Bulletin of the Chemists and Technologists of Macedonia, Vol. 23, No. 2, pp. 87–92 (2004) ISSN 0350 – 0136

GHTMDD – 441 Received: April 20, 2004 Accepted: October 10, 2004

UDC: 547.82–304.1 : 543.422.4

Short communication

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-cyclo-hexadiene; 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.

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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 2benzylpyridine 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-d₄ (99.95 % D, Aldrich). Except for the benzylic bands, the IR spectrum of DNBP-d2 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, photocolored with UV light and subsequently bleached with visible light. Fig. 1 shows the regions where the bands from the v(CH), v(NH), v(ND) and v(OD) modes are expected.

Upon photocoloration with UV light (360-460 nm), bands from v(NH) (3385 cm^{-1}) and

v(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 \rightarrow NH. The assignment of the v(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 v(NH), the band from the symmetric benzylic stretching mode $v_7(CH)$ 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 t	empera	ture								7 K				
37.1	low	Polycrystal in KBr matrix						37.1		in film ^b	Polycrystal in KE					Br matrix Bleached ^c			
Yellow		Blue			Bleached			Yellow		3517 vw		Yellow		Blue			Ble	eacned	
										3317	* ***	3210	m	3211	m		3211	m	
		3385	W	n						3385	vw								
3115	VW	3115	VW		3114	vw		3113	W	2102		3120	W	3120	W		3120	W	
3103	W	3103	W		3103	W		3102	W	3102	W	3107	W	3108	W		3108	W	
3088	vw	3088	VW		3088	VW		3086	W	3086	vw	3090	VW	2054			2054		
3051 3012	W W	3051 3012	W W		3051 3012	W W		3051 3011	W W	3052 3012	W W	3054 3011	vw vw	3054 3011	vw vw		3054 3011	vw vw	
2957	VW	2957	VW		2958	VW		2956	W	2956	VW	2960	VW	2959	VW		2959	VW	
2925	vw	2929	vw		2926	VW		2730	**	2730	* **	2932	vw	2932	vw		2932	vw	
												2891	VW	2891	vw		2891	vw	
2878	vw	2877	vw	\downarrow	2878	vw		2875	vw	2872	vw	2882	VW	2882	vw		2882	vw	
2859	VW	2863	vw		2859	vw						2864	$\mathbf{v}\mathbf{w}$	2864	vw		2864	$\mathbf{v}\mathbf{w}$	
												2851	VW	2851	vw		2851	VW	
2758	VW	2756	VW		2758	vw		2754	vw	2755	vw	2763	VW	2763	VW		2763	VW	
										1697	W					•			
												1648	VW	1648	VW	1	1648	VW	
		1/2/			1627					1626	**	1643	VW	1643	vw	^	1643	vw	
		1636 1630	VW ch	n	1637 1629	VW ch	1			1636	VW	1637	vw	1637	VW	T	1637	vw	
1610	m	1610	sh m		1610	sh m	\downarrow					1614	m	1614	m		1614	m	
1603	m	1603	m		1603	m		1603	m	1602	m	1605	m	1605	m		1605	m	
1589	m	1589	m		1589	m		1588	m	1588	m	1591	m	1591	m		1591	m	
1577	sh	1577	sh		1577	vw						1577	sh	1577	sh		1577	sh	
1568	w	1568	W	\downarrow	1568	w		1568	w	1569	w	1568	W	1568	W		1568	W	
1559	vw	1559	W	\uparrow	1560	vw	\downarrow					1559	sh	1559	VW	\uparrow	1560	vw	\downarrow
1540	S	1539	S		1541	VS						1542	S	1542	S	\downarrow	1542	S	\uparrow
												1537	m	1537	m		1538	m	\uparrow
1525	VS	1525	VS		1529	VS		1527	VS	1527	VS	1526	VS	1526	VS		1526	VS	
												1523	sh	1523	VS	1	1524	VS	\downarrow
										1.500		1515	m	1515	m		1515	m	
1.502		1502	1		1502					1508	sh	1509	sh	1509	sh		1509	sh	
1502	sh	1502	sh		1502 1490	sh vw						1500 1491	sh	1500 1490	sh		1500 1490	sh	
1475	m	1475	m		1476	m		1474	m	1474	m	1476	vw m	1476	vw m		1476	vw m	
1459	VW	1459	VW		1458	VW		17/7	111	17/7	111	1458	VW	1459	VW		1459	VW	
1.07		1.07			1.00	• • •						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		1427	m	
												1411	W	1411	W		1411	W	
1408	W	1408	W		1408	w		1407	wm	1407	W	1405	VW	1405	VW		1405	VW	
												1392	vw	1392	VW		1392	vw	
1255		1254			1254							1362	sh	1362	sh		1362	sh	
1355 1347	S S	1354 1347	s s		1354 1347	S S		1345	***	1345	***	1360 1348	S	1360 1348	S		1360 1348	s s	↑
1347	5	1347	5		1347	5		1343	VS	1343	VS	1348	s sh	1341	s sh		1346	s sh	ı
												1324	VW	1324	VW		1324	VW	
										1309	vw	1521	• • • •	1321	• • • •		1321	• • • •	
														1302	W	n	1302	W	\downarrow
		1291	m	n								1291	vw	1291	sh		1291	sh	
1287	vw	1284	sh		1285	vw		1285	sh	1285	m	1283	vw	1284	vw		1284	vw	
1267	vw	1269	vw		1268	vw		1268	VW	1267	sh	1267	vw	1268	W		1268	W	
														1251	vw	n	1251	vw	\downarrow
1242	VW	1245	VW		1242	VW	\downarrow	1242	VW			1244	VW	1244	vw		1244	VW	
										1239	VW			1238	vw		1237	vw	\
										1212		1016		1225	VW	n	1225	VW	\downarrow
		1211								1212	VW	1216	VW	1215	VW		1215	VW	
1204	17117	1211	VW	n	1204	1/11/		1203	X/XX7			1205	17117	1205	17117		1205	17317	
1204	vw	1205	vw		1204	VW		1203	vw			1203	vw	1205	vw sh	n	1198	vw sh	\downarrow
1192	w	1192	W		1193	W		1192	W	1193	vw	1193	w	1193	W	11	1193	W	*
11/2	**	11/2	**		11/5	**		11/2	**	11/3	* **	1188	sh	1188	sh		1188	sh	
												1173	VW	1173	vw		1173	VW	
		1164	vw	n						1164	VW			1165	vw	n	1164	vw	\downarrow
1149	W	1148	W		1150	W		1148	wm	1147	wm	1153	W	1153	W		1153	W	

