

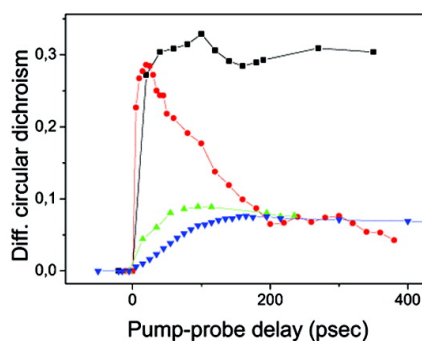
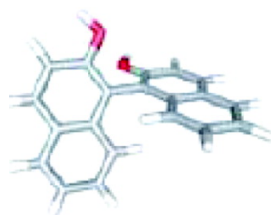
Article

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Conformational Changes in Photoexcited (*R*)-(+)-1,1'-Bi-2-naphthol Studied by Time-Resolved Circular Dichroism

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Abstract: Conformational changes following photoexcitation of (*R*)-(+)-1,1'-bi-2-naphthol are studied with a time-resolved circular dichroism (CD) experiment. Two wavelengths are investigated. For $\lambda = 237$ nm, we observe a bleaching of the ground-state absorption and a transient CD structure. Thanks to a coupled-oscillator calculation, we can attribute this effect to a decrease of the dihedral angle. For $\lambda = 245$ nm, excited-state absorption and CD are observed. All these effects are solvent-dependent. In particular, it is shown that dynamics is slower in a protic solvent, which is attributed to hydrogen-bonding of the hydroxy groups with the solvent.

1. Introduction

Conformational changes in excited molecules represent a fundamental process in chemical physics and have been studied in many molecules.¹ This is particularly important in compounds such as biaryls where two π -systems are linked by a single bond. In such cases, the dihedral angle φ between the two moieties is strongly dependent on the π - π interaction and can therefore undergo a large change after photoexcitation of the π -electrons. This process is well documented for many compounds,² and it is known, for example, that the dihedral angle in biphenyl decreases from 45° in the S_0 state to 0° in the S_1 state.³ On the other hand, information on the dynamics of such processes is rather scarce because such phenomena generally occur on a very rapid time scale and time-resolved techniques sensitive to conformation are not widespread. Picosecond dynamics in 1,1'-binaphthyl was studied by Eisenthal in the 1980s,^{4,5} and more recently, dynamics in biphenyl was studied with femtosecond resolution.⁶ Both experiments relied on time-resolved absorption spectroscopy. However, because such experiments are not directly sensitive to molecular conformation, conclusions about the dihedral angle could only be obtained thanks to quantum chemical calculations.

In the work described in this article, we chose to investigate this process with a more direct experimental signature of conformation. Due to subtle equilibrium between opposing forces such as geometrical hindrance or electronic interactions,

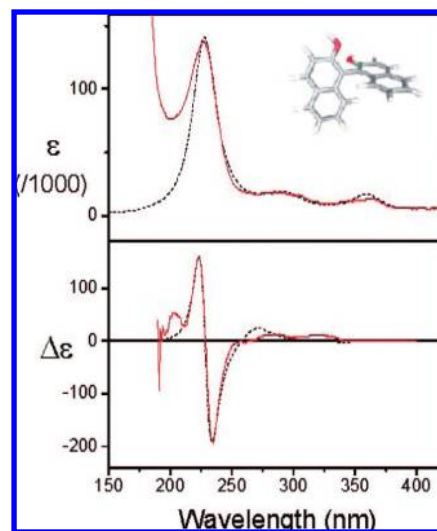


Figure 1. Absorption and CD spectra of (*R*)-(+)-1,1'-bi-2-naphthol (in $M^{-1} cm^{-1}$; solid line). The dashed lines are fits obtained with the coupled-oscillator calculation. A sketch of the molecule is shown in the inset.

stable forms of biaryls are chiral molecules, existing as two mirror-images. Such molecules, when isolated under a pure enantiomeric form, display circular dichroism (CD), which is known to be a very sensitive probe of molecular conformation.⁷ Taking advantage of a time-resolved CD measurement technique that we have recently developed,⁸ we have investigated the dynamics of conformational changes in (*R*)-(+)-1,1'-bi-2-naphthol (BINOL) from an experimental point of view. A sketch of BINOL can be seen in Figure 1. A more detailed chemical structure is displayed in the Supporting Information. More precisely, we have conducted a subpicosecond pump-probe

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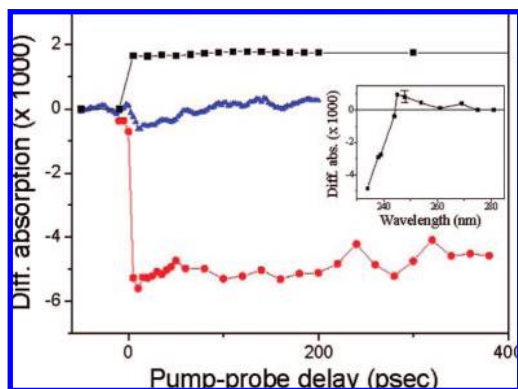


Figure 2. Differential absorption of BINOL dissolved in ethanol as a function of the pump–probe delay for three wavelengths: 237 (red circles), 244 (blue triangles), and 245 nm (black squares). The inset shows the differential absorption spectrum measured for a pump–probe delay equal to 100 ps. A typical error bar is indicated.

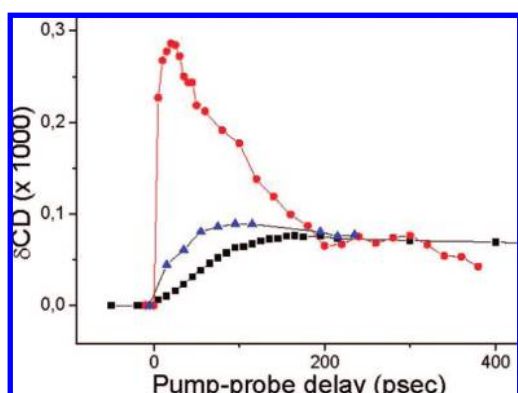


Figure 3. Pump-induced CD as a function of the pump–probe delay. BINOL in ethanol (red circles, $\lambda = 237$ nm; black squares, $\lambda = 245$ nm), and BINOL in cyclohexane (blue triangles, $\lambda = 245$ nm).

experiment where we probed the CD in the 1B_b band after photoexcitation. This band, which lies in the far-UV (220 nm), corresponds to the absorption of π -electrons along the naphthalene long axis and gives rise to a strong CD structure due to Davydov excitonic coupling.⁹ This CD structure is therefore a very sensitive probe of the relative position of the two naphthalene rings, and changes in the dihedral angle are expected to have a strong signature in the CD signal.

2. Experiment

2.1. Time-Resolved CD Measurements in the UV. In order to carry out time-resolved experiments in the far-UV, we have developed a laser source based on a 150 fs, 1 kHz titanium–sapphire laser. A tunable probe is obtained after amplification of a white-light continuum in a two-stage, BBO-based optical parametric amplifier. This yields visible pulses that we convert into the UV range either by frequency-doubling or by sum-frequency-generation with the second harmonic of the laser (400 nm). These pulses are used as probe pulses. They are tunable between 220 and 350 nm with a pulse energy around 50 nJ. The pump pulses are readily obtained after frequency-tripling the Titanium-Sapphire laser (267 nm, 300 nJ) and then focused onto the sample where they excite the π -electrons. Although the pump wavelength corresponds to a weak absorption in BINOL (see Figure 1), the energy is sufficient to excite 10–20% of the molecules and to obtain measurable effects.

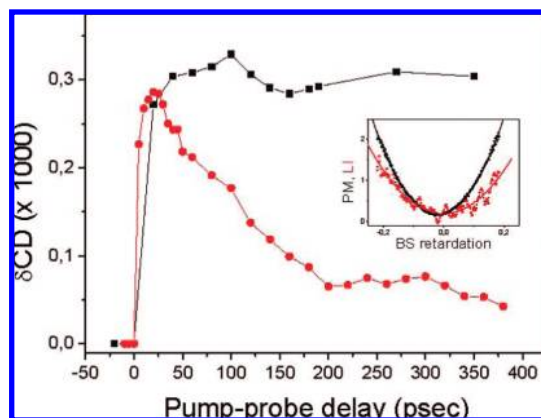


Figure 4. Time-resolved CD at $\lambda = 237$ nm for BINOL in ethanol (red circles) and in ethylene-glycol (black squares). The inset shows the raw data. Time-resolved CD is obtained by comparing the quadratic coefficients and the minimum positions for the PM and LI parabolas.

