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Intramolecular excimer formation in model compounds for polyesters. Diesters from 2-naphthol and aliphatic dicarboxylic acids

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The propensity for the formation of bends in the flexible spacer in polyesters containing naphthyl units has been examined by the study of the fluorescence of a series of diesters. Steady state fluorescence spectra have been measured for the diesters Naph–OOC–$(CH_2)_m$–COO–Naph, $m = 2$–6, 'Naph' = 2-naphthyl, in dilute solution in solvents of differing viscosity, η. The dependence of the degree of intramolecular excimer formation on m, under circumstances where the dynamics of rotational isomerism in the flexible spacer is suppressed, is evaluated by extrapolation of the measurements to infinite η. The extrapolated results exhibit an odd–even effect, with the more intense excimer emission being observed when m is odd. The odd–even effect is rationalized by a rotational isomeric state analysis of the diesters.

(Keywords: conformation; excimer; fluorescence)

INTRODUCTION

If A denotes a group that is capable of forming an excimer, the dependence of the intensity of excimer emission on m in poly$(A–B_m)$ can provide information about the conformation and dynamics of B_m[1–4]. Here B is a conformationally flexible group, and m denotes the size of the flexible spacer. The excimer might be populated as a consequence of intramolecular energy migration in the polymer, but the influence of energy migration can be eliminated by studying the dimeric compound represented by $A–B_m–A$ instead of the macromolecule with repeating sequence $A–B_m$. This approach has recently been used for diesters with $A = C_6H_5–COO–$[5], as well as for diesters in which A is the 1- or 2-isomer of Naph–COO–[6,7], where Naph denotes naphthyl. A rotational isomeric state[8] analysis of the population of conformations of the flexible spacer at equilibrium was used to rationalize the dependence on m of the measured values of I_D/I_M in media of very high viscosity. Here I_D/I_M denotes the ratio of the intensities of excimer and monomer emission.

That approach is applied here to a series of diesters that are structural isomers of a series considered earlier. In both series, $B = CH_2$, and A contains a naphthalene ring that is singly substituted at position 2. In the series studied earlier[5] (*Figure 1a*), A was 2-Naph–COO–, and in the present series (*Figure 1b*) it is 2-Naph–OOC–. The reversal in direction of the ester group will, of course, influence the conformations accessible to the flexible spacer. The experimental results for I_D/I_M are presented here, along with the theoretical analysis based on rotational isomeric state theory.

EXPERIMENTAL DETAILS

Materials

Aldrich was the source of all solvents (spectrophotometric grade or 98% purity), reactants and 2-naphthyl acetate, which was used as a model compound. None of the solvents exhibited any stray bands in the fluorescence measurements. The diesters depicted in *Figure 1b* were synthesized from 2-naphthol (β-naphthol) and the acid chlorides of succinic, glutaric, adipic, pimelic and suberic acids, in the presence of triethylamine in chloroform at room temperature. The reaction mixture was washed several times, alternating between water and an aqueous solution of sodium bicarbonate. The diester from the organic phase was recrystallized twice from chloroform/methanol. T.l.c., n.m.r. and thermal analysis were used to characterize the diesters and the 2-naphthyl acetate. Melting points were 68° for the model compound and 162, 133, 134, 107 and 137° ($\pm 0.5°$) for the diesters with $m = 2$–6, respectively.

