Intramolecular formation of excimers in model compounds for polyesters containing naphthalene units: α,ω-diesters from 1-naphthoic acid and five glycols

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The fluorescence of the α,ω-diesters of $HO(CH_2)_mOH$, $m = 2\text{--}6$, and 1-naphthoic acid has been characterized in dilute solution in solvents of different viscosity, η. The ratio of the intensity of the emission from intramolecular excimers and from individual naphthalene moieties, denoted by I_D/I_M, depends on m and on η. Extrapolation to a medium of infinite η shows a lower equilibrium contribution to the formation of intramolecular excimers than that observed previously in an analogous series of α,ω-diesters based on 2-naphthoic acid. With the series based on 1-naphthoic acid, a weak odd–even effect is observed, with the maximum value of I_D/I_M at $m = 5$. An equilibrium rotational isomeric state analysis can rationalize the observation of the odd–even effect and the occurrence of the maximum at $m = 5$. In media of low η, there is a substantial dynamic contribution to I_D/I_M.

INTRODUCTION

Fluorescence from intramolecular excimers formed by chromophores that are nearest neighbours can be detected from a wide variety of polymers in dilute solution. The polymers of this kind that are of interest in the present work can be represented by the repeating sequence $-A-B_m-$, where A denotes a chromophore that can participate in the formation of an excimer, and B is a flexible spacer. Consider the case where the optical properties of A, or the size of m, cause energy migration to be negligible. Then the dominant mechanism for the formation of an excimer will depend upon the relationship between the fluorescence lifetime of A, denoted by τ_f, and the time required for conversion of B_m from one rotational isomer to another, which is denoted by τ_r. If $\tau_f \ll \tau_r$, as seen, for example, in cases where A is terephthalate or isophthalate[1,2], the dominant mechanism for the formation of an excimer must be via minor adjustments in dihedral and/or bond angles within potential-energy wells. Consequently the dependence of I_D/I_M on m is susceptible to rationalization by conventional equilibrium rotational isomeric state theory[3], which provides the probabilities for observation of all of the rotational isomers of B_m[4,5]. Here I_D and I_M denote the intensities of the emission from the excimer and monomer, respectively.

Another mechanism for population of the excimer is activated as τ_f increases relative to τ_r. Now the conformation of B_m can change from one rotational isomer to another during the lifetime of the excited state. Consequently the dynamics of the rotational isomerism, which

was ignored when $\tau_f \ll \tau_r$, must now be considered in the evaluation of the dependence of I_D/I_M on m. This task requires utilization of dynamic rotational isomeric state theory[6-9], instead of the more widely known equilibrium rotational isomeric state theory[3]. Specifically, in the event that thermal dissociation of the excimer is negligible, the theory must produce the rate of first passage from the set of rotational isomers of $A-B_m-A$ that do not place the pendant As in a geometry conducive to formation of an excimer to the set of rotational isomers that do fulfil the geometric requirements[1,10].

The values of τ_f for A and τ_r for $-B_m-$ may satisfy the relationship $\tau_r < \tau_f$ in solvents of low viscosity η, but convert to the relationship $\tau_r > \tau_f$ in solvents of higher η, and finally to $\tau_r \gg \tau_f$ in the limit where η becomes infinite. In the last system, conventional equilibrium rotational isomeric state theory should be able to rationalize the dependence on m of the limiting values of I_D/I_M at infinite η. Dynamic rotational isomeric state theory would rationalize the dependence on m of different sensitivities of I_D/I_M to changes in η. The experimental characterization required for this purpose is reported here for model compounds for polyesters formed from either 1,4- or 1,5-naphthalene dicarboxylic acid and $HO(CH_2)_mOH$, $m = 2\text{--}6$. We also report the analysis, via conventional rotational isomeric state theory, of the values of I_D/I_M in the limit of infinite η. The model compounds are the α,ω-diesters of naphthoic acid and $HO(CH_2)_mOH$, which are depicted at the top of *Figure 1*. Use of these model compounds rigorously excludes any complications that might arise from energy migration, which might otherwise be a problem in view of the size of the Forster radius[11] for self-transfer in chromophores based on naphthalene.
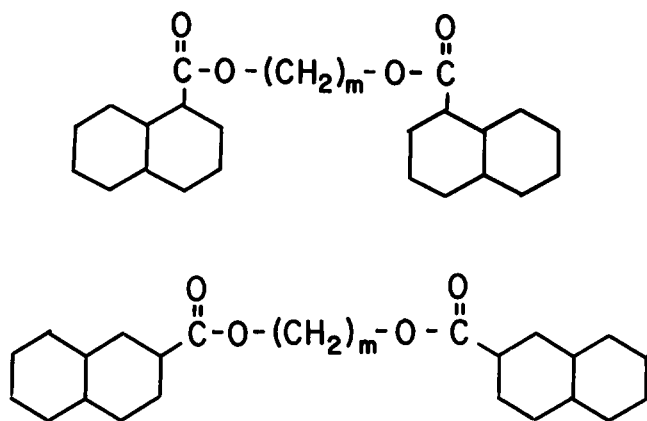
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Figure 1 Structures of the α,ω-diesters of 1-naphthoic acid (top) and 2-naphthoic acid (bottom)

