

STEADY-STATE INFRARED EVIDENCE OF THE PHOTOINDUCED ACI-NITRO TAUTOMER OF SOLID 2-(2',4'-DINITROBENZYL)PYRIDINE

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By using selective photoirradiation and lifetime extension by isotopic substitution, the photoinduced unstable aci-nitro tautomer OH of 2-(2',4'-dinitrobenzyl)pyridine is produced in IR-detectable amounts in thin polycrystalline film. The selectively deuterated form of OH absorbs at 2606 cm^{-1} and is stable with minutes at ambient conditions.

Key words: 2-(2',4'-dinitrobenzyl)pyridine; isotope effect; photochromism; solid-state reactions

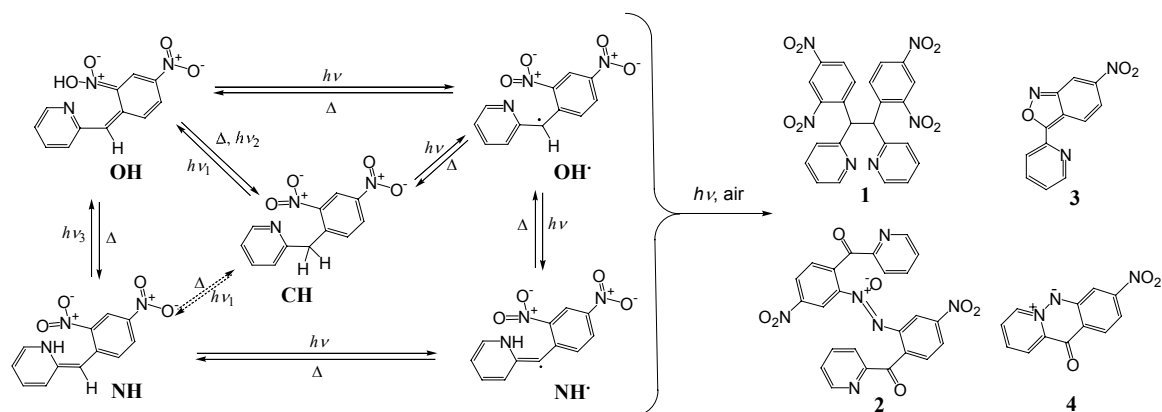
INTRODUCTION

Photochromic nitrobenzylpyridines (NBPs) have been attracting scientific attention since the first discovery of their solid-state photochromism in 1925 [1]. The NBPs are already employed as phototriggers in caged bioactive compounds [2]. The long lifetime of the photoinduced colored form and the large difference between the second hyperpolarizabilities of the colorless and colored forms indicate that the NBPs can be used for photomodulation of the second harmonic generation [3]. Another potential use of the NBPs is as phototrigger units in electrical nano-circuits. Detailed knowledge of the reaction mechanism is crucial for practical application of the NBPs in the nano-electronics.

The simplified reaction mechanism is outlined in Scheme 1: mainly by means of photoinduced and thermally-activated nitro-assisted proton transfer, the excited stable colorless form CH (2-(2',4'-dinitrobenzyl)pyridine; $\lambda_{\text{max}} = 250\text{ nm}$) is converted, *via* the unstable aci-nitro tautomer OH (6-aci-nitro-2-nitro-5-(2'-pyridylmethylene)-1,3-cyclohexadiene; lifetime: > seconds in the solid state, microseconds in solution, $\lambda_{\text{max}} = 430\text{ nm}$), into blue enamine tautomer NH (2-(2',4'-dinitrophenylmethylidene)-1,2-dihydropyridine; lifetime: hours in the solid state, seconds in solution, $\lambda_{\text{max}} = 600\text{ nm}$) [4]. Additional low-yield open-shell reactions

which include two carbon-centered radicals (OH and NH) account for the crystalline photofatigue (products 1–4) [5]. Although an appreciable quantum of diffraction and spectroscopic data on the isomers CH and NH is available now [4], neither diffraction nor steady-state infrared spectroscopic data exist on the short-lived isomer OH. The creation and existence of the OH form, have been, however, undoubtedly confirmed with UV/vis spectroscopy [6, 7]. The OH produced through the open-shell routes was detected with fast temperature-resolved difference IR spectroscopy [5].

In order to extend the lifetime of the OH form and produce it in IR-detectable amounts, selective irradiation and deuteration were simultaneously employed. Thereby the selective irradiation was crucial for selective increase of the population of the OH form, despite that it is thermodynamically less stable than the NH form. The deuteration was intended to extend the lifetime of the OH form by slowing its thermal decay due to the notable isotopic kinetic effect [8]. In addition, to decrease the strong filtering effect of the blue NH form, instead of the usual pellet method, the experiments were performed with thin microcrystalline layers of 2-(2',4'-dinitrobenzyl)pyridine (DNBP) deposited on an IR-transparent carrier crystal.