Absorption spectra

Absorption spectra were measured with a Hewlett–Packard 8451A diode array spectrophotometer. Freshly

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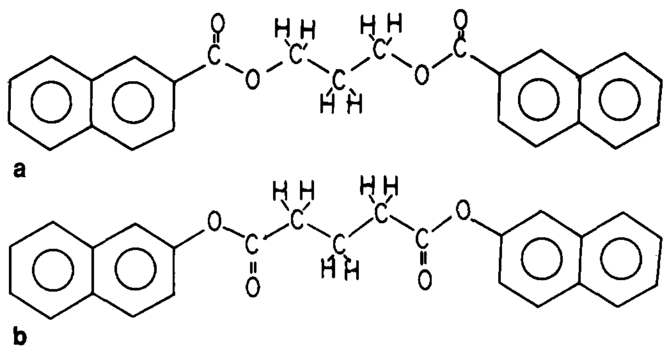

Figure 1 Covalent structures of the isomeric diesters derived from (a) 2-naphthoic acid chloride and a glycol, and (b) from 2-naphthol and a diacid chloride

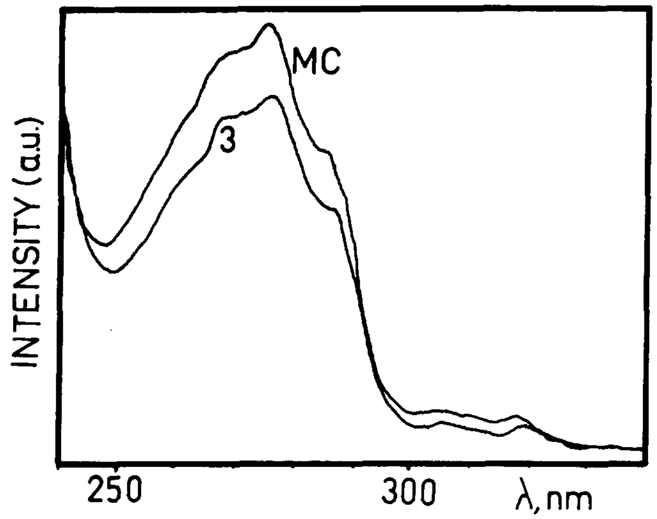

Figure 2 Absorption spectra for freshly prepared solutions in 1-propanol of 2-naphthyl acetate (MC) and the diester with $m = 3$ (3)

prepared solutions show similar features in ethylene glycol and in the various alcohols used as solvents. Illustrative spectra (for the model compound and the diester with $m = 3$, in 1-propanol at 25°) are depicted in *Figure 2*. There is a maximum at 276 nm and shoulders at 268 and 286 nm. A much weaker absorption is apparent near 320 nm. With time, new absorption bands appear at about 318 and 338 nm. The appearance of these new bands is accelerated by heating, and is faster in ethylene glycol as the solvent than in $H(CH_2)_n$–OH as a solvent. The focus here will be on the spectral properties of freshly prepared solutions.

Fluorescence

Fluorescence measurements were performed at 25° using an SLM 8000C fluorometer, equipped with a double monochromator in the excitation path. Slit widths were 8 and 4 nm for excitation and emission paths, respectively. The polarizers were set to magic angle conditions.

Figure 3 depicts excitation spectra from freshly prepared solutions of 2-naphthyl acetate and the diesters with $m = 2$ and 3. Each excitation spectrum shows four bands, located at about 290, 304, 318 and 266 nm. The maximum is near 290 nm. The emission was monitored at 336 nm in *Figure 3*. Similar spectra are obtained when the emission for freshly prepared solutions is monitored at other locations in this vicinity. With old solutions, in contrast, the excitation spectrum changes when the wavelength for monitoring the emission increases from 336 to 350 nm. The old solution then shows the strongest excitation band at 334 nm, and there is a shoulder near 320 nm.

Emission spectra were obtained at 25° for freshly prepared solutions, using excitation at 286 nm. Typical absorbances at the wavelength of excitation were in the range 0.1–0.2. *Figure 4* depicts the emission spectra when they are normalized at 336 nm, which is the location of the maximum intensity. The model compound also shows shoulders at 324 and 350 nm. The diester with $m = 2$ has a normalized emission spectrum that is indistinguishable from that of the model compound, 2-naphthyl acetate. The diesters with larger spacers exhibit an additional emission band at lower energies. This new band is most intense in the diester with $m = 3$. It seems to be located

