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Structure of the Photocolored 2-(2′,4′-Dinitrobenzyl)pyridine Crystal: Two-Photon Induced Solid-State Proton Transfer with Minor Structural Perturbation

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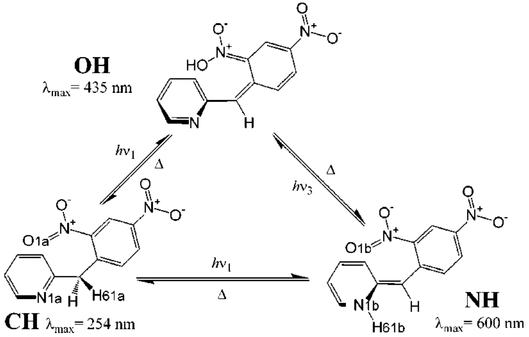
The potential applicability of photochromic solids as controllable molecular media in the photon-based molecular devices, that is, memories and switches, has turned such materials into an expanding research field.[1] One of the most intriguing photochemical reactions known for over 70 years[2] is the photoinduced and thermally activated proton transfer (PT) between the colorless **CH** and blue **NH** forms of 2-(2′,4′-dinitrobenzyl)pyridine (DNBP) (Scheme 1).

Spectroscopic observations[4] suggest that the photoexcited **CH** isomerizes to the **NH** form either by a direct **CH** → **NH** reaction or through an intermediate aci-nitro structure (**OH**). Transient spectroscopic measurements in the solid state have revealed a long-lived species consistent with a triplet state or a metastable ground-state tautomer.[4e] Theoretical results[5] supported the latter alternative, indicating that the **CH** ↔ **NH** reaction in a crystal proceeds through an **OH**-like intermediate. Considerably high photoconversions (∼16%) reported in thin crystalline layers[6] ensure that **NH** is not produced exclusively at crystal defects. Although the photochromism of DNBP[2] and the structure of **CH** in the colorless crystal[7] have been known for quite some time, direct crystallographic evidence for the **NH** and **OH** isomers has been lacking. By employing the two-photon excitation technique, we have accomplished preparation of diffraction-quality single crystals with high concentrations of the **NH** blue isomer. The following reports the results of its X-ray analysis.

To increase the population of the **NH** form in a single crystal[8] while retaining low concentrations of the **OH** isomer several experimental problems had to be solved. First, relaxation of the **NH** form by thermal isomerization (Scheme 1) was minimized by using low temperatures. Second, partial crystal decay upon prolonged UV irradiation—which leads to the formation of light-absorbing, yellow-brownish, photoinactive side-products[9] that prevent reaction in the crystal interior—had to be avoided. A third obstacle preventing the accumulation of the **NH** tautomer is that incident light can be strongly self-filtered by a thin (several micrometers) blue layer at the crystal surface, preventing further excitation of the **CH** form.[7] Resonant two-photon excitation has been shown to be useful for efficient photoconversion in similar cases.[10] Therefore, irradiation conditions were optimized to reduce the inherent and induced filter effects from the blue species and from the side products, respectively. These conditions involved short irradiation times with intense monochromatic light to (1) excite the absorption tail of the **CH** form, (2) bleach the yellow-absorbing **OH** tautomer, and (3) remain unabsorbed by the **NH** isomer. While twice the wavelength of the yellow maximum (∼508 nm) falls on the low-frequency side of the broad blue **NH** absorption (λ_{max} = 600 nm, Figure 1) and should not decrease the **NH** isomer significantly, it approaches the **OH** shoulder (λ_{max} = 435 nm) and could eventually suppress the concentration of the **OH** isomer. After several trials with wavelengths $\lambda \leq 508$ nm (i.e., away from the 600 nm maximum and closer to the 435 nm one), good photoconversion was achieved upon 0.5 h exposure of a DNBP single crystal to pulses with $\lambda = 502$ nm.[11] As the **NH** and **OH** have only higher transitions around $\lambda/2$, such irradiation was less likely to excite these isomers by a double-photon event.

Scheme 1. Proton Transfer Reactions[3] in Crystalline DNBP



The molecular structure[12] of the **CH** isomer in the blue crystal resembled that before irradiation. When the **CH** part was refined anisotropically, additional peaks from the non-hydrogen atoms of the product molecule and the transferred proton, except for the *o*-nitro nitrogen atom, were observed in the difference Fourier map. Subsequently, both closely overlapped molecules were refined within the isotropic model. This afforded occupancy of 32.8% for the **NH** photoproduct. That conversion to the **NH** form had occurred up to 36.4% was confirmed from the fitted UV/vis spectrum. Under these conditions, the **OH** form had accumulated to less than 0.5%.

The **NH** isomer in the disordered blue crystal (Figure 2; atoms of **CH** and **NH** are labeled with a and b, respectively) evidences only minor structural rearrangement. The dynamic proton is transferred over a distance of nearly 3.16 Å from H61a to H61b. The active oxygen O1a is 2.28(2) Å far from the proton H61a in **CH**; after PT and structural relaxation it (O1b) is placed 2.88(1) Å away from the transferred proton H61b and 3.19(1) Å from the allyl proton H62b. The final separation between the heavy centers O1b and N1b amounts 3.13(1) Å. The planar phenyl ring slightly shifts within its plane together with the *p*-nitro group. Relative orientation of N2−O1 to the phenyl ring is retained (O1−N2−C8−C7 in **CH** and **NH** equals 30.4 and 30.9°, respectively), while N2−O1 is rotated around C8−N2 (C7−C8−N2−O2 decreases from 153.8 to 145.6°) in **NH**. The loss of planarity of the pyridine ring shows rehybridization in the 2-benzylpyridyl fragment, consistent with the enamine structure of **NH**. Resonance with the allyl

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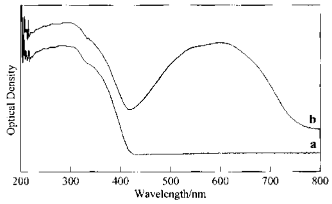

Figure 1. UV/vis spectra of (a) colorless and (b) blue DNBP in KBr.

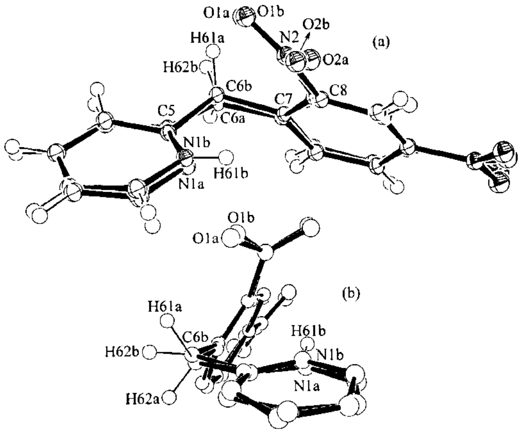

Figure 2. Perspective views (50% probability ellipsoids) of the molecular structure of the blue crystal with overlapped **CH** (occ ≈ 67.2%) and **NH** (occ ≈ 32.8%) isomers along two directions (a, b). Phenyl and pyridyl H-atoms in the plot (b) are omitted for clarity.

bridge shifts the bridging carbon atom C6 for 0.2 Å and the remaining proton from H62a to H62b.

The X-ray structure of the blue crystal and the high yield of **NH** have several important implications for the proposed reaction mechanism in DNBP-type photochromics (Scheme 1): (a) The structure of the photoproduct represents the first direct evidence that the blue coloration of DNBP exposed to light can be assigned to the **NH** enamine tautomer. (b) Since there are no significant intermolecular interactions in the crystal structure of the **NH** and **CH** forms, the PT in the solid state clearly is an intramolecular process. (c) The PT reaction can proceed despite the unfavorable donor−acceptor orientation in the reactant **CH** (C6a−H61a- - -N1a = 40.2°). As the structure of the product is very similar to that of the reactant, it is likely that the **OH** form may be an intermediate between the **CH** and **NH** forms. The *o*-nitro group abstracts H61[13] and by reorientation it delivers it to the nitrogen acceptor (Figure 2). Since there is considerably large void space around the *o*-nitro-group, the other oxygen atom is unhindered for simultaneous shift backward. The relative position of the aromatic rings remains nearly unaltered and the proton is free to undergo the reverse series of events, which accounts for the thermal reversibility of the PT. The **NH** structure thus supports the indications[5b] that the **CH** ↔ **NH** reaction can only proceed by participation of the nitro group. The photoinactivity of some DNBP-type compounds can be rationalized by consideration of the rotational freedom of the *o*-nitro group. (d) The high **NH** yield with scarcely populated **OH** in our two-photon experiment supports the presumptions[5] about the existence of an additional short-lived species which can produce **NH** from the excited **CH** effectively, even during low concentration of **OH**. Experimental and theoretical studies are now underway to characterize this transient.

In summary, the structure of the blue **NH** isomer produced by two-photon excitation in a single crystal of DNBP is detailed here. It represents the first crystallographic characterization of a blue species in the DNBP photochromic family. From the result, the photocoloration of solid DNBP is attributed to a *nitro-assisted proton transfer* mechanism. The reaction is feasible for compounds with nitro group(s), which is in the vicinity of an acidified hydrogen and a convenient basic target, and requires no significant structural perturbation in the solid state.

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Supporting Information Available: X-ray crystallographic data for the colorless and blue crystals (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) The lifetimes (ref 5a) of the **NH** and **OH** forms are 5.5 × 10^3 s (198 K) and 750 s (325 K). The activation energies in the solid state are in the range 3.9−96.5 kJ/mol (ref 4c).

(4) For examples, see: (a) Hardwick, R.; Mosher, H. S.; Passailaigue, P. *Trans. Faraday. Soc.* **1960**, *56*, 44. (b) Yokoyama, K.; Kobayashi, T. *Chem. Phys. Lett.* **1982**, *85*, 175. (c) Sixl, H.; Warta, R. *Chem. Phys.* **1985**, *94*, 147. (d) Corval, A.; Kuldová, K.; Eichen, Y.; Pikramenou, Z.; Lehn, J. M.; Trommsdorff, H. P. *J. Phys. Chem.* **1996**, *100*, 19315. (e) Casalegno, R.; Corval, A.; Kuldová, K.; Ziane, O.; Trommsdorff, H. P. *J. Lumin.* **1997**, *72−74*, 78.

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(8) DNBP was synthesized by nitration of 2-benzylpyridine (Tokyo Kasei), purified by column chromatography (Al_2O_3, gradient elution with CH_2Cl_2/hexane) and recrystallized from EtOH. Repeated recrystallizations from EtOH yielded crystals suitable for X-ray diffraction.

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(11) The 355-nm harmonic of a pulsed Quanta-Ray Nd:YAG laser was used to pump a Quanta-Ray MOPO−SL optical parametric oscillator. The output pulse with frequency of 10 Hz was tuned to 502 nm, close to the doubled maximum absorption of the yellow crystal (254 nm), where the yield was sufficient for structure analysis. To avoid melting, DNBP crystal of good quality affixed on a glass fiber was covered with glass capillary and inserted into a Dewar filled with liquid nitrogen. After irradiation of 0.5 h with $\lambda = 502$ nm, the crystal was inserted directly into cold N_2 stream on the goniometer head and the data were collected with a CCD SMART diffractometer.

(12) The structure was solved by direct methods (Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G. Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined (Sheldrick, G. M. E. *SHELXL-97*, Program for crystal structure refinement, University of Göttingen, Germany, 1997) on F^2 against all reflections. Except for the refined benzylic hydrogen atoms, all hydrogens were included according to the riding model. To avoid correlation between the heavily overlapped structures, the isotropic thermal parameters on the analogous atoms were constrained equal. Crystal data: $C_{12}H_9N_3O_4$, monoclinic, $P2_1/c$ (blue) $a = 9.9727(1)$ Å, $b = 15.2094(1)$ Å, $c = 7.6778(1)$ Å, $\beta = 101.106(1)^o$, $Z = 4$, $T = 77$ K, $R = 0.0476$, GOF = 1.059. The highest residual peak was located near to the isotropic *p*-nitro oxygen atom (0.46 e$Å^{-3}$).

(13) In all theoretical models of **OH** (details will be reported elsewhere), the phenyl ring was nonplanar with partially double C−N bond. The **OH** isomer represents a broad and flat local minimum on the high potential energy barrier for **CH** ↔ **NH** proton jump.

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