The results are compared with those reported recently[12] for the related series at which 1-naphthoic acid is replaced by 2-naphthoic acid, as depicted at the bottom of *Figure 1*.

EXPERIMENTAL

Materials

The α,ω-diesters were synthesized by reaction of 1-naphthoyl chloride and $HO(CH_2)_mOH$ in the presence of triethylamine in chloroform at ambient temperature. The model compound, methyl 1-naphthoate, was synthesized by the same procedure, with substitution of methanol for the glycol. Purification was carried out as described earlier, and the purified samples were characterized by thin-layer chromatography and nuclear magnetic resonance spectroscopy[12]. The solvents were purchased from Aldrich and used without further purification.

Fluorescence

Steady-state measurements were performed at 20°C with an SLM 8000C fluorometer equipped with a double monochromator in the excitation path. Slits were 4 nm for excitation and for emission. The polarizers were set for magic-angle conditions[13]. Solvent blanks were measured and subtracted from the observed spectra. Typical absorbances at the wavelength of excitation, 298 nm, were about 0.1.

CHARACTERIZATION OF THE EXCIMERS IN THE α,ω-DIESTERS

Figure 2 depicts the absorption spectrum of methyl 1-naphthoate in ethylene glycol. The spectrum exhibits a maximum at 298 nm and a shoulder at 320 nm. The α,ω-diesters exhibited similar absorption spectra. Excitation for the fluorescence measurements was at 298 nm. The excitation and emission spectra of methyl 1-naphthoate are depicted in *Figure 3*. The excitation spectrum, which was measured using the emission at 400 nm, exhibits the maximum and shoulder that are apparent in the absorption spectrum. The emission spectrum was obtained with excitation at 298 nm, which is the location of the maximum in the absorption band. Similar excitation spectra are obtained with the α,ω-diesters, but the emission spectra are different, as will be shown below.

The shape of the excitation spectrum is not affected by changes in the wavelength for the emission.

The details of the shape of the emission band for methyl 1-naphthoate depend upon the solvent used in the measurement. In ethylene glycol the emission exhibits two overlapping bands of nearly equal intensity, as shown in *Figure 3*. The peaks are located at 376 and 395 nm. The positions of these two peaks are somewhat different in other solvents, and their relative intensity changes. For example, in methanol the same sample exhibits an emission with a peak at 371 nm and a shoulder at 390 nm. In this work, I_M will denote the intensity at the peak of higher energy in the emission spectrum of methyl 1-naphthoate. The location of this peak varies from 364 to 378 nm, depending on the solvent.

