

$J = 15.8\text{Hz}$ and 1.2Hz , 1H, H-6'), 7.01 (*dd*, $J = 15.8\text{Hz}$ and 5.5Hz , 1H, H-5'), 7.15 (*d*, $J = 8.0\text{Hz}$, 1H, H-6).

1-[(*E*)-5,6-didexoy-2,3-O-isopropylidene- β -D-ribo-hept-5-enodialdo-1,4-furanosyl] uracil (**22**). To a solution of **11** (0.50g, 1.8 mmol) in dimethyl sulfoxide (10 ml), trifluoroacetic acid (0.065 ml) and *N,N'*-dicyclohexylcarbodiimide (1.09g, 5.3 mmol) were added. After 10 hr, **10** (0.52g, 1.8 mmol) was added and stirring was continued for a further 24 hr at room temperature. The product was isolated by the procedure which was used for **12** to afford, after chromatography on silica gel, **22** as a pale yellow foam (0.32g, 62%), R_f 0.65 (toluene-acetone, v/v 1:1); $^1\text{H NMR}$ (CDCl_3) δ 1.39 and 1.61 (*s*, 3H, CMe_2), 4.68-5.04 (*m*, 2H, H-3'), H-4'), 5.18 (*dd*, $J = 6.0\text{Hz}$ and 0.5Hz , 1H, H-2'), 5.57 (*d*, $J = 0.5\text{Hz}$, 1H, H-1'), 5.77 (*d*, $J = 8.0\text{Hz}$, 1H, H-5), 6.25 (*ddd*, $J = 16.0\text{Hz}$, 7.5Hz , and 1.0Hz , 1H, H-6'), 7.00 (*dd*, $J = 16.0\text{Hz}$ and 5.0Hz , 1H, H-5'), 7.27 (*d*, $J = 8.0\text{Hz}$, 1H, H-6), 9.62 (*d*, $J = 7.5\text{Hz}$, 1H, H-7'). *Anal.* Calcd., for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_6$: C, 54.54; H, 5.23; N, 9.09. Found: C, 54.48; H, 5.13; N, 9.12.

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^{13}C NMR Study of Segmental Motions of *n*-Heptane in Neat Liquid

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Carbon-13 nuclear spin-lattice relaxation times have been measured over the range of temperature from 213K to 353K for carbons in *n*-heptane in neat liquid. The experimental data have been analyzed to obtain informations of segmental motions in the chain polymers by employing a model which describes jumps between several discrete states with different lifetimes. The overall reorientation of the molecule is assumed to be isotropic rotational diffusion. From the above analysis the activation energies of each C-C bond reorientation as well as the overall reorientation have been obtained through the Arrhenius-type temperature dependence.

Introduction

Study of segmental motions in chain polymers plays an important role in understanding their physical properties.^{1,2} Particularly, since the membrane transport in living cells is closely related to segmental motions of acyl chains in the phospholipid bilayer which is a building block of cellular membranes, the investigation of segmental motions of chain molecules becomes an important task in the field of life science these days.³⁻⁵

In the past, studies on the dynamics of polymer chains were

mainly based on the stochastic approach and the results were rather qualitative. This might be inevitable when one deals with long polymer chains. Explicit roles of segmental motions in the polymer chain dynamics should become clear once we understand first the dynamics of rather short chain molecules such as *n*-hexane, *n*-heptane, etc.

Reorientation of small molecules in liquid has been widely studied experimentally and theoretically.⁶ Several models are commonly used to describe molecular reorientation including internal rotations of side groups. Of these, rotational diffu-

sion,^{7,9} jump diffusion,^{8,10} and extended rotational diffusion¹¹⁻¹⁴ models have been used in the analysis of the internal rotation of a methyl group. Segmental motions of normal alkanes may be viewed as successive internal rotations of C-C bonds and the above theoretical models can be used to investigate the chain dynamics.

