

DFT STRUCTURE OPTIMIZATION AND VIBRATIONAL SPECTRA OF THE PHOTOCROMIC 2-(2',4'-DINITROBENZYL)PYRIDINE*

C. FLOARE^{1,3*}, S. ASTILEAN², M. BOGDAN¹, O. COZAR²

¹ National Institute for Research and Development of Isotopic and Molecular Technologies,
P.O. Box 700, 400293, Cluj-Napoca 5, Romania

² Babeş-Bolyai University, Faculty of Physics, Kogălniceanu 1, RO-3400 Cluj-Napoca, Romania

* Corresponding author: cfloare@s3.itim-cj.ro

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Ab initio density functional calculations were performed on the CH₂ pale yellow stable tautomer of 2-(2',4'-dinitrobenzyl)pyridine and on his photoinduced dark blue NH tautomer. We used B3LYP hybrid functional with 6-31G(d), 6-31G** and 6-31++G** basis sets. Good agreement is found between the calculated and experimental structures and vibrational spectra. The discrepancies are associated with the fact that the experimental values are obtained from a crystal, the theoretical ones being calculated in the gas phase.

Key words: 2-(2',4'-dinitrobenzyl)pyridine, α -DNBP, photochemistry, *ab initio* calculations, DFT, vibrational spectra.

1. INTRODUCTION

The pale yellow crystals of 2-(2',4'-dinitrobenzyl)pyridine, C₁₂H₉N₃O₄, also referred to as α -DNBP, or in solution in different solvents, when irradiated with ultraviolet light, undergo a characteristic change of color from pale yellow to blue-violet caused by a reversible photoinduced or thermally activated proton transfer (PT) reaction [1, 2]. The metastable tautomer is relatively long-lived (4.7 s in ethanol [3] and approximately 4.6 h in the crystal [4]). This kind of bi-stable system which undergoes a proton-transfer reaction to produce long-lived species are of great interest for its potential application as an optical switch for optical data processing and optical data storage [3] and for the development of molecular protonic devices [7].

Spectroscopic investigations [2–6] concluded that the photoexcited CH₂ form isomerizes to the quinoid NH blue form, either directly CH₂ \rightarrow NH or through an intermediate aci-nitro structure (Fig. 1).

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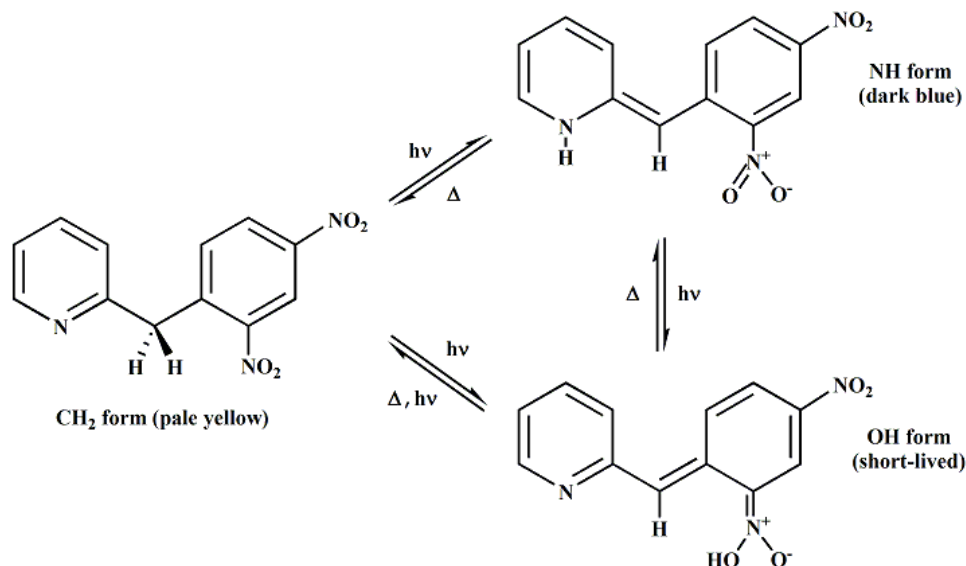


Fig. 1. – Tautomeric forms of α -DNBP.

Although the crystal structure of the CH_2 form is known since 1968 [8], only recently Y. Ohashi group have accomplished the preparation of diffraction-quality single crystals with high concentration of NH blue isomer, employing two-photon excitation technique, and determined its structure [9].

The aim of this study is that, by means of *ab initio* density functional calculations performed on the stable CH_2 and photoinduced NH tautomers, to throw light upon their geometric structure and vibrational spectrum and to make a full assignment of the fundamental bands.

2. COMPUTATIONS

Structure optimization and vibrational spectra calculations for the 2-(2',4'-dinitrobenzyl)pyridine $-\text{CH}_2$ and $-\text{NH}$ tautomers were performed with Becke's three-parameter density functional hybrid method containing the Lee, Yang and Parr gradient-corrected correlation functional (B3LYP) [8], using GAUSSIAN 98 program package [9]. For CH_2 stable tautomer the 6-31G(d), 6-31G** and 6-31++G** split-valence basis sets were used, to quantify the influence of the additional polarization and diffuse functions on the calculations. For the NH tautomer only the 6-31G(d) basis set was used.

The calculations have been performed, partly on a Silicon Graphics O2 workstation (processor MIPS R12000 at 300 MHz with 512 Mb RAM) and partly on a computer with Intel architecture (processor Intel Celeron at 2.4 GHz,

1Gb RAM) running Windows OS, using the 'Opt' and 'Freq' options from Gaussian.

