Picosecond dynamics of conformational changes in 1,1' binaphthyl

C. V. Shank, E. P. Ippen, and O. Teschke[a)]

Bell Telephone Laboratories, Holmdel, New Jersey 07733

K. B. Eisenthal

Columbia University, New York, New York 10027

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Optically induced conformational changes in 1,1' binaphthyl in different liquids have been studied on a picosecond time scale with subpicosecond optical pulses from a passively modelocked cw dye laser. The technique used was to measure the risetime of an excited state absorption induced by a 307.5 nm pulse and monitored with a 615 nm probing pulse. The risetime was found to be nonexponential with a 2.5±0.5 psec rapid initial rise followed by a slower component which varied from 11 to 22 psec depending on solvent viscosity. The orientational relaxation of the molecule in its equilibrium excited state configuration was also obtained.

The advent of ultrashort subpicosecond optical pulses[1,2] and the development of measurement techniques[3] on this time scale have provided the means to investigate the dynamical properties of molecules. The subject of the present work is the dynamics of excited state conformational changes in the double molecule 1, 1'-binaphthyl.

The electronic properties of systems composed of two identical parts have been a subject of keen experimental and theoretical interest for a number of years. Excimers represent one example of the changes in electronic properties resulting from the interactions between two identical moieties, one being in an excited and the other in the ground electronic state. The coupling between the two electronic systems leads to the formation of a transient species, the excimer, which has markedly different spectral properties from the isolated chromophores. Another example of systems composed of two identical parts is double molecules such as the biaryls, i.e., biphenyl, binaphthyl, binathryl, etc. They consist of two planar aromatic molecules connected by a carbon–carbon bond. Unlike the excimers, the relative orientations of the two molecules are severally constrained by the bond joining them. The structure of 1, 1'-binaphthyl is shown in Fig. 1.

Earlier spectroscopic work by Friedel and Orchin,[4] Hochstrasser,[5] and by Post, Langelaar, and Van Voorst[6] demonstrated that the absorption spectrum of 1, 1'-binaphphthyl in solution is essentially the same as the alkylated naphthylenes, i.e., in the ground state and naphthalene moieties are very weakly interacting. This suggests a ground state configuration close to perpendicular since in this configuration interactions between the π-electronic systems are minimized. These spectroscopic results are in agreement with structural studies of crystalline 1, 1'-binaphthyl. It was also found that the emission of 1, 1'-binaphthyl in a glass at low temperatures, 77 °K, is very similar to naphthalene emission both in structure and lifetime. However, in solution at room temperature the 1, 1'-binaphthyl fluorescence is significantly red shifted (~4000 cm^{-1}), structureless, and found to decrease in lifetime by an order of magnitude compared with the fluorescence at 77 °K. This points to a twisting of the naphthalene moieties into a more coplanar arrangement in the excited state which results in appreciable coupling between the π-electronic systems.

In the present work the kinetics of the structural change that occurs in the excited singlet state of 1, 1'-binaphthyl in a variety of solvents at room temperature were investigated. Using picosecond laser pulses the dynamics of the twisting motion along the excited state potential surface from the perpendicular configuration characteristic of the ground state to the more coplanar configuration of the excited state were determined. In addition to the twisting motion which changes the relative orientation of the naphthane moieties, the rotational motion of 1, 1'-binaphthyl in its equilibrium excited state configuration was also obtained.

The approach used was to excite 1, 1'-binaphthyl with a picosecond light pulse at 3075 Å and to monitor the motion towards coplanarity by probing with a second picosecond laser pulse the increase in excited-state absorption as 6150 Å. The excited state absorption at 6150 Å is characteristic of the equilibrium "coplanar" excited state configuration and is significantly stronger than the excited state absorption at this wavelength for the orthogonal configuration.

