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Bifunctional Photochromism Based on Photoinduced Nitro-Assisted Proton Transfer

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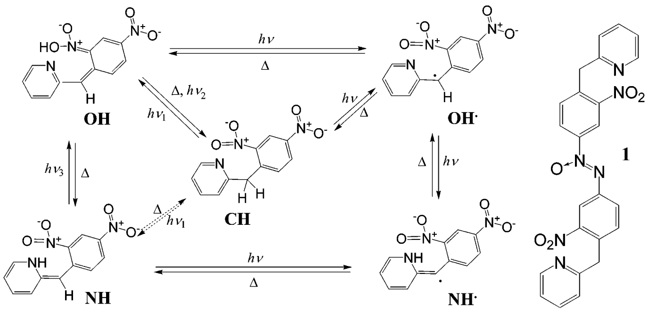
Newly recognized potentials for application as switching units in electrical nanocircuits and photon-based memory devices have revived research interest in photochromic compounds during the last two decades.[1] Because an appreciable number of photochromic families are already known, most of the recent efforts have been directed toward modification of the existing photochromic compounds, preferably the ones that are active in the crystalline state, aimed to prepare more stable and fatigue-resistant photoresponsive materials.[2] Another goal that has been addressed recently is design of polystable photoactive systems, for example, by co-crystallization of structurally similar molecules[3] or by combination of several photoactive units in the same molecule.[4−6] Such polyfunctional molecules are advantageous relative to their monofunctional analogues with respect to a larger change of the physical properties upon photoirradiation (e.g., nonlinear optical properties),[7] potential use in energy quenching,[8] and nondestructive optical readout.[9] Here we report on the preparation, spectroscopy, structure, and solid-state photochromism of the first photoactive bifunctional molecule based on the *ortho*-nitrobenzylpyridine (NBP) unit, which is capable of nitro-assisted proton transfer (NAPT) and could serve as a prototypic compound for a new concept of design of nitro-based polystable switching materials.

Scheme 1. Proton-Transfer and Radical Reactions of the NBP Unit (left) and the Chemical Structure of the Dimer 1 (right)



Scheme 1 shows the reaction diagram of the NBP moiety which undergoes NAPT among three forms, CH, NH, and OH.[10] At low temperatures, the NAPT is thermally deactivated, so that usually cryogenically irradiated NBPs are not photoactive. If such NBPs are subsequently warmed in the dark, they show latent photochromism—delayed color change due to low-yield open-shell reactions including radicals.[11] The NBP group is the most-used trigger unit for controlled release of bioactive compounds and fluorescent dyes in caged compounds.[12−14] Nevertheless, as a result of the negligible structural perturbation it requires, the NAPT mechanism seems to be very advantageous for preservation of the crystallinity during prolonged operation.[15,16] Furthermore, the NBPs are promising for optical control of nonlinear optical properties.[7] To increase the number of possible states, a new strategy was employed in this study based on combination of a *polyfunctional* system (i.e., having more than one photochromic unit) and a *polystable* system (i.e., having more than two photoisomers of each group) within the same molecule. In general, an *n*-stable molecule with *m* photoactive units can have n^m ground states, while a bistable molecule with a single photoactive unit can have only $2^1 = 2$ states. Therefore, the polystable, polyfunctional molecule could, in principle, exist in $n^m/2$ times more states relative to a bistable monofunctional one. In this study two photoactive NBP units were coupled into the azoxy dimer **1**. The two polymorphs of **1**, obtained through a simple synthetic procedure, are photoactive in the single crystalline state and show “inverted” temperature dependence of the photochromic activity. The visible absorption maximum of the colored form of the dimer is strongly red-shifted from the respective monomer and appears at the highest wavelength reported so far in the NBP photochromic family. Further-

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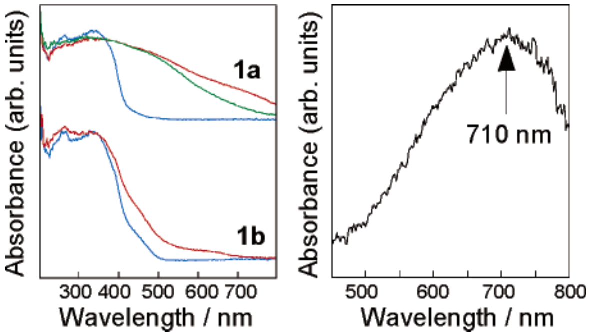

Figure 1. Left: UV/vis spectra of powdered recrystallized **1a** and **1b** recorded in reflection mode in the KBr matrix in the dark (blue), after short-term UV irradiation (red) and after thermal bleaching of **1a** exposed to several minutes of UV irradiation (green). Right: difference spectrum of **1a** before and after the bleaching. These spectra are reproducible for short-term UV irradiation, but permanent coloration from red products is obtained during prolonged irradiation (e.g., **1a**).

more, the triclinic polymorph can be obtained as crystals with millimeter dimensions which upon coloration absorb in the near-IR region.

The dimer **1** was prepared, together with 2-(4′-amino-2′-nitrobenzyl)pyridine (**2**) and very small amounts of 2-(2′-amino-4′-nitrobenzyl)pyridine (**3**) by aerobic reduction of 2-(2′,4′-dinitrobenzyl)pyridine (**4**) with H_2S. Alternatively, it can be prepared by acidic oxidation of **2** with peroxide.[17] Recrystallization of **1** afforded pale yellow parelellepiped triclinic ($P\bar{1}$, **1a**) and bright yellow needle monoclinic ($P2_1/n$, **1b**) crystals. Plate polygonal crystals of **1a** of millimeter dimenions can be grown by slow evaporation from ethanol.

The UV/vis spectra of the two forms of **1** are shown in Figure 1. Upon UV irradiation (λ < 400 nm) solid **1a** and **1b** change their color, the coloration being dependent on the polymorph, its physical state, and irradiation conditions. At 298 K, short (<1 s) or diffuse UV irradiation turn powdered **1a** deep blue, but prolonged or intense irradiation result in a red-brown color as a result of photolysis. With moderately intense light irradiation, the spectral change is reversible. In the dark, the blue color remains visible for 1 day. The UV/vis spectrum of the resulting blue product(s) indicates that a mixture of products is obtained with different kinetics of the thermal bleaching. To obtain the part of the spectrum which is bleachable in 1 day, the difference spectrum was calculated by subtraction of the spectrum of the powdered sample bleached thermally by standing 1 day in the dark from the spectrum of the same sample recorded immediately after the coloration by exposure to UV light. The resulting difference spectrum exhibits a broad absorption band starting from 500 nm, with a maximum at 710 nm, full width at half-intensity of about 200 nm, and low-wavelength tail extending above 800 nm into the near-IR region (Figure 1). To our knowledge, the absorption maximum at 710 nm of the blue **1a** is the longest wavelength of a blue species within the entire family of photochromic NBP compounds. The large shift from the blue form of the monomer **4** (550 nm) is clearly a result of the extended conjugation of **1a**. Contrary to **1a**, the blue coloration of irradiated powdered **1b** at 298 K is hardly noticeable and disappears completely within 1 min from the irradiation offset. If crystalline **1a** and **1b** are irradiated below 173 K, their photochromic properties are inverted. As expected from the thermal deactivation of the NAPT, photoirradiated **1a** remains almost colorless,[17] while even a very short UV flash turns **1b** intensively blue-green. The color in the latter case is stable at 173 K but disappears completely in several minutes if the sample is warmed to 298 K.