Scheme 1. Reaction mechanism of the NBPs exemplified on the parent compound DNBP. The reactions denoted with broken arrows are characteristic for liquid state

EXPERIMENTAL

DNBP, either synthesized by nitration of 2-benzylpyridine or obtained from commercial sources, was purified and repeatedly recrystallized from EtOH prior to the use. The isotopomer deuterated selectively in the benzylic positions, DNBP- d_2 , was prepared from finely powdered protiated sample (110 mg), dissolved under argon in dry THF (2 mL) and EtOH- d_1 (7 mL, 99 % D, Cambridge Isotope Laboratories) with catalytic amounts of Et₃N, sealed in an ampoule and kept at *ca.* 250 K in water bath for a week [8]. The solid obtained on evaporation under reduced pressure, was purified with thin layer chromatography (Al₂O₃, 10 % ethyl acetate in hexane, $R_f = 0.17$) and recrystallized from methanol- d_4 (99.95 % D, Aldrich). Except for the benzylic bands, the IR spectrum of DNBP- d_2 resembled closely that of DNBP.

For investigation of the photochromism, the deuterated samples were irradiated according to two regimes. For photocoloration the ranges of 360–460 nm and > 700 nm were cut (filter C-39B) from the output of high-pressure mercury lamp, while for photobleaching the range of 490–750 nm was sharp-cut (filter Y-51) from the output of xenon arc lamp. The irradiation time varied according to the experiment.

The FT IR spectra were recorded with Jasco FT IR 350 instrument (32/16 scans, res. 4 cm⁻¹). KBr pellets or thin microcrystalline layers served as samples. In the latter case, thinly sliced KBr crystals were coated with DNBP by instant dipping into solution of the compound in anhydrous acetone and dried in air. The phase identity of DNBP crystallized from ethanol and acetone was confirmed by X-ray diffraction.

RESULTS AND DISCUSSION

The infrared spectra of colored and bleached polycrystalline samples of DNBP were recorded in KBr matrix and as thin films. The detailed vibrational data for the protiated DNBP samples are listed in Table 1. In order to increase the photoconversion of CH to NH and OH, thin films of DNBP and DNBP- d_2 were deposited on the carrier crystals, photocolorated with UV light and subsequently bleached with visible light. Fig. 1 shows the regions where the bands from the $\nu(\text{CH})$, $\nu(\text{NH})$, $\nu(\text{ND})$ and $\nu(\text{OD})$ modes are expected.

Upon photocoloration with UV light (360–460 nm), bands from $\nu(\text{NH})$ (3385 cm⁻¹) and

$\nu(\text{ND})$ (2507 cm⁻¹) modes of the NH form appeared in the spectra of DNBP and DNBP- d_2 , respectively, mostly due to the photoreaction CH→NH. The assignment of the $\nu(\text{NH})$ mode is corroborated by the value of the isotopic shift (1.35) and its identical decay rate with the characteristic strong NH bands in the mid-IR region [4]. Simultaneously with the evolution of $\nu(\text{NH})$, the band from the symmetric benzylic stretching mode $\nu_7(\text{CH})$ at *ca.* 2880 cm⁻¹ decreased in the spectrum of DNBP, indicating photodecay of CH, as expected [9] from spectra of model compounds.

Table 1

Infrared data (cm^{-1}) of protiated 2-(2',4'-dinitrophenyl)pyridine (DNBP) in the 4000–400 cm^{-1} region^a

		Room temperature						7 K										
		Polycrystal in KBr matrix			Thin film ^b			Polycrystal in KBr matrix			Bleached ^c							
		Yellow	Blue	Bleached	Yellow	Blue	Yellow	Blue	Yellow	Blue	Bleached ^c	Yellow	Blue	Bleached ^c				
							3517	vw										
									3210	m	3211	m	3211	m				
3115	vw	3385	w	n	3114	vw	3385	vw	3120	w	3120	w	3120	w				
3103	w	3115	vw		3103	w	3102	w	3107	w	3108	w	3108	w				
3088	vw	3088	vw		3088	vw	3086	w	3086	vw	3090	vw						
3051	w	3051	w		3051	w	3051	w	3052	w	3054	vw	3054	vw				
3012	w	3012	w		3012	w	3011	w	3012	w	3011	vw	3011	vw				
2957	vw	2957	vw		2958	vw	2956	w	2956	vw	2960	vw	2959	vw				
2925	vw	2929	vw		2926	vw			2932	vw	2932	vw	2932	vw				
									2891	vw	2891	vw	2891	vw				
2878	vw	2877	vw	↓	2878	vw	2875	vw	2872	vw	2882	vw	2882	vw				
2859	vw	2863	vw		2859	vw			2864	vw	2864	vw	2864	vw				
									2851	vw	2851	vw	2851	vw				
2758	vw	2756	vw		2758	vw	2754	vw	2755	vw	2763	vw	2763	vw				
								1697	w									
									1648	vw	1648	vw	↑	1648	vw			
									1643	vw	1643	vw		1643	vw			
									1637	vw	1637	vw	↑	1637	vw			
		1636	vw	n	1637	vw												
		1630	sh		1629	sh	↓											
1610	m	1610	m		1610	m			1614	m	1614	m	1614	m				
1603	m	1603	m		1603	m	1603	m	1602	m	1605	m	1605	m				
1589	m	1589	m		1589	m	1588	m	1588	m	1591	m	1591	m				
1577	sh	1577	sh		1577	vw			1577	sh	1577	sh	1577	sh				
1568	w	1568	w	↓	1568	w	1568	w	1569	w	1568	w	1568	w				
1559	vw	1559	w	↑	1560	vw	↓		1559	sh	1559	vw	↑	1560	vw	↓		
1540	s	1539	s		1541	vs			1542	s	1542	s	↓	1542	s	↑		
									1537	m	1537	m		1538	m	↑		
1525	vs	1525	vs		1529	vs	1527	vs	1527	vs	1526	vs	1526	vs				
									1523	sh	1523	vs	↑	1524	vs	↓		
									1515	m	1515	m		1515	m			
									1509	sh	1509	sh		1509	sh			
1502	sh	1502	sh		1502	sh		1508	sh	1500	sh	1500	sh	1500	sh			
					1490	vw				1491	vw	1490	vw	1490	vw			
1475	m	1475	m		1476	m	1474	m	1474	m	1476	m	1476	m				
1459	vw	1459	vw		1458	vw				1458	vw	1459	vw	1459	vw			
										1447	w	1447	w	1447	w			
										1434	vw	1434	vw	1434	vw			
1427	m	1427	m		1428	m	1427	m	1430	m	1427	m	1427	m				
										1411	w	1411	w	1411	w			
1408	w	1408	w		1408	w	1407	w	1407	w	1405	vw	1405	vw	1405	vw		
										1392	vw	1392	vw	1392	vw			
										1362	sh	1362	sh	1362	sh			
1355	s	1354	s		1354	s				1360	s	1360	s	1360	s			
1347	s	1347	s		1347	s	1345	vs	1345	vs	1348	s	1348	s	1348	s	↑	
										1341	sh	1341	sh	1341	sh			
										1324	vw	1324	vw	1324	vw			
									1309	vw								
											1302	w	n	1302	w	↓		
1287	vw	1291	m	n	1285	vw	1285	sh	1285	m	1291	vw	1291	sh	1291	sh		
1267	vw	1284	sh		1268	vw	1268	vw	1267	sh	1283	vw	1284	vw	1284	vw		
											1267	vw	1268	w	↑	1268	w	↓
													1251	vw	n	1251	vw	↓
1242	vw	1245	vw		1242	vw	↓	1242	vw		1244	vw	1244	vw	1244	vw		
													1238	vw	n	1237	vw	↓
													1225	vw	n	1225	vw	↓
													1215	vw		1215	vw	
1204	vw	1211	vw	n	1204	vw	1203	vw			1205	vw	1205	vw	1205	vw		
											1200	sh	n	1198	sh		↓	
1192	w	1192	w		1193	w	1192	w	1193	vw	1193	w	1193	w	1193	w		
											1188	sh	1188	sh	1188	sh		
											1173	vw	1173	vw	1173	vw		
													1165	vw	n	1164	vw	↓
1149	w	1164	vw	n	1150	w	1148	w	1147	w	1153	w	1153	w	1153	w		

