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1,3-di-2,2′-Naphthylpropane as a fluorescent probe for silica surfaces

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Abstract

The bifunctional molecule 1,3-di-2,2′-naphthylpropane, N(3)N, has been investigated as a thermodynamic surface interaction probe of silica surfaces. Adsorption of N(3)N onto a silica surface from cyclohexane follows a Freundlich adsorption isotherm, demonstrating a range of weak interactions between the molecule and surface active sites. A moderate excimer emission ($\lambda_{max} = 400$ nm) observed at room temperature for low probe concentrations (below 5% of a monolayer) is attributed to an intramolecular process. Our results indicate that at low surface coverages more than 70% of the isolated bichromophoric molecules exist in an intramolecular excimer form. Thermodynamic data obtained from fluorescence studies reveal that excimer emission increases concurrently with a decrease in monomer emission as the temperature is raised. From an Arrhenius plot of the data an activation energy of about 2.2 kcal mol^{-1} is calculated for the intramolecular excimer formation on silica surface. Gas phase molecular mechanics calculations predict an activation energy of 2.3 kcal mol^{-1} for the interconversion of an *anti–gauche* conformer (non-excimer emitting) to a *gauche–gauche* conformer responsible for intramolecular excimer emission. Since the calculation does not take into account surface interactions, the *anti–gauche* conformation may not be the predominant non-excimer emitting species present on silica surface.

Keywords: 1,3-di-2,2′-naphthylpropane; Fluorescence; Singlet excimer; Intramolecular processes; Fluorescent probe

1. Introduction

Fluorescent molecular probes for interrogating solid surfaces have received much attention in recent years [1]. Because of its unusually long fluorescence lifetime, ability to form an excimer and sensitivity of its structured fluorescence spectrum to polarity of the environment, pyrene [2] has been widely used as a molecular probe to study the surfaces of silica [3], alumina [4], titania and other semiconductors [5], calcium fluoride [6], clays [7] and zeolites [8]. The disadvantage of this molecule, however, is its ability to form an intermolecular excimer through ground state aggregation even at very low surface coverages [9]. This makes it difficult to interpret results from studies of dynamic intramolecular excimer formation on surfaces. Results from our photochemical studies of other polycyclic aromatic hydrocarbons (PAHs) on silica and alumina have revealed that most of these PAHs tend either to aggregate or to crystallize on the surface when adsorbed from cyclohexane solutions [10,11]. We have shown that aggregation, even at very low surface coverages (1% of a monolayer), can sometimes lead to a structured emission as observed for anthracene (due to a stable pair form) [11] while crystallization gives rise to an emission corresponding to the crystalline form of the molecule as seen for phenanthrene on silica [12]. Bifunctional molecules capable of forming intramolecular excimers, on the contrary, offer the advantage of using significantly lower concentrations to avoid ground state aggregation phenomena. Leermakers and coworkers [13] first reported the observation of an intramolecular excimer emission from bifunctional molecule 1,3-diphenylpropane in silica–cyclohexane slurries. Bauer and coworkers [14] studied the photophysics of the bifunctional molecule 1,3-di-1,1′-pyrenylpropane on dry silica and concluded that the observed enhancement in excimer-like emission was due to a ground state intramolecular process induced by surface interactions. A later study by Avnir et al. [15] on the contrary, attributed the enhanced excimer-like emission from the same molecule to an intermolecular process involving ground state aggregates. Two explanations were advanced for the observed aggregation phenomenon leading to an excimer–like emission in this bifunctional molecule. The first invokes formation of a "domino-like" chain between pyrene moieties of close neighbors while the second is based on the non-homogeneous nature of adsorbing sites and assumes that crevices of the surface may cause the molecule to deviate from a stretched ground state conformation into a bent structure. The observed