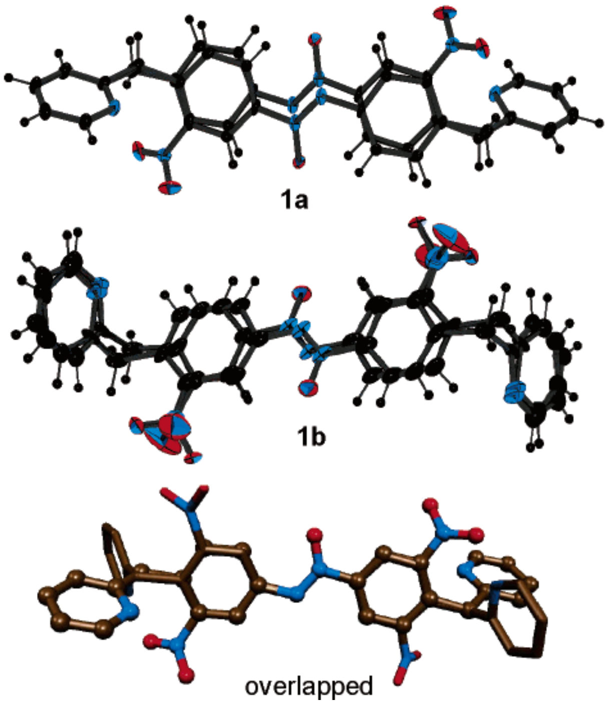

Figure 2. ORTEP diagrams of the molecular structures of the colorless forms of **1a** and **1b** (each 1:1 disordered over two positions, 50% probability level). Bottom: overlapped representation of the structures of **1a** (ball-and-stick model) and **1b** (stick model).

To unravel the different temperature behaviors of the photochromic properties of **1a** and **1b** and especially the unexpected photoactivity of **1b** at low temperature, the structures of both unirradiated crystals were determined at 293 and 78 K[18] and are presented as thermal ellipsoid diagrams in Figure 2. Both structures are practically unaffected by the temperature. The $-CH_2-C_6H_3(NO_2)-N{=}N(\rightarrow O)-C_6H_3(NO_2)-CH_2-$ portion of the molecule of **1a**, except for the nitro groups, was refined as a disordered entity across a center of inversion with an occupancy 0.5 of all atoms. The N═N and N→O distances are 1.254(5) and 1.271(5) Å, respectively. When referenced to the C1—C4 axis, the nitro group lies on the same side as the N→O linkage, being twisted by 35.2(3)° with respect to the phenyl ring. Similarly to the other photochromic NBPs,[10,16] the nitro group (the proton chaperon) and the pyridyl nitrogen (the proton acceptor) are placed on the same side of the benzyl bridge plane. Therefore, the structure of **1a** corresponds with

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the photoactivity and the long lifetime (hours) of its blue form at room temperature.[15] Accordingly, the inactivity of the crystals of **1a** at 78 K is ascribed to thermal deactivation of the NAPT. In **1b**, the entire molecule is disordered over the center of symmetry, and all atoms were assigned half occupancy. Contrary to in **1a**, the nitro group and the N→O bond are positioned on opposite sides. The unprimed and primed nitro groups are twisted by 63.4(6)° and 41.4(4)° from the respective phenyl rings. Similarly to the nonphotochromic NBPs,[16] the nitro group and the pyridyl ring are positioned on opposite sides of the benzyl bridge plane and NAPT is not likely to occur. Therefore, the inverted temperature dependence of the photoactivity of **1b** is probably due to latent photochromism, similarly to what was proposed for the monomer compound **4**.[11] Namely, although due to the unfavorable relative juxtaposition and large distance between the proton donor (methylene group) and proton acceptor (pyridyl nitrogen) the geometry of **1b** is not favorable for NAPT, the creation of radicals, which does not seem to be apparently related to geometrical conditions, may be still active. At temperatures as high as 78 K one portion of the radicals is already decayed to the colored form NH, which results in the blue color. The creation of radicals may be enhanced by the powder state of **1b** used to record the UV/vis spectra. It should be noted that single crystals of **1a** also exhibit latent photochromism. If flashed with UV light at 78 K through quartz windows and then warmed to room temperature in the dark, they develop weak absorption bands at 560, 630, and 1100 nm at 220 K. This observation conforms to the photoactivity of **1a** at ambient temperature. Extensive literature search[19] showed that the weak band at 1100 nm is the first near-IR band reported for a blue NBP compound. Most of the previous spectroscopic studies of NBPs have been devoted to the difference between the colorless and colored forms in the visible region. Near-IR absorptions controllable by visible light are important for quenching of the absorbed energy[8] and nondestructive optical readout.[9]

In both crystals, the non-centrosymmetric molecules of **1** are packed over the center of symmetry. Therefore, independent operation of the two photoactive units of each molecule within the centrosymmetric crystals can only proceed at single-molecule level, with preservation of the overall crystal symmetry. To investigate the possibilities for energy slicing by stepwise switching of a single molecule among the possible states, the energies of the nine possible ground-state isomers of **1** were calculated at the B3LYP/6-31G(d) level. The results indicate that approximately 70 kcal mol^{-1} (293 kJ mol^{-1}) can be stored by each molecule between the highest-energy (OHOH) and the lowest-energy (CHCH) forms. The energy splits between the consecutive steps in the cascade are in the range 15−20 kcal mol^{-1} (63−84 kJ mol^{-1}), which corresponds to the resulting energy portions upon ground-state deexcitation from OHOH to CHCH.

In summary, the first bifunctional molecule based on NAPT, with each functionality having three and the whole molecule having nine possible closed-shell states, was prepared in two crystalline forms. Because of the larger number of possible ground states, the compound represents a model for design of NBP-based materials for memory devices with an increased density of storable information. Despite that the structure of each crystalline form remains practically unaffected by the temperature, as a result of the difference in the reaction mechanisms the two forms exhibit inverted temperature dependence of the photochromic activity. The low-temperature photoactivity of the monoclinic form, whose molecular conformation is unfavorable for proton transfer, is probably due to latent photochromism caused by radical reactions. Therefore, this compound (**1**) is capable of dual-mode switching in the solid state—by closed-shell (proton transfer) and open-shell (hydrogen atom transfer) reactions. The mechanism and, consequently, the photochromic properties are ultimately determined by the actual molecular conformation in the solid state. In addition, the UV spectra of crystalline **1** show for the first time that, by extension of the molecular conjugation, both visible and near-IR absorption maxima of the photoinduced colored NBPs can be tuned and shifted to lower energies. The near-IR absorption may have application potentials for media capable of nondestructive readout. If combined with larger molecular cages, this and similar NBP compounds can be also employed for synthesis of photoactive inclusion complexes.[20]

Syntheses. **4** (1.0 g) suspended in EtOH (20 mL) with 1 mL of ammonia was bubbled with H_2S, initially for 4 h at 273−283 K and under reflux 2 h afterward. After removal of the solvent, the product was extracted to an acidic aqueous solution containing a small amount of HCl, neutralized with diluted NaOH solution, and extracted with CH_2Cl_2. A total of 0.82 g of yellow-brownish solid was recovered from the organic layer and purified on an Al_2O_3 column (hexane, gradient elution with CH_2Cl_2) to yield **1** (607 mg) as an orange solid and **2** (83 mg) as a yellow solid. The compound was alternatively prepared by the following method: 100 mg of **2**, 0.8 mL of 98% acetic acid, 0.2 mL of 35% H_2O_2, and one drop of 96% H_2SO_4 were mixed, and the solution was kept for 2 days in the dark. Precipitate formed upon addition of 1 mL of distilled water and a 20% aqueous solution of NaOH. The solution was extracted with toluene, and the organic extract was dried over anhydrous $MgSO_4$ and evaporated to give 71 mg of **1** as an orange solid. The product was recrystallized from an acetone/EtOH mixture and purified with column chromatography on a short column (Al_2O_3, CH_2Cl_2). TLC (Al_2O_3/EtOAc:hexane = 3:7): 0.16 (**2**), 0.42 (**1**). The first recrystallization of **1** from EtOH afforded long, thin colorless to pale-yellow needles of **1b**. Further recrystallizations from EtOH or acetone/EtOH af-

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(19) Review article on the photochromism of *ortho*-NBPs: Naumov, P. *J. Mol. Struct.* **2005**, in press.

(20) To demonstrate the possibilities for incorporation of polystable NAPT-based photochromic molecules in more complex structures, **1** was included into the cavity of γ-cyclodextrin (γCD) by mixing a solution of γCD in MeOH to which a drop of water was added (to dissolve the γCD), with a solution of **1** in MeOH. Upon several seconds of irradiation with UV light from a high-pressure mercury lamp at 298 K, the large colorless crystals of the adduct **1**@γCD turn blue. The coloration depends on the exposure time and at ambient conditions is completely thermally bleachable. The crystals of **1**@γCD can be cycled between the colorless and the blue forms several times without visible residual coloration.

forded either **1b** concomitantly with yellow plates of **1a** or **1a** only. **1b** was also obtained from the CH_2Cl_2/hexane mixture. Several orange crystals of **3** were also isolated from the batch of **1** recrystallized from EtOAc/EtOH. The identity of **2**−**4** was confirmed by X-ray diffraction.

