Experimental Evidence for a Highly Reversible Excited State Equilibrium between s-Cis and s-Trans Rotational Isomers of 2-Methoxynaphthalene in Solution

Ioanna Balomenou and George Pistolis*

Contribution from the NCSR “Demokritos” Institute of Physical Chemistry, 153 10 Athens, Greece

Received June 25, 2007; E-mail: pistolis@chem.demokritos.gr

Abstract: Detailed studies on the kinetics and the thermodynamics of the excited-state torsional isomerization of the title molecule (1) relative to exocyclic C2–O bond, when dissolved in 3-methylpentane, are reported by means of nontime- and time-resolved fluorescence spectroscopy. Over the broad temperature range studied, 1 exists in spectrally distinct, thermally equilibrated s-cis and s-trans conformations in the ground state (S0). In the lowest excited singlet state (S1) and above 260 K a pure adiabatic interconversion channel is activated that interconverts s-cis* and s-trans* conformers through a nearly fully reversible isomerization pathway with an activation energy of about 29 kJ/mol. The excited-state equilibrium constant is found to be remarkably temperature-independent just barely exceeding 1 above 260 K. Contrary to the predominantly irreversible photosomerization mechanism generally observed in related compounds, this work provides insights into the high reversibility of an excited-state rotameric equilibration in solution.

1. Introduction

Rotational isomerism in the excited state is a photochemical mechanism which interconverts s-cis* and s-trans* conformers during their lifetime, upon rotation about the single bond that joins a suitable conjugated group to an aromatic moiety (Aryl−C=−).1−7 Manifestation of the rotational isomerization in the singlet excited state of 2-vinyl-anthracene (2VA) and its α- or β′-dialkyl derivatives was originally reported from Barbara and co-workers,1 and later 2VA was reinvestigated by others.2 Thereafter the above photodynamic scheme was demonstrated in similar systems including 3,3′-dimethylstilbene,3 2-anthryl-ethylenes,4 N-methoxy-1-(2-anthryl)ethanimine derivatives,5 and 1,3-di-(3′-thioklythenyl)benzene.6 The one-way photochemical adiabatic isomerization of aromatic olefins has also been comprehensively reviewed by Arai and Tokumaru.7

It is generally accepted that the above torsional photosomerization process proceeds one way2−4,7 (forward), from the higher to the lower energy rotamer; the opposite way (reverse), if existing, is not significant and has no substantial effect on the observable thermal activation parameters.1 Very recently the above photodynamic scheme was demonstrated experimentally for 2-methoxynaphthalene and some of its derivatives in solution.8 In the above work it is proposed that one-way interconversion from the s-cis* into the s-trans* conformations, within their singlet excited-state lifetimes, takes place.8 The s-cis and s-trans configuration are assigned according to the orientation of the methoxy group relative to the long axis of the anthracene subunit. However, the absence of pure rotameric spectroscopic analysis and the lack of accurate theoretical methods to date, capable of reliably handling the sizable electronic features of 2-methoxynaphthalene and its derivatives,8 prevent an in-depth kinetic analysis for these compounds. On the contrary, the simpler analogue 2-methoxynaphthalene (1) has been extensively studied by jet-cooling spectroscopy and ab initio calculations,9 although so far it is unexplored in the condensed phase. We now report mainly on the excited-state dynamics of rotameric interconversion of 1, addressing specifically the issue of possible new kinetic manifestations on torsional isomerization in solution. The general scheme of our investigations is given below.

2. Experimental Section

2.1. Materials: 2-Methoxynaphthalene (1) was purchased from Fluka and was first purified by vacuum sublimation and then by recrystallization from a mixture of methanol and chloroform. 3-Methylpentane


(3MP) was filtered through a water-cooled chromatographic column packed with a combination of silica gel (activity grade I) in the lower half and basic alumina (super active) in the upper half. Finally, it was distilled in a glass-filled column under an argon atmosphere.