We have considered all π -diastereoisomers of the NH tautomer, Z-I, Z-II, E-I and E-II, presented in Fig. 2. All calculations of harmonic wavenumbers were performed for the fully optimized geometry at the same level of theory. No imaginary frequencies were obtained, proving that a local or a global minimum on the potential energy surface was found.

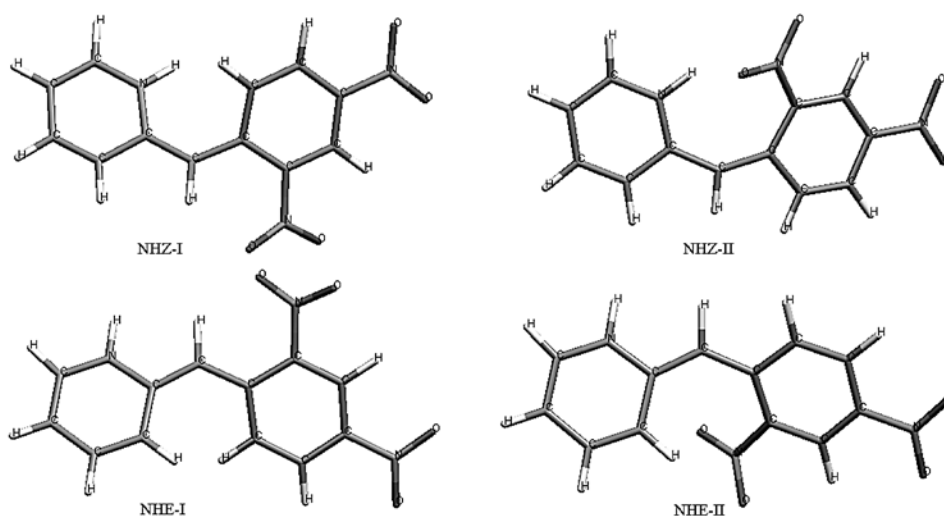


Fig. 2. – π -diastereoisomers of α -DNBP, NH form.

3. RESULTS AND DISCUSSION

The three tautomeric forms of 2-(2',4'-dinitrobenzyl)pyridine – CH₂, NH and OH are depicted in Fig.1 and the molecular structure of the NH π -diastereoisomers – Z and E in Fig. 2. The results obtained for the optimized structures for CH₂ and NH tautomers are compared in Tables 1 and 2, with the available crystallographic data [9]. Vibrational calculated infrared wavenumbers and an approximate description of modes are presented in Tables 3 and 4.

3.1. STRUCTURE OF 2-(2',4'-DINITROBENZYL)PYRIDINE CH₂ TAUTOMER

All three X-ray diffraction studies performed for the CH₂ form of α -DNBP agree that the angle between the two aromatic rings is around 65°: 114° [8], 65.1° [4] and 64.07° [9]. This angle, approximated by the torsion angle C5-C6-C7-C8 (Fig. 3), is in agreement with the value found from our calculations with

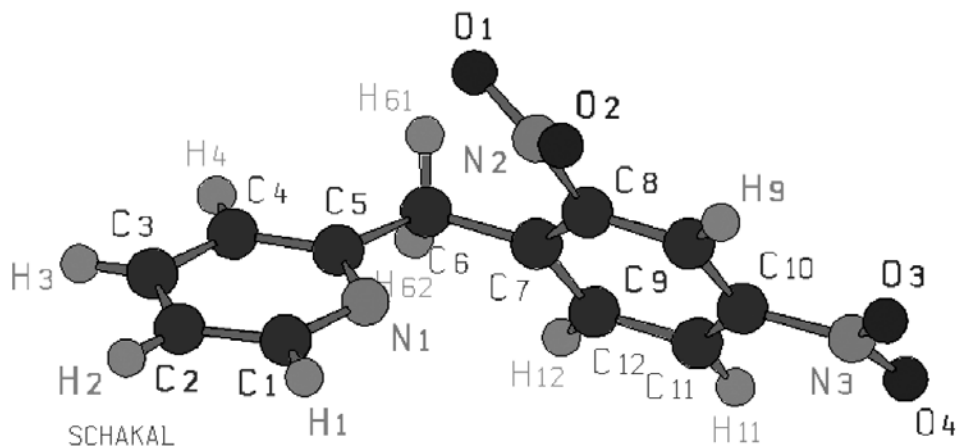


Fig. 3. – Experimental structure of α -DNBP [9], CH₂ form, and atoms numbering.

Table 1

Bond lengths (Å) and bond angles (deg.) for α -DNBP, CH₂ form

CH2	X-ray ^a	B3LYP		
		6-31G(d)	6-31G**	6-31++G**
E (a.u.)		-927.64844	-927.662262	-927.700045
C5-C6	1.523	1.526	1.526	1.526
C6-C7	1.513	1.513	1.512	1.513
O1-H61	2.408	2.257	2.255	2.278
C5-C6-C7	114.8	113.3	113.4	113.7
C4-C5-C6-C7	-173.5	-145.4	-145.9	-148.9
C5-C6-C7-C8	-64.1	-72.7	-72.6	-73.5
C9-C8-N2-O1	147.6	146.3	146.6	145.7
C9-C8-N2-O2	-30.5	-30.8	-30.6	-31.7
C9-C10-N3-O4	-167	179.5	179.5	179.5
C9-C10-N3-O3	11.5	-0.5	-0.5	-0.5
C11-C10-N3-O4	12.3	0.4	0.4	0.4