The probe pulses are sent on to the sample after passing through a variable delay line. The pump/probe cross-correlation was measured by two-photon absorption in cyclohexane and yields a 1 ps time resolution for this experiment.

Pump-induced CD was measured thanks to a new technique detailed in ref 8. The sample is placed between the crossed-polarizer and analyzer, and the ellipticity of the probe is accessed through a Babinet-Soleil compensator (BS) by recording the transmitted probe intensity (hereafter called the “PM” signal) as a function of the BS retardation θ . A mechanical chopper is inserted on the pump path, and a lock-in amplifier allows us to measure the modulated part of the PM signal (hereafter called the “LI” signal). We briefly review the principle of the measurement here. When measuring simultaneously the PM and the LI signals for small BS retardation, we obtain two parabolas:

$$PM = \theta^2 + C_1 \quad (1)$$

$$LI = -\delta\alpha L \theta^2 - \frac{\delta CD}{2} \theta + C_2 \quad (2)$$

In these equations, C_1 and C_2 are constant, $\delta\alpha L$ is the pump-induced absorption change, and δCD is the pump-induced CD change. Examination of the formulas shows that comparing the quadratic coefficients of the PM and LI parabolas directly yields $\delta\alpha L$ and that the LI parabola is shifted compared to the PM one by $\delta CD / 4\delta\alpha L$. This shift is easily measurable (especially when $\delta\alpha L$ is smaller than 0.1), and this technique allows δCD to be detected in the 10^{-4} range. Examples of the measured parabolas are given in the inset of Figure 4 (below). The experiment involves measuring the PM and LI parabolas for a fixed pump–probe delay and extracting the pump-induced absorption and CD according to eqs 1 and 2. This procedure is repeated for each pump–probe delay. Extreme care is taken to have the same polarization directions for the pump and the probe to avoid any pump-induced birefringence artifact. We checked with a racemic mixture of ruthenium-tris(bipyridyl) that there were no such birefringence artifacts in the CD measurements.

This technique can appear to be quite indirect, but it presents many advantages compared to more conventional ones relying on probe polarization modulation. First, as it only involves linearly polarized beams, it is much less prone to artifacts, which represents a tremendous challenge in conventional techniques. Second, it is much less sensitive to laser fluctuations because information is obtained through a parabolic fit of the raw data. This technique is furthermore very general and can be employed in all spectral ranges.

2.2. Sample Characteristics. Our sample consists of enantiomerically pure (*R*)-(+)-1,1'-bi-2-naphthol purchased from Sigma-Aldrich (99%). A sketch of the molecule is given in Figure 1.

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Various solvents are used for the experiments, and the concentration is about 0.2 mM for all the samples. Note that no dimerization is expected at such concentrations. The solution is placed in a 1 mm thick fused silica cuvette. The pH solution was neutral, and the BINOL molecule is protonated in its ground state ($pK_a = 9.5$). Although the excited-state pK_a is about 2.8, proton transfers are too slow in 2-naphthol to be effective during the excited-state lifetime, and we can suppose that deprotonation in the excited state is negligible.¹⁰

The steady-state absorption and CD spectra of BINOL dissolved in ethanol are shown in Figure 1. The large structure around 220 nm is attributed to the 1B_b band, which is polarized along the long axis of each naphthalene moiety.⁹ The CD spectrum displays a very strong bisignate structure which originates in the excitonic coupling of the two naphthalene transitions. This assignment allows us to give a very simple description of the CD in terms of geometrical parameters. In order to verify that point, we have carried out a classical calculation of the CD due to the dipole–dipole coupling between the two moieties. This calculation, based on the polarizability theory by Applequist,¹¹ is detailed in the Supporting Information. The fits of the absorption and the CD spectra obtained with the same parameters are displayed in Figure 1. They yield a dihedral angle of 104° , in good agreement with measured and calculated values in solution.¹² This good agreement makes us confident in interpreting the CD data in terms of geometrical information.