Figures 4 and *5* depict emission spectra for methyl 1-naphthoate and the α,ω-diesters prepared from $HO(CH_2)_mOH$ and 1-naphthoic acid, with $m = 2$–6. The spectra in *Figure 4* were obtained in ethylene glycol, for which $\eta = 19.90$ cP at 20°C, and the spectra in *Figure 5* were obtained in methanol, for which $\eta = 0.597$ cP at this temperature. The broad band at high wavelength in the
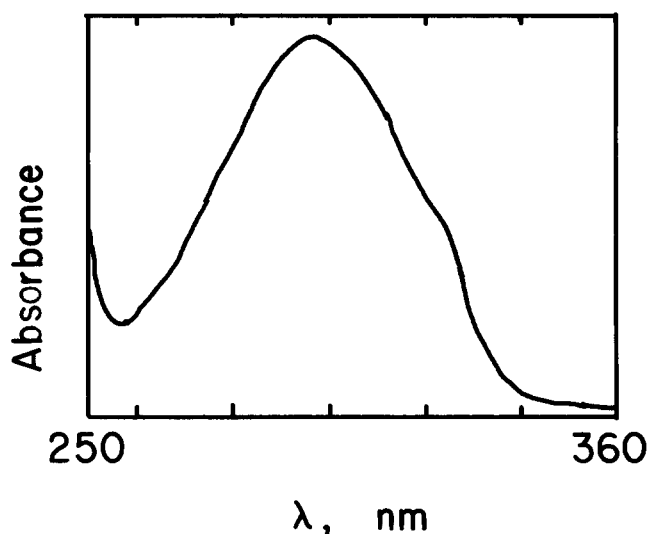

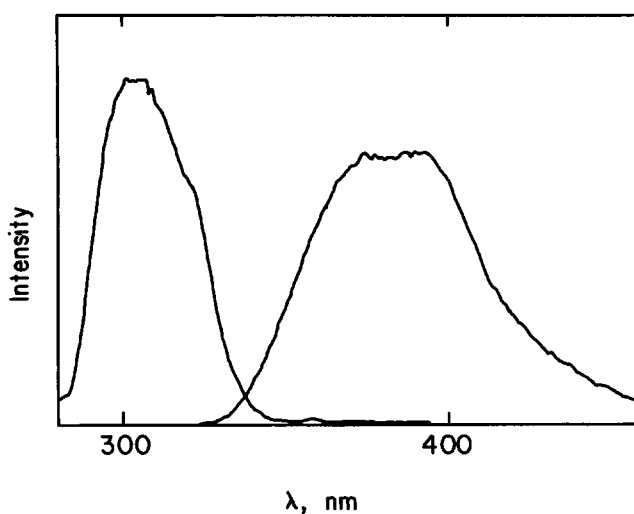**Figure 2** Absorption spectrum of methyl 1-naphthoate in ethylene glycol

Figure 3 Excitation (left) and emission (right) spectra for methyl 1-naphthoate in ethylene glycol
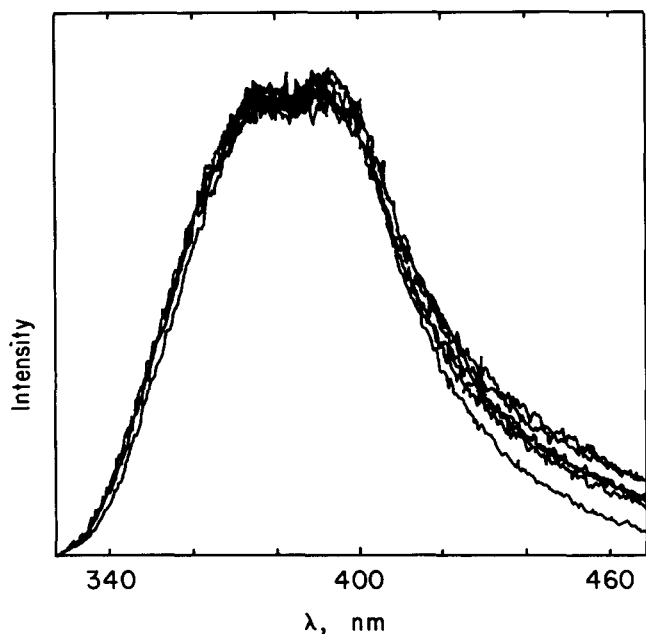
Figure 4 Emission spectra for methyl 1-naphthoate and the α,ω-diesters of $HO(CH_2)_mOH$ and 1-naphthoic acid. The spectra were measured in ethylene glycol, and they are normalized at 376 nm. At 450 nm, the two spectra with the highest intensities are those for the diesters with odd values of m, and the spectrum with the weakest intensity is the one for methyl 1-naphthoate. The three diesters with even values of m produce the spectra of intermediate intensities at 450 nm
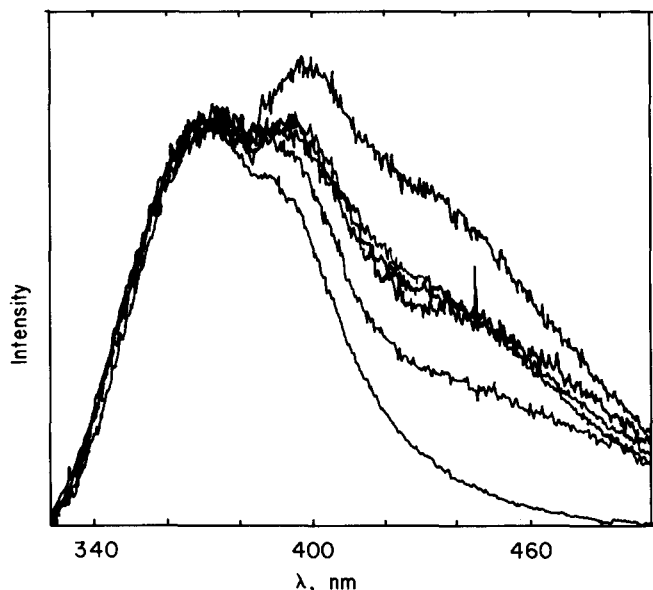