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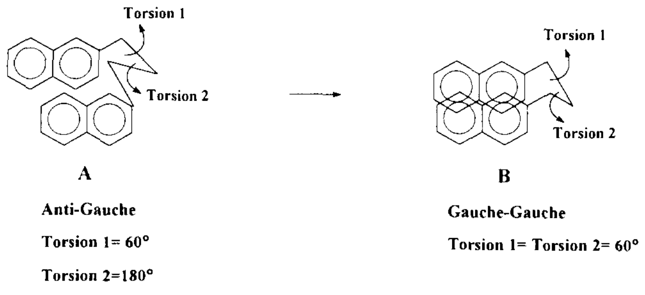
discrepancies between these reports with regard to the nature of the excimer from bifunctional pyrene on dry silica prompted us to use a different probe for investigating silica surfaces. It has been reported that room temperature emission of 1,3-di-2,2′-naphthylpropane, N(3)N, in solution is almost entirely due to a thermally activated intramolecular excimer [16]. We have employed N(3)N as a thermodynamic fluorescent probe on silica surfaces in an attempt to evaluate the role of surface interactions in inducing or inhibiting intramolecular excimer formation.



2. Experimental details

Synthesis of 1,3-di-2,2′-naphthylpropane, N(3)N, and 1,3-di-1,2′-naphthylpropane, 1N(3)N2, was carried out using a literature method [16]. Starting materials 2-naphthaldehyde (Aldrich 98%, Aldrich Chemical Company Inc., Milwaukee, WI), 2-acetonaphthone (Aldrich 99%) and 1-naphthaldehyde (Aldrich 98%) were used as received. Pyrene (Aldrich, 99%) and 2-methylnaphthalene (Aldrich, 98%) were recrystallized twice from cyclohexane before use. All solvents used were high performance liquid chromatography grade (Baker Analyzed, Phillipsburg, NJ). Silica-60 (Baker Analyzed, 60–200 mesh) was activated at 200 °C for at least 24 h before use. The N_2 Branauer–Emmett–Teller (BET) surface area and pore size distribution for silica were measured on an Autosorb-1 (Quantachrome Corporation, Boynton Beach, FL) gas sorption instrument [17]. The surface area determined by BET measurement is 274 $m^2\ g^{-1}$ with an average pore radius of ca. 60 Å [17]. The adsorption of N(3)N and 1N(3)N2 onto silica from a cyclohexane slurry was carried out in the similar manner to that reported earlier [11,18]. Percentage monolayer surface coverage was calculated by fractal theory as previously described [11,18] using an area of $9 \times 10^{-19}\ m^2$ molecule^{-1} for N(3)N. Samples for fluorescence measurements were prepared in a degassing tube equipped with a 1 cm quartz sidearm cell. Tubes were degassed to a pressure of 2×10^{-6} Torr and sealed under vacuum with a flame.

Absorption and diffuse reflectance spectra were recorded on a Cary 4E UV–visible spectrophotometer (Varian) equipped with an integrating sphere. Diffuse reflectance measurements were carried out on silica samples immediately after adsorption of N(3)N by applying a layer of solid on top of a thin layer of rubber cement on a glass slide and were corrected for background silica. Fluorescence spectra were obtained from the front face of the 1 cm quartz cell containing the solid sample and were corrected for instrumental response and background silica-60.

3. Results and discussion

Adsorption of N(3)N on silica obeys a modified Freundlich adsorption isotherm demonstrating a range of weak interactions between the molecules and surface active sites. The equilibrium adsorption potential calculated by the method described previously [18] indicates that the range of interactions falls between 2 and 6 kcal mol^{-1}. Fig. 1 compares the absorption spectrum of N(3)N in cyclohexane (spectrum A) with diffuse reflectance spectra of the molecule on dry silica at various surface loadings. Spectra B, C and D correspond to 0.24%, 2.4% and 10.2% respectively of a monolayer. The appearance of a new red-shifted broad band centered around 350 nm for the highest surface coverage (spectrum D, 10.2% of a monolayer) may indicate some ground state pairing and/or crystallization consistent with our previous studies of other PAHs on silica [10,11,17]. Therefore, except for some peak broadening and red shifting, no significant change is observed in the absorption of N(3)N on silica. The dependence of N(3)N fluorescence on surface loading for dry silica at room temperature is shown in Fig. 2. The data show that (a) excimer emission $\lambda_{max} = 400$ nm, is present at surface loadings as low as 0.24% of a monolayer where no ground state pairs and/or crystals form as revealed by diffuse reflectance results of Fig. 1 and (b) contribution from excimer emission increases with increasing surface coverage. Emission spectra for similar loadings of 2-methylnaphthalene/silica (1.2% of a monolayer) and N(3)N/silica (0.6% of a monolayer) show that more than 70% of the N(3)N molecules exist in excimer form. Each mole of

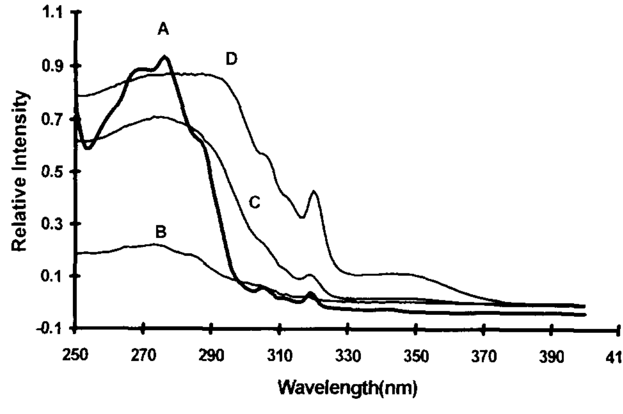


Fig. 1. Absorption spectrum of N(3)N in cyclohexane (spectrum A, 1.5×10^{-4} M) and diffuse reflectance on dry silica for 0.24% (spectrum B), 2.4% (spectrum C) and 10.2% (spectrum D) of a monolayer.

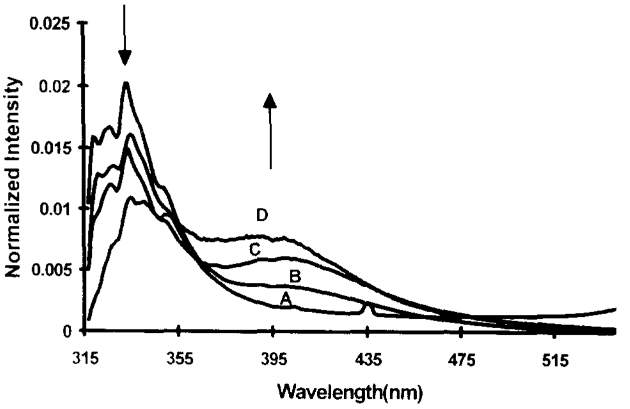


Fig. 2. Variation in the emission (corrected) spectra of N(3)N on dry silica as a function of surface coverage (degassed, room temperature, front face, $\lambda_{ex}=290$ nm; spectra were normalized relative to total area): spectrum A, 0.06% of a monolayer; spectrum B, 0.24% of a monolayer; spectrum C, 2.4% of a monolayer; spectrum D, 5% of a monolayer.

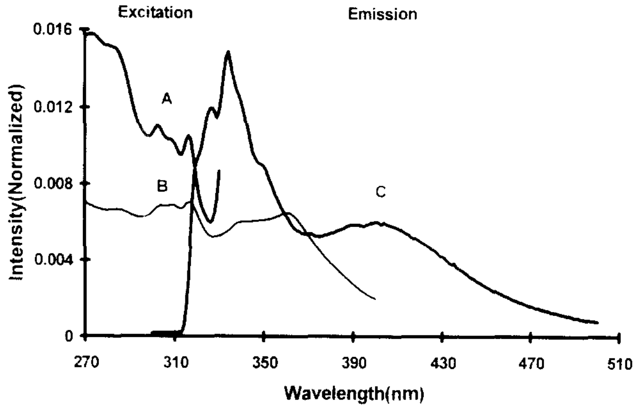


Fig. 3. Emission (spectrum C, $\lambda_{ex}=290$ nm) and excitation spectra of N(3)N on dry silica for 2.4% of a monolayer monitored at 340 nm (spectrum A) and 440 nm (spectrum B); front face, degassed, room temperature, corrected for silica background. Spectra were normalized relative to total area.