2.2. Instrumentation and Methods: Absorption spectra were recorded on a Perkin-Elmer Lambda-16 spectrophotometer. Steady-state fluorescence spectra were accomplished by the Perkin-Elmer model LS-50B and the Edinburgh Instruments model FS-900 spectrofluorometer. Fluorescence lifetimes \( \tau \) were determined using the time-correlated single-photon counter FL900, of the above Edinburgh Instruments setup, which is capable of measuring lifetimes down to 100 ps. For measurements at ambient temperatures, the samples were degassed by using the freeze–pump–thaw technique six or more times. For low-temperature experiments samples were degassed by bubbling nitrogen (99.9999%). As standard a reference for quantum yield measurements, a sealed cryogenic rectangular quartz cuvette was enclosed in a helium atmosphere. Special care was taken to ensure that the samples, at every temperature. The temperature dependence of the solvent index of refraction \( \eta(T) \) was corrected by using a third-order polynomial:

\[
\eta(T) = \eta_0 + B_0 T + B_1 T^2 + B_2 T^3
\]

\( \eta_0 = (9.273 \pm 0.04 \times 10^{-3}) \) for 3MP. \( B_0 = 0.54 \pm 0.02 \). Samples above 6 °C were thermostated to ±0.1 °C using a circulating water bath. For low-temperature measurements, a sealed cryogenic rectangular quartz cuvette was enclosed in a copper block mounted on the coldfinger of a liquid nitrogen cryostat (Oxford Instruments, PE1704). All the experiments were accomplished under a helium atmosphere. Special care was taken to ensure that the glass formed by the frozen solvent was not cracked. To avoid any deviation in spectral analysis, we subtracted the solvent’s spectra from the samples, at every temperature. The dependence of density \( \rho \) on temperature \( T \) was corrected by using a third-order polynomial:

\[
\rho(T) = \rho_0 + B_0 T + B_2 T^2 + B_3 T^3
\]

\( \rho_0 = (9.273 \pm 0.04 \times 10^{-3}) \) for 3MP.

3. Results and Discussion

3.1. Spectroscopy below 260 K. Figure 1 displays the temperature dependence of the absorption spectrum of 1 dissolved in 3MP, upon cooling stepwise from 296 to 77 K. As clearly shown the weak absorption band (~333 nm) gradually disappears whereas several isosbestic points emerge across the absorption spectrum. The above features strongly suggest the existence, in the ground state, of two discrete forms A and B (see also Figure 1, right bottom insert).

The fluorescence spectra, on the other hand, also show quite remarkable characteristics (Figure 1 right top insert). When the sample is preferentially excited at an isosbestic point of the absorption band, the total integrated fluorescence intensity increases with decreasing temperature indicating an augmentation of the absolute quantum yield from 0.36 ± 0.02 at ambient temperatures to 0.7 ± 0.04 below 130 K (see also Figure 2; Table 1). Furthermore, the relative intensity mainly of the "0–0" emission peak is strongly temperature dependent and

\[
\begin{align*}
\text{Table 1. Fluorescence Quantum Yields (Φ), Lifetimes (τ), Radiative (k) and Nonradiative Rates Constants (k_{nr}), Absorption} & \\
\text{Transition Origins of A and B Rotameric Isomers of 1 Obtained at Low Temperatures} & \\
\hline
\text{rotamer} & \Phi & \tau & k_f \times 10^7 & k_{nr} \times 10^7 & \Delta\varepsilon & \varepsilon_0 & \varepsilon_{1\rightarrow0} \\
\hline
A^0 & 0.72 & 13.0 & 5.54 & 2.15 & 30525 & 30583 \\
B^0 & 0.68 & 13.0 & 5.23 & 2.46 & 29895 & 29980 \\
\hline
\end{align*}
\]

* “Limiting” values ±130 K. * Obtained at 160 K. * Uncertainties in low-temperature quantum yields <8%. * Uncertainties in recovered lifetimes and rates <5% and <8%, respectively.

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The remarkable increase of the molar extinction coefficient increases sharply, by analogy to the “0→0” absorption transition, with decreasing temperature. After analysis of the above experimental data we find that the reason for the increase of quantum yield is a consequence of an increase of the radiative rate constant \(k_{\text{A}}\) of the A* emitting species. The fluorescence spectra of I below ~130 K, likewise to the absorption spectra at these temperatures, have no appreciable changes. This latter observation provides additional evidence that practically the spectrum of I is due entirely to the more stable form A at low temperatures.

Below 260 K the barrier controlled isomerization rate, in the excited state, is much slower than the fluorescence decay, that is, \(k_1 + k_{-1} < k_{A}\). As a consequence, A* and B* do not interconvert during their lifetime and decay independently according to the so-called NEER (nonequilibration of excited rotamers) rule. Therefore, direct excitation at an appropriate wavelength in which B absorbs solely will give pure B* emission. Indeed, the dramatic photoselection observed with excitation at \(\lambda \geq 333\) nm (Figure 2b) provides further evidence that there is an additional species B in the ground state which is thermodynamically less stable and absorbs at longer wavelengths than the dominant one (A). The pure spectra of A can be easily obtained below 130 K. As becomes evident from the above spectroscopic analysis, the high-energy part (329 ± 3 nm) of the fluorescence spectrum shown in Figure 2a contains no contribution from B* emission and therefore is a signature of the emission of the A* rotamer only (see also Figure 2b). Consequently, this wavelength region can serve for monitoring fluorescence decay traces of pure A* at any temperature. The absolute quantum yields and the recovered fluorescence lifetimes as a function of temperature for both emitting species are also given in Figure 2c,d. For both emitting species A* and B* below 260 K, the fluorescence intensity versus time can be fitted very successfully with a single-exponential function. The results clearly show the following: (1) the “limiting” quantum yields of the A* and B* rotamer respectively are, within experimental uncertainty (<8%) closely identical, namely, \(\Phi_{0,A} = 0.72\) and \(\Phi_{0,B} = 0.68\), and (2) they have indistinguishable lifetimes below 160 K (\(\tau_{0,A} = \tau_{0,B} = 13.0 ± 0.2\) ns). The most important photophysical parameters are summarized in Table 1.

### 3.1.1. Assignment of A and B Rotamers: The “0→0” electronic transition of the high-energy rotamer A of I in 3MP

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**Figure 2.** Normalized absorption-fluorescence spectra, quantum yields, and lifetimes of I in 3MP. (a) Absorption spectrum (left) and fluorescence spectra (right) excited selectively (see arrows for \(\lambda_{\text{exc}} = 0.1\) nm), at room temperature; scattered excitation light has been removed. (b) Pure emission spectra of A* and B* rotamers. Emission of A* is obtained at 77 K in a dilute solution of ~3 × 10⁻⁵ M. For pure B* emission a solution of ~2 × 10⁻⁴ M at 160 K was used (see arrows for \(\lambda_{\text{exc}} = 0.1\) nm). (c) Lifetimes of A* and B*; excitation and emission observation wavelengths (exc/em) were, respectively, 322 ± 5/328 ± 3 nm for A* and 335 ± 2/345 ± 7 nm for B* below 260 K. Above 260 K coupled biexponential kinetics was observed (see part B). (d) Absolute quantum yields (\(\Phi\)) at varying temperatures corrected for refractive index variation with temperature (excitation wavelengths as in Figure 2b).
occurs at 30 525 cm\(^{-1}\) (327.6 nm) and is close to that observed in jet-cooled \(I^0\) (31 028 cm\(^{-1}\)). Furthermore, the separation of the \(S_1\) – \(S_0\) electronic origin transitions of the A and B rotameric forms of I observed in the present work (630 cm\(^{-1}\)) nearly coincides with the one obtained from the jet-spectra of \(I^0\) (660 cm\(^{-1}\)). The above configurations A and B have been assigned respectively to a cis (syn, \(\varphi = 0^\circ\)) and a trans (anti, \(\varphi = 180^\circ\)) conformation.\(^{15,16}\) The syn and anti are denoted by the dihedral angle \(\varphi\) (C\(_1\) – C\(_2\) – O\(_{11}\) – C\(_{12}\)) of the methoxy group relative to the naphthalene plane. Our analysis on the fluorescence and fluorescence excitation spectrum vibronic features at cryogenic temperatures (4.2 K) also suggest the s-cis configuration.\(^{15}\) A crystallographic analysis at 173 K proves that I crystallizes as a nearly planar molecule with the methoxy group adopting a syn-periplanar conformation with respect to the C\(_1\) atom.\(^{16}\) Finally, from \(^1\)H and \(^13\)C nuclear magnetic resonance experiments of I in carbon tetrachloride solutions, a conformational preference of the cis- over the trans-configuration is found;\(^{17}\) quantitative analysis led to an approximate population ratio of 19:1 between cis and trans rotameric isomers at 305 K.\(^{17}\) We therefore assign the A form as the s-cis rotamer which isomerizes to the s-trans analogue as temperature increases. The equilibrium constant for \(S_0\) (\(K_{s0} = [B]/[A]\)) is estimated to be \(\sim 0.07\) at 296 K from the absorption spectra.\(^{18}\) This estimate corresponds to a \(\Delta H_{s0}^0\) of \(6.5\) kJ/mol (\(\sim 550\) cm\(^{-1}\)). For comparison a value of \(\sim 0.05\) for I in carbon tetrachloride can be estimated (see above). A value of \(\sim 0.1\) for the analogues rotamers of 2-vinylanthracene in cyclohexane has also been reported.\(^{19}\)

