Long-lived Photoinduced Proton Transfer Processes

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Irradiation of the phenanthroline–dinitrobenzyl compound **3** generates, *via* a photoinduced proton transfer process, a long-lived tautomer having a lifetime about 5 × 10^3 times longer than that of the parent compound **1a**.

Photoinduced electron transfer processes have been studied extensively both as models for natural photosynthesis and for energy conversion purposes. Proton-based systems undergoing long-lived, long-range photoinduced proton transfer (PIPT) may allow the preparation of optical switches for optical data processing and storage applications such as optical memories based on frequency-selective spectral hole burning[1–7] and optical information processing.[8] They also represent the basic components of molecular protonic devices.[9] Proton transfer (PT) can also be utilised for the transformation of light energy into a thermodynamic potential,[10,11] as is the case for natural PT systems.[12]

PT reactions present a number of interesting properties: (i) they are in most cases reversible, and can be used for many cycles; (ii) they do not require large structural changes and can therefore take place in the solid state, amorphous or crystalline, even at low temperatures; (iii) the lifetime of the proton-transferred states ranges from the picosecond regime to days and more at very low temperatures.

Long-term optical memories require a system which possesses bistability, *i.e.* two thermally stable states, and which can be photoconverted selectively and reversibly from one state to the other.

A promising PIPT system is the photoinduced tautomerism of 2,4-dinitrotoluene derivatives[13–18] and, in particular, the photoconversion of 2-(2,4-dinitrobenzyl)pyridine **1** (α-DNBP) to its 'NH' tautomer **1a** (Fig. 1)† which takes place in solution[16] and in the crystalline state[17] as well as when the compound was adsorbed on solid matrices.[18] Although this system was already reported in 1925,[13] little is known about the relation between molecular structure and proton transfer properties.

In view of designing new PIPT systems exhibiting longer lifetimes of the tautomers, two new molecules **2** and **3** have been synthesised *via* compounds **4**,[19] **5**, **6**[20] and **7**, according to Schemes 1 and 2.‡ In these derivatives, hydrogen bonding between the transferred proton and the additional adjacent pyridine nitrogen may stabilize the transferred state and retard the back PT reaction. We present here a comparative study of some of the thermodynamic, kinetic and spectroscopic properties of **2** and **3**.

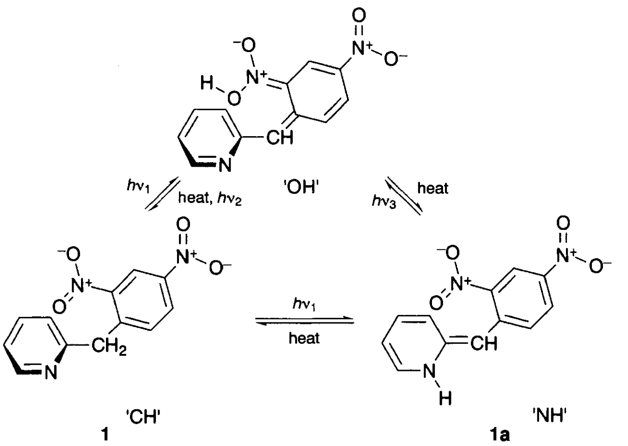
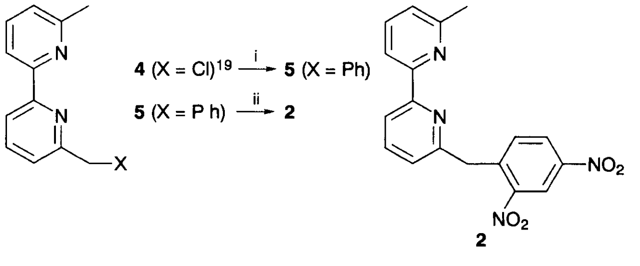


Fig. 1 Photochemical and thermal interconversion processes of the 'CH', 'OH' and 'NH' tautomers of **1**[16,17]

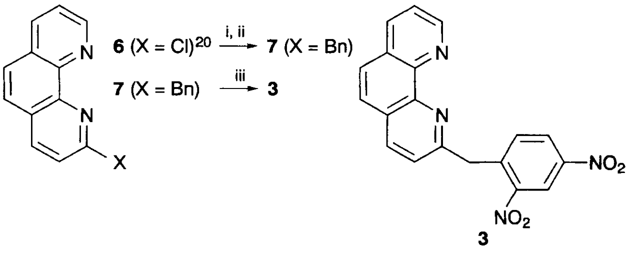
Compounds **2** and **3** were found not to be photochromic in the crystalline state, although the crystal structure of **3**[21] exhibits internal coordinates of the dinitrobenzylpyridine part that are similar to those reported for **1** which is photochromic in the crystalline state.[22] This may indicate the operation of intermolecular effects in these solid state PIPT processes.

In solution, **2** and **3** were found to generate a metastable, blue to blue–purple form upon near-UV§ irradiation with a quantum yield *ca.* 0.1.[23] By analogy with **1a**[16] and in view of the visible spectra similarities, these forms can be considered to be the 'NH' tautomers of **2** and **3**.