Figure 5 Emission spectra for methyl 1-naphthoate and the α,ω-diesters of $HO(CH_2)_mOH$ and 1-naphthoic acid. The spectra were measured in methanol, and they are normalized at 371 nm. At 450 nm, the spectra, in order of decreasing intensity, are $m=5$, $m=3$, 4 and 6, $m=2$ and methyl 1-naphthoate

spectra for the diesters in methanol is attributed to the intramolecular formation of excimers. This band is barely detectable in the more viscous solvent, ethylene glycol. For a quantitative measure of the importance of the emission from the excimer, we adopt the ratio I_D/I_M, which is calculated as:

$$I_D/I_M = [I(m, 450) - I(0, 450)]/I(\text{norm}) \quad (1)$$

where $I(m, 450)$ denotes the intensity at 450 nm for the diester with m methylene units, $I(0, 450)$ denotes the intensity at 450 nm for methyl 1-naphthoate and $I(\text{norm})$ denotes the intensity at the wavelength used for normalization of the spectra.

The fluorescence was also measured in mixtures of methanol and ethylene glycol. The results are presented in *Figure 6* as a function of $1/\eta$. All five diesters exhibit a decrease in I_D/I_M as η increases. The decrease in I_D/I_M is approximately linear in $1/\eta$ in the solvents with $\eta > 2.5$ cP. In less viscous solvents, I_D/I_M depends less strongly on η. Qualitatively similar behaviour was observed previously in the related series obtained from 2-naphthoic acid[12]. In this latter series, the deviations from linearity in I_D/I_M vs. $1/\eta$ became apparent at somewhat higher viscosity, near 4 cP. An odd-even effect is observed in all of the solvents, with I_D/I_M always being largest at $m=5$, and next largest at $m=3$. The values of I_D/I_M for the three samples with even m are most easily distinguishable from one another in the solvents of low viscosity, in which the sample with $m=2$ has a distinctly smaller value of I_D/I_M than the samples with $m=4$ or 6.

Measurements were also performed using as solvents the seven alcohols in the series $H(CH_2)_nOH$, $n=1-7$. The results are depicted in *Figure 7* as I_D/I_M vs. $1/\eta$. The qualitative features in this figure bear a close resemblance to those found in *Figure 6*.

The straight lines through the data at the higher viscosities in *Figures 6* and 7 define an intercept and a slope that provide different types of information about the population of excimers. The intercept at infinite η, denoted by $(I_D/I_M)_\infty$, can be taken to be proportional to the population of intramolecular excimers in the absence of rotational isomerism of the flexible spacer during the lifetime of the singlet excited state. Theoretical methods based on equilibrium statistics should be used to rationalize the intercepts. The initial slope, denoted by $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$, can be taken to be proportional to the ability of the flexible spacer to undergo dynamic rotational isomerism during the lifetime of the singlet excited state so that a non-excimer-forming conformation is converted into one that will form an excimer. *Tables 1* and 2 present the values of $(I_D/I_M)_\infty$ and $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$, respectively, that are obtained from *Figures 6* and 7.
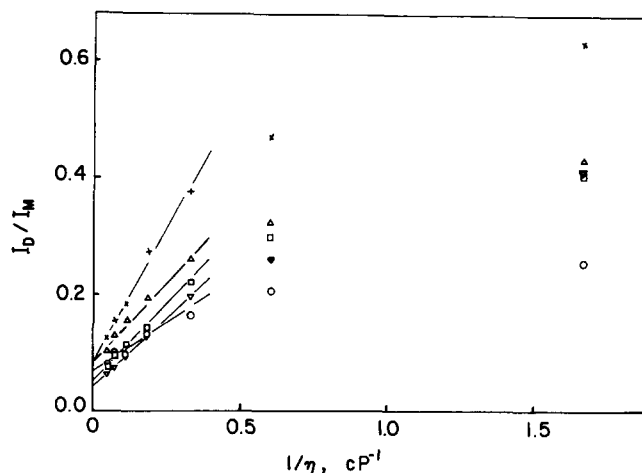

Figure 6 I_D/I_M vs. $1/\eta$ for five α,ω-diesters in mixtures of methanol and ethylene glycol. The values of m are 2 ($\bigcirc$), 3 ($\triangle$), 4 ($\square$), 5 ($\times$) and 6 ($\triangledown$)

The values of $(I_D/I_M)_\infty$ in *Table 1* show that the extrapolation to infinite viscosity retains an influence of the method used to manipulate η. Somewhat larger intercepts are obtained from the data in the methanol–ethylene glycol system than from the seven members of the $H(CH_2)_nOH$ series. However, the odd–even effect is readily apparent, with the average values of $(I_D/I_M)_\infty$ at odd m being distinctly larger than the averages obtained at even m. The values of $(I_D/I_M)_\infty$ in *Table 1* are smaller than those obtained previously[12] with the related series based on 2-naphthoic acid. Consideration of the equilibrium population of the various conformations of the flexible spacer should be used to rationalize the odd–even effect and the fact that $(I_D/I_M)_\infty$ is smaller in the series based on 1-naphthoic acid than in the series based on 2-naphthoic acid.

The values of $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$ for the α,ω-diesters from 1-naphthoic acid in *Table 2* depend somewhat on the means used to manipulate η, being about two-thirds as large in the $H(CH_2)_nOH$ series as in the mixtures of methanol and ethylene glycol. However, the two series
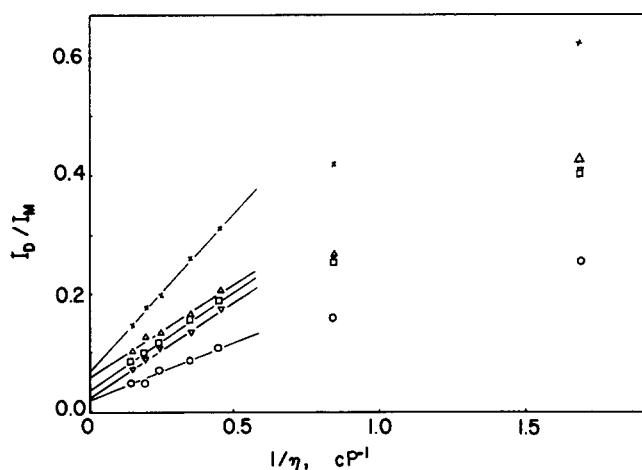
of results compare quite nicely when each is normalized to the result obtained at $m = 5$, as shown by the entries in parentheses in *Table 2*. The values of $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$ decrease in the order $m = 5 > m = 3$, 4, $6 > m = 2$. Comparison of the second and fourth columns in *Table 2* shows that the values of $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$ are smaller in the series obtained from 1-naphthoic acid than in the analogous series obtained from 2-naphthoic acid. Consideration of the dynamics of the rotational isomerism of the flexible spacer will be required to explain the trends with changing m, and also the smaller values of $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$ in the series based on 1-naphthoic acid.

