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Intramolecular Excimer Formation Dynamics of *meso*-Bis[1-(2-pyrenyl)ethyl] Ether Studied by Single-Photon Timing with Simultaneous Analysis

R. Andriessen, F. C. De Schryver,* and N. Boens

Chemistry Department, K. Universiteit Leuven, Celestijnenlaan 200F,
B-3030 Heverlee-Leuven, Belgium

N. Ikeda and H. Masuhara

Department of Polymer Science and Engineering, Kyoto Institute of Technology,
Matsugasaki, Kyoto 606, Japan. Received July 19, 1988

ABSTRACT: The excited-state kinetics of *meso*-bis[1-(2-pyrenyl)ethyl] ether is reinvestigated in isooctane. With the use of nonstationary fluorescence techniques, kinetic and thermodynamic parameters of intramolecular excimer formation are obtained, and the existence of two conformers in the ground state of this compound is demonstrated.

Introduction

The photophysics of 2,4-diarylpentanes[1–4] and bis(1-arylethyl) ethers[5,6] as first-order model compounds for vinyl polymers[7] elucidated a number of features of the behavior of these compounds in solution. A more detailed knowledge of the molecular dynamics of these systems, in the ground and excited states, is being acquired.

The distribution of the possible conformers in the ground state has been intensively investigated by means of ^{1}H NMR spectroscopy.[8–10] In the case of *meso*- and *rac*-2,4-di(2-pyrenyl)pentane (D2PP), one can obtain information about the ground-state distribution of the con-

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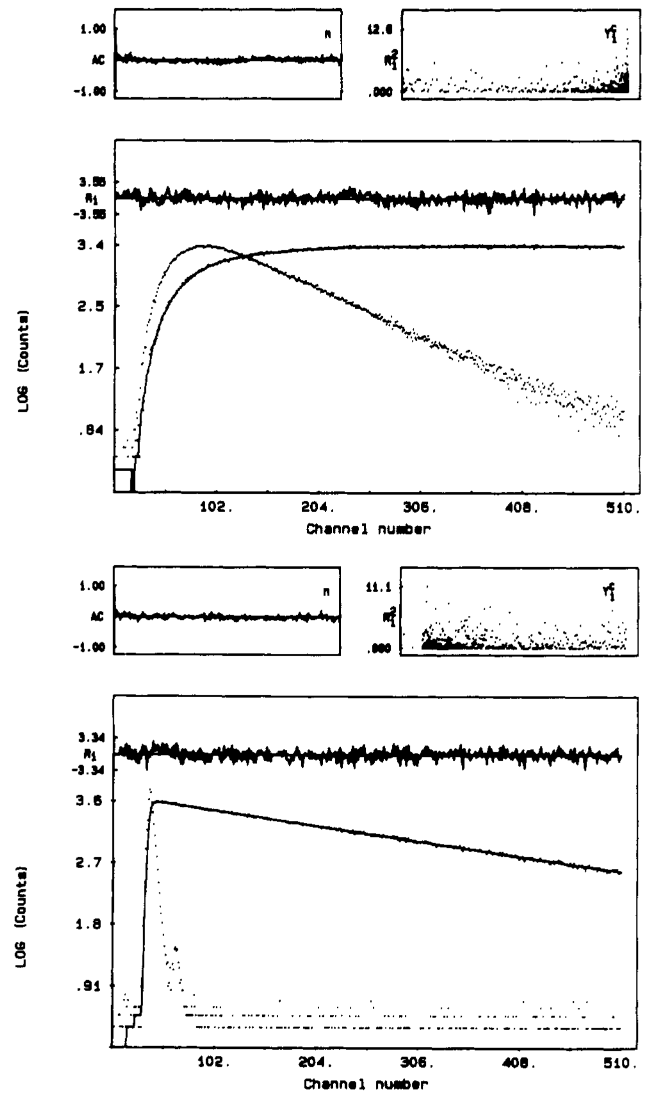