The BINOL molecules were excited with a 267 nm pump beam which corresponds to the third-harmonic of the titanium–sapphire radiation. We could not generate other wavelengths with a sufficient energy for efficient pumping, and although the absorption is rather weak at 267 nm, it is nevertheless likely to excite both 1B_b and 1L_a transitions. In order to gain insight into the characteristics of BINOL after this excitation, we first performed excited-state absorption measurements in the 235–280 nm range. Results are displayed in Figure 2. Pump–probe curves are plotted for three wavelengths, 237, 244, and 245 nm, whereas the inset shows the differential absorption as a function of the wavelength. Two different zones are observable. For wavelengths shorter than 244 nm, we observe a bleaching behavior, which shows that we do excite the 1B_b transition. In contrast, for wavelengths longer than 244 nm, the dominant effect is an induced absorption, likely due to the electrons excited in the 1B_b band. The changes in optical density are very weak, meaning that the excited-state and the ground-state absorptions have a large overlap. It is worth noting that no dynamics is observable in Figure 2 for 237 and 245 nm. This feature is consistent with a previous study which showed that the intramolecular transfer of the excitation between the two moieties was done in less than 1 ps¹³ and that the excited-state lifetime is in around 5 ns.¹⁰ It also proves that the electronic relaxation can be neglected on our time scale and that no dynamical information can be obtained from these time-resolved absorption measurements. We have nevertheless observed a relaxation for the 244 nm curve with a time constant comparable to the one observed in time-resolved CD (*vide infra*), probably originating from a very slight shift in the electronic band when conformational relaxation occurs. This feature is rendered visible at this wavelength because ground-state absorption bleaching and excited-state absorption almost perfectly compensate each other, and it is likely that the solvent response will slightly affect the excited-state absorption.

3. Results and Discussion

3.1. Conformational Changes. In a first set of experiments, we studied time-resolved CD in the bleaching zone ($\lambda = 237$ nm) for samples dissolved in ethanol. The results are displayed in Figure 3 (red circles), where the CD change is plotted in optical density units. They show that, right after excitation by the pump, an increase of the CD is observed. But one has to keep in mind that the steady-state CD at this wavelength is *negative* (see Figure 1), which indicates that excitation by the pump induces a *decrease* of CD in absolute values. This feature is consistent with the expected bleaching of the 1B_b transition, but sorting out the contributions of both the bleaching and excited-state absorption is difficult due to the large uncertainty in the fraction of excited molecules. The steady-state CD at 237 nm being equal to -3.5×10^{-3} , and estimating that 12% of the molecules are excited, would yield $\delta CD = 4.2 \times 10^{-4}$ for the bleaching alone, indicating that the contribution of the excited state is *negative* and of the order of -10^{-4} , corresponding to $\Delta\epsilon \approx -40 \text{ M}^{-1} \text{ cm}^{-1}$.

When considering longer delays, one observes that the CD goes down, which indicates that the excited-state CD, which is *negative*, *increases* in absolute values, whereas the absorption remains constant. Let us now discuss this feature. This CD change cannot be due to a change in the electronic state of the BINOL since it does not show up in absorption, nor to a mere change in the molecule's orientation, even though such reorientation effects are likely on this time scale. Indeed, BINOL involves two transitions oriented at about 90° , which confers on this molecule a 2D character and makes it much less sensitive to reorientation effects. This feature could be checked in absorption as well as in CD thanks to our calculation of anisotropic CD.¹⁴ It is similar to what we had observed in carboxy-myoglobin.¹⁵ From an experimental point of view, this is confirmed by the fact that we do not observe any time evolution of the absorption changes. Finally, we are confident in attributing the change in CD to a change in the molecule's conformation and, more precisely, to a change in its dihedral angle. We have examined the consequence of a change in the dihedral angle on the CD according to the calculation described in the Supporting Information. Considering that the dihedral angle at equilibrium is about 100° , we see that an increase (in absolute value) in the CD corresponds to a decrease in φ . From our calculation, it is not possible to obtain a quantitative value of φ since nothing is known about the spectroscopic properties of the excited state, but our data are qualitatively consistent with such a decrease. We can remark that the excited-state CD undergoes a 3-fold increase, which is consistent with a 20–30° change in the dihedral angle (see Supporting Information). This is in agreement with previous studies¹⁶ which estimated that BINOL undergoes a change from a *trans* ($\varphi = 103^\circ$) to a *cis* ($\varphi = 69^\circ$) configuration after photoexcitation. We can, therefore, conclude that we observe in a very direct way the dynamics of the change in the dihedral angle in BINOL thanks to our time-resolved CD measurement.