ROTATIONAL ISOMERIC STATE ANALYSIS OF THE EQUILIBRIUM POPULATIONS

Except for the obvious change in the site of attachment of the ester group to the naphthalene ring, and the accompanying change in the rotational potential for the C^{ar}–C bond (see next paragraph), the rotational isomeric state model adopted here is identical with the one used previously[12] in the analysis of the α,ω-diesters of 2-naphthoic acid. The analysis must identify all rotational isomers that have two six-membered rings in each naphthalene group oriented so that the normals to their planes are parallel, the line joining the centres is parallel to the normals and the centres are separated by ~ 350 pm. Some tolerance in these objectives must be allowed, because the theoretical formalism does not sample conformational space continuously. The statistical weights used and the tolerances are exactly the same as those used previously[12].

Calculation of the conformational energy, using the Tripos force field in Sybyl 5.2 for the molecular modelling, as a function of the rotation about the C^{ar}–C bond in methyl 1-naphthoate yields four minima. These minima occur at $\pm 45°$ and $\pm 135°$ if the naphthalene is constrained to remain planar. The minima move to $\pm 30°$ and $\pm 150°$ if distortions in the naphthalene ring are allowed. In either case, the conformational energies at the four minima are not distinguishable, and hence all four rotational isomers at the C^{ar}–C bond are weighted equally. An equivalent treatment of methyl 2-naphthoate yields two minima, at $0°$ and $180°$, with the ester group in the plane of the naphthalene ring. These minima are suppressed in methyl 1-naphthoate because of the repulsive interaction of the oxygen atoms in the ester group with the C^{ar} at position 8 in the adjacent ring when the ester group and naphthalene ring are coplanar.

The observations that I_D/I_M is smaller in the α,ω-diesters of 1-naphthoic acid than in the α,ω-diesters of

Figure 7 I_D/I_M vs. $1/\eta$ for five α,ω-diesters in seven alcohols, $H(CH_2)_nOH$ with $n = 1$–7. The values of m for the diesters are 2 (○), 3 (△), 4 (□), 5 (×) and 6 (▽)

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

m	CH_3OH–$HOCH_2CH_2OH$	$H(CH_2)_nOH$	Range
2	0.065	0.026	0.045 ± 0.020
3	0.084	0.061	0.072 ± 0.012
4	0.047	0.033	0.040 ± 0.007
5	0.082	0.069	0.075 ± 0.007
6	0.037	0.027	0.032 ± 0.005

Table 2 Values of $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$ (cP)^a

m	α,ω-Diesters of 1-naphthoic acid		α,ω-Diesters of 2-naphthoic acid
	CH_3OH–$HOCH_2CH_2OH$	$H(CH_2)_nOH$	CH_3OH–$HOCH_2CH_2OH$
2	0.30 (0.33)	0.19 (0.34)	0.83 (0.48)
3	0.53 (0.59)	0.32 (0.57)	1.47 (0.85)
4	0.51 (0.57)	0.35 (0.62)	1.35 (0.78)
5	0.90 (1.00)	0.56 (1.00)	1.14 (0.66)
6	0.46 (0.51)	0.33 (0.59)	1.73 (1.00)

^{a} Values in parentheses are normalized to the largest $[\partial(I_D/I_M)/\partial(1/\eta)]_\infty$ in each series. The data for the α,ω-diesters of 2-naphthoic acid are from ref. 12

Table 3 Probabilities for conformations conducive to formation of an excimer, using three different assumptions about long-range interactions and two different assumption for the dihedral angle at C^{ar}–C (see text for further details)

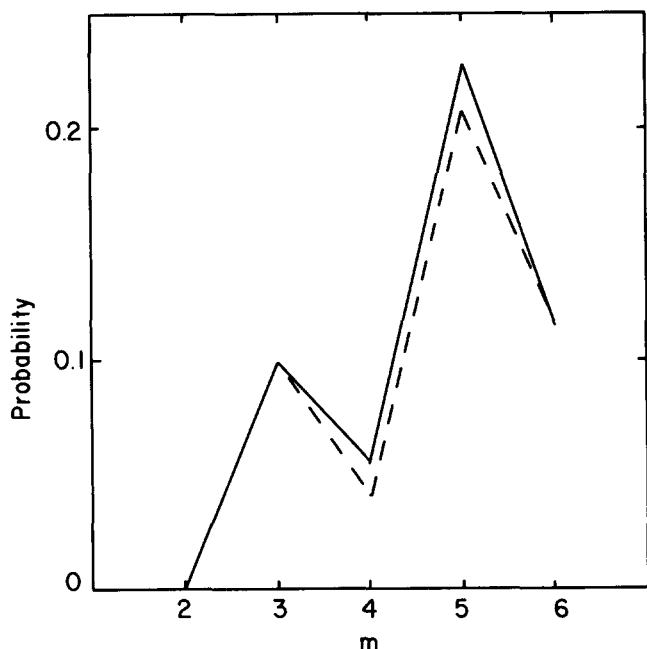|	None		Ring		Ester	
m	45°	30°	45°	30°	45°	30°
2	0.0008	0.0010	0.0006	0.0002	0.0003	0.0000
3	0.099	0.099	0.011	0.020	0.099	0.085
4	0.042	0.056	0.014	0.015	0.042	0.055
5	0.209	0.229	0.055	0.066	0.113	0.109
6	0.113	0.115	0.027	0.024	0.110	0.112