Figure 1. Fluorescence decay curves of *meso*-B2PEE in isooctane at -43.5 °C: λ_{exc} = 330 nm, λ_{anal} = 500 nm, channel width = 0.019 ns (top) and 0.488 ns (bottom), λ_1^{-1} = 1.53 ns, λ_2^{-1} = 96.81 ns, χ_ν^2 = 1.048 (top) and 1.043 (bottom) (Durbin-Watson = 1.83 (top) and 1.87 (bottom)).

formers of these products by means of ^{1}H NMR spectroscopy according to the method described by Bovey.[11]

Time-resolved fluorescence studies make it possible to elucidate the excited-state processes of these products.[4] Zachariasse et al.[9] reported recently a deviation from unity[12] of the ratio of the preexponentials in the excimer region for *meso*-2DPP. This was attributed to the presence of a preformed "excimer conformation" in the ground state. This, in turn, suggested the existence of the TT conformation in the ground state at room temperature. ^{1}H NMR analysis of *meso*-D2PP confirmed the presence of about 10% TT conformation in toluene at room temperature. An instantaneous formation of excimer after excitation of TT does change the kinetic analysis of the time-resolved fluorescence decays.[9]

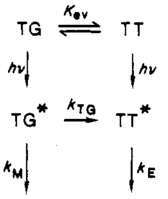
Earlier single-curve calculations of SPT measurements of *meso*-bis[1-(2-pyrenyl)ethyl] ether (B2PEE) revealed no significant deviation from unity within the experimental error for the ratio of preexponentials in the excimer region of *meso*-B2PEE, and so it was assumed that only the TG/GT conformer could be present.[8]

Picosecond laser absorption measurements revealed the existence of a preformed excimer in the ground state for *meso*-B2PEE because an instantaneous rise of excimer component within a pulse width was observed.[13] This suggested also the presence of the TT conformer in the ground state which forms an excimer without any significant conformational change.

Table I
Decay Parameters of *meso*-B2PEE at Different Temperatures in Isooctane

temp, °C	λ_1^{-1}, ns	λ_2^{-1}, ns	$-A_{21}/A_{22}$
-90	8.88	99.03	0.894
-80	5.02	97.55	0.861
-70	3.60	98.21	0.822
-43.5	1.53	96.81	0.719
-30	1.03	94.52	0.669
-15	0.73	93.50	0.626
0	0.52	91.14	0.565
17.5	0.42	88.23	0.507
33.5	0.35	85.60	0.427
50.5	0.33	80.37	0.342

Scheme I



Those data and the availability of global analysis[14-16] led us to reevaluate the fluorescence decay of *meso*-B2PEE by analyzing simultaneously decays at different wavelengths and time increments.

Experimental Section

The same experimental setup has been used as described before[8] except that the decays were analyzed globally. All measurements were done in isooctane (Merck UVASOL).

Results and Discussion

A two-exponential decay is observed for *meso*-B2PEE in the excimer region (Figure 1) over a temperature range from 183 to 223 K: a growing-in component, which is ascribed to the formation of the excimer from the locally excited state, and one decay, which is ascribed to the decay of the excimer. Picosecond time-resolved transient absorption measurements show a rise time of the excimer at room temperature of about 300 ps,[13] which is in good agreement with the 0.38 ns we obtained with the SPT technique.

Measurements at different time increments can be linked in the simultaneous analysis of multiple-decay curves, giving more accurate values for the decay parameters, and it is clear, as is pointed out in Table I, that the ratios of preexponentials in the excimer region at different temperatures do not equal unity.

Taking the existence of the TT conformer into account leads to Scheme I, in which TT* represents the excimer conformation and TG* the locally excited state.