^a Ref. [9]

6-31G(d) basis set, 72.6°. However the theory predicts a tilt angle C4-C5-C6-C7 of -145.5°, when experimentally [9] a value of -173.5° was found. We associate these differences to the fact that the experimental studies were performed on solid crystal structure our calculations being performed in the gas phase. The obtained C-C distances between the methylene carbon atom and that of the pyridine and benzene ring are 1.526 and 1.513 Å, respectively, which are in

great agreement with the experimental values 1.523 and 1.513 Å. For the C-C-C angle at the methylene carbon atom found to be 114.1 [8] or 114.8 [9], we have obtained the value of 113.3°. The distance between the oxygen atom from the *ortho*-nitro group and the hydrogen atom of the methylene group is 2.257 Å with 6-31G(d) basis set, increasing at 2.278 Å after the addition of polarization and diffusion functions to all atoms. The experimental value is 2.4 Å.

The *ortho*-nitro group is twisted with an angle of 32° [8], 31.7° [4] or 30.5° [9] from the benzene ring, pointing towards the hydrogen of the methylene group. The values obtained from our calculations, ranging from 30.8 to 31.7, agree with the experimental values. The greatest discrepancy is found between the theoretical and experimental values of the twisting angle of the *para*-nitro group. Experimentally has been found a twisting angle of 12.3°, and theoretically the *para*-nitro group lies nearly in the dinitrobenzyl ring plane (angle of deviation 0.4°). As suggested by G. N. Andreev *et al.* [12], a possible explanation for this discrepancy is that (as for the tilt angle between the pyridine and dinitrobenzyl rings) the experimental study is carried out in crystal state, the theoretical calculations being performed in a gas state, where the molecule is free from interactions with other molecules.

3.2. STRUCTURE OF 2-(2',4'-DINITROBENZYL)PYRIDINE NH PHOTOINDUCED TAUTOMER

For all π -diastereoisomers (NHZ-I, NHZ-II, NHE-I and NHE-II) of the NH tautomer (Fig. 2) we have performed geometry optimizations and vibrational spectra calculations at the level B3LYP/6-31G(d). In all cases we have obtained only positive values of frequencies which prove that the stationary points found on the PES are local minimums. The X-ray crystallographic asymmetric unit of the blue crystal containing the overlapped CH₂ and NH isomers obtained by P. Naumov [9], is presented in Fig. 4. We can remark the close similarity between the two structures. Due to the unfavorable donor-acceptor in the reactant CH₂ (C6a-H61a---N1a = 40.2°), the PT mechanism proposed for the reaction is that the *ortho*-nitro group abstracts H61 and by reorientation it delivers to the nitrogen acceptor, being clearly an intramolecular process.

The atoms numbering for the NH experimental structure [9] is depicted in Fig. 5, the Table 2 containing the results from our calculations for all four optimized NH π -diastereoisomers, compared with the experimental values. We must mention that as in the additional data of [9], the table of positional parameters for the blue crystal of 2-(2',4'-dinitrobenzyl)pyridine contains the two overlapped tautomers (CH₂ and NH), the structure presented in Fig. 5 as well as the experimental values in Table 2, are only for the NH structure characterized by the suffix "B".

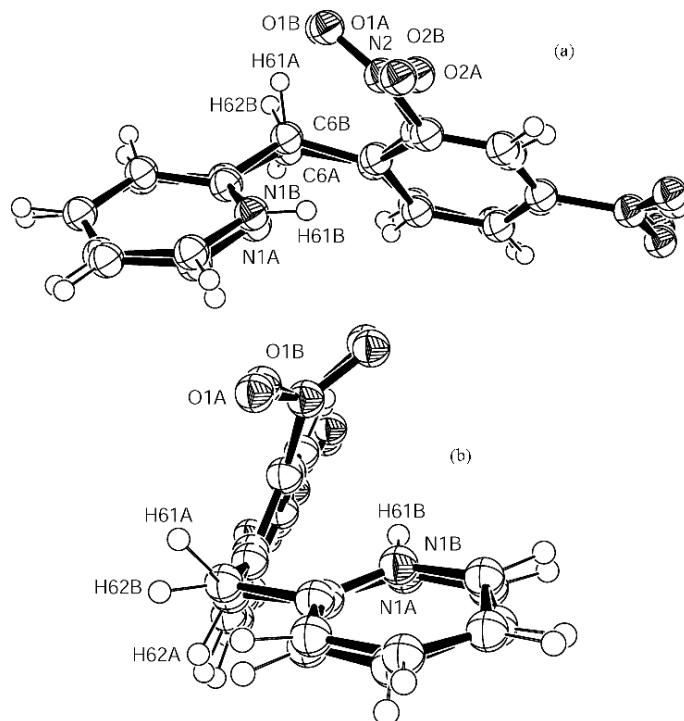


Fig. 4. – Views of the molecular experimental structure of the blue crystal with overlapped CH₂ and NH isomers [9].