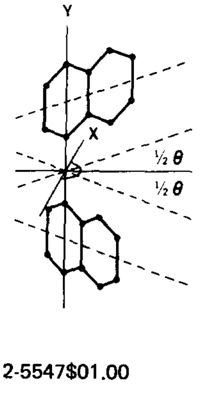

FIG. 1. Structure of 1, 1'-binaphthyl in the Cartesian coordinate system.

[a)] Work done while on a leave of absence from the Universidade Estadual de Campinas, Campinas, S. P., Brazil.

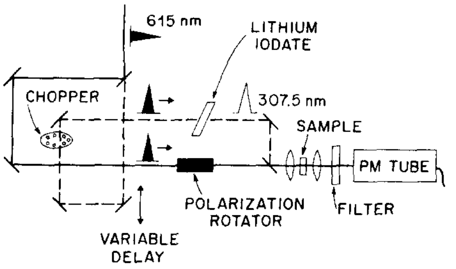

FIG. 2. Experimental arrangement.

EXPERIMENT

The source of optical pulses used in this experiment was a cavity-dumped and passively modelocked cw dye laser.[2] The pulses generated by this laser are less than 1 psec half-width with an intensity of 5×10^3 W and a pulse repetition rate of 10^5/sec. The output wavelength was 6150 Å. Subpicosecond pulses in the ultraviolet at 3075 Å were obtained by frequency doubling in lithium iodate with approximately 15% efficiency.[7]

The experimental configuration is shown in Fig. 2. The visible optical pulse train is split into a pump and a probe beam. The pump beam passes through the lithium iodate crystal and second harmonic is generated. The probe beam passes through a variable delay and polarization rotator and is recombined with the ultraviolet pump using a dichroic beam splitter. The two beams are adjusted for collinearity and focused into a cell containing the sample with a 25 mm focal length lens. The 6150 Å probe beam is selected using the appropriate filters and fed into the photomultiplier. The intense uv beam is used to excite the binaphthyl solution, and the excited state absorption is monitored as a small modulation on the visible probe beam. The pump beam is chopped mechanically, and the probe beam modulation is detected using phase sensitive detection. With this system absorption changes as small as 10^{-4} are readily detected.

The time delay is varied with a stepping motor and translation stage in one arm of the interferometer. The stepping motor drive also increments a multichannel analyzer which allows accumulation and signal averaging over a time period from minutes to hours.

Experiments were performed with various combinations of pump and probe beam polarizations. In Fig. 3 we have plotted the experimentally measured probe pulse absorption induced by ultraviolet pumping pulse in 1,1′-binaphthyl in benzene for the case when the pump and probe beam polarization were parallel. The risetime for the process was found to be nearly exponential with a 2.5 ± 0.5 psec lifetime. In the case when the pump and probe polarizations were perpendicular, a different temporal behavior was observed for the same benzene solutions, as depicted in Fig. 4. Noting the change in time scales, we observe a two component risetime with a fast component of 2.5 ± 0.5 psec and slow rise of 11 ± 3 psec. The above measurements were repeated for two other solvents: *t*-butyl benzene and *n*-heptanol.

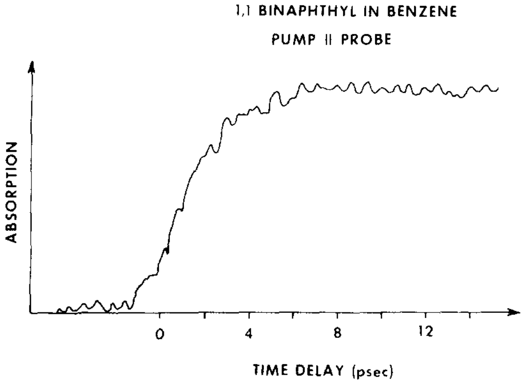

FIG. 3. Induced absorption vs time for pump (307.5 nm) and probe (615 nm) polarizations parallel for 1,1′-binaphthyl in benzene.