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		Dolmar	tol in 10	D		emperat	ure		n film ^b	7 K									
Yellow		Polycrystal in KBr matrix Blue Bleached						Val		Yel	low	Polycrystal in KBr matrix				nahad ^c			
			biue	Bleached				Yellow Blue			1147		Blue 1147 w			Bleached ^c 1147 w			
		1142	sh	n								114/	W	1147	w VW	n	1147	w VW	\downarrow
		1142	511	11										1134	sh	n	1134	sh	\downarrow
1126	vw	1122	wm		1126	WV	\downarrow	1121	VW			1123	vw	1128	VW	11	1128	VW	•
1120	v vv	1122	WIII		1120	VV V	•	1121	V VV	1121	w	1119	VW	1120	VW		1119	VW	\downarrow
1097	w	1096	W		1097	W		1095	vw	1095	w	1097	W	1097	VW		1097	VW	•
1097	w	1090	w		1097	w		1093	VW	1093	w	1082	sh	1082	sh		1082	sh	
												1062	W	1062	W		1068	W	
1064	w	1064	W		1064	W		1063	W	1063	w	1062	W	1062	W		1062	W	
1050	W	1050	W		1051	W		1050	VW	1050	vw	1052	W	1051	W		1051	W	
1050	**	1020	vw	n	1019	vw		1050	* **	1020	vw	1019	vw	1019	VW		1019	vw	
995	wm	995	wm	11	995	wm		995	wm	994	wm	996	wm	996	wm		996	wm	
,,,	,,,,,,,	990	sh	n	,,,	******		,,,,	******	,,,	******	,,,	******	,,,	***111		,,,	******	
980	vw	980	VW	••	980	vw		980	vw			982	w	982	W		982	W	
960	vw	960	vw		960	vw		, , ,	• • •			960	vw	960	vw		960	vw	
, 00		, 00			, 00	• • • •				944	vw	, 00		, , ,			, 00		
932	vw	934	vw		933	vw	\uparrow	929	sh	· · ·		934	vw	933	vw		933	vw	
		930	sh	n	,		•							,			,		
920	w	920	W	••	920	w		917	w	917	sh	923	w	923	W		923	w	
,_0	••	,_0			720	••		, , ,		, . ,	511	,	••	913	sh	n	913	sh	
900	wm	900	wm		900	wm		899	wm	900	wm	900	wm	900	wm		900	wm	
885	sh	885	sh		885	W				882	sh	888	VW	888	vw		888	vw	
		870	vw	n										871	sh	n	871	sh	
857	w	857	w		857	w		856	W	856	w	858	wm	858	wm		858	wm	
														847	sh	n	847	sh	
836	wm	836	wm		836	wm		834	wm	834	wm	837	wm	837	wm		837	wm	
												830	W	830	w		830	w	
810	W	810	W		811	w		810	w	812	W	811	W	811	w		811	w	
												794	VW	794	vw		794	vw	
												772	sh	773	$\mathbf{v}\mathbf{w}$	\uparrow	773	vw	\downarrow
759	m	759	m		759	m		759	m	757	wm	762	m						
												757	sh	757	sh		757	sh	
736	wm	736	wm		736	wm		735	m	736	m	737	wm	737	wm		737	wm	
726	w	726	\mathbf{W}		726	W		726	sh			726	W	726	W		726	W	
709	wm	709	wm		709	wm		708	wm	708	W	711	wm	711	wm		711	wm	
697	W	697	\mathbf{W}		697	W		695	W	696	W	696	W	696	W		696	W	
		681	\mathbf{W}	n	681	VW	\downarrow							682	VW	n	682	$\mathbf{v}\mathbf{w}$	\downarrow
670	VW	671	vw		670	VW								672	$\mathbf{v}\mathbf{w}$	n	672	$\mathbf{v}\mathbf{w}$	
665	VW	665	vw																
650	W	650	W		651	W		650	W	649	W	651	W	651	W		651	w	
																	643	VW	\uparrow
629	VW	628	vw		629	VW		628	VW	628	VW	629	VW	629	VW		629	VW	
					615	VW	\uparrow			616	VW			615	sh		615	sh	
604	vw	604	vw		604	VW		603	W	602	W	605	VW	605	$\mathbf{v}\mathbf{w}$		605	VW	
586	VW	586	vw									586	VW	586	VW		586	VW	
																	577	sh	n
														567	$\mathbf{v}\mathbf{w}$	n	567	VW	
																	555	sh	n
										543	sh						545	sh	n
								520		501				501			538	sh	n
								530	vw	531	sh			531	sh		531	sh	\uparrow
														521	sh	n	521	sh	
513	VW	514	VW		514	vw		512	wm	515	VW	514	W	514	W		514	W	
		400						401		400				504	VW	n	504	sh	\uparrow
470		489	VW	n	470			491	VW	490	VW	400		400			400		
478	VW	479	VW		478	vw		476	vw	476	W	480	W	480	W		480	W	
1.00		460			462			166				162		462			470	sh	n
462	VW	462	VW		462	vw		466	vw			462	W	462	W		462	W	•
														449	sh	n	449	VW	\uparrow
422		400			422			421		421		42.5		42.5			442	VW	n
433	W	432	W		433	W		431	VW	431	vw	435	W	435	W	•	435	W	
					421	VW	n	420	VW	420	VW	425	VW	425	VW	1	425	VW	