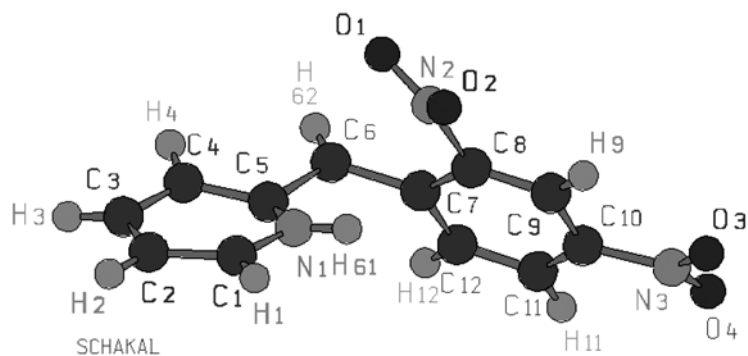


Fig. 5. – Experimental structure of α -DNBP [9], NH form, and atoms numbering.

If we compare the energies of the NH tautomers with the energy of the CH₂ tautomer at the same level of theory (Table 1) we can observe that, in accordance with our expectations, the CH₂ tautomer is the most stable. The energy differences between the CH₂ structure and NH-isomers, representing the heat of conversion from NH to CH₂, are: 58.881 kJ/mol (NHZ-I/CH₂), 57.157 kJ/mol

Table 2

Bond lengths (Å) and bond angles (deg.) of a-DNBP NH form

NH	X-ray ^a	B3LYP 6-31G(d)			
		NHZ-I	NHZ-II	NHE-I	NHE-II
E (a.u.)		-927.626028	-927.626685	-927.625383	-927.620466
C5-C6	1.621	1.389	1.404	1.388	1.387
C6-C7	1.562	1.432	1.427	1.432	1.432
N1-H61	0.88	1.012	1.024	1.013	1.012
O1-H61	2.877	5.200	1.688	4.055	4.452
O2-H61	2.775	5.987	3.175	6.047	6.185
C5-C6-C7	108.3	128.2	138.9	127.9	131.1
C4-C5-C6-C7	-177.4	-174.7	-165.6	12.7	8.9
C5-C6-C7-C8	-69.9	-153.1	-19.2	-154.6	27.1
C9-C8-N2-O1	143.9	158.9	159.5	160.3	-145.9
C9-C8-N2-O2	-39.4	-20.4	-17.8	-19.1	32.6
C9-C10-N3-O4	-159.4	178.5	-178.1	178.9	178.5
C9-C10-N3-O3	14.7	-1.4	2.1	-0.9	-1.5
C11-C10-N3-O4	17	-2.5	0.0	-2.1	-0.3

^a Ref. [9]

(NHZ-II/CH₂), 60.577 kJ/mol (NHE-I/CH₂) and 73.494 kJ/mol (NHE-II/CH₂), respectively. These values show that the most stable NH isomer is NHZ-II followed by NHZ-I, the most unstable being NHE-II. This result differs from that obtained by Andreev *et al.* [12] performed at the Hartree-Fock level using 6-21G** basis set, where the NHE-II isomer was found to be the more stable. In this paper, however, the NHZ-II structure hasn't been optimized as the computation procedure failed because the program did not meet the convergence criteria. Even if between the values of the conformational parameters for the optimized NHZ-II isomer and the experimental one exist some differences, as we can observe in Table 2, the NHZ-II is the NH isomer being the most similar to the reactant CH₂. The fact that this structure is the most stable between the all four NH π -diastereoisomers, agree with the experimental data, mentioned above, that the conformations of the reactant (CH₂ form) and product (NH form) are closely similar.

While in the CH₂ form the methylene carbon is tetrahedral, it became planar in the NH form, and the C-C_{py} has a higher bond order in all optimized structures of the NH tautomers, the C-C_{ph} bond being almost a pure single bond. Experimentally, the values of these bonds are, C-C_{py} (1.621 Å) and C-C_{ph} (1.562 Å), while those calculated for the NHZ-II isomer are 1.404 Å and

1.427 Å, respectively. For the N1-H61 distance found experimentally to be 0.88 Å, we have obtained a value of 1.024 Å for NHZ-II isomer, a little bit longer than for all other NH isomers due to the strong hydrogen bonds between H61 atom with O2 and N2 atoms, as we will see. One of the greatest discrepancies is found for the angle between the pyridine and benzene ring planes. If experimentally this angle approximated by the torsion angle C5-C6-C7-C8 is almost identical in the CH₂ and NH tautomers, the calculated values are rather different. The NHZ-II structure is nearly planar, the H61 atom forming hydrogen bonds with the O1 atom (H61-O1 = 1.688 Å) and with the N2 atom (H61-N2 = 2.351 Å). The *ortho*-nitro group is deviated in a similar manner from the benzene ring plane but with half angle than in the experimental structure, also because the calculated structure is more planar than the experimental one. The *para*-nitro group is almost conjugated with the plane of the benzene ring in all calculated structures, the tilt observed in the experimental structure being essentially due to the crystallographic packing intermolecular interactions not taken into account by our gas phase calculations.

3.3. VIBRATIONAL SPECTRA OF 2-(2',4'-DINITROBENZYL)PYRIDINE TAUTOMERS

The first important vibrational spectroscopy study of α -DNBP is the 1959 article of Hardwick *et al.* [2] where, beside the observation that the reversible photochemical reaction takes place also in the liquid state, the authors reported also a comparison between the IR spectra of CH₂ and NH tautomers. From that time other IR [5, 13, 16] or Raman [14–16] studies have been published. As an experimental hint, we mention that in a Raman study, as the NH and OH tautomers absorbs in visible, a laser excitation light of 1.064 μm is the better to be used.

