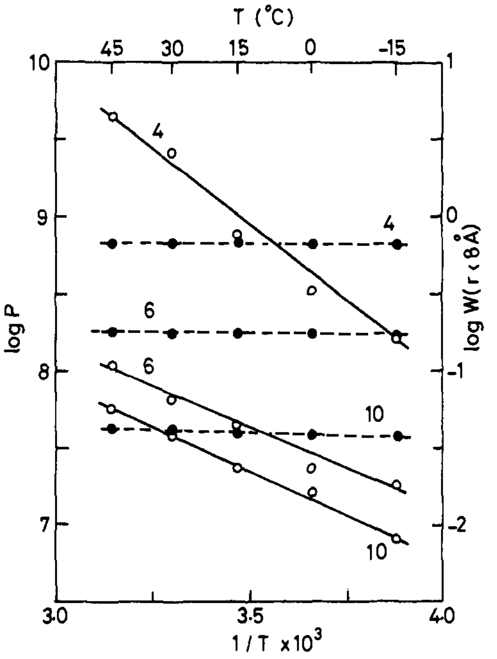

Figure 8. The Arrhenius plots of the observed frequency P in HMPA solution (—o—) and of the calculated values of $W(r \leqslant 8$ Å) (- -●- -). Numbers in the figure indicate the number of methylene units n.

nation may account for this discrepancy. Namely, in the present model, mutual orientations of two naphthyl groups as well as strong binding energy of the excimer are not taken into account, whereas they are predominantly important factors in the excimer formation. Indeed, in the excimer, a parallel sandwich structure with the interplanar distance being about 2.5 Å appears to be essential.[8] This situation is actually realized when the trimethylene unit takes $g^{\pm}g^{\pm}g^{\mp}g^{\mp}$ conformations. However, these two conformations are not included in the present calculation because of the steric overlaps between the two naphthyl groups. When the steric repulsive force is compensated for by the binding force of the excimer, the excimer formation at $n = 3$ will be much more increased than found in this calculation. The dependence of proximity and mutual orientation has been studied by us and will be reported in the forthcoming paper.

Temperature Dependence of P and $W(r \leqslant r_0)$. The good applicability of eq 9 to the diffusion-controlled intramolecular electron transfer may cause the following question: Is the static limit actually the case for this system or does eq 9 hold even in the dynamic case? In the latter case, $\langle\tau\rangle_1 \approx \langle\tau\rangle_2$, being irrespective of the chain length. This can be rationalized by the following argument. Since the mobility of terminal methylene units may be much larger than that of the middle part of a polymethylene chain, it is likely that $\langle\tau\rangle_1$ is determined only by the mobility of the terminal group. Hence, $\langle\tau\rangle_1$ may be independent of the chain length and approximately equal to $\langle\tau\rangle_2$. If this is the case, $\langle\tau\rangle_1$ can be evaluated from eq 6. For example, the observed frequency P for $n = 6$ was 4.4×10^7 s^{-1} in HMPA at 15 °C, whereas the calculated value of $W(r \leqslant 8$ Å) is 0.177 at 15 °C. Accordingly, $\langle\tau\rangle_1$ is evaluated to be 2.0×10^{-9} s, which is a highly probable value (see below). It cannot be concluded, however, at this stage whether the static or the dynamic case is the present one.

A decisive answer will be obtained by a careful inspection of the temperature dependence of P and $W(r \leqslant r_0)$. If the experimental results are of the static case, the temperature dependence of P should mainly be governed by the temperature dependence of $W(r \leqslant r_0)$ because the activation energy of the intrinsic rate constant k has been found to be very low (~1 kcal/mol). On the other hand, if they are of the dynamic case, the temperature dependence will be governed by $\langle\tau\rangle_1$ as well as by $W(r \leqslant r_0)$. Obviously, $\langle\tau\rangle_1$ decreases when the temperature increases. The Arrhenius plots of the observed frequencies of electron transfer P in HMPA and that of $W(r \leqslant 8$ Å) are shown in Figure 8. It clearly reveals that the temperature dependence of P is substantially greater than that of $W(r < 8$ Å), while the latter increased only slightly with temperature, indicating that conformations with $r \leqslant 8$ Å are relatively unstable. Similarly, the observed values of P in DME solution show a larger temperature dependence than that of $W(r \leqslant 8$ Å).