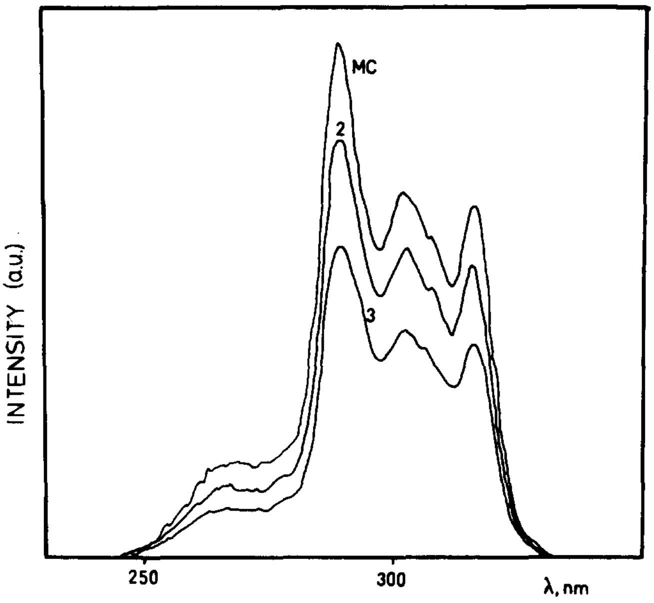

Figure 3 Excitation spectra at 25° for freshly prepared solutions of 2-naphthyl acetate (MC) and the diesters with $m = 2$ or 3 (2 or 3, respectively). Emission is monitored at 336 nm. The solvent is 1-propanol

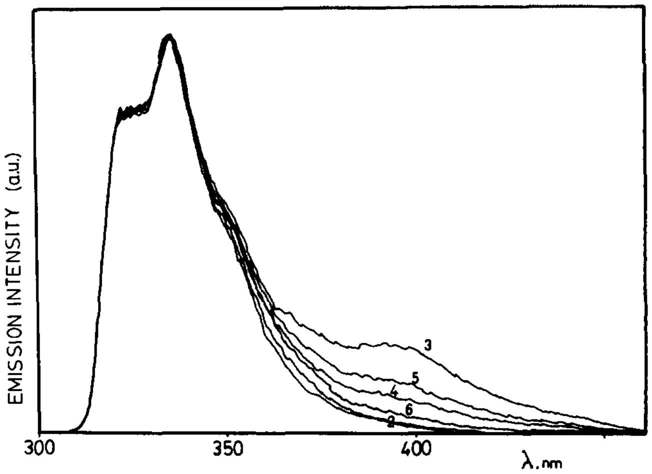

Figure 4 Normalized (at 336 nm) emission spectra at 25° in 1-propanol for naphthyl acetate and for the diesters with $m = 2$–6 (2–6, respectively). Excitation is at 286 nm

at about 400 nm. This band is attributed to emission from an intramolecular excimer.

The fluorescence lifetimes of the model compounds, 2-methyl naphthoate and 2-naphthyl acetate, are 7.4 and 6.6 ns, respectively, in methanol.

DEPENDENCE OF EXCIMER EMISSION ON m AND η

The dependence of excimer emission on m and the viscosity of the solvent, η, was monitored as I_D/I_M, using the intensities at 400 and 336 nm, respectively, according to:

$$I_D/I_M = [I_{d,400} - I_{m,400}]/I_{336} \qquad (1)$$

where 'd' and 'm' as subscripts denote the spectra, normalized at 336 nm, for the diester and model compound, respectively. The viscosity of the solvent was manipulated isothermally by using mixtures of methanol and ethylene glycol, and by using the $H-(CH_2)_n-OH$ with $n = 1-7$. The latter series will be used for the analysis because the spectra are less time dependent (the influence of ageing has a more rapid onset in ethylene glycol than in $H-(CH_2)_n-OH$). The results are depicted in *Figure 5* as I_D/I_M *versus* $1/\eta$. No convincing trend is apparent upon the change in η. This result for 2-Naph-OOC-$(CH_2)_m$-OOC-2-Naph stands in contrast with the behaviour of the structural isomers, 2-Naph-COO-$(CH_2)_m$-COO-2-Naph for which I_D/I_M decreases as η increases[6].

