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Molecular and crystal structures, vibrational studies and quantum chemical calculations of 3 and 5-nitroderivatives of 2-amino-4-methylpyridine

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HIGHLIGHTS

- The crystal structures of 3- and 5-nitroderivatives of 2-amino-4methylpyridine were studied.
- ► These structures exhibit layered arrangement with a dimeric N-H…N motif.
- The IR and Raman wavenumbers have been calculated from the optimized geometry of monomers and dimers.
- ► X-ray, IR, Raman and DFT methods confirm the existence of intermolecular N-H…N bonds.

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Introduction

The pyridine derivatives are widely used in the syntheses of various biologically active compounds and have attracted

G R A P H I C A L A B S T R A C T



ABSTRACT

The crystal structures of 2-amino-4-methyl-3-nitropyridine (**I**), 2-amino-4-methyl-3,5-dinitropyridine (**II**) and 2-amino-4-methyl-5-nitropyridine (**III**) have been determined. The compounds crystallize in the monoclinic $P2_1/n$, triclinic P-1 and monoclinic C2/c space groups, respectively. These structures are stabilized by a combination of N–H…N and N–H…O hydrogen bonds and exhibit layered arrangement with a dimeric N–H…N motif in which the molecular units are related by inversion centre. The molecular structures of the studied compounds have been determined using the DFT B3LYP/6-311G(2d,2p) approach and compared to those derived from X-ray studies. The IR and Raman wavenumbers have been calculated from the optimized geometry of monomers and dimers formed in the unit cell and compared to the experimental values obtained from the spectra.

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interest of numerous studies [1–4]. The pyridine ring appears in a large number of natural substances such as vitamin B5, vitamin B6, pyridoxal and pyridoxamine; and drugs such as nifedipine, nichetamine, sulphapyridine. Some of pyridine derivatives show antimicrobial, antifungal, antibacterial, pesticidal, antiallergic, antihypertensive, antitumor or analgesic properties [5–10].

On the other hand, substituted pyridine compounds such as 2aminopyridines [11–13] and their nitro derivatives are useful as building blocks of nonlinear optical materials [14–18].

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Scheme 1. The molecular formulas of I-III compounds.

The present work is a continuation of our systematic studies on the 2-aminopyridine derivatives with different substituents at various ring positions [19–22]. The relationships between the structure of these compounds and their hybrid salts have also been studied [23–26]. The knowledge of their crystal and molecular structures and their relation to the vibrational characteristics can be applied in the discussion of their biological activity and the role of hydrogen bonds in it. Therefore we report the preparation methods, structures, spectroscopic properties and quantum chemical calculations of 2-amino-4-methyl-3-nitropyridine (I), 2-amino-4methyl-3,5-dinitropyridine (II) and 2-amino-4-methyl-5-nitropyridine (III) (Scheme 1).

The IR and Raman spectra of 2-amino-4-methyl-3-nitropyridine (I) are reported in the Spectral Database for Organic Compounds (SDBS), (SDBS No: 29780) [27]. These data have been compared to the spectra of other derivatives studied in the present paper. In the similar way, although the crystal structure of I has been determined at ambient temperature by other authors [28] recently, the complementary X-ray studies at low temperatures for I–III derivatives are reported in this paper.

Experimental

Synthesis

The syntheses of several 2-aminonitropyridines were described previously by Talik and Talik [29]. Their methods were applied in the syntheses of I-III compounds using commercially available 2amino-4-methylpyridine (Fluka, >99%). These compounds were obtained as follows: 25 g of appropriate 2-amino-4-methylpyridine were dissolved in 125 cm³ of concentrated H₂SO₄ (Fluka, 96%). The reaction mixture was cooled under intensive stirring to $0 \,^{\circ}$ C by adding ice mixed with NaCl. Subsequently, 37.5 cm³ of HNO₃ (Chempur, 65%, $d = 1.4 \text{ g/cm}^3$) were added in small portions keeping the temperature below 10 °C. Then the mixture was stirred for 1.5 h with continuous cooling, and kept at ambient temperature for 1 h. Next, the reaction mixture was heated in a water bath for half an hour at 40 °C, 1 h in the temperature range 60–70 °C and half an hour in a boiling water bath. Then, the whole reaction mixture was cooled to ambient temperature, poured on ice and neutralized with ammonia to a slightly alkaline pH. The solid reaction product was filtered off under vacuum. Two nitro isomers (3 and 5) were separated by steam distillation. More volatile 3- nitro isomