Reversible Photoswitching of Second-Order Nonlinear Optical Properties in an Organic Photochromic Crystal

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Introduction

In the recent years, there has been a tremendous number of studies dealing with organic molecules and materials for nonlinear optics (NLO),[1−3] owing to the increasing need for cheap and easily processable materials in photonics applications. Many organic molecules possess intrinsic molecular NLO properties that can beat the usual inorganic crystals. However, one of the main challenges to make these organic molecules suitable for practical applications is the design of materials. For example, to get an efficient material for quadratic NLO properties ($\chi^{(2)} \neq 0$), molecules have to be arranged in a noncentrosymmetric fashion in order to avoid the annihilation of molecular quadratic hyperpolarizability (β).

Interest for organic systems also arises from the possibility of combining other properties in the same material, to make them more valuable. We have been focusing our studies on organic molecules and materials exhibiting both NLO properties and photochromism. In previous works on poled polymers, we showed that the latter property could modulate the former, owing to the switching between two molecular species (e.g. DR1, an azobenzene derivative,[4] and spiropyran and furylfulgide).[5] However, reversibility of the photochemical reaction does not necessarily imply reversibility of NLO properties of the material. In fact, in polymers, the randomization of the molecular orientation inside the bulk leads to an irreversible decay of the NLO properties and eventually to a centrosymmetric structure. Other studies regarding photoswitching of NLO properties have been performed in solutions on photochromes such as diarylethene[6] and nitrobenzylpyridine derivatives,[7] but none of them were done on real material. To the best of our knowledge, the only paper on completely reversible photoinduced change of material's NLO properties reports on transient phenomena in Langmuir−Blodgett film supported ruthenium−tris(bipyridine) complex derivative.[8]

The present work deals with *N*-salicylidene-4-bromoaniline (**1**), known to yield reversible photochromic reaction in crystalline state due to proton transfer (Figure 1). Compound **1**, like other *N*-salicylideneaniline ("anil") compounds, is known to exhibit photochromism in various states (solution, crystal, rigid glass, and organic matrix), and the first studies date back to the beginning of the century.[9−13] It is interesting to point out that the solid-state photochemical activation is weak, owing to the small structural change during the reaction. Moreover, **1a** crystallizes in a noncentrosymmetric structure.[14] It belongs to the $Pca2_1$ space group (orthorhombic), which is among the 14 most frequently encountered noncentrosymmetric ones.[15] Second-order NLO properties are studied by second harmonic generation (SHG).

Experimental Section

Synthesis. Compound **1a** has been synthesized using a straightforward method. By mixing a solution of salicylaldehyde (Aldrich) in methanol (0.61 g in 10 cm^3) and a solution of 4-bromoaniline (Aldrich) in methanol (0.86 g in 10 cm^3), yellow crystals precipitated in about an hour. These were filtered, and recrystallized from methanol. mp 109 °C (lit. 109 °C).[6] Anal. Calcd for $C_{13}H_{10}NOBr$: C, 56.55%; H, 3.65%; N, 5.07%; O, 5.79%; Br, 28.94%. Found: C, 56.47%; H, 3.87%; N, 4.86%; O, 5.91%; Br, 29.07%. For further studies, these crystals are put between two microscope glass slides, melt on a hot plate, and cooled slowly to room temperature.

Photochromism. The absorption spectrum of **1a** (Figure 2) was taken on a Cary 5E (Varian) spectrophotometer. Photochromic properties of **1** were studied by alternate irradiations with UV light at 365 nm (450W Xe/Hg lamp, 10 nm wide band-pass filter) and with visible light at 490 nm (same lamp, analogous filter). During irradiation, a probe beam detected by a diode array through a spectrometer (Princeton Instruments) allowed us to follow in situ the absorption changes in the UV−visible region.

SHG Measurements. The fundamental beam (1064 nm) of a Nd:YAG picosecond laser (30 ps pulse width, 10 Hz repetition rate) was focused on the sample. Alternately, we used a 1907 nm fundamental beam, Raman-shifted from the fundamental of a Nd:YAG nanosecond laser (10 ns pulse width, 10 Hz repetition rate, focused in a 50 atm 1 m long hydrogen cell). In both cases, the second harmonic beam was selected through a 10 nm wide band-pass filter and collected by an appropriate photomultiplier. The SHG signal was read on an ultrafast oscilloscope (Tektronix TDS620B).

Results and Discussion

Photochromism. The photochromic character of compound **1** is checked. Upon UV irradiation, a reddish

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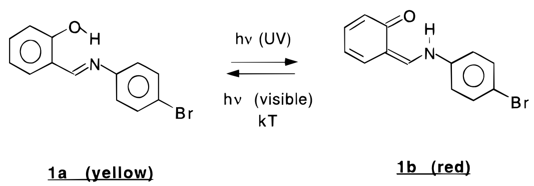

Figure 1. Photochromic reaction of *N*-salicylidene-4-bromoaniline (**1**).

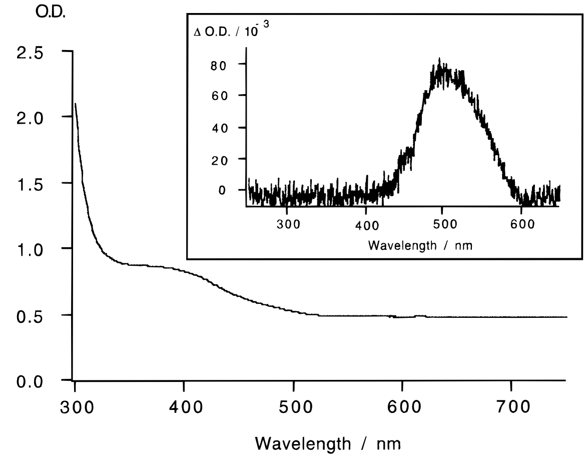

Figure 2. Absorption spectrum of **1a** (OD, optical density). Inset shows the differential spectrum (ΔO.D.) between before (**1a**) and after (**1a** + **1b**) UV irradiation.

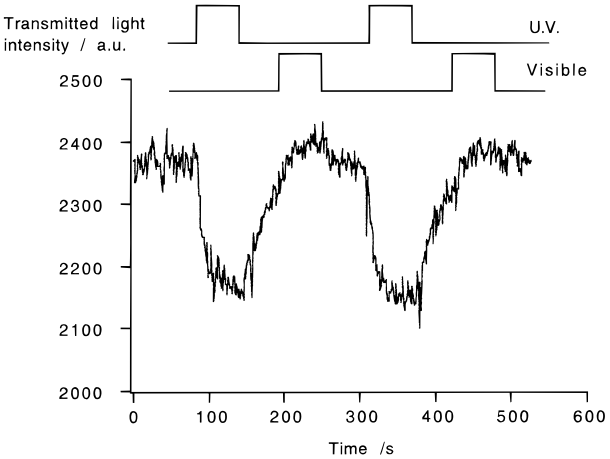

Figure 3. Transmitted light intensity at 500 nm: variations during UV irradiation—thermal decay—visible irradiation cycles.

color appears, and an equilibrium between the two isomers is reached after about 30 s of irradiation (Figure 3). The absorption difference between **1a** and the equilibrium is shown in Figure 2. The red color vanishes either under visible irradiation or by leaving the sample in the dark. In this latter case, the color almost completely disappears in half a minute, and a fairly good exponential fitting yields a rate constant of 3×10^{-2} s^{-1}. This value is 1 order of magnitude higher than for the *N*-salicylideneaniline itself (2×10^{-3} s^{-1}).[11] A subsequent irradiation through a narrow band-pass filter in the visible helps the back reaction to complete (Figure 3). Quantitative measurements of quantum yields and conversion ratio could not be done because of high diffusion and low absorption change.