Extrapolation of the data in *Figure 5* to $1/\eta = 0$ yields $(I_D/I_M)_\infty$, the estimate of I_D/I_M in a solvent of infinite viscosity, where the dynamics of internal rotational isomerism over potential barriers is completely suppressed. The numerical values are 0, 0.17, 0.065, 0.083 and 0.021 for the diesters with $m = 2$, 3, 4, 5 and 6, respectively. The results display an odd-even effect, with the larger values of $(I_D/I_M)_\infty$ being observed when m is odd. In *Table 1* these values are compared with those reported previously[6] for the isomeric series, 2-Naph-COO-$(CH_2)_m$-OOC-2-Naph. Clearly the extrapolated values of $(I_D/I_M)_\infty$ are smaller in the present series than in the previous one.

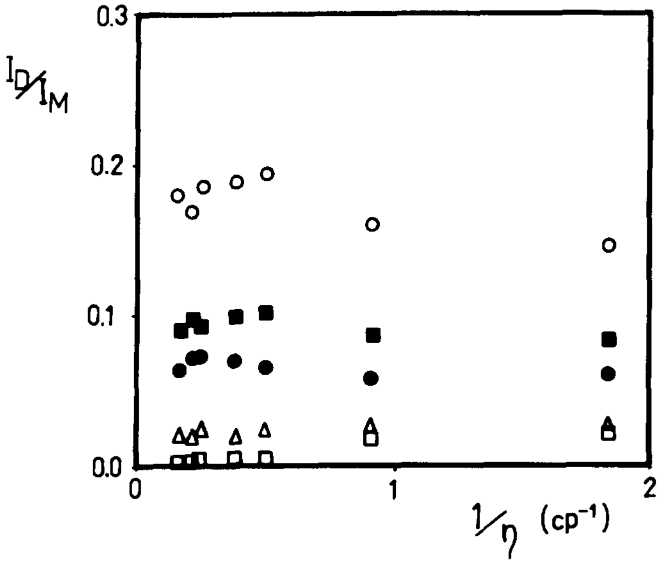

Figure 5 Dependence of I_D/I_M for the diesters on $1/\eta$ at 25°C in $H-(CH_2)_n-OH$, $n = 1-7$. The values of m are: (□) 2; (○) 3; (●) 4; (■) 5 and (△) 6

Table 1 Extrapolated values of $(I_D/I_M)_\infty$

m	N-OOC-$(CH_2)_m$-COO-N	N-COO-$(CH_2)_m$-OOC-N
2	0.00 ± 0.00	0.12 ± 0.03
3	0.17 ± 0.02	0.24 ± 0.05
4	0.06 ± 0.01	0.10 ± 0.02
5	0.08 ± 0.03	0.20 ± 0.01
6	0.02 ± 0.00	0.12 ± 0.01

'N' denotes 2-naphthyl. The results for N-COO-$(CH_2)_m$-OOC-N are from ref. 6, using isothermal methanol:ethylene glycol mixtures and thermal variation of ethylene glycol solutions to manipulate η

Table 2 Bond lengths and bond angles

Bond lengths (Å)	Bond angles (°)
$C^{ar}-C^{ar} = 1.40$	$C^{ar}-C^{ar}-C^{ar} = 120$
$C^{ar}-O = 1.30$†	$C^{ar}-C^{ar}-O = 120$
$C^*-O = 1.32$†	$C^{ar}-O-C^* = 122.9$†
$C^*-CH_2 = 1.50$†	$O-C^*-CH_2 = 118.3$†
$CH_2-CH_2 = 1.53$	$C^*-CH_2-CH_2 = 109.9$†
	$CH_2-CH_2-CH_2 = 112$

Values denoted by † have been optimized by minimization of conformational energies of naphthyl propionate. All other parameters are taken from Mendicuti *et al.*[2]

THEORETICAL INTERPRETATION OF $(I_D/I_M)_\infty$

Geometry

Figure 1b depicts 2-Naph-OOC-$(CH_2)_3$-COO-2-Naph in the conformation that has *trans* states (taken as $\phi = 180°$) at all of the bonds in the flexible spacer. The geometry of the ester group was optimized with Sybyl[9] by minimizing the energy of naphthyl propionate. The geometry of the remainder of the molecule is standard, and was taken from Mendicuti *et al.*[2]. The bond lengths and bond angles are summarized in *Table 2*.

Dihedral angles

The dihedral angles will be denoted by ϕ for the C-C bonds and by Φ for the $C^{ar}-O$ bonds, where C^{ar} denotes a carbon atom in the naphthalene ring system. There are four equally weighted states at the $C^{ar}-O$ bond with dihedral angles of $0° \pm \Delta\Phi$ and $180° \pm \Delta\Phi$. The out-of-plane rotation for the $C^{ar}-O$ bond (angle $\Delta\Phi$) was fixed at 60° (even for the energy minimization) according to the results reported by Hummel and Flory[10] for phenyl acetate. Their results are in agreement with the X-ray analysis[11,12], and they also permit calculation of accurate dipole moments for several *meta*-chlorophenyl esters[13-17]. With the exception of the diester with $m = 2$, neither the geometry nor the value of $\Delta\Phi$ is critical for the properties that are calculated here.

Three states denoted by t, g^+, g^- were used for each C^*-CH_2 bond (C^* denotes the carbonyl carbon atom) and the m-1 CH_2-CH_2 bonds. Each of these states was assigned three dihedral angles. The central of these three dihedral angles was 180° for t, and $\mp 60°$ for $g^\pm$. The other two dihedral angles for each state were located $\pm\Delta\phi$ from the central angle. Differences in conformational energy produced by rotations of $\pm\Delta\phi$ from t, g, or g^- were ignored. The purpose of $\Delta\phi$ is to mimic the effect of the rapid torsional oscillations that can occur within each rotational isomeric potential well. The value was uniformly assigned as $\Delta\phi = 20°$, as was done previously[6].

Statistical weights

The statistical weights used for the first- and second-order interactions in the t, g^+, g^- states at the C–C bonds are presented in *Table 3*. Most of these parameters have been used before in calculations of this type[2,18,19]. Three of these parameters deserve special attention here.

The factor ω_2 for the diester with $m = 3$ is the statistical weight for the second-order interaction C* ... C*. The computed probability for excimer formation in this diester increases sharply with ω_2 (decreases with E_{ω_2}) because all excimer forming conformations place the central two bonds in the state $g^{\pm}g^{\mp}$. The value assigned here to E_{ω_2}, 0.8 kcal mol^{-1}, provides the best agreement between computation and experiment.

The energy E_{σ_1} is usually[20,21] taken to be slightly smaller than E_{σ_2}. The preference for *trans versus gauche* states is supposed to be smaller in C^*CH_2–CH_2CH_2 than in CH_2CH_2–CH_2CH_2. Strictly speaking, the value of E_{σ_1} should be different at $m = 2$ and at larger values of m. However, the successful prediction of a very low probability of excimer formation at $m = 2$ results from the assignment of ω_2, and is insensitive to plausible variation in σ_1 after the assignment of ω_2 has been made. For this reason no attempt has been made to resolve a unique value of E_{σ_1} at $m = 2$.

The value of E_σ is more difficult to assign. Very different results for this parameter, ranging from positive (*trans* strongly favoured) to negative (*gauche* strongly favoured) have been reported. The status of this parameter has been reviewed by Abe[20], who uses $E_\sigma = 1.2$ kcal mol^{-1}, and by Riande and Guzmán, who used a value near zero. The range used in the calculations reported here is -1–2 kcal mol^{-1}.

Results of the calculations

The two naphthalene rings in most of the diesters can be brought into a face-to-face 'sandwich' geometry by appropriate adjustments in the dihedral angles at the CH_2–CH_2, C^*–CH_2 and C^{ar}–O bonds. Here C* and C^{ar} denote carbonyl and aromatic carbon atoms, respectively. The criteria adopted for a geometry classified as conducive to the formation of an excimer were the same as those used previously for 2-Naph–COO–$(CH_2)_m$–OOC-2-Naph[6].

$$z_{\min} < |z| < z_{\max} \tag{2}$$

$$r^2 - z^2 < (x^2 + y^2)_{\max} \tag{3}$$

$$0 < \psi < \psi_{\max} \tag{4}$$

Table 3 Energies of first- and second-order interactions

Parameter	Order	Interaction	Energy (kcal mol^{-1})
σ	First	OOC^*–CH_2CH_2	Variable
σ_1 ($m = 2$)	First	OOC^*CH_2–CH_2C^*	0.3
σ_1 ($m \geqslant 3$)	First	C^*CH_2–CH_2CH_2	0.3
σ_2	First	CH_2CH_2–CH_2CH_2	0.5
ω	Second	$CH_2 \ldots CH_2$	2.0
ω_1 ($m = 2$)	Second	$OOC^* \ldots C^*$	2.0
ω_1 ($m > 2$)	Second	$OOC^* \ldots CH_2$	0.6
ω_2 ($m = 3$)	Second	$C^* \ldots C^*$	0.8
ω_2 ($m > 3$)	Second	$CH_2 \ldots C^*$	∞

First-order parameters represent the energy of *gauche* states over *trans* states, and second-order parameters are the penalty for the 'pentane effect' encountered when two successive bonds occupy *gauche* states of opposite sign

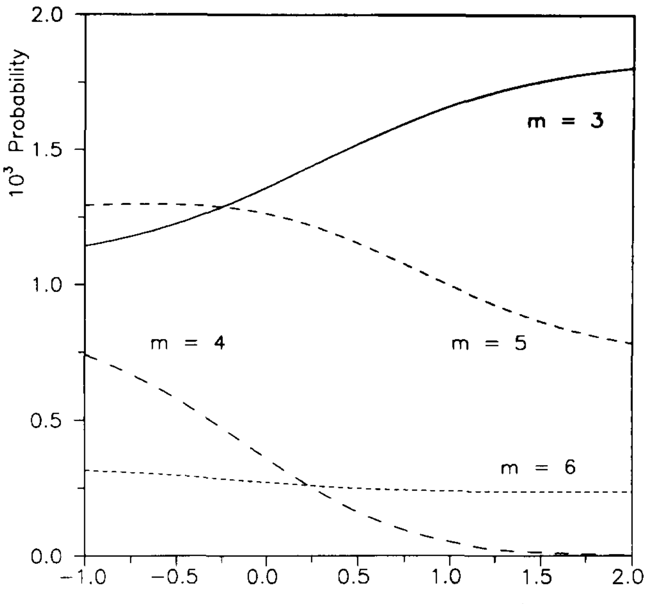

Figure 6 Dependence of p on E_σ for $m = 3$–6

These criteria use a distance between the centres of the rings of $z_{\min}$ and $z_{\max}$ (3.35 and 3.90 Å), a maximum radial offset between the centres of the rings of $(x^2 + y^2)^{1/2}_{\max}$ (1.35 Å) and an upper limit of $\psi_{\max}$ (40°) for the angle between the normals to the planes of the rings. All three criteria must be satisfied simultaneously if a conformation is to be classified as capable of forming an excimer. The results reported here are the sums of the probabilities for conformations in which there is an overlap of one or both rings.