The major differences between the infrared spectra of the stable and the blue form of α -DNBP are the decrease of the intensity of the pyridine stretching band -C=N- at 1567 cm^{-1} and a simultaneous development of a new band at 3388 cm^{-1} [5], which was associated to the stretching of N-H group, as a result of the analysis of the shift and the magnitude of this band for deuterium labeled compound d₂- α -DNBP.

Andreev *et al.* [12] reported, at a later time, from the difference IR spectrum between the NH and CH₂ isomers, the following bands characteristic to the blue NH tautomer: 489, 682, 990, 1123, 1142, 1165, 1293, 1635 and 3389 cm^{-1} . In the case of the Raman analysis the only remarkable difference between the spectra of CH₂ and NH forms of α -DNBP crystal is the strong band at 1296 cm^{-1} [16] or 1293 cm^{-1} [12].

In the Tables 3 and 4 we compare the experimental values of IR and Raman frequencies, for the stable CH₂ and photoinduced NH blue tautomer of

Table 3

Experimental and *ab initio* calculated vibrational spectrum of α -DNBP CH₂ form

ν [cm ⁻¹] Raman ^a	ν [cm ⁻¹] IR ^a	(a) ^b	(a1) ^b	IR _{int.} (a) ^c	(b) ^b	(c) ^b	Approx. description
515vw	516w	536	516	1.7	536	532	$\rho(\text{NO}_2)$; $\nu_{\text{bz}}(\text{CC})$; $\delta(\text{CH})$
		586	563	0.6	585	583	$\nu_{\text{bz}}(\text{CC})$; $\rho(\text{NO}_2)$; $\rho(\text{CH})$
605vw	605vw	612	589	4.3	612	610	$\nu_{\text{py}}(\text{CC})$; $\delta(\text{CH}_2)$; $\delta(\text{CH})$
630vw	629vw	642	617	1.6	641	640	$\nu_{\text{py}}(\text{CC})$
652w	651w	663	637	1.2	663	661	$\nu_{\text{py}}(\text{CC})$
	697w	707	680	22.8	707	705	$\delta(\text{NO}_2)$; $\nu_{\text{py}}(\text{CC})$; $\delta(\text{CH})$
709vw	709m	725	697	16.6	724	720	dnBz. out of plane def
	726w	750	721	12.4	749	747	Py. & dnBz. out of plane def
736vw	736m	756	727	17.8	755	752	
	759s	770	741	42.9	770	765	$\omega_{\text{py}}(\text{CH})$
764vw		778	748	1.7	777	776	$\omega(\text{N}_2\text{N}_3)$; $\omega(\text{CH})$
813w	811w	830	798	12.2	829	826	$\nu_{\text{sym}}(\text{C}_5\text{C}_6\text{C}_7)$; $\omega_{\text{bz}}(\text{CH})$
	830w	840	807	2.1	839	837	$\nu_{\text{asym}}(\text{C}_5\text{C}_6\text{C}_7)$; $\omega_{\text{bz}}(\text{CH})$; $\nu_{\text{py}}(\text{CC})$
836m	837m	847	814	27.4	847	843	$\sigma(\text{NO}_2)$; $\nu_{\text{bz}}(\text{CC})$
859vw	858m	877	843	14.1	876	873	$\omega_{\text{bz}}(\text{CH})$
884vw		903	868	0.3	903	900	$\omega_{\text{py}}(\text{CH})$
900vw	900m	937	901	22.7	937	932	$\nu_{\text{bz}}(\text{CC})$; $\sigma(\text{NO}_2)$; $\rho(\text{H}_6\text{H}_6\text{H}_2)$
922vw	921w	953	916	18.3	950	948	$\delta(\text{C}_9\text{H}_9)$
933vw	933vw	955	918	1.5	952	951	$\tau_{\text{bz}}(\text{CH})$; $\rho(\text{H}_6\text{H}_6\text{H}_2)$; $\tau_{\text{py}}(\text{CH})$
		982	944	0.9	983	986	$\tau_{\text{py}}(\text{CH})$
	961vw	991	952	0.0	992	996	$\tau_{\text{bz}}(\text{CH})$
	980vw	1007	968	0.0	1010	1012	$\tau_{\text{py}}(\text{CH})$
996m	996m	1015	976	8.7	1014	1013	$\nu_{\text{py}}(\text{CC})$; $\nu_{\text{py}}(\text{CN})$ breathing
		1078	1036	2.3	1075	1071	
1052m	1051w	1089	1047	33.3	1085	1084	$\sigma(\text{H}_9\text{H}_{11})$; $\nu_{\text{bz}}(\text{CC})$
	1065w	1127	1083	4.1	1123	1120	$\sigma(\text{H}_2\text{H}_4)$; $\nu_{\text{py}}(\text{CC})$
1098vw	1098w	1151	1106	12.8	1148	1144	$\nu_{\text{bz}}(\text{CC})$; $\tau(\text{H}_6\text{H}_6\text{H}_2)$; $\nu(\text{CO})$
1127w	1127vw	1172	1126	16.8	1167	1165	$\sigma(\text{H}_{12}\text{H}_{11})$
1153w	1148w	1187	1141	2.5	1181	1178	$\sigma(\text{H}_2\text{H}_3)$; $\sigma(\text{H}_3\text{H}_4)$
		1209	1163	12.0	1202	1201	$\tau(\text{H}_6\text{H}_6\text{H}_2)$; $\sigma(\text{H}_{12}\text{H}_{11})$
1194w	1193w	1227	1179	6.2	1222	1221	$\nu(\text{C}_6\text{C}_7)$; $\rho(\text{CH})$ (C6H61)
1205m	1204vw	1243	1195	12.7	1237	1232	$\nu(\text{C}_5\text{C}_6)$; $\rho(\text{CH})$ (C6H62)
1243vw	1242vw	1299	1249	0.3	1293	1291	$\nu_{\text{py}}(\text{CC})$; $\omega(\text{H}_6\text{H}_6\text{H}_2)$; $\rho_{\text{bz}}(\text{CH})$