X-ray Diffraction.[18] The data were collected from samples in the dark in ω-scanning mode with a Siemens SMART diffractometer equipped with a charge-coupled device detector and liquid nitrogen cryosystem. Several crystals were measured for each polymorph to confirm their identity. The structures were solved with direct methods and refined with the least-squares method.[18] Structure determination and crystal data are as follows. **1a**: $C_{24}H_{18}N_6O_5$, orange-yellow plate, 300 × 300 × 50 μm, $M_r = 470.44$, triclinic, $a = 7.2765(2)$, $b = 7.5673(1)$, $c = 11.2579(3)$ Å, $\alpha = 86.385(1)$, $\beta = 80.176(2)$, $\gamma = 61.485(1)°$, $V = 536.59(5)$ Å^3, $T = 78(2)$ K, space group $P\bar{1}$, $Z = 1$, μ(Mo Kα) = 0.106 mm^{-1}, $\rho_{calc} = 1.456$ g·cm^{-3}, $\theta_{max} = 27.5°$, $\lambda = 0.710\,73$ Å, reflns/unique 3838:2426, params/rest 158:52, $R = 5.83\%$ [1840 reflns with $F_o > 4\sigma(F_o)$] and $R = 7.64\%$ (all 2426 reflns), max peak/hole 0.67:−0.66 e·A^{-3}. The phenyl rings were refined as hexagons with sides of 1.39 Å. The temperature factors of the primed atoms were set equal to those of the unprimed atoms. Additionally, the thermal vibrations of the carbon and nitrogen atoms were restrained to be nearly isotropic, and several distance restraints were also used. **1b**: $C_{24}H_{18}N_6O_5$, colorless to yellowish needle, 400 × 120 × 40 μm, $M_r = 470.44$, monoclinic, $a = 9.9484(5)$, $b = 4.1968(2)$, $c = 25.6637(13)$ Å, $\beta = 92.623(2)°$, $V = 1070.37(14)$ Å^3, $T = 78(2)$ K, space group $P2_1/n$, $Z = 2$, μ(Mo Kα) = 0.11 mm^{-1}, $\rho_{calc} = 1.460$ g·cm^{-3}, $\theta_{max} = 25°$, $\lambda = 0.710\,73$ Å, reflns/unique 7085:2453, params/rest 179:240, $R = 9.86\%$ [1282 reflns with $F_o > 4\sigma(F_o)$] and $R = 16.53\%$ (2453 reflns), peak/hole 0.52:−0.45 e·A^{-3}. The diffraction intensities of several measured crystals were not as optimal and only half satisfied the $I > 2\sigma(I)$ criterion. The benzyl and pyridyl rings were refined as regular hexagons. The disorder was treated by applying a number of restraints.

UV/vis Spectra. The spectra were recorded in reflection mode from powders or crystals of the sample in KBr with a Jasco V-560 spectrometer. The UV/vis/NIR spectra from a single crystal of **1** were recorded on an UV-3100 PC spectrometer (Shimadzu) with Oxford cryostat. The hexagonal plate single crystalline sample (size of the largest side: 0.9 × 1.5 × 0.6 × 1.5 × 1.0 × 1.3 mm) was pressed in a KBr pellet and irradiated with UV light from Hg lamp filtered with filter L-39 ($\lambda_{max} = 405$, 436 nm) for 200 s. The irradiation was conducted in 10 s shots separated by 20 s dark intervals to avoid overheating of the sample.

Theoretical Calculations. All theoretical calculations were performed with the Gaussian 98 program suite[21] running on a SGI ORIGIN2000 supercomputer. The energies of the optimal stable ground-state structures of the possible isomers of **1** were calculated using the density functional theory [the B3LYP method with the 6-31G(d) basis set].[22,23]

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Supporting Information Available: X-ray crystallographic files for **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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