### 3.2. Spectroscopy above 260 K

Above 260 K a pure adiabatic interconversion channel in the excited state between A\(^*\) and B\(^*\) rotamers is switched on, as manifested by dynamic fluorescence analysis (vide infra). I follows the fluorescence kinetics commonly observed in analogous systems.\(^{1}\) Briefly, coupled biexponential kinetics with a short (\(t_1\)) and a long (\(t_2\)) lifetime component showing no wavelength dependence, was observed.

\[
I(t, \lambda) = A_1(\lambda) \exp(-t/t_1) + A_2(\lambda) \exp(-t/t_2) \tag{1}
\]

At the high-energy part of the fluorescence spectrum, both \(A_1\) and \(A_2\) are positive. When decay traces are detected at emission wavelengths where the B\(^*\) (s-trans) rotamer considerably emits, \(A_1\) becomes negative demonstrating s-cis\(^*\) and s-trans\(^*\) rotameric interconversion.

For a given hypothetical adiabatic photodynamic model, as in Scheme 1, if the nonisomerization rate constants \(k_A = 1/\tau_{0A}\) and \(k_B = 1/\tau_{0B}\) are equal then the solution of the coupled differential equations for the A\(^*\) and B\(^*\) deactivating processes leads explicitely to the simple but very important relations\(^{18}\)

\[
\tau_2^{-1} = \tau_{0B}^{-1} - \tau_{0A}^{-1} \tag{2}
\]

and

\[
\tau_1^{-1} - \tau_2^{-1} = k_1 + k_{-1} - k_{\text{sum}} \tag{3}
\]

Analysis of the time-resolved fluorescence decay traces indicates the following (see Table 1): (1) \(\tau_2\) remains exceptionally independent of temperature and within experimental error is equal to \(\tau_{0B} \approx \tau_{0A} \approx 13.3\) ns obtained at low temperatures; this provides additional evidence with respect to the adiabaticity of the isomerization and the equality of the nonisomerization rate constants (\(k_A = k_B\)).\(^{13}\) (2) The fluorescence decay traces, selected at a narrow wavelength region signed by the emission of the A\(^*\) rotamer only (328 ± 2.0 nm) (Figure 2b), can be strictly fitted to a biexponential function; this is also a signature for the reversibility of the excited-state reaction,\(^{18}\) and (3) the amplitude ratio \(A_2/A_1\) is nontemperature dependent and close to 1 (see also Figure 3a; insert). From the decay times \(t_1\) and \(t_2\) and the amplitude ratio \(A_2/A_1\) together with the “limiting” lifetime \(\tau_{0A}\), the forward rate constant \(k_1\) can be unambiguously determined;\(^{19}\) \(k_{-1}\) is then obtained from \(k_{\text{sum}}\). In fact, the above procedure should be slightly corrected for the fraction of the initially excited [B\(^*\)]\(^*\) resulting from direct excitation of the ground state population of the B (s-trans) isomer.\(^{20}\)

#### 3.2.1. Energy Barriers, Thermodynamics, and Reaction Coordinate

From the recovered rate constants in an Arrhenius analysis (Figure 3a and Table 2), the \(S_1\) thermal activation parameters can be evaluated. If the forward and reverse reaction were, in principle, to have different activation energies \(E_{A}^f\) and \(E_{A}^\text{re}\), respectively, then \(\ln k_{\text{sum}}/\tau_{0}\) would be nonlinear because \(k_{\text{sum}}\), in fact, follows a biexponential form (eq 4).

\[
k_{\text{sum}} = k_0^f \exp\left(\frac{E_{A}^f}{RT}\right) + k_0^{\text{re}} \exp\left(\frac{E_{A}^\text{re}}{RT}\right) \tag{4}
\]

\(k_0^f\) and \(k_0^{\text{re}}\) are Arrhenius frequency factors for the forward and reverse reaction, respectively. The unexpected linearity of \(\ln k_{\text{sum}}\) (Figure 3a) can be explained only if either (a) the forward (\(k_1\)) and reverse (\(k_{-1}\)) reaction do have approximately indistinguishable energy barriers or (b) the forward predominates.

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Figure 3. (a) An Arrhenius plot of \( k_{sum} \), \( k_{1} \), and \( k_{-1} \). Open and filled circles represent noncorrected and corrected values, respectively, for the presence of \( K_{eq}^{i}(T) \). (Insert) Ratio of preexponential factors vs \( T \). (b) Original steady-state fluorescence spectra at varying \( T \) obtained with selective excitation at an isosbestic point (323.6 ± 0.1 nm). (Insert) Excited-state equilibrium constant \( K_{eq}^{S1} \) vs \( T \) estimated from dynamic (black circles) and static (green circles) fluorescence spectroscopy.

Table 2. Temperature Dependence of the Observed Lifetimes, \( ^{ab} \) Ratio of Preexponential Factors (\( A_{2}/A_{1} \)), and Recovered Rate Constants \( ^{b} \) of 1 in 3-Methylpentane \([1] = 5 \times 10^{-5} \) M (Exc: 320 ± 5 nm; Em: 328 ± 2.0 nm)

<table>
<thead>
<tr>
<th>T, K</th>
<th>( t_{1}, ) ns</th>
<th>( t_{2}, ) ns</th>
<th>( k_{sum} \times 10^{6} ) s(^{-1} )</th>
<th>( (A_{2}/A_{1}) )</th>
<th>( k_{1} \times 10^{6} ) s(^{-1} )</th>
<th>( k_{-1} \times 10^{6} ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>279</td>
<td>4.84</td>
<td>13.12</td>
<td>1.30</td>
<td>0.85</td>
<td>0.74</td>
<td>0.55</td>
</tr>
<tr>
<td>287</td>
<td>3.85</td>
<td>13.20</td>
<td>1.84</td>
<td>0.74</td>
<td>1.10</td>
<td>0.73</td>
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<tr>
<td>296</td>
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<td>13.24</td>
<td>2.77</td>
<td>0.77</td>
<td>1.64</td>
<td>1.12</td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>331</td>
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<td>13.70</td>
<td>9.34</td>
<td>0.80</td>
<td>5.54</td>
<td>3.80</td>
</tr>
</tbody>
</table>

\(^{a}\) The statistical parameter \( \chi^{2} \) was between 1.00 and 1.07. \(^{b}\) Uncertainties in lifetimes and \( k_{sum} \) <5%; uncertainties in preexponential factors and recovered rates <10%.

significantly over the reverse; \(^{1b}\) that is, the isomerization reaction is in fact predominantly irreversible (\( k_{sum} \approx k_{1} \)). An Arrhenius analysis of the \( k_{sum} \) and the individual \( k_{1} \) and \( k_{-1} \) gives respectively \( E_{a} = 29.1 \) kJ/mol, \( E_{1} = 29.0 \) kJ/mol, and \( E_{-1} = 29.3 \) kJ/mol which are actually indistinguishable. An insignificant variation within <3% was found when the corresponding noncorrected values, for the presence of the ground state equilibrium \( K_{eq}^{i}(T) \), were employed. It should be noted that three independent sets of experiments were carried out to determine the uncertainty associated with each point. We were unable to observe differences in rate constants and energy barriers exceeding remarkably the experimental error (<10%).

Besides the dynamic fluorescence spectroscopy findings, we have also made an indirect determination of the excited-state isomerization kinetics from static quantum yield measurements. We found that above 260 K the overall fluorescence quantum yield \( \Phi \) of a dilute solution of I in 3MP is completely independent from both temperature and wavelength of excitation, within experimental uncertainty (\( \Phi = 0.36 \pm 0.02 \))\(^{1}\) (see also Figure 2d, \( T > 260 \) K). On the basis of the above and previous findings in part A, it is easy to show that the ratio of the individual quantum yields of the s-trans\(^{b} \) (B\(^{+} \)) and s-cis\(^{a} \) (A\(^{+} \)) species is given by\(^{21}\)

\[
\Phi_{B^{+}}/\Phi_{A^{+}} \approx K_{eq}^{S1}
\]  

Interestingly, as seen in Figure 3b, the effect of temperature on the steady-state fluorescence spectra, after excitation at an isosbestic point (323.6 ± 0.1 nm), is actually insignificant. After detailed analysis of the above spectra, we find the following:

(a) From the ratio of fluorescence intensities at the origin emission maxima 329 (A\(^{+} \)) and 336 nm (B\(^{+} \)) (pure B\(^{+} \) intensity was retrieved by subtracting the portion of A\(^{+} \) emission at 336 nm according to the pure rotameric spectral analysis made before; see Figure 2b), one obtains\(^{21} \) \( K_{eq}^{S1} \) values of 1.17, 1.27, and 1.36 at 287, 306, and 331 K, respectively; these values just barely exceed 1 and are in excellent agreement with those recovered from dynamic fluorescence kinetic analysis (\( K_{eq}^{S1} \) vs \( T \) according to the following relations: \( \chi^{2} = \sigma^{2} = 2104. \) (b) Yoshihara, T.; Druzhinin, S. I.; Zachariasse, K. A. J. Am. Chem. Soc. 2004, 126, 8535.

The above suggest that for the present interconversion process, both the standard (\( \Delta H^{c} \)) and the free reaction enthalpy (\( \Delta G^{c} \)) for \( T > 260 \) K should be very close to 0.\(^{22}\) From the Arrhenius frequency factors for the forward (\( k_{1} \)) and reverse...
(23) Reaction enthalpy: $\Delta H^\circ = E_{\text{trans}} - E_{\text{cis}} \approx 0.3 \text{ kJ/mol.}$ Free reaction enthalpy: $\Delta H^\circ = -RT \ln (k_{\text{cis}}/k_{\text{trans}})$. Reaction entropy: $\Delta S^\circ = RT \ln k_{\text{cis}}/k_{\text{trans}} = 2.15 \pm 0.5 \times 10^{11} \text{ s}^{-1}$ and $E_{\text{trans}} = (1.6 \pm 0.5) \times 10^{12} \text{ s}^{-1}$ are frequency factors for the forward and reverse reaction, respectively, obtained from Arrhenius plots in Figure 3.


hindrance in S\textsubscript{0} is also supported from theoretical methods in the case of the s-cis form\textsuperscript{9b} of 1 and of the simpler analogue methoxybenzene.\textsuperscript{27} Most likely, contrary to S\textsubscript{1}, electronic and steric asymmetric interactions induced by a distorted sp\textsuperscript{2} hybridized oxygen atom might in principle be responsible for the observed energy gap between the two rotamers in S\textsubscript{0}.

Finally it is interesting to note that, if one combines the energy separation of the two electronic origin transitions of the two rotamers experimentally obtained from gas-phase vibronic spectroscopy\textsuperscript{9a} (660 cm\textsuperscript{-1}) with their ground state energy gap calculated from an ab initio study\textsuperscript{9b} (the s-trans form lies \textasciitilde700 cm\textsuperscript{-1} higher in energy than the s-cis analogue), then one indirectly obtains an estimation of only \textasciitilde40 cm\textsuperscript{-1} (\textasciitilde0.5 kJ/mol) for the energy gap between the two rotamers in S\textsubscript{1}. That is, the two rotamers are nearly isoenergetic in S\textsubscript{1} supporting thus our conclusions in the present work reached by straightforward kinetic analysis.

4. Conclusions

The results from this work provide the first detailed insights into the\textsuperscript{27} high reversibility of an excited-state rotameric equilibration in solution. Our findings clearly demonstrate that, above 260 K, s-cis\textsuperscript{*} and s-trans\textsuperscript{*} rotational isomers of 2-methoxynaphthalene interconvert through very close lying energy barriers with respect to the forward and reverse isomerization pathway. This leads to an excited-state equilibrium constant very close to 1, which is not noticeably affected over the temperature region studied. To the best of our knowledge, in contrast to the generally accepted photodynamic scheme of related compounds, this is the first experimental manifestation of a nearly fully reversible torsional photoisomerization in solution.


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