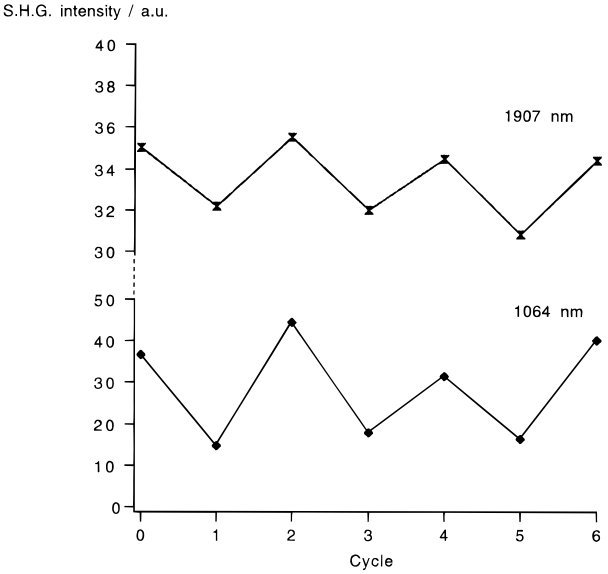

Figure 4. Photoswitching of SHG at 1907 nm (upper curve) and at 1064 nm (lower curve). SHG values are not to be compared between both curves. On the *x* axis, odd numbers correspond to "after UV irradiation" and even numbers correspond to "after visible irradiation".

Table 1. Theoretical β_0 Values of Compounds 1a and 1b[a]

	1a	1b
$\beta/10^{-30}$ esu	2.3	1.3
$\beta_x/10^{-30}$ esu	2.0	0.1
$\beta_y/10^{-30}$ esu	0.3	1.3
$\beta_z/10^{-30}$ esu	1.1	0.3

[a] In both cases, the molecule lies almost in the *xy* plane, and the *x* axis is along the Br−C bond.

This photochromic behavior is rather common in "anil" compounds. However, some "anils" (e.g. *N*-salicylidene-4-chloroaniline) show no photochromism in bulk but thermochromism, and both properties are exclusive according to Cohen and co-workers.[11] These phenomena are largely topochemically dominated: a subtle difference in the substituents can drastically change the photochromic behavior in crystals, as this has also been observed recently in some diarylethenes.[16]

NLO Properties. A totally reversible SHG intensity change, correlated to the change of the molecular species, is observed (Figure 4). The irradiation cycles are identical with those of Figure 3, but since in situ measurements are not possible in our SHG setup, the overall evolution of the SHG intensity is not followed. Odd abscissa correspond to 10 s after switching the UV irradiation off and even abscissa to 10 s after switching the visible irradiation off. The modulation is not a totally "on/off" type: the SHG intensity drop is about 60% at 1064 nm and 10% at 1907 nm. Theoretical calculations by the finite field method using the molecular orbital program MOPAC [17] gives β_0 (off resonance β) = 2.3×10^{-30} esu (Table 1) for **1a**, based on crystallographic data. For **1b**, the geometry is unknown and β_0, after AM1 optimization, is found to be 1.3×10^{-30} esu. Since theoretical β values are very sensitive to the geometry, it is not reliable as an absolute value. However, the difference between the two calculated β values can explain the switching of SHG during the **1a** → **1b** reaction. Another remarkable feature is that the

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main component of β is not in the same direction in the two isomers (Table 1). This feature can also generate an NLO property change during the photochromic process. The "self-absorption" of the second harmonic beam at 532 nm by the red compound (**1b**) may contribute to the drastic drop of SHG intensity at 1064 nm. On the other hand, resonance enhancement should have an opposite effect. We do not have any clear explanation for such a different modulation intensity between 1064 nm (60%) and 1907 nm (10%).

Compound **1a** exhibits SHG both at 1064 and 1907 nm. At 1064 nm, the second harmonic green light can be observed with the naked eye. Since the lattice volume and the density of the compound are known,[14] weighting the sample and measuring the surface of the glass substrate yields 75 μm as a rough estimation of the average thickness. The sample is far less diffusing than the usual urea powder reference. Hence, a quartz crystal (Y-cut, 3 mm thick, $d_{11} = 0.5$ pm/V) is used as reference. At 1907 nm, its maximum SHG signal is only 4 times **1a**'s for a thickness ratio of 40. Therefore, *N*-salicylidene-4-bromoaniline can be considered as a competitive material, though not optimized yet.

Conclusion

Totally reversible photoswitching of second-order NLO properties in photochromic crystals was performed without any loss of the noncentrosymmetric order. With this material, we are stepping beyond the molecules and toward the device. One of its advantages is that no wide movement of the molecule is required for the proton transfer, making the photochemical process easy to proceed. The flexibility of organic chemistry will probably extend this new family of functional materials by optimizing the yield of the photochromic conversion, the NLO response itself both on the molecular and on the material's scales, and finally the amplitude of the change in NLO response.

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