Dynamics of chain molecules may be characterized by conformational changes about each C-C bond. Conformational changes between the *trans*(*t*) and *gauche*^{*}(*g*^{*}) forms or *trans* and *gauche*⁻(*g*⁻) forms can best be described by the jump model which describes jumps between several discrete states. Recently, London and Avitabile¹⁵ proposed a modified version of the jump model to calculate the carbon-13 nuclear relaxation times for hydrocarbon chains. By assuming independent rotations about C-C bonds and disallowing direct jumps between *g*^{*} and *g*⁻ states, they described each internal rotation in terms of two parameters, τ_t , the lifetime of a *trans* state, and σ , the equilibrium ratio of *gauche* to *trans* states: $\sigma = \tau_g/2\tau_t$, with τ_g , the lifetime of a *gauche* state. These parameters are empirically introduced in rate equations for the probabilities of being in each one of three states. These probabilities are necessary to evaluate the ensemble average in the rotational correlation function through the conditional probabilities of moving from one state to another.

The purpose of the present work is to apply the above method of London and Avitabile¹⁵ to obtain the lifetime of a *trans* state for each C-C bond from the carbon-13 nuclear magnetic relaxation measurements. From the temperature dependence of the lifetimes the activation energy which corresponds to the jump barrier height is evaluated. In order to make the analysis tractable we assume here that σ is the same for all C-C bonds and its value is obtained from the fact that the energy difference ΔE between the *gauche* minimum and the *trans* minimum for liquid *n*-butane is 800 cal/mol¹ and σ may be expressed in the Arrhenius-type expression: $\sigma = \exp(-\Delta E/RT)$.

Carbon-13 nuclear spin-lattice relaxation time contains contributions from several relaxation mechanisms. The dipole-dipole and spin-rotation interactions are known to be the major contributions. These contributions may be separated by measuring the nuclear Overhauser enhancement (NOE) factor¹⁶ and it is well known that the spin-rotational relaxation mechanism does not contribute significantly to the spin-lattice relaxation time for the hydrocarbon chain molecules.¹⁷ We confirm this by measuring the NOE factors for *n*-heptane.

Theory

The spin-lattice relaxation time of the *N*-th carbon-13 nucleus due to the dipole-dipole interactions with the nearest neighboring protons in the extreme narrowing limit is given by¹⁸

$$\frac{1}{T_1} = \frac{L \gamma_H^2 \gamma_C^2 \hbar^2}{r_{CH}^6} \int_0^\infty G_N(\tau) d\tau \quad (1)$$

where γ 's are the magnetogyric ratios of corresponding nuclei, r_{CH} is the C-H bond length and L is the number of protons bonded to the *N*-th carbon counted from the central zeroth carbon. The relevant reorientational correlation function $G_N(\tau)$ is given by London and Avitabile as¹⁵

$$G_N(\tau) = \left[\frac{\sigma}{(1+2\sigma)^2} \right]^N \sum_{abc \dots n} \sum_{a'c' \dots n'} \exp(-6D_0 \tau) \times A_{aa'} d_{ab}(\beta) d_{a'b'}(\beta) \dots A_{nn'} d_{nn'}(-\beta) d_{n'n'}(-\beta) \times A_{nn'} d_{no}(\beta) d_{n'o}(\beta) \exp[-2\pi i(n-n')/3] \quad (2)$$

where all summations run from -2 to +2 and D_0 is the isotropic overall rotational diffusion constant; β is the polar angle between successive carbon-carbon bonds along the chain (70.5° for the present case); $d_{ab}(\sigma)$ is the reduced Wigner rotation matrix element.¹⁹ Elements of the **A** matrix are tabulated in their paper and these contain informations of the probabilities that a bond is in a given state at any time and the conditional probabilities of moving from one state to another in terms of the lifetimes of the *trans* and *gauche* states, τ_t and τ_g , and the equilibrium ratio of *gauche* to *trans* states, σ .

Explicit expressions of the above correlation functions for *t*'^c successive carbons in *n*-heptane become

$$G_0(\tau) = \exp(-6D_0 \tau) \quad (3)$$

$$G_1(\tau) = \frac{\sigma}{(1+2\sigma)^2} \sum_a \exp(-6D_0 \tau) A_{aa}(\tau, \tau_1, \sigma) d_{aa}(\beta) d_{aa}(\beta) \quad (4)$$

$$G_2(\tau) = \left[\frac{\sigma}{(1+2\sigma)^2} \right]^2 \sum_{ab} \sum_{b'} \exp(-6D_0 \tau) A_{aa}(\tau, \tau_1, \sigma) \times d_{ab}(\beta) d_{ab'}(\beta) A_{bb'}(\tau, \tau_2, \sigma) d_{bb'}(-\beta) d_{bb'}(-\beta) \times \exp[-i(b-b')2\pi/3] \quad (5)$$

$$G_3(\tau) = \left[\frac{\sigma}{(1+2\sigma)^2} \right]^2 \sum_{abc} \sum_{c'} \exp(-6D_0 \tau) A_{aa}(\tau, \tau_1, \sigma) \times d_{ab}(\beta) d_{ab'}(\beta) A_{bb'}(\tau, \tau_2, \sigma) d_{bc}(-\beta) d_{b'c'}(-\beta) \times B_{cc'}(\tau, \tau_e) d_{c*}(\beta) d_{c*}(\beta) \quad (6)$$

The expressions in Eqs. (3)~(5) are obtained directly from Eq. (2) but we introduced a modification in Eq. (2) to obtain Eq. (6). Since the third carbon corresponds to the terminal group in *n*-heptane the reorientational dynamics of this group may be simply described by jumps between three equally probable sites. This is the original jump model proposed by Woessner²⁰ and Wallach⁸ and later corrected by Versmold.¹⁰ The elements of the **B** matrix are given in terms of the jump rate $1/\tau_e$ from one site to another as¹⁰

$$B_{ij}(\tau, \tau_e) = \begin{cases} 1 & , \text{ for } i=j=0 \\ \exp(-3\tau/2\tau_e) & , \text{ for } 0 \neq i=j+3n \quad (n=0, \pm 1) \\ 0 & , \text{ for } i \neq j+3n \quad (n=0, \pm 1) \end{cases} \quad (7)$$

where all the indices are restricted to the values 0, ±1, and ±2. Notice that the elements of **A** matrix contain the explicit dependence of the lifetime of the *trans* state for the first carbon group, τ_1 , or τ_2 for the second carbon.

In order to utilize Eqs. (3)~(6) for the analysis of experimental data we assume that σ is the same for all C-C bonds and the relaxation rates of the *trans* and *gauche* states follow the Arrhenius-type relations:

$$\begin{aligned} 1/\tau_g &= A_g \exp(-E_g/RT) \\ 1/2\tau_t &= A_t \exp(-E_t/RT) \end{aligned} \quad (8)$$

Then, σ can be expressed in terms of the energy difference, $\Delta E = E_t - E_g$, between the *trans* and *gauche* minima:

$$\sigma = \exp(-\Delta E/RT) \quad (9)$$

Again we assume that the pre-exponential factors are the same. The value of ΔE ranges from 0.5~1.0 kcal/mol for various

alkanes¹ and we take the value of 0.8 kcal/mol which is reported for liquid n-butane in our calculation.

Experimental

n-Heptane, a spectroscopic grade, was purchased from the Merck & Co. and used without further purification. The sample in a 12mm tube bearing a 5mm inner coaxial tube filled with a field-lock substance was degassed by repeating the freeze pump thaw cycles 5 times and the tube was sealed under N₂ of 1.0 atm. DMSO-*d*₆ was used as a field-lock substance at high temperature while acetone-*d*₆ was used at low temperature. The temperature in the probe was measured with the Omega digital thermometer and was maintained within the accuracy of $\pm 1^\circ\text{C}$ throughout the experiment.

All data were obtained with the Varian XL-100 NMR spectrometer operating at 25.16 MHz for ¹³C. The spin-lattice relaxation times (*T*₁) for all carbons were determined simultaneously by the standard inversion recovery method.^{21,22} The pulse sequence utilized in these measurements was (*T*_d-180°-*t*-90°)_{*n*} in which *t* is experimentally varied and *T*_d is set to be 8*T*₁. Intensities obtained from the spectra were used to calculate the relaxation times using the relation.

$$\ln(A_\infty - A_t) = -\ln 2A_\infty - t/T_1 \quad (10)$$

where *A*_∞ is the equilibrium amplitude of the fully relaxed peak and *A*_{*t*} is the amplitude of the peak at some pulse interval time *t*. The NOE factors (*η*) were determined by the gated proton noise decoupling technique^{21,22} in which they were calculated from the ratio of signal intensities, (*S*-*S*₀)/*S*₀, obtained with and without noise irradiation of proton nuclei with a pulse delay of about 10*T*₁. Both *T*₁ and *η* were determined from the NMR spectra which were obtained by accumulating 2~5 FID (free induction decay) signals and then performing the Fourier transformation. Each data represents an average of at least 10 independent measurements at each temperature. Particularly, *T*₁ values were calculated by treating the peak heights with the least square method and only spectra with the reproducibility within $\pm 10\%$ were included in the calculation.

Results and Discussion

Experimentally observed spin-lattice relaxation times for carbon-13 nuclei in liquid n-heptane at various temperatures are listed in Table 1 and corresponding relaxation rates are plotted in Figure 1. Also the dependence of the spin-lattice relaxation time on the carbon position in the chain is plotted in Figure 2. In order to compare the relaxation times for all the carbons directly with one another the values of the terminal carbon (C₃) are multiplied by 3/2.¹⁷ Measurements of the NOE factors give the value of 1.98 for all the carbons in n-heptane up to the temperature of 313K and as the temperature is increased further the NOE factors decrease only slightly. This fact confirms that the relaxation mechanism is dominantly due to the dipole-dipole interaction for n-heptane as for other hydrocarbon chain molecules.

From the experimental data we observe that at each temperature there is a progressive increase in *T*₁ values from the central carbon to the terminal carbon (Figure 2). Also the

relaxation rate decreases rapidly at low temperature whereas it decreases rather slowly at high temperature for each carbon (Figure 1). In order to analyze these data we adopt the theory of London and Avitabile¹⁵ which was described earlier and the results are presented in Table 2. In the second column the overall reorientational correlation time, $\tau_c = 1/6D_0$, is listed. This value is obtained from the relaxation time of the central carbon assuming the rotational diffusional model for the overall reorientation via Eq. (3). The lifetimes of the trans state for the next (*τ*₁) and the second next (*τ*₂) carbons to the central carbon are listed in the third and fourth columns. Relaxation times of the corresponding carbons are analyzed via Eqs. (4) and (5) which take into consideration the conformational

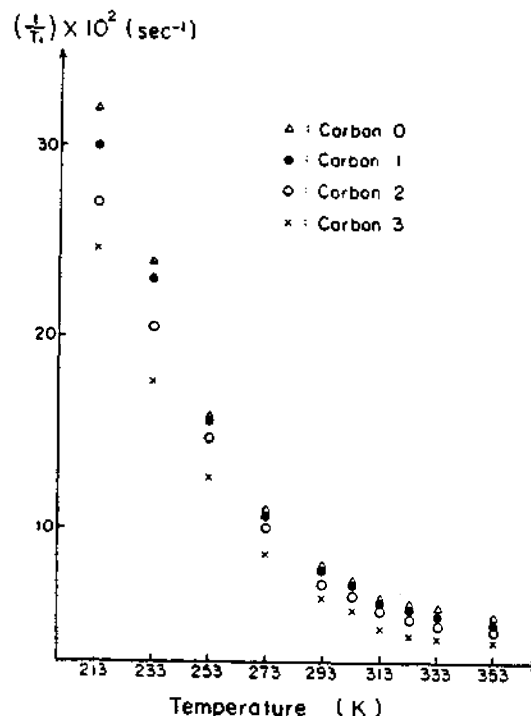


Figure 1. Observed spin-lattice relaxation rate, $1/T_1$, as a function of temperature.

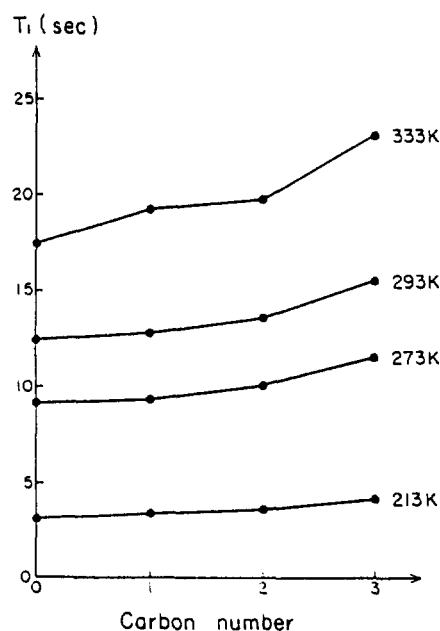


Figure 2. Observed spin-lattice relaxation time, *T*₁, as a function of position in the chain at several temperature.