When going to a wavelength pertaining to the excited-state absorption region ($\lambda = 245$ nm), things are somewhat different. In that case, the steady-state CD is very small, and we observe

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the onset of a new CD feature which builds up in a time comparable with the relaxation observed in the bleaching zone (Figure 3). The final CD is of the order of $+30 \text{ M}^{-1} \text{ cm}^{-1}$. However, the dynamics is more complicated and cannot be fitted with a simple exponential curve. This feature is likely to come from the interplay between the aforementioned change in the dihedral angle and electronic relaxation in the excited state, as already observed in the differential absorption curve at $\lambda = 244 \text{ nm}$.

3.2. Solvent Dependence. We also studied time-resolved CD in the bleaching zone ($\lambda = 237 \text{ nm}$) for various solvents. The results are displayed in Figure 4. The two curves correspond to two solvents with very different viscosities: ethanol (1.074 cP) and ethylene glycol (16.1 cP). It is very obvious that the relaxation time observed in CD is strongly solvent-dependent. In ethanol, the pump-induced CD can be fitted with a single exponential with a 100 ps time constant, whereas in ethylene-glycol, no relaxation is observed on the time scale of the measurement. Another experiment was also carried out for a 3:97 (vol) mixture of the two solvents, yielding an intermediate result with a 130 ps relaxation time.

From Figure 4, it is very clear that the higher the viscosity, the longer the relaxation time. When ethanol is changed to the ethylene-glycol/ethanol mixture, the viscosity at 25°C changes from 1.07 to 1.2 cP,¹⁷ whereas the relaxation times go from 100 ± 10 to 130 ± 20 ps. This effect is expected and has already been thoroughly studied in refs 4 and 5 thanks to the Kramers' equation. We note, however, that the time of our measurements are much longer than in refs 4 and 5. This difference is due to the fact that the molecules studied are not exactly the same. In refs 4 and 5, the molecule is binaphthyl, whereas here we study binaphthol. Although the two molecules are very similar, a major difference lies in the presence of two hydroxy groups in BINOL. These groups are not expected to change dramatically the electronic states, and the conclusions concerning the dihedral angle are therefore expected to be very close. In contrast, these two hydroxy groups may lead to dramatic change in the dynamics of the conformational changes because they are prone to form hydrogen bonds in protic solvents such as ethanol or

ethylene-glycol. In order to check that point, we carried out the experiment at $\lambda = 245 \text{ nm}$ in a nonprotic solvent, cyclohexane (Figure 3). Cyclohexane has a viscosity of 1.02 cP at 17°C , close to that of ethanol, but we observed a 40% decrease in the time constant of the CD changes between the two solvents. This shows that hydroxy groups indeed slow down dynamical processes in protic solvents due to hydrogen-bonding and that this effect is canceled out in nonprotic solvents. This feature is in agreement with solvatochromism studies of 2-naphthol which show that hydrogen-bonding plays a dominant role in the solvation effects.¹⁸

4. Conclusion

We have performed time-resolved circular dichroism measurements in BINOL at two wavelengths. In the first case, ground-state absorption bleaching is observed, and after an instantaneous change, the CD undergoes a relaxation process which is strongly solvent-dependent. We attribute this relaxation to the change in the molecule's conformation and, more precisely, to a decrease of the dihedral angle between the two moieties. The dynamics of this dihedral angle change is directly measurable from the dynamics of the CD signal. For the other wavelength, excited-state absorption dominates, and the onset of a CD signal associated with this new absorption process is observed. Measurements made in protic/nonprotic solvents show that the dynamics is slower in protic solvents, illustrating the effect of hydrogen-bonding on the solute-solvent interaction and dynamics.

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Supporting Information Available: Detailed calculation of the CD spectrum of BINOL with the coupled oscillator model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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