Figure 8 Dependence of m of probabilities calculated from rotational isomeric state theory with inclusion of first- and second-order interactions, and values of the dihedral angle at C^{ar}–C that rotate the ester groups 30° (full lines) or 45° (broken lines) from the plane of the naphthalene ring

2-naphthoic acid can be explained by the differences in the conformational preferences at the C^{ae}–C bond. Rotation away from 0° or 180° at the C^{ar}–C bond renders the ester group non-coplanar with the naphthalene ring. It brings the oxygen atoms of the ester group into a position where they inhibit the approach of a second naphthalene group that is required for the formation of the planar sandwich geometry that characterizes a singlet excimer of naphthalene[14].

Table 3 presents the sums of the probabilities for occupancy of all conformations that satisfy the criteria for formation of an excimer, based on two different assignments for the dihedral angle at C^{ar}–C and on three different assumptions about the role of interactions of higher than second order. Under 'None' are listed the results obtained upon consideration of no interactions of range longer than second order. In addition to the first- and second-order interactions, interactions of long range involving C(5), C(6), C(7) and C(8), as well as their pendant hydrogen atoms, are considered in the entries under the columns headed 'Ring'. Conformations are discarded if these two rings interfere with one another.

Finally, interactions of long range involving the ester groups are considered under the columns headed 'Ester'. In the entries under this heading, all conformations in which the carbonyl carbon atoms are separated by less than 268 pm are discarded. Two sets of data are presented under each heading. The data tabulated under '45°' use dihedral angles at the C^{ar}–C bond that are at the conformational energy minima when the naphthalene ring is restricted to be planar. The sets of data tabulated under '30°' employ dihedral angles at the minima when the naphthalene is subject to distortion.

In the first two columns of data in *Table 3*, the largest entry is the one at $m = 5$. Also the entry for $m = 3$ is larger than the entries for $m = 2$ and 4. Consequently, the appearance of an odd–even effect in I_D/I_M, and the appearance of the maximum at $m = 5$, can be rationalized in a qualitative fashion by consideration of first- and second-order interactions only. The results are depicted in *Figure 8*. Comparison with the values of $(I_D/I_M)_\infty$ in *Table 1* shows that, while the theoretical analysis correctly identifies the maximum and the odd–even effect, it underestimates the importance of excimers at $m = 2$, and does not capture the fact that nearly identical values of $(I_D/I_M)_\infty$ are obtained at $m = 3$ and 5.

Specific inclusion of the higher-order interactions involving C(7), C(8), C(9) and C(10) of the naphthalene rings, as well as their pendant hydrogen atoms, reduces the values of the probabilities for every value of m and choice of dihedral angle at C^{ar}–C, as shown by the entries in the third and fourth columns of data in *Table 3*. The maximum still occurs at $m = 5$ in each column. The odd–even effect is retained if the dihedral angle at C^{ar}–C is assigned the values obtained in the optimized structures, but not if it is 45°. Specific inclusion of the long-range interactions of the two ester groups has the greatest effect on the values at $m = 5$, as can be seen by comparing the last two columns of data in *Table 3* with the first two columns. The maximum remains at $m = 5$ only if the dihedral angle at C^{ar}–C is at 45°. When this dihedral angle is decreased to 30°, the maximum moves to $m = 6$. Specific inclusion of these two types of long-range interactions does not appreciably improve the qualitative rationalization that was achieved through consideration of interactions no higher than second order.

ACKNOWLEDGEMENTS

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