N(3)N is equivalent to 2 mol of 2-methylnaphthalene. In solution at room temperature, the emission of N(3)N is almost entirely due to intramolecular excimers [16]. Although the majority of N(3)N molecules introduced on the surface assume a conformation that leads to excimer emission, the interaction between naphthyl moieties and surface silanol groups apparently provides a barrier to conformational interconversion causing about 30% of the molecules to exist in non-excimer emitting conformations. The observed monomer emission can be attributed to these conformations. The information obtained from the excitation spectra monitored at wavelengths corresponding to monomer and excimer can be utilized to identify the intramolecular or intermolecular nature of the excimer. For example, the excitation spectrum of intermolecular pyrene excimer on dry silica formed by aggregation and/or microcrystallization [9,14,19–21] is red shifted relative to the excitation spectrum of the monomer. Furthermore, the maxima and minima of the two spectra are anticoincident. Anticoincident behavior in the excimer and monomer excitation spectra, which we have also observed for several other PAHs on dry silica, has been explained by Lochmuller and Wenzel [21] to result from competition between two species (monomer and aggregates and/or microcrystals) for the incident light. Absorption of a significant portion of the incident light by the monomers at wavelengths of its maximum absorbance will cause minima in the excimer excitation spectrum. On the contrary, good overlap of both excitation spectra implies presence of a dynamic excimer in the system. Fig. 3 shows the emission (spectrum C) and excitation spectra for N(3)N/silica (2.4% of a monolayer) monitored at wavelengths corresponding to monomer (spectrum A, $\lambda_m=340$ nm) and excimer (spectrum B, $\lambda_m=440$ nm) emissions. Both excitation spectra A and B resemble the absorption spectrum of N(3)N on silica. The absence of any red shifting in spectrum B confirms the intramolecular nature of the excimer. Additional support for the intramolecular nature of the excimer was provided by examining the corresponding isomer 1N(3)N2 on silica. We see no significant intramolecular excimer formation in solution by 1N(3)N2 at room temperature consistent with the earlier report of Chandross and Dempster [16] who observed very little excimer emission in solution for concentrations as high as 10^{-3} M. Fig. 4 compares the observed emission from both isomers on silica. Absence of any excimer emission (intramolecular or intermolecular) from 1N(3)N2 at surface coverages up to 3% of a monolayer (spectrum B) substantiates the intramolecular nature of the excimer observed from N(3)N at very low surface coverages.

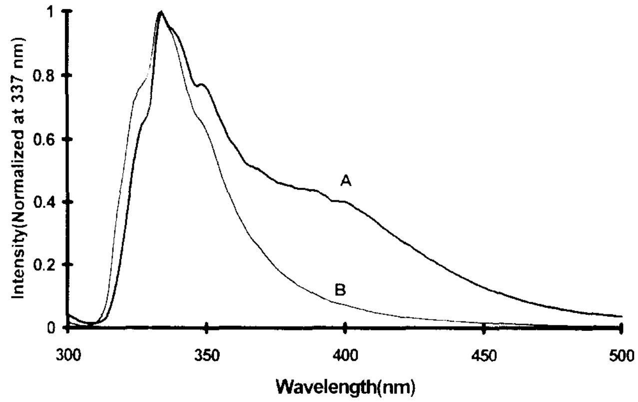


Fig. 4. Comparison of the normalized emission spectrum of N(3)N (spectrum A, 6×10^{-6} mol g^{-1}, 1.2% of a monolayer) and 1N(3)N2 (spectrum B, 1.7×10^{-5} mol g^{-1}, 3.4% of a monolayer) on dry silica; front face, degassed, room temperature, $\lambda_{ex}=290$ nm, corrected for silica background. Spectra were normalized at 337 nm.