SUMMARY OF RESULTS

A number of common features were observed in the temporal behavior of the induced absorption in all the solutions studied. When the probe beam (615 nm) and the excitation beam (307.5 nm) polarizations were adjusted to be parallel, the induced absorption risetime was found to be nearly exponential with a time constant of 2.5 ± 0.5 psec. In the case where the pump and excitation polarizations were adjusted to be orthogonal, the temporal behavior was found to be more complex. A rapid initial rise was observed followed by a slower nearly exponential rise. In all solvents the fast risetime was found to be 2.5 ± 0.5 psec as in the parallel probe case just described. The slow component risetime varied slightly with solvent: 11 ± 3 psec in benzene, 12 ± 3 psec in *t*-butyl benzene, and 22 ± 4 psec in *n*-heptanol. After rising to a constant value, the absorption for the orthogonal case was at about twice the level reached in the parallel case.

ANALYSIS: EXCITED STATES STRUCTURAL CHANGE

Calculations and room temperature x-ray measurements indicate that 1,1′-binaphthyl in the ground state is slightly inclined towards the *cis* configuration, i.e., 20° from the orthogonal configuration.[8,9] Assuming therefore that this *cis* inclination is the dominant form for the ground state molecule, the excitation of 1,1′-

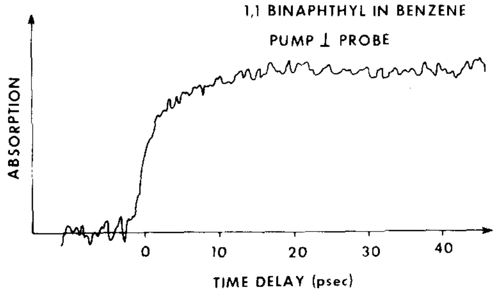

FIG. 4. Induced absorption vs time delay for pump (307.5 nm) and probe (615 nm) polarizations perpendicular for 1,1′-binaphthyl in benzene.

binaphthyl produces an excited state molecule which is also *cis* inclined immediately after absorption. The changes in the attractive vs repulsive interactions between the rings on excitation to S_1 (e.g., charge and exciton resonance effects) drive the molecule from the nearly orthogonal configuration to the more coplanar one. It is not known if the equilibrium coplanar configuration of the excited singlet molecule is the *cis* form or the *trans* form. We therefore do not know if the absorption kinetics are due to a *cis* to *trans* configuration change or some other process. One possibility involves the crossing or hopping between *cis* potential surfaces as the naphthalene moieties twist from the initial slightly inclined *cis* form toward the coplanar *cis* configuration.

The rate of passage across the different potential surfaces is determined by the factors which contribute to radiationless transitions and include the electronic matrix elements and Franck–Condon factors with the key mode being the twisting motion. The kinetic measurements could then reflect both the rate of relaxation on a given potential surface as the internal rotation occurs and potential surface crossing. The very fast 2.5 psec component could be a rapid relaxation on a given surface corresponding to twisting from the initial slightly inclined *cis* position to some intermediate angle. This would then be followed by the slower potential surface crossing to the final excited state equilibrium surface yielding the slower observed component. It is to be noted that from these experiments we cannot separate a crossing between *cis* potential surfaces from isomerization to the *trans* form.

We have chosen to present our results in a simple kinetic formulation which is consistent with our data but which may not be unique. The formulation includes the following steps:

(1) Excitation: $A(\theta_0)+\hbar\omega_2\, A^*(\theta_0)$,

(2) Rapid relaxation: $A^*(\theta_0) \xrightarrow{k_1} A_1^*(\theta_{eq}<\theta<\theta_0)$,

(3) Potential crossing: $A_1^*(\theta) \xrightarrow{k_2} A_2^*(\theta)$,

(4) Rapid relaxation: $A_2^*(\theta) \xrightarrow{k_3} A_2^*(\theta_{eq})$,

(5) Probe measurements: $A_i^*+h\omega_1 \rightarrow A^{**}$.