(continues)

Table 3 (continued)

ν [cm ⁻¹] Raman ^a	ν [cm ⁻¹] IR ^a	(a) ^b	(a1) ^b	IR _{int.} (a) ^c	(b) ^b	(c) ^b	Approx. description
1268vw	1268vw	1307	1257	4.7	1302	1301	$\rho_{bz}(\text{CH})$
1285w	1289vw	1328	1276	2.2	1322	1318	$\nu_{py}(\text{CC}); \rho_{py}(\text{CH})$ (C6H62)
1321w		1371	1318	0.5	1366	1364	$\nu_{bz}(\text{CC}); \rho_{py}(\text{CH}); \omega(\text{H61H62})$
1346vs	1349m	1388	1334	1.5	1382	1378	$\nu_{bz}(\text{CC}); \rho_{py}(\text{CH})$ (C6H61)
1360vs	1356s	1398	1344	424.8	1398	1383	$\nu_{sym}(\text{O3N3O4})$
1394vw		1412	1358	121.1	1412	1400	$\nu_{sym}(\text{O1N2O2})$
1406vw	1409w	1447	1391	3.5	1443	1437	$\nu_{bz}(\text{CC}); \rho_{bz}(\text{CH})$
1427vw	1428m	1480	1423	35.8	1475	1468	$\rho_{bz}(\text{CH})$
1440vw	1443w	1500	1442	24.7	1483	1480	$\sigma(\text{C6H61-C6H62})$
		1521	1462	34.4	1515	1509	$\rho(\text{CH})$
1478vw	1476m	1526	1467	1.8	1521	1516	$\rho(\text{CH})$
1528m	1526s	1617	1554	89.5	1615	1595	$\nu_{bz}(\text{CC}); \nu_{asym}(\text{NO}_2)$
		1633	1570	10.3	1630	1613	$\nu_{py}(\text{CC}); \nu_{py}(\text{CN})$
1544m	1542vs	1637	1574	56.5	1636	1622	$\nu_{bz}(\text{CC}); \nu_{asym}(\text{NO}_2)$
1569w	1568w	1647	1584	77.0	1645	1636	$\nu_{py}(\text{CC}); \nu_{py}(\text{CN})$
1590m	1603m	1671	1606	82.7	1670	1653	$\nu_{bz}(\text{CC}); \nu_{asym}(\text{NO}_2)$
1612s	1612m	1674	1610	173.2	1674	1657	$\nu_{bz}(\text{CC}); \nu_{asym}(\text{NO}_2)$
2860vw	2862vw	3081	2962	15.4	3076	3074	$\nu(\text{C6H61}); \nu(\text{C6H62})$ sym
2936m		3127	3006	3.3	3125	3118	$\nu(\text{C6H61}); \nu(\text{C6H62})$ asym
2958w	2959vw	3182	3059	14.4	3174	3178	$\nu(\text{C1H1})$ asym
3012w	3013w	3192	3069	2.9	3188	3187	$\nu(\text{C3H3}); \nu(\text{C4H4})$ asym
3053m	3053w	3205	3081	2.4	3202	3200	$\nu(\text{C12H12})$
3067m		3206	3082	24.0	3202	3201	$\nu(\text{C3H3}); \nu(\text{C4H4}); \nu(\text{C2H2})$
3091m	3089w	3220	3096	17.9	3216	3215	$\nu(\text{C2H2}); \nu(\text{C3H3})$ sym
	3104w	3255	3129	2.1	3248	3244	$\nu(\text{C11H11})$
	3117w	3276	3149	15.5	3269	3261	$\nu(\text{C9H9})$

^a Experimental values are taken from [12], preceded by 19 lower frequency normal vibrations.

^b Calculated with: B3LYP/6-31G(d) unscaled and scaled by 0.9614 [17] (a, a1), B3LYP/6-31G** unscaled (b), B3LYP/6-31++G** unscaled (c).

^c IR calculated intensities for (a).

Abbreviations: Py - pyridine ring, dnBz - dinitrobenzyl ring, Relative intensities (s, strong; m, medium; w, weak; v, very; sh, shoulder), Vibrational modes (ν -stretching, δ -bending, ρ -rocking, τ -twist, ω -wagging), sym-symmetric, asym-asymmetric.