To obtain the activation barrier for interconversion from monomer emitting conformations to conformers that emit as excimer, the thermodynamics of the system was investigated. Fig. 5 shows the temperature dependence of intramolecular excimer formation on the silica surface for a sample with 1.2% of a monolayer. It can be seen from the spectral changes that an increase in excimer emission is accompanied by a decrease in monomer emission intensity as the temperature

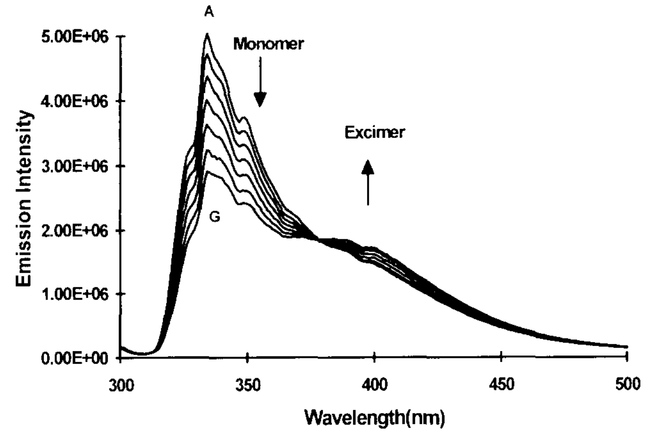


Fig. 5. Temperature dependence of intramolecular excimer formation by N(3)N on dry silica (1.2% of a monolayer, 6×10^{-6} mol g^{-1}); front face, degassed, corrected for silica background. Spectra A–G were obtained at −7 °C, −2 °C, 6 °C, 15 °C, 25 °C, 35 °C and 45 °C respectively.

is raised from −7 °C to 45 °C. The presence of an isosbestic point at about 376 nm is consistent with a process involving transformation of one species into another (in this case monomer to excimer). It should be noted that, when a similar study was carried out for pyrene adsorbed on silica at a surface coverage where intermolecular excimers were present (3% of a monolayer), the opposite behavior was observed. In that case an increase in temperature was accompanied by a decrease in excimer emission and concurrent increase in monomer emission. This implies that slow diffusion of molecular pairs (aggregates), responsible for the intermolecular excimer, away from each other leads to a increase in monomer emission at the expense of excimer. Wang and Harris [22] have reported a value of 10^{-20} cm^2 s^{-1} for the diffusion coefficient of pyrene on silica at room temperature.

The interaction between an excited and a ground state naphthalene chromophore linked by a propane chain can be represented by Scheme 1, similar to that of Ghiggino et al. [23], where k_{ICM} and k_{FM} are the radiationless and radiative decay rates for the excited monomer and k_{ICD}, k_{FD} are the corresponding rates for the excimer. Using the steady state approximation, kinetic analysis yields the following equation for the ratio of excimer to monomer emission intensities [24]:

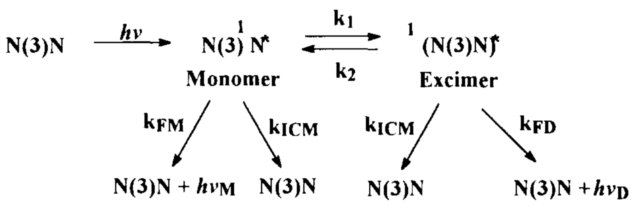
$$I_D/I_M=k_1(k_{FD}/k_{FM})/(k_2+k_{ICD}+k_{FD}) \quad (1)$$

Assuming $k_2 \ll k_{FD}$, Eq. (1) simplifies to

$$I_D/I_M=k_1\tau_D k_{FD}/k_{FM} \quad (2)$$

where $\tau_D=(k_{ICD}+k_{FD})^{-1}$ is the lifetime of the excimer. It has been shown in homogeneous solutions as well as micelles and biomembranes [25–29] that a linear relationship between $\ln(I_D/I_M)$ and $1/T$ is observed where the slope yields the activation energy E_a for excimer formation. Temperature dependence of k_1 can be incorporated into Eq. (2) to give

$$I_D/I_M=Le^{-E_a/RT} \quad (3)$$



Scheme 1.

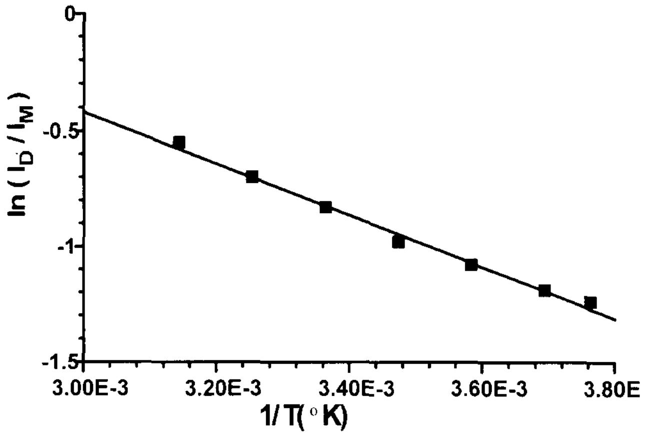


Fig. 6. Arrhenius plot of $\ln(I_D/I_M)$ vs. $1/T$ for N(3)N on dry silica (1.2% of a monolayer, 6×10^{-6} mol g^{-1}); I_D corresponds to excimer emission intensity at 420 nm and I_M is the intensity of monomer emission at 327 nm.

where $L=\tau_D k_{FD}/k_{FM}$. Eq. (3) predicts a linear relationship between $\ln(I_D/I_M)$ and $1/T$. Fig. 6 shows a plot of $\ln(I_D/I_M)$ vs. $1/T$ for the thermodynamic data. From the slope of the line a value of 2.2 kcal mol^{-1} is calculated for the activation energy of intramolecular excimer formation (k_1). The activation energy for intramolecular excimer formation in solution has been reported to be 4 kcal mol^{-1} [16]. Since adsorption of N(3)N on silica is carried out at room temperature, the majority of adsorbed molecules will be expected to be in a conformation that emit as excimer (intramolecular) provided that surface interactions are not important. The fact that only about 70% of the molecules retain this conformation implies that surface interactions cause a deviation from this excimer emitting conformation to another conformation where naphthyl moieties do not overlap. Gas phase molecular mechanics calculation (using the PC model) of the torsional barrier to conformational interconversion of the propane chain predicts a value of 2.3 kcal mol^{-1} for the activation energy required for intramolecular excimer formation. This is the energy required to convert the *anti–gauche* conformation (conformation A) to a *gauche–gauche* conformation (conformation B) where maximum overlap of the π systems takes place between the two naphthyl groups. These calculations predict higher activation energies for the interconversion of other conformations to a *gauche–gauche*. For example, the calculated activation energy for the interconversion of *anti–anti* to *gauche–gauche* is about 3.5 kcal mol^{-1}.