TABLE 1: Observed Spin-lattice Relaxation Times, T_1 , for Carbon-13 nuclei in n-heptane at Various Temperatures

Temp. (K)	T_1 (sec)			
	C_0	C_1	C_2	C_3^a
213	3.12	3.32	3.60	4.07
233	4.15	4.34	4.91	5.66
253	6.35	6.40	6.75	7.98
273	9.06	9.38	10.1	11.7
293	12.5	12.9	13.7	15.8
303	13.9	14.3	15.2	18.0
313	15.8	15.9	17.2	21.0
323	16.5	17.3	18.5	22.8
333	17.5	19.2	19.9	23.1
353	19.1	20.9	22.2	24.3

^a Observed $T_1 \times 3/2$.TABLE 2: Various Reorientational Correlation Times for Carbon-13 Nuclei in n-heptane at Various Temperatures.^a

Temp. (K)	τ_0	τ_{11}	τ_{12}	τ_e
213	0.746	22.4	10.9	6.07
233	0.561	23.3	6.93	3.23
253	0.367	87.9	11.9	2.25
273	0.257	13.1	5.29	1.67
293	0.186	10.1	4.60	1.31
303	0.167	10.0	4.06	0.975
313	0.147	39.9	2.91	0.713
323	0.141	4.82	2.83	0.639
333	0.133	2.19	3.71	0.879
353	0.122	2.03	2.20	1.20
E_a (kcal/mol)	2.09	2.56	1.67	2.17

^a In 10^{-11} sec.

changes between trans and gauche states. The terminal carbon group is analyzed by the jump model between three equally probable sites and the jump rate, $1/\tau_e$, is calculated from the relaxation time of the terminal carbon via Eq. (6) and the results are listed in the last column in terms of τ_e vs. temperature. In our calculation the C-H bond length is taken to be 1.09 Å for all the carbons.

From the temperature dependence of these properties we calculate the activation energies through the Arrhenius-type plots (Figure 3) by the least square fitting method. These values are given at the bottom of each column in Table 2. The activation energy for the overall reorientation is 2.09 kcal/mol which is of the same order of magnitude as other short chain n-alkanes.²³ The activation energy for the relaxation process of the trans state for noncentral carbon shows a decreasing tendency toward the terminal carbon. However, the activation energy for the terminal carbon itself increases again. It may be interpreted that the internal rotation around the C-C bond becomes easier toward the chain end but the internal rotation of the terminal group itself becomes difficult again. Other workers²³ reported a continuing decrease in the activation energy to the end for longer hydrocarbon chains but their method of analysis is different from the present work. Since the present analysis is rather sensitive to the variation in the experimental values of T_1 and computational errors may be accumulated toward

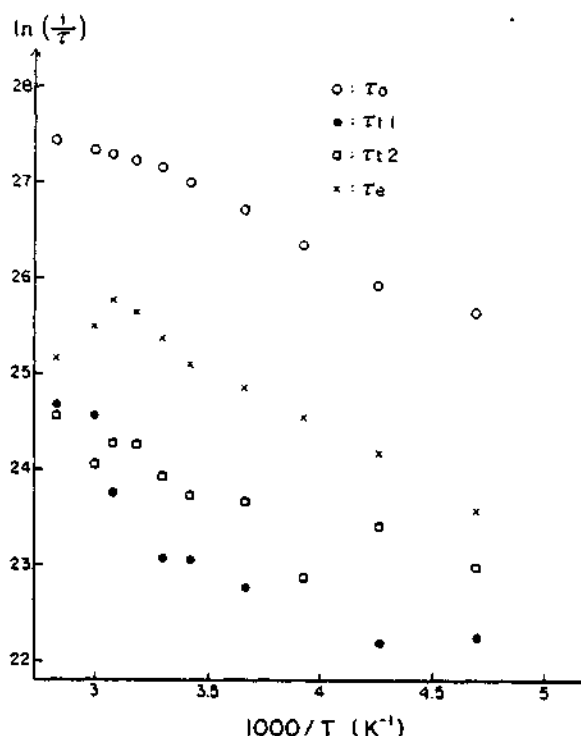


Figure 3. The Arrhenius-type temperature dependence of various reorientational correlation times.

the terminal group analysis, more studies on other systems with various theoretical models are needed in the future.