To clarify this problem further, let us discuss it more quantitatively. The activation energy of $W(r \leqslant 8$ Å) is 0–0.4 kcal/mol for all chain lengths calculated. The activation energy of k is estimated to be 1 kcal/mol.[7] Accordingly, the total activation energy in the static case should amount to about 1–1.4 kcal/mol, which is evidently much less than the observed values in HMPA (~5 kcal/mol) or those in DME (~3 kcal/mol).[7] On the other hand, in the dynamic case the evaluation of the activation energy of $\langle\tau\rangle_1$ cannot be made so straightforwardly. We, however, can accept as reasonable an assumption that the translational motion of naphthyl groups attached to polymer ends and that of a free naphthyl group are equally governed by the hydrodynamic interaction with the surrounding solvent molecules. If this is the case, the activation energies of $\langle\tau\rangle_1$ and $\langle\tau\rangle_2$ may be substituted by the activation energy of the diffusion of solvent. The latter quantity has been reported to be 3.9 kcal/mol for HMPA.[8] Therefore the total activation energy for the dynamic case is about 4 kcal/mol, which is comparable to the observed value. It is interesting to note that hydrodynamic force appears to play an important role for the segmental movement of such small molecules as one of $n = 5$ or 6 as well as high polymers. The susceptivity to the hydrodynamic force has been reported for the intramolecular excimer formation in even shorter chains by Wang and Morawetz.[23]

The observed activation energies for $n = 3$ and 4 are exceptionally higher than the calculated ones. This may result from the peculiarities of intramolecular electron transfer in $n = 3$ and 4, which has been discussed in the original paper.[8] The observed high activation energies strongly suggest contributions of highly strained conformations to electron transfer, or the presence of a different transfer mechanism in these short chains. In any case, the behavior of short chains deserves further investigation.

The temperature dependence of P/k_{ex} is also calculated on the basis of the static model (eq 9). The result agrees excellently with that of the observed one when $n \leqslant 4$, implying that $\langle\tau\rangle_1$ and $\langle\tau\rangle_2$ will have nearly the same temperature dependence. Obviously, this is consistent with the preceding discussion.

Evaluation of $\langle\tau\rangle_1$ and Comparison with Fluorescence Depolarization Data. Let us now discuss the mean lifetime of conformations for $r \leqslant 8$ Å, $\langle\tau\rangle_1$. We can estimate this value from eq 6, using the calculated value of $W(r \leqslant 8$ Å) and the experimentally obtained P. The $\langle\tau\rangle_1$ obtained for $n = 6$, 10, and 16 in HMPA and DME solutions are listed in Table IV. Seemingly, these values lie in a reasonable range for the motion of terminal groups of a polymer chain. Although the mean lifetime appears to decrease with the increase of chain length, the accuracy of the present calculation may be insufficient for a detailed discussion. Despite the uncertainties, however, it is clearly shown that the activation energies in HMPA solution are substantially higher than those in DME solution. The higher activation energies in HMPA solution reflect the higher activation energy of the viscosity of HMPA (3.9 kcal/mol) than that of DME (1.95 kcal/mol).[7,9]

The lifetime calculated here will be compared with the ro-

Table IV. The Mean Lifetime of Favorable Conformations with $r \leqslant 8$ Å, $\langle\tau\rangle_1$ in HMPA and DME Solutions (ns)

		Temp, °C					
n	Solvent	−75	−45	−15	15	45	$\Delta E^{\ddagger}$, kcal/mol[c]
6	HMPA[a]			4.9	2.0	0.81	4.6
10	HMPA			2.4	0.89	0.39	4.9
16	HMPA			1.9	0.78	0.41	4.1
6	DME[b]	45	13	4.4	2.7		3.7
10	DME	13	5.3	2.0	1.4		3.2
16	DME	9.1	3.6	1.7	1.2		2.9

[a] Hexamethylphosphoric triamide. [b] Dimethoxyethane containing 2% HMPA. [c] Activation energy.

tational relaxation time ρ obtained in the fluorescence depolarization of a perylene group attached to the end of a polystyrene chain reported by Uchida et al.[24] Their polymer sample had its perylene moiety attached to the polymer end in such a way that the transition moment of the luminophore was parallel to the bond connecting the luminophore. Hence, the rotation around the terminal bond made little contribution to the depolarization and the observed relaxation time reflected the translational mobility of the terminal group. They reported the results for a polystyrene chain with the molecular weight of 2400 (degrees of polymerization of 23) at 30 °C, which was 1.6×10^{-9} s in benzene, 2.6×10^{-9} s in cyclohexane, and 5.2×10^{-9} s in cyclohexanone. The relaxation time increased slightly with increasing molecular weight of the polymer. They decreased when the temperature increased, and their activation energies were 4.8 kcal/mol in benzene, 4.2 kcal/mol in cyclohexane, and 4.0 kcal/mol in cyclohexanone, which were a little higher than the values for the solvent viscosities. Obviously, these values are in accordance with those in Table IV.

Conclusions

The static and the dynamic models of the intramolecular electron transfer in $\alpha N(CH_2)_n\alpha N^-\cdot$ system have been studied theoretically. The chain length dependence of the frequencies of electron transfer is successfully determined by the equilibrium probability to find the polymer system in a favorable conformation for the reaction, i.e., a conformation where the two terminal naphthyl groups are closer than 8 Å. The dynamic model has been strongly supported by the substantially higher activation energy than that of the equilibrium probability. From the viewpoint of the dynamic model, the mean lifetime of the favorable conformation has been calculated and found to be independent of chain length. The calculated values of the mean lifetime are in accordance with the data obtained in the fluorescence depolarization study.

Finally, we should remark on some basic assumptions of the present calculation. Our major assumptions are (1) the active sphere model for the transfer probability p_i, the proximity and orientational dependence being neglected, (2) the rotational isomeric state model for very short chains, and (3) the equality of the relaxation times, $\langle\tau\rangle_1$ and $\langle\tau\rangle_2$. However, although their precise meaning cannot be clearly defined now, we can assess the validity of calculation at least when $n > 4$. In any case, the range of uncertainties in P/k_{ex} will be expected to be within a factor of 2 or 3, which is not important in a log-log plot of Figure 7.

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Appendix

In the theoretical section the two limiting cases, the static and dynamic cases, were treated. Here the intermediate of the two limiting cases will be considered. As before, k_i is defined as an intrinsic rate of electron transfer for the ith conformation, whose lifetime is τ_i. The probability p_i of the electron transfer during τ_i is obtained as follows. If $q(t)$ is the probability of an electron to be located on one of the terminal naphthyl groups at time t, then that for the second naphthyl group is equal to $(1 - q)$. The differential equation to be solved is

$$\frac{dq}{dt} = k_i(1 - q) - k_i q \tag{A1}$$

The solution at $t = \tau_i$ under an initial condition $q = 0$ at $t = 0$ is

$$p_i = q(\tau_i) = \frac{1}{2}[1 - \exp(-2k_i\tau_i)] \tag{A2}$$

In the static case, $k_i\tau_i \ll 1$ and p_i is equal to $k_i\tau_i$. In the dynamic case, $k_i\tau_i \gg 1$ and p_i is equal to $1/2$. Substitution of eq A2 into eq 1 in the text leads to

$$P = \langle 1 - \exp(-2k_i\tau_i)\rangle / 2\langle\tau\rangle \tag{A3}$$

For the use of the above equation, each value of k_i and τ_i should be specified. For the illustrative purpose, we can assume that $k_i = k$ for $r \leqslant r_0$ and $k_i = 0$ for $r > r_0$ as before (see eq 3 in the text) and that all τ_i's are equal to τ. Then eq A3 is reduced to

$$P = \frac{[1 - \exp(-2k\tau)]}{2\tau} W(r \leqslant r_0) \tag{A4}$$

Accepting $\tau = 2 \times 10^{-9}$ s, $[1 - \exp(-2k\tau)]/2\tau$ is calculated as a function of k and plotted in Figure 9. It should be noticed that the transition from the static limit to the dynamic limit occurs in a relatively small range of the rate constant k. This finding justifies the assumption of the two limiting cases in the text.