The transition moment for absorption of the 307.5 nm exciting pulse [Step (1)] is assumed to be along the direction of the carbon–carbon bond joining the two naphthalene moieties. This direction corresponds to the short axes of the naphthalene groups and is consistent with the close similarity of the naphthalene and 1,1'-binaphthyl absorption spectra. The excited state absorption of the probe pulse from $A^*(\theta_0)$, the slightly inclined excited state *cis* form, is neglected based on the weak 615 nm excited state absorption observed at 77 °K.[6] As the molecule twists toward the more coplanar form, an absorption appears at 615 nm. In our kinetic model we assume that an absorption appears from state $A_1^*(\theta)$ with a fast rate constant k_1. As the molecule continues to twist, a second contribution from $A_2^*(\theta)$ begins to appear at the point of a potential surface crossing with a slower rate constant k_2. Since $k_3 \gg k_2$ the absorption experimentally observed is due to $A_2^*(\theta_{eq})$. The rate of appearance for this absorption is determined by k_2 with the rapid k_3 process obscured by the slower step.

Solving the kinetic equations we obtain

$$A_1^*(t)=A^*(0)\,\frac{k_1}{k_2-k_1}\left(e^{-k_1t}-e^{-k_2t}\right), \tag{1}$$

$$A_2^*(t)=A^*(0)+A^*(0)\,\frac{1}{k_2-k_1}\left(k_1e^{-k_2t}-k_2e^{-k_1t}\right), \tag{2}$$

where $A^*(0)$ is the excited state population immediately after the excitation pulse.

The probe change in transmission

$$\Delta T_{\parallel}=\frac{\Delta I_{\parallel}(t)}{I_0}\approx -\,\alpha_{\parallel}(t)l \tag{3}$$

for $\alpha_{\parallel}(t)l \ll 1$. The quantity l is the cell length and $\alpha_{\parallel}$ is the change in absorption coefficient for parallel polarizations. A similar expression is obtained for the orthogonal case.

The polarization behavior indicates that transitions of different symmetry are involved in the excited state absorptions from states A_1^* and A_2^*. To obtain agreement with our measurements of $\alpha_{\parallel}(t)$ and $\alpha_{\perp}(t)$ the following assumptions are made: The absorption from $A_1^*(t)$ contains two orthogonal transitions. One, μ_1, is parallel to the excitation transition μ_0 from the ground to excited state of 1,1'-binaphthyl. The other transition μ_1' is orthogonal to μ_0. The excited state absorption from $A_2^*(t)$ contains a single transition moment μ_2' which is orthogonal to μ_0. With these assumptions the absorption coefficients are given by

$$\alpha_{\parallel}(t)\sim\langle|\mu_1\cdot\hat{e}_{\parallel}|^2|\mu_0\cdot\hat{e}_{\parallel}|^2\rangle A_1^*(t)+\langle|\mu_1'\cdot\hat{e}_{\parallel}|^2|\mu_0\cdot\hat{e}_{\parallel}|^2\rangle A_1^*(t)+\langle|\mu_2'\cdot\hat{e}_{\parallel}|^2\rangle|\mu_0\cdot\hat{e}_{\parallel}|^2\rangle A_2^*(t), \tag{4}$$

$$\alpha_{\perp}(t)=\langle|\mu_1\cdot\hat{e}_{\perp}|^2|\mu_0\cdot\hat{e}_{\parallel}|^2\rangle A_1^*(t)+\langle|\mu_1'\cdot\hat{e}_{\perp}|^2|\mu_0\cdot\hat{e}_{\parallel}|^2\rangle A_1^*(t)+\langle|\mu_2'\cdot\hat{e}_{\perp}|^2|\mu_0\cdot\hat{e}_{\parallel}|^2\rangle A_2^*(t), \tag{5}$$

where $\hat{e}_{\parallel}$ is the unit vector parallel to the polarization of the exciting light and $\hat{e}_{\perp}$ is the perpendicular unit vector. The average is over all angles. Substituting Eqs. (1) and (2) into (4) and (5) we obtain