At low temperatures, when there is a linearity in the plot of the ratio of the quantum yields of monomer and excimer fluorescence versus the reciprocal of the temperature,[8] the return from the excimer to the locally excited state is neglectable and one can assume that the system obeys Scheme I. The differential equations are than given by

$$d[TG^*]/dt = -X_G[TG^*] \tag{1}$$

$$d[TT^*]/dt = k_{TG}[TG^*] - X_T[TT^*] \tag{2}$$

where

$$X_G = k_M + k_{TG}$$
$$X_T = k_E$$

Table II
Kinetic and Thermodynamic Parameters of *meso*-B2PEE in Isooctane

$E_{TG} = 12 \pm 2$ kJ mol^{-1}	$E_{GT} = 16 \pm 2$ kJ mol^{-1}
$k_{TG}° = 3.1 \times 10^{11}$ s^{-1}	$k_{GT}° = 1.12 \times 10^{12}$ s^{-1}
$\Delta H° = -4 \pm 1.2$ kJ mol^{-1}	$\Delta S° = 11 \pm 3$ J mol^{-1} K^{-1}

In this case the boundary condition [TT*] at $t = 0$ is equal to zero no longer applies, and one has to take the equilibrium constant, K_{ev}, into account:

$$K_{ev} = \frac{[TT]_{\text{ground state}}}{[TG]_{\text{ground state}}} = \frac{[TT^*]_{t=0}}{[TG^*]_{t=0}} \qquad (3)$$

Using this condition, the time dependencies of TG* and TT* are expressed as

$$[TG^*](t) = [TG^*]_{t=0} \exp(-X_G t) \qquad (4)$$

$$[TT^*](t) = \left[\frac{k_{TG}}{K_{ev}(X_T - X_G)}\right][TT^*]_{t=0} \exp(-X_G t) + \left[1 - \frac{k_{TG}}{K_{ev}(X_T - X_G)}\right][TT^*]_{t=0} \exp(-X_T t) \qquad (5)$$

Therefore, at low temperatures, $10^9\lambda_1 = X_G$ and $10^9\lambda_2 = X_T$.

The decay of the locally excited state is globally analyzed as a two-exponential function which could be linked with the decay times found in the excimer region. The reason for this two-exponential decay, instead of a one-exponential decay, is due to the overlap with the large excimer band even at 377 nm. The excimer state shows a two-exponential decay as described. The following expression can now be derived from eq 5:

$$K_{ev} = (|A_{22}|/|A_{21}| - 1)k_{TG}/(X_G - X_T) \qquad (6)$$

Using eq 6, one can calculate the amount of molecules in the TT conformation in the ground state. At room temperature about 9% of the molecules of *meso*-B2PEE in isooctane are in the TT conformation, whereas at 51 °C already 16% of the molecules are in the TT conformation. Apparently some of the pyrene chromophores tend to come together to produce a kind of self-solvating situation in which the negative effect on the entropy by lowering the state of disorder is compensated for by the favorable van der Waals interactions between the aromatic rings.

The variation of K_{ev} with temperature can be used to determine $\Delta H°$ and $\Delta S°$ for the conformational equilibrium in the ground state between TG/GT and TT. Their values are 8.5 kJ mol^{-1} and -5.5 J mol^{-1} K^{-1}, respectively.

The SPT measurements enable us also to calculate the entropy and enthalpy changes in the excited state for the excimer formation. At higher temperatures, where return from the excimer state to the locally excited state becomes possible, the rate constant, k_{GT}, can be calculated with

$$k_{GT} = 10^9(\lambda_1 + \lambda_2) - k_M - k_{TG} - k_E \qquad (7)$$

The values are shown in Table II and correspond to the linear free energy relationship for excimers found by Zachariasse et al.[17]

Conclusion

Simultaneous analysis of SPT data enabled us to obtain more detailed information about the molecular dynamics of *meso*-B2PEE, and in this special case, fluorescence measurements make it possible to calculate the thermodynamics of this system in the ground state. The analysis showed that at 25 °C about 10% of the TT conformer is present.

Acknowledgment. We are indebted to the F.K.F.O., the F.G.W.O., and the Ministry of Scientific Programming for financial assistance to the laboratory. R.A. thanks the N.F.W.O. for a doctoral fellowship.

Registry No. B2PEE, 108346-77-6.

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