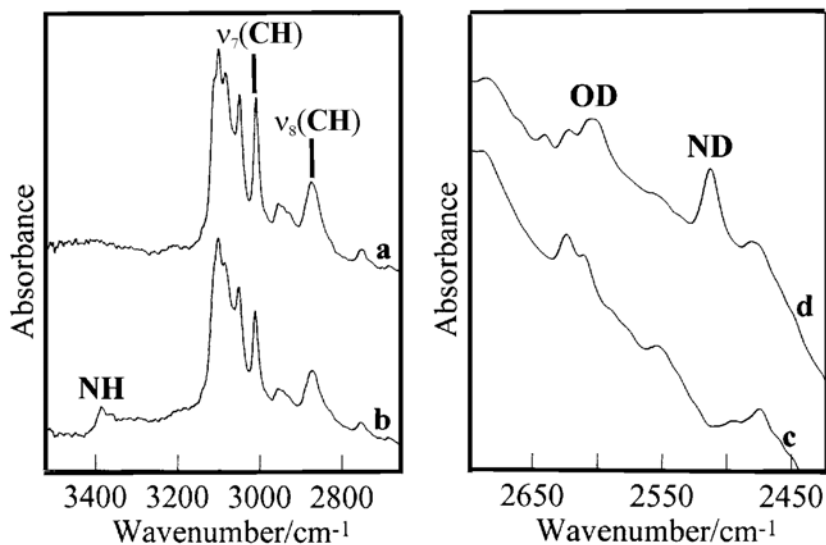


Fig. 1. FTIR spectra of protiated and deuterated thin films of DNBP and DNBP- d_2 at 298 K: (a) colorless, (b) blue, after 15 minutes of UV irradiation with mercury lamp (filter C-39B), (c) colorless DNBP- d_2 , (d) after 10 minutes irradiation with mercury lamp (filter C-39B) and bleaching with xenon lamp

After partial photobleaching with visible light (490–750 nm), novel band at 2606 cm^{-1} from the $\nu(\text{OD})$ mode of deuterated OH was clearly observed in the spectrum of DNBP- d_2 (Fig. 1d), mostly due to the photoreaction $\text{NH} \rightarrow \text{OH}$. The band was persistent with minutes at ambient conditions and is not likely to originate from by-products due to their low yield in the solid state [5]. The observation of the $\nu(\text{OH})$ band represents the first steady-state infrared evidence of creation of the OH isomer at ambient conditions in the solid state. The accumulation of the partially deuterated OH to IR-detectable quantities owes to the relatively high photoconversion in the microcrystalline film and the nearly four-fold extension of its lifetime by the kinetic isotopic effect ($k_{\text{H}}/k_{\text{D}} = 3.8$) [8]. The detection of the respective $\nu(\text{OH})$ band was obscured by its weak intensity and the low signal-to-noise ratio in the water-absorbing region.

CONCLUSIONS

Although the existence of the OH isomer has been clearly established by absorption spectroscopy, no IR bands corresponding to the $\nu(\text{OH})$ mode have been reported yet. The high effective photoconversion in UV-photocolored and subsequently bleached thin solid layers provided the first infrared evidence of the OH isomer: the $\nu(\text{OD})$ band appeared at 2606 cm^{-1} , together with the

An additional very weak unassigned band at 2641 cm^{-1} may be due to another, less-strongly hydrogen-bonded conformer of the ground-state OH minima, for example, with the aci-nitro proton pointing towards the benzylic carbon or away from both the benzylic carbon and the pyridyl nitrogen. Namely, fifteen stable ground-state OH conformers were obtained by unrestricted optimization of a monomolecular model at the B3PW1/6-31G(d) level [4] (the detailed results of the theoretical analysis will be published elsewhere). More detailed investigation should unravel the origin of this band.

The deuterated forms of all three isomers CH, NH and OH co-exist in the partially bleached sample. No attempts for quantitative measurements were made due to the lack of precise knowledge of their absorption characteristics.

$\nu(\text{ND})$ mode at 2507 cm^{-1} . The accumulation of OH to IR-detectable amounts owes to the high transparency to light of the film and nearly four-fold extension of its lifetime of OH due to the kinetic isotope effect.

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Резиме

**ИНФРАЦРВЕН ДОКАЗ ЗА ФОТОИНДУЦИРАНИОТ АЦИ-НИТРОИЗОМЕР
НА 2-(2',4'-ДИНИТРОБЕНЗИЛ)ПИРИДИН ВО ЦВРСТА ФАЗА**

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Клучни зборови: 2-(2',4'-динитробензил)пиридин; изотопски ефект; реакции во цврста фаза; фотохромизам

Со селективно озрачување и продолжување на времето на живот со изотопска замена, фотоиндуцираниот нестабилен аци-нитроизомер ОН на 2-(2',4'-динитробензил)пиридин прв пат е добиен во тенок

поликристален филм во принос што може да се детектира со инфрацрвена спектроскопија. Селективно деутерираниот облик на ОН апсорбира на 2606 cm^{-1} и при обични услови е стабилен со минути.