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Reactions of Thianthrene Cation Radical Perchlorate with Azo-bis-2-phenoxy-2-propane and Azo-bis-2-(p-nitrophenoxy)-2-propane

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Thianthrene cation radical perchlorate (**1**) reacted with azo-bis-2-phenoxy-2-propane (**6**) to give thianthrene (**2**), *cis*-thianthrene-5,10-dioxide, 5-(*p*-hydroxyphenyl) thianthrenium perchlorate (**10**), acetone, phenol, and 5-(2-propenyl) thianthrenium perchlorate (**11**) when the mole ratio of **1** to **6** was 1:1. Among the products, **11** was a new compound. However, when the corresponding mole ratio was 5:1, **11** was not formed. Similar result was obtained for azo-bis-2-(*p*-nitrophenoxy)-2-propane.

Introduction

Some years ago we have investigated the reaction of thianthrene cation radical perchlorate (**1**) with azobisisobutyronitrile (AIBN) in acetonitrile at solvent reflux temperature in order to obtain information about the coupling nature between a cation radical and a free radical.¹ From this reaction were obtained thianthrene (**2**), thianthrene 5-oxide (**3**), *cis*-thianthrene-5,10-dioxide (**4**), 5-acetylthianthrenium perchlorate (**5**), and 5-(2-thianthreniumyl)thianthrene perchlorate. No coupling product between **1** and cyanoisopropyl radical was detected. In addition, it was realized that a canonical form of cyanoisopropyl radical caused the reaction complicated. Therefore, it was necessary to change CN group of AIBN with other group of which resonance form would not be expected to involve either in the reaction with **1** or in the cross-coupling reaction of the radical itself. We synthesized azo-bis-2-(phenoxy)-2-propane (**6**) according to the known method² and run the reaction with **1**. Surprisingly, the azo compound (**6**) underwent rapidly the reaction with **1** in acetonitrile at room temperature. We wish to report the result in this paper.

Experimental

Thianthrene (**2**) and thianthrene cation radical perchlorate (**1**) were prepared by the methods described elsewhere.³ Acetonitrile was Kanto Chemical Corporation Extra pure and was refluxed with phosphorus pentoxide for 3 hours, followed by refluxing with calcium hydride for 2 hours. The distillate was stored over molecular sieve (4Å). Hydrazine hydrate (80%) was from Kanto. Column chromatography was performed with Merck silica gel (70-230 ASTM mesh, 0.063-0.2mm). All chromatographic solvents were distilled prior to use. Ultraviolet

spectra were obtained with a Beckman 5270 spectrometer. Infrared spectra were obtained using a Perkin-Elmer 283 infrared spectrometer. All infrared spectra were taken using potassium bromide pellets, unless otherwise indicated. ¹H NMR spectra were recorded on a Varian EM-360A spectrometer and chemical shifts were relative to tetramethylsilane. Melting points were measured using a Fisher-Jones melting point apparatus and uncorrected.

Preparation of methyl methylketazine (7). The compound was prepared by the reaction of acetone with 80% hydrazine hydrate in ether according to the known procedure.⁴

Preparation of azo-bis-2-chloro-2-propane (8). The title compound was prepared by bubbling of chlorine gas into **7** in petroleum ether at 0°C. The reaction mixture was worked up as in the literature.⁵ Chlorine gas was generated by the reaction of KMnO₄ with conc. HCl which was passed through water, followed by conc. H₂SO₄.

Preparation of azo-bis-2-phenoxy-2-propane (6). To a 180 ml of 75% aq. ethanol containing 5.4g (0.14 mmol) of NaOH was added 15g (0.16 mmol) of phenol. After the solution cooled to room temperature, 12.9g (0.07 mol) of **8** was added little by little by which time yellow precipitates were formed. The reaction mixture was additionally stirred for 30 min, followed by dilution with 160 ml of water. The yellow solid was filtered, washed with water, followed by recrystallization from methanol, yielding 4.2g (20%) of white solid: mp 90-90.5°C (lit.² 90-90.5°C); IR (KBr) 1595, 1490 (-N=N-)cm⁻¹; ¹H NMR (CDCl₃) δ 1.45 (s, 12H, CH₃), 6.90-7.20 (m, 10H, C₆H₅).

Preparation of azo-bis-2-(p-nitrophenoxy)-2-propane (9). To a 90 ml of 75% aq. methanol containing 3.5g (0.088 mol) of NaOH was added 12.5g (0.089 mol) of *p*-nitrophenol. The mixture was stirred at about 40°C to cause a homogeneous solu-