$$\alpha_{\parallel}(t)\sim A^*(0)|\mu_2'|^2\left[1-\frac{k_1}{k_1-k_2}\left(\frac{3|\mu_1|^2+|\mu_1'|^2}{|\mu_2'|^2}-\frac{k_2}{k_1}\right)e^{-k_1t}-\frac{k_1}{k_1-k_2}\left(1-\frac{3|\mu_1|^2+|\mu_1'|^2}{|\mu_2'|^2}\right)e^{-k_2t}\right], \tag{6}$$

$$\alpha_{\perp}(t)=2A^*(0)|\mu_2'|^2\left[1-\frac{k_1}{k_1-k_2}\left(\frac{|\mu_1|^2+2|\mu_1'|^2}{2|\mu_2'|^2}-\frac{k_2}{k_1}\right)e^{-k_1t}-\frac{k_1}{k_1-k_2}\left(1-\frac{|\mu_1|^2+2|\mu_1'|^2}{2|\mu_2'|^2}\right)e^{-k_2t}\right]. \tag{7}$$

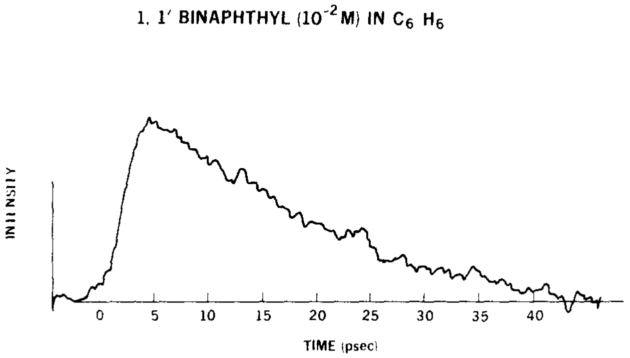

FIG. 5. Induced anisotropy vs time delay for 1, 1′-binaphthyl in benzene.

An unusual aspect of our experimental results is the apparent difference in the kinetic behavior of the absorption coefficients $\alpha_{\parallel}(t)$ and $\alpha_{\perp}(t)$. It is common, and to be expected in photoselection experiments, to find that the amplitude of $\alpha_{\parallel}(t)$ and $\alpha_{\perp}(t)$ differ, but not for the dynamics to be polarization dependent. With the formulation contained in Eqs. (6) and (7) we can describe the interesting features of our experimental observations. Two component risetimes with rates k_1 and k_2 are clearly indicated for both $\alpha_{\parallel}(t)$ and $\alpha_{\perp}(t)$. A good fit to the experimental data, for example, in the case of benzene solution can be obtained for $|\mu_1|^2/|\mu_2'|^2 = 0.08$, $|\mu_1'|^2/|\mu_2'|^2 = 0.7$. With these constants the fast rate k_1 dominates for $\alpha_{\parallel}(t)$ and contributions from both k_1 and k_2 are observed for $\alpha_{\perp}(t)$. Also the ratio of amplitudes $\alpha_{\perp}(\infty)/\alpha_{\parallel}(\infty) \sim 2$ is consistent with the experimental observations.

The absence of a viscosity dependence in the fast component of $\alpha_{\parallel}(t)$ or $\alpha_{\perp}(t)$ suggests that the k_1 process does not involve any significant motion of the solvent molecules in rotation from $A^*(\theta_0)$ to $A_1^*(\theta)$. Although we do observe a change in the slow component of $\alpha_{\perp}(t)$ in going from benzene to t-butyl benzene to n-heptanol the viscosity dependence is certainly not the simple linear dependence found for Debye-type rotational diffusion. Similar observations have been made of the viscosity dependence of the nonradiative ground state relaxation in the triphenylmethane dyes.[10-13] Relaxation in the triphenylmethanes is thought to involve a change in the relative orientations of the phenyl rings. The rate of ring rotation is found to have a nonlinear viscosity dependence, deviating from a simple Debye interpretation. The role of viscosity in the rates of internal rotational motions of molecules in solutions remains to be explored.