^a Acronyms and symbols: vw – very weak, w – weak, wm – weak to medium, m – medium, s – strong, vs – very strong, sh – shoulder, ↑ – increased intensity, ↓ – decreased intensity, n – new band.

^b Bleaching of the blend produced only minor spectral changes that were difficult to follow even after 3 h of irradiation. From what could be observed, the bands at 3385 (vw), 1285 (w), 1164 (vw) and 420 cm⁻¹ (vw) disappeared, those positioned at 1309 (w) and 1122 cm⁻¹ (w) decreased and those at 616 (vw), 531 (vw), 565 (vw), 499 (vw), 445 cm⁻¹ (vw) increased in intensity.

^c Due to the low reaction rate, the pellet was not bleached completely; the reported spectrum corresponds to 30 minutes of irradiation.

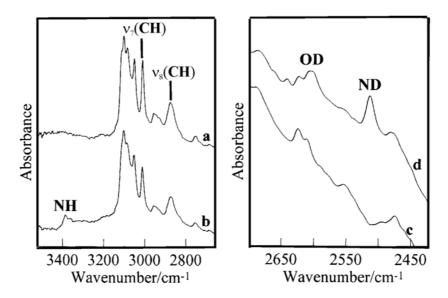


Fig. 1. FTIR spectra of protiated and deuterated thin films of DNBP and DNBP- d_2 at 298 K: (a) colorless, (b) blue, after 15 minutes of UV irradiation with mercury lamp (filter C-39B), (c) colorless DNBP- d_2 , (d) after 10 minutes irradiation with mercury lamp (filter C-39B) and bleaching with xenon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

After partial photobleaching with visible light (490–750 nm), novel band at 2606 cm⁻¹ from the v(OD) mode of deuterated OH was clearly observed in the spectrum of DNBP- d_2 (Fig. 1d), mostly due to the photoreaction NH-OH. The band was persistent with minutes at ambient conditions and is not likely to originate from byproducts due to their low yield in the solid state [5]. The observation of the v(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 $(k_H/k_D = 3.8)$ [8]. The detection of the respective v(OH) band was obscured by its weak intensity and the low signal-tonoise ratio in the water-absorbing region.

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 confomers 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.

CONCLUSIONS

Although the existence of the OH isomer has been clearly established by absorption spectroscopy, no IR bands corresponding to the $\nu(OH)$ 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 $\nu(OD)$ band appeared at 2606 cm⁻¹, together with the

v(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 fourfold extension of its lifetime of OH due to the kinetic isotope effect.

Acknowledgements: This work was supported by Tokyo Institute of Technology, Tokyo, Japan.

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Резиме

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

Панче Наумов

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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.