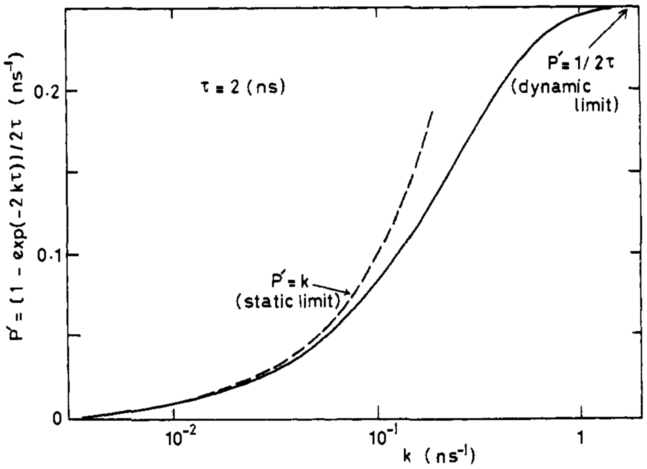

Figure 9. Dependence of the frequency factor, $[1 - \exp(-2k\tau)]/2\tau$, of the intramolecular electron transfer upon the intrinsic rate constant k. $\tau = 2 \times 10^{-9}$ s.

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(25) There is ½ probability for the electron to remain on the original naphthyl moiety or to be transferred to the other one during each encounter.

Electron Transfer Quenching of Fluorine Substituted Aryl Alkyl Ketones. ^{19}F Polarization via the Triplet Mechanism

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Abstract: The interaction of photoexcited α,α,α-trifluoroacetophenone (**1**) and several of its derivatives with dimethoxybenzene (**3**) results in concentration and acidity dependent ^{19}F polarization. The effects observed at low concentrations and in acidic solutions are compatible with the radical pair theory whereas the results obtained at high reactant concentrations in neutral solutions can be explained by a mechanism involving preferential intersystem crossing to one triplet sublevel, fast electron transfer quenching of the polarized triplet, and electron–nuclear cross relaxation in the resulting radical ions. The signal direction observed for the CF$_3$ group (enhanced absorption) can be explained by predominantly scalar cross relaxation, whereas the emission observed for meta and para fluorines requires a predominantly dipolar cross relaxation mechanisms. The kinetic requirements for this polarization mechanism are delineated and the probability of quenching an electron spin polarized triplet is formulated.

Ten years ago, the first reported cases of chemically induced nuclear spin polarization[1,2] were explained by invoking a mechanism featuring electron–nuclear cross relaxation in free radicals[3,4] in a way similar to the Overhauser effect. However, this mechanism was soon found to be unsatisfactory because it fails to explain or is in conflict with experimental results such as the multiplet effect[2,4] and the dependence on the mechanism of product formation[5] or the spin multiplicity of the precursor.[6] An alternative polarization mechanism, proposed by Closs and co-workers[7] and by Kaptein,[8] is based on hyperfine induced singlet–triplet mixing in radical pairs. This so-called radical pair theory, in the initially proposed form or in later, refined versions,[9,10] has been remarkably successful and can account satisfactorily for the overwhelming majority of nuclear spin polarization effects reported during the last 10 years.[11-14]

Nevertheless, the nuclear spin polarization phenomena observed in a limited number of reactions are not compatible with the radical pair theory. Among these are the effects observed in the following reactions: the irradiation of anthraquinone[15] and several derivatives of benzoquinone[16] as well as phenazine[17] and several diazanaphthalenes[18] in the apparent absence of a reaction partner; the photolysis of pyruvic acid;[19] and the illumination of benzoquinone or tetrafluorobenzoquinone in the presence of suitable reactants.[20,21] The effects observed in these reactions have been explained by mechanistic schemes involving a cross relaxation step.

In continuing our studies of potential electron transfer reactions by the CIDNP technique[22-25] we have recently reported CIDNP effects observed during the irradiation of α,α,α-trifluoroacetophenone (**1**, TFA) in the presence of 1,4-diazabicylo[2.2.2]octane (**2**, Dabco) or 1,4-dimethoxybenzene (**3**, DMB). These results were independently observed by Thomas and Wagner.[26] The intensity, signal direction, and mode of these effects depend on the concentration of both quencher and ketone, an observation which led us to conclude that two different polarization mechanisms are operative in this system. The polarization observed at low concentrations of quencher and ketone is compatible with the radical pair theory whereas the polarization observed at higher concentrations of the reactants is compatible with the so-called triplet mechanism.[20,21]

In this publication, we present a more detailed discussion of the system TFA–DMB, including the kinetic formulation of the probability of quenching an electron spin polarized triplet state. In addition, we discuss the acidity dependence of the polarization at high quencher concentrations and we report CIDNP effects observed during the electron transfer quenching of the *m*- and *p*-fluoro derivatives of TFA and of two homologues, pentafluoropropiophenone and heptaflu-