As the excited state molecule undergoes the internal rotation (twisting) it can also undergo an overall molecular rotation. Our measurements show that the molecular rotation is slow compared with the internal rotation for the liquids used in these studies. The method used to measure the molecular rotation[14] was a null method[15] which is more sensitive than measuring $I_{\parallel}(t)$ and $I_{\perp}(t)$. The null technique involves excitation with 307.5 nm light polarized along the laboratory z axis (what we have called the parallel reference direction) and the probe light (615 nm) polarized at 45° to the z axis. An analyzer orthogonal to the probe light is placed after the cell. If the real and imaginary parts of the refractive indices for the parallel and perpendicular directions are equal, then no light will pass through the analyzer. An optical anisotropy is induced in the system if both the ground and excited molecules have unequal absorption strengths along different molecular axes. The magnitude of the anisotropy is determined primarily by the dichroism rather than the birefringence. The intensity of transmitted light is given by

$$I_T(t) = |\hat{e}_A \cdot \mathbf{E}_T(t)|^2,$$

where

$$e_A = \frac{1}{\sqrt{2}}(\hat{e}_z - \hat{e}_y),$$

$$\mathbf{E}_T = \frac{1}{\sqrt{2}}(E_0 e^{-\alpha_z l} e^{i\phi_z} + E_0 e^{-\alpha_y l} e^{i\phi_y}). \tag{8}$$

Neglecting the induced birefringence and assuming small optical densities, we obtain

$$\frac{I_T(t)}{I_0} = [\alpha_z(t) - \alpha_y(t)]^2 l^2. \tag{9}$$

If there is no molecular rotation, then $\alpha_z(t)$ and $\alpha_y(t)$ are given by the expressions for $\alpha_{\parallel}(t)$ and $\alpha_{\perp}(t)$, respectively, Eqs. (6) and (7). Treating the molecular rotation as an isotropic rotational diffusion and assuming that the rotational times are long compared with the times for internal rotation, the expression becomes

$$\frac{I_T(t)}{I_0} = Cl^2 e^{-2t/\tau_{or}},$$

where C is a constant dependent on the induced anisotropy and τ_{or} is the orientational relaxation time. In the Debye–Stokes–Einstein hydrodynamic model, τ_{or} is related to the solution viscosity η and the hydrodynamic volume of the excited 1, 1′-binaphthyl molecule by the expression $\tau_{or} = \eta V/kT$.

Near zero time delay between pump and probe, the above equations do not describe the experimental situation because of the formation time of the induced dichroism. The formation time arises, of course, as a result of the intramolecular twist. The delay in the induced anisotropy is clearly seen in Fig. 5 to be about 5 psec. The actual time delay is somewhat longer because the experimental result plotted in Fig. 4 is the square of induced anisotropy owing to the quadratic dependence of transmission through crossed polarizers. Out on the tail of this curve the decay becomes nearly exponential with a time constant of 13.5 psec, implying a rotational relaxation time for the entire molecule in the benzene solution of 27 ± 5 psec. The values for the other solvents are 40 ± 5 in t-butylbenzene, and 300 ± 50 in n-heptanol. The ratios of the rotational relaxation times in benzene to t-butylbenzene to n-heptanol should be 1 : 1.5 : 11 if the Debye relaxation is applicable. The measured ratios are 1 : 1.6 : 9.3, which agree, within our experimental errors, with the rotational diffusion values. We therefore conclude that the rotational motion of 1, 1′-binaphthyl in its equilibrated excited state conformation can be described by the Debye–Stokes–Einstein model.

CONCLUSIONS

The results presented here represent the first observations of time resolved configurational changes of a double molecule on a picosecond time scale. By monitoring an induced dichroic absorption associated with a twisting of the double molecule we have been able to determine the complex dynamics of the configurational change consisting of at least two resolved rate processes. The influence of viscosity on these rate processes has been shown to deviate from a simple Debye process. Orientational relaxation of the double molecule has been shown to obey a simple linear relationship with viscosity.

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