None of the 9^3 conformations allowed to the diester with $m = 2$ simultaneously satisfies inequalities (2)–(4). The sequences $g^{\pm}g^{\mp}g^{\pm}$ are the only ones that give orientations in which those inequalities are almost fulfilled. In fact, the restrictions on ψ and z are satisfied, but the distance $(x^2 + y^2)^{1/2}$ is at least 1.9 Å. The three inequalities (2)–(4) can be satisfied by either increasing the displacement $\Delta\phi$ allowed at the rotational states in the skeleton, or by a small modification in the geometry of the ester group. Values of 124, 118 and 109° are required respectively for the bond angles C^{ar}–O–C^*, O–C^*–CH_2, and C^*–CH_2–CH_2, instead of the values 122.9, 118.3 and 109.9° that are assigned in *Table 2*. Even after adjustment of the geometry of the ester groups, the compound with $m = 2$ is the one in which the probability of an excimer is smallest (roughly four orders of magnitude smaller than for the compound with $m = 3$). The probability remains small because the excimer forming conformations are weighted by ω^2, and E_ω is 2 kcal mol^{-1}.

Figure 6 depicts p as a function of E_σ for $m = 3$–6. Here p denotes the sum of the probabilities for those conformations that meet the criteria for the formation of an excimer by the overlap of one or both rings. The

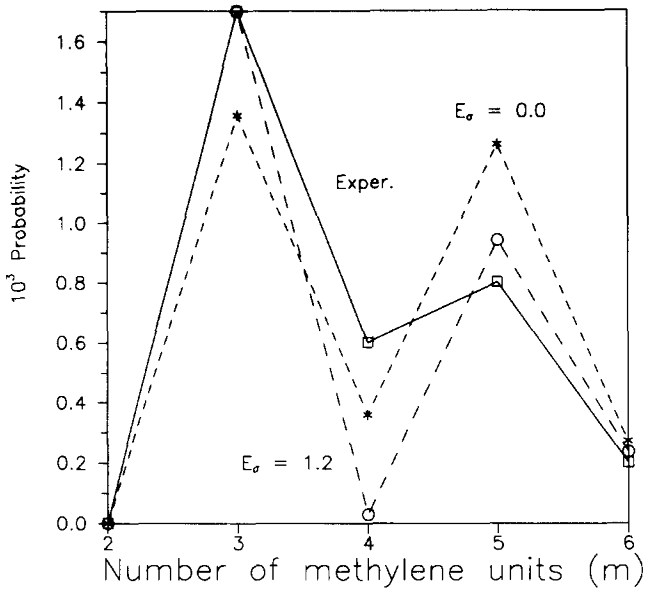

Figure 7 Dependence of p on m when E_σ is assigned at 0.0 or 1.2 kcal mol^{-1} (dashed lines). The solid line is the experimental results for I_D/I_M, scaled by the constant factor of 10^{-2}

odd–even effect, with larger values of p at $m = 3$ or 5 than at $m = 4$ or 6, is retained when E_σ is varied over a rather wide range.

Figure 7 depicts, using dashed lines, the results for p, as a function of m, when E_σ is assigned the values used by Abe[20] and by Riande and Guzmán[21]. The solid line is the experimental result for I_D/I_M, scaled by the constant factor of 10^{-2}. It is difficult to decide which of these two values of E_σ provides the better fit to the experimental results. The larger value of E_σ provides the better prediction at $m = 5$, and the smaller value provides the better prediction at $m = 4$. There is little basis for a preference when m is 2, 3 or 6.

The rotational isomeric state analysis clearly accunts for the observation of the odd–even effect in I_D/I_M in media of very high viscosity. The inability of the rotational isomeric state analysis to define uniquely the value of E_σ is remininscent of the rather large range of values that have been estimated for this parameter by previous workers[20,21].

ACKNOWLEDGEMENT

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