α -DNBP taken from [12], with our *ab initio* DFT calculated infrared values. We also present an approximate description of the vibrational normal modes. If for the CH₂ stable tautomer we have performed the calculations using the B3LYP density functional method and three basis sets 6-31G(d), 6-31G** and 6-31++G**,

Table 4

Experimental and *ab initio* calculated vibrational spectrum of α -DNBP, NH isomer

ν [cm ⁻¹] Raman ^a	ν [cm ⁻¹] IR ^a	Z-I ^b	Z-II ^b	IR _{int.} Z-II ^c	E-I ^b	E-II ^b	Approx. description for NHZ-II isomer
	463w	438	448	1.8	440	438	dnBz. out of plane def
478vw	480w	479	482	4.0	466	466	dnBz. out of plane def; ω (CH)
		505	497	18.9	500	481	ρ (O1O2)(O3O4); ω_{py} (CH)
515w	515w	521	521	6.8	518	518	dnBz. out of plane def; ω_{py} (CH)
	525w	549	557	4.1	551	559	dnBz. out of plane def
	584vw	598	600	7.0	599	594	ν_{py} (CC); ν_{py} (CN)
605vw	601vw	621	630	0.2	615	616	ν_{py} (CC); ν_{py} (CN)
630vw	627vw	646	638	5.0	638	625	ν_{bz} (CC)
652m	649w	655	669	3.2	647	639	dnBz. & Py. out of plane def
	682w	678	691	16.5	677	672	Py. out of plane def
709vw	709m	693	701	19.7	688	680	ν_{bz} (CC); σ (NO ₂)
	726m	701	717	35.7	698	704	ω (CH)(N3)
736vw	737m	718	727	16.8	722	718	ω (CH); δ (N1H62); ω (N2,N3)
	759vs	725	735	16.9	724	725	
764vw		745	764	42.4	744	742	ω (CH); δ (N1H62); δ (C6H62)
		769	769	14.1	781	749	δ (N1H61); σ (NO ₂); ν_{bz} (CC)
		797	799	32.4	792	789	
813w	811m	812	806	24.6	812	808	
836m	837m	830	822	5.5	819	825	ω (CH)
859vw	858m	840	839	38.1	841	835	
884vw	886vw	849	866	42.0	849	854	ν_{py} (CC); ν_{bz} (CC)
900vw	900m	902	915	7.3	903	900	τ (H1H2)
922vw	921m	908	920	9.2	909	912	ν_{bz} (CC); τ (H1H61)
933vw		933	932	8.6	930	924	δ (H9)
		962	951	1.2	956	951	τ (H11H12)
	990m	965	962	0.6	965	966	τ (H3H4)
996m		969	982	66.6	978	976	ν_{py} (CC); ν_{py} (CN)
	1019w	997	1011	7.0	1003	1007	ν_{py} (CC); ρ (H3H4); σ (H1H4)
1052m	1049w	1041	1051	23.3	1042	1044	ν_{bz} (CC); σ (H9H11)
	1095w	1081	1090	77.4	1081	1084	ρ_{py} (CH); ν_{bz} (CC)
	1123w	1111	1112	192.3	1109	1112	ν_{bz} (CC); ρ_{py} (CH)
	1142w	1123	1132	175.2	1120	1126	σ_{bz} (H11H12)
1153m		1148	1153	30.1	1152	1152	σ (H2H3); σ (H3H4)
	1165w	1191	1194	193.0	1195	1205	σ_{py} (CH); ν (C6C7); ρ (H62H12)

(continues)

Table 4 (continued)

ν [cm ⁻¹] Raman ^a	ν [cm ⁻¹] IR ^a	Z-I ^b	Z-II ^b	IR _{int.} Z-II ^c	E-I ^b	E-II ^b	Approx. description for NHZ-II isomer
1205m		1211	1199	22.7	1210	1208	$\nu_{\text{sym}}(\text{C5C6C7})$
	1211vw	1233	1233	6.4	1247	1237	$\rho_{\text{py}}(\text{CH}); \rho_{\text{ph}}(\text{CH})$
1243vw	1243vw	1258	1249	261	1265	1262	$\rho_{\text{py}}(\text{CH}); \rho_{\text{bz}}(\text{CH}); \nu_{\text{sym}}(\text{NO}_2)$
		1295	1270	57.6	1296	1302	$\nu_{\text{py}}(\text{CC}); \rho_{\text{bz}}(\text{CH}); \rho_{\text{bz}}(\text{CH})$
1293s	1292s	1315	1321	1424	1305	1318	$\nu_{\text{sym}}(\text{O3N3O4})$
		1328	1328	51.8	1320	1328	$\nu_{\text{ph}}(\text{CC}); \rho_{\text{bz}}(\text{CH}); \nu_{\text{sym}}(\text{NO}_2)$
1346vs	1345sh	1354	1368	47.3	1343	1344	$\nu_{\text{bz}}(\text{CC}); \rho_{\text{py}}(\text{CH}); \nu_{\text{py}}(\text{CN})$
1360vs	1361s	1369	1374	64.7	1367	1370	$\nu_{\text{bz}}(\text{CC}); \rho_{\text{py}}(\text{CH}); \nu_{\text{sym}}(\text{NO}_2)$
1406w	1409m	1395	1412	32.0	1398	1389	C6H62 def; $\nu_{\text{bz}}(\text{CC}); \nu_{\text{py}}(\text{CC})$
1427vw	1428m	1411	1428	117.2	1434	1449	Py. $\rho(\text{CH}); \text{NH def}; \nu(\text{CN})$
		1448	1458	45.1	1453	1456	Bz. $\rho(\text{CH})$ & $\rho(\text{C6H62})$
1478vw	1476m	1460	1467	14.5	1482	1482	Py. $\rho(\text{CH})$ & $\rho(\text{C6H62})$
		1513	1512	79.8	1512	1509	$\nu_{\text{asym}}(\text{NO}_2); \text{dnBz. \& Py. stretch.}$
1528m	1528s	1537	1523	374.8	1525	1532	
1544m	1543s	1549	1545	244.9	1547	1548	$\delta(\text{C6H62}); \nu(\text{C5C6})$
	1559m	1575	1567	652.2	1569	1572	$\nu_{\text{asym}}(\text{NO}_2); \text{dnBz. \& Py. stretch.}$
1569w	1574m	1585	1590	474.6	1585	1584	
1612s	1604m	1603	1605	17.5	1599	1598	dnBz. & Py. stretch.
	1634w	1630	1623	117.1	1629	1633	
2936m		3082	3050	5.5	3082	3022	$\nu(\text{C6H62})$
2958w	2960vw	3084	3080	9.8	3103	3074	$\nu(\text{C12H12})$
3012vw	3013w	3105	3082	4.2	3108	3087	$\nu(\text{C3H3}); \nu(\text{C4H4})$ asym
3053m	3053w	3108	3101	9.4	3121	3109	$\nu(\text{C4H4}); \nu(\text{C3H3})$ sym
3067m		3123	3109	1.1	3125	3126	$\nu(\text{C1H1}); \nu(\text{C2H2})$ asym
3091m		3125	3125	5.4	3127	3127	$\nu(\text{C1H1}); \nu(\text{C2H2})$ sym
	3104m	3150	3128	2.0	3133	3135	$\nu(\text{C11H11})$
	3111w	3157	3153	17.1	3153	3147	$\nu(\text{C9H9})$
	3389vw	3460	3230	75.1	3460	3464	$\nu(\text{N1H61})$

^a Experimental values are taken from [12], preceded by 16 lower frequency normal vibrations.

^b Calculated with: B3LYP/6-31G(d) scaled by 0.9614 [17] for NHZ-I, NHZ-II, NHE-I, NHE-II, NH isomers.

^c IR calculated intensities for NHZ-II.

IR intensity and Raman activity

Abbreviations: Py - pyridine ring, dnBz - dinitrobenzyl ring, Relative intensities (s, strong; m, medium; w, weak; v, very; sh, shoulder), Vibrational modes (ν -stretching, δ -bending, ρ -rocking, τ -twist, ω -wagging), sym-symmetric, asym-asymmetric.

for all four NH π -diastereoisomers the computations were performed with the same density functional (B3LYP) but only with the 6-31G(d) basis set.

To quantify the degree of correlation between the experimental and calculated wavenumbers, for all NH isomers we have computed the value

$$D = \frac{1}{N} \sqrt{\sum_{i=1}^N (v_{calc.} - v_{exp.})^2}, \quad (1)$$

where N represents the number of normal modes taken into account, $v_{exp.}$ the experimental values [12] and $v_{calc.}$ the calculated ones. We obtained the values: 4.49, 3.97, 4.79, 4.17 cm^{-1} , for Z-I, Z-II, E-I and E-II NH isomers, excluding only the last mode – $\nu(\text{N1H61})$, which is greatly sub-estimated due to the hydrogen bonds N1-H61-O1 and N1-H61-N2 mentioned above. We observe that the better correlation is obtained for the NHZ-II isomer, which ensures us, one time again that this NH isomer is the most stable.

We finally add that from our calculations for all NH isomers the NH stretching is predicted at the right place, as being the most energetic vibrational mode, another improvement compared with the results obtained in [12], where one of the $\nu(\text{CH})$ is predicted to be with higher frequency than the $\nu(\text{NH})$.

4. CONCLUSIONS

Structure optimization and vibrational analysis were performed on the 2-(2',4'-dinitrobenzyl)pyridine stable CH_2 tautomer and on all four NH π -diastereoisomers, using the density functional B3LYP with the basis sets 6-31G(d), 6-31G** and 6-31++G**. In all cases no imaginary frequency modes were obtained, proving that the optimized structures are local minimums on the potential energy surface (PES). Contrary to the reference [12] we didn't have any problem with the optimization of the NHZ-II isomer, which finally proved to be the most stable NH isomer. The fact that the structure of this NH isomer is the most similar with that of the original CH_2 form, agree with the finding that the structures of the reactant (CH_2) and product (NH) are very similar [9]. In our calculations, however, the angle between the pyridine and benzene ring planes differ with 8° (50°), for the CH_2 (NH) forms. This difference may be the consequence of not taking into account the intermolecular interactions due to crystal packing, the theoretical calculations being performed in the gas phase. The twist of the *p*-nitro group from the benzene ring plane is clearly due to the crystal packing as observed in [12].

As the experimental wavenumbers are anharmonic by nature and our calculated wavenumbers use the harmonic approximation, and also because the

theoretical structures ignore the crystal packing, the calculated vibrational frequencies, even scaled, agree only in part with the experimental ones. Nevertheless, for the NH isomers, the closest resemblance between the calculated and experimental frequencies was found for the NHZ-II isomer, which ensures us, one time again, that this NH isomer is the most stable. Consequently, we can assume that in the blue NH form of α -DNBP not much strain is developed in the crystal, the structure remaining practically identical with that of the pale yellow crystal, as observed experimentally. The great difference between the lifetimes of the NH form in the solid state (hours) and in the liquid state (ms), we think that can be associated essentially with the existence in the liquid of other types of mechanisms, besides the intramolecular proton transfer, to produce the N-H blue tautomer, as for example the one where the proton is transferred to the N atom or abstracted from it *via* the solvent.

We finally consider that a great improvement in the theoretical description of the structural and vibrational solid state properties of this system can be obtained at the same level of theory performing the calculations on a periodic structure.

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