The lifetimes of the PT 'NH' forms of **1–3** were found to be strongly solvent-dependent. In aprotic solvents, they are significantly longer for **2** and **3** than for **1**, while in protic solvents such as ethanol, they are similar. Fig. 2 displays the temperature dependence of the lifetimes of the 'NH' tautomeric forms of **1**, **2** and **3** in ethanol and toluene. Table 1 presents the kinetic parameters. It appears that upon adding a neighbouring nitrogen site that may establish a hydrogen bond to the transferred proton in the 'NH' form, retardation of the back PT reaction can be achieved. For instance, at 295 K the lifetime of **1** in ethanol was 4.7 s, while **2** and **3** showed lifetimes of 0.32 and 33.5 s, respectively. In toluene, the differences in lifetimes were found to be more important; the lifetime of **1** dropped to 0.02 s, while for **2** and **3** it increased to 0.44 and 125 s, respectively. Thus, the replacement of the pyridine group in **1** by a 9,10-phenanthroline group in **3** leads to a marked increase



Scheme 1 *Reagents and conditions*: i, $AlCl_3$, C_6H_6, reflux, 72 h, 94%; ii, HNO_3, H_2SO_4, room temp., 2 h, 83%



Scheme 2 *Reagents and conditions*: i, $PhCH{=}PBu_3$, DME, reflux, 16 h; ii, Na_2CO_3, H_2O, reflux, 4 h, 88%; iii, HNO_3, H_2SO_4, room temp., 2 h, 70%

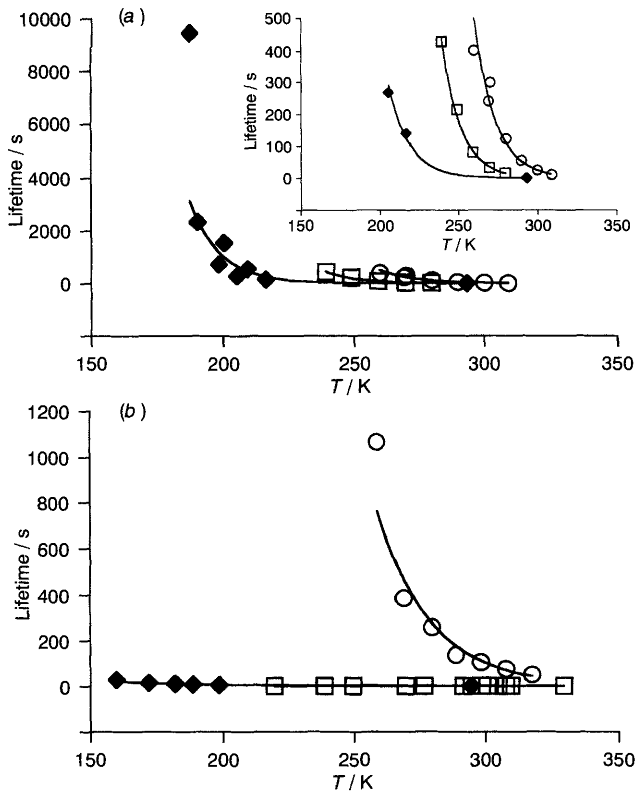


Fig. 2 Lifetimes for the back conversion of the 'NH' tautomer to the 'CH' tautomer for **1** (□), **2** (◆) and **3** (○) as a function of temperature in dry ethanol (*a*) or toluene (*b*) solution. Insert: expansion of the 0–500 s domain.

Table 1 Lifetimes at 295 K, Arrhenius activation energy E_a and preexponential factor *A* for the back-conversion of form 'NH' to form 'CH' for **1**, **2** and **3**[a]

Compound	Solvent	Lifetime/s	E_a/ kcal mol^{-1}	A/s^{-1}
1	Ethanol	4.7	11.1	2.8×10^7
2	Ethanol	0.32[b]	10.0	5.8×10^7
3	Ethanol	33.5[c]	14.0	1.5×10^8
1	Toluene	0.02	2.8	8700
2	Toluene	0.44	2.7	175
3	Toluene	125[d]	8.2	3400

[a] See Fig. 1. [b] Extrapolated from 0.38 s measured at 293 K. [c] Extrapolated from 25 s measured at 299.6 K. [d] Extrapolated from 104 s measured at 298.7 K.

in the lifetime of the coloured tautomeric 'NH' form, by a particularly large factor of about 5×10^3 in the apolar solvent toluene.[24]

Immobilisation of **1–3** in different polymers gave photochromic films in which the lifetime of the blue 'NH' tautomer varied from a few min to several h.[25]

The results described here give access to systems undergoing long-lived PIPT reactions which are of interest for the design of molecular protonic devices[9] as well as for various procedures of optical information storage and processing.

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Footnotes

† The 'NH' tautomer **1a** (Fig. 1), as well as the analogous forms of **2** and **3**, may in principle exist in two configurations having the dinitrophenyl group in *cis* or *trans* position with respect to the pyridyl nitrogen; their geometry and interconversion barrier will depend on the double bond character. Further studies are necessary in order to clarify this point.

‡ All new compounds gave spectroscopic and microanalytical data in agreement with their structure.

§ The light sources used were the 3rd harmonic of a YAG laser at 355 nm and a mercury lamp fitted with a Melles Griot 'UG1' filter.

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