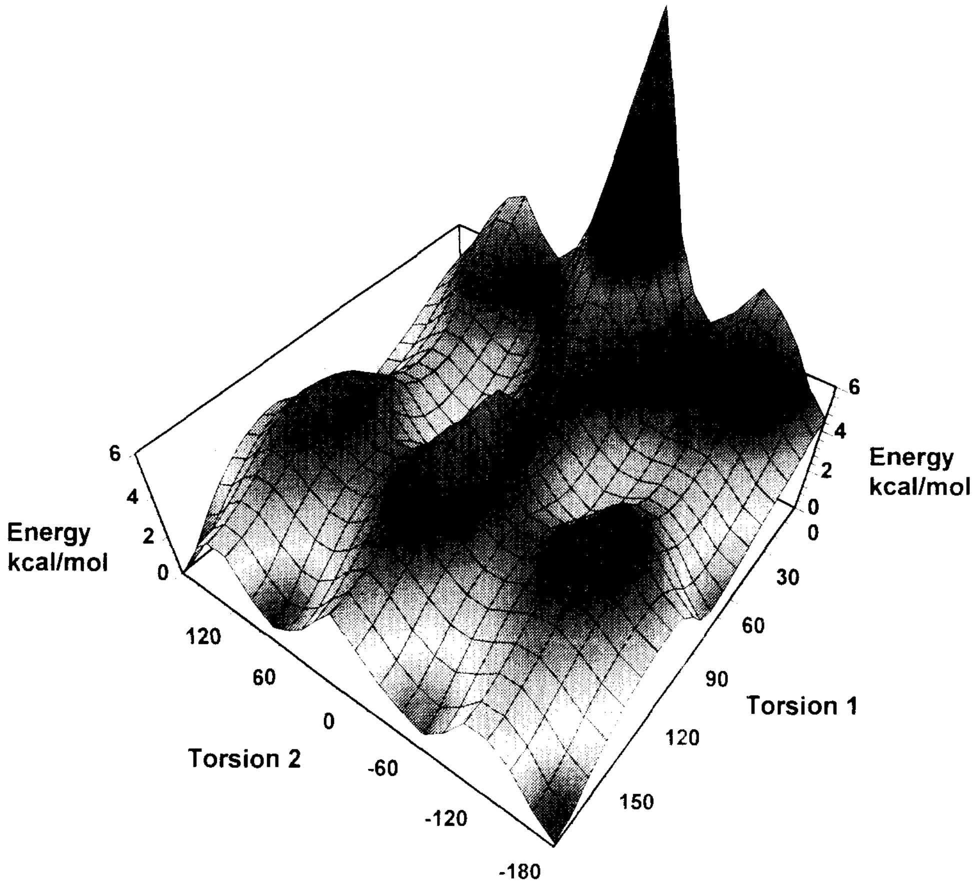
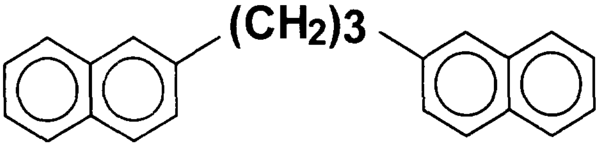


Fig. 7. Map of energy surfaces for the interconversion of the *anti* (180°) to *gauche* (60°) conformation in propane chain for N(3)N molecule in the gas phase.



1,3-di-2,2'-Naphthylpropan

N(3)N

Fig. 7 shows the map of energy surfaces for the interconversion of different conformations obtained by the isomeric rotational states approximation. Although the observed activation energy agrees well with the calculated value for an *anti–gauche* conformation, we cannot conclude that this is the only non-excimer emitting conformer present on silica because gas phase calculations do not take into account surface interactions. Nevertheless, the observed activation energy may result from an average of all contributing conformations of the molecule experiencing different degrees of interaction with silica surface.

4. Conclusion

Our fluorescence results show that the emission of the bifunctional molecule N(3)N adsorbed on dry silica is mainly due to intramolecular excimer at very low surface coverages. The observed monomer emission, which accounts for about 30% of the molecules, apparently results from geometrical constraints imposed by surface interactions. These weak interactions cause the molecule to assume conformations other than the *gauche–gauche* (which is responsible for intramolecular excimer) that are non-excimer emitting. Thermodynamic data indicate that the activation energy for intramolecular excimer formation by these molecules is about 2.2 kcal mol^{-1}. Although molecular mechanics calculation predicts an activation energy of 2.3 kcal mol^{-1} for the interconversion of *anti–gauche* to *gauche–gauche* conformation in the gas phase, the good agreement between the observed and calculated value does not warrant the presence of *anti–gauche* on silica as the predominant species because calculations do not take into account surface interactions. Depending on the extent of these interactions, the observed activation energy could be an average of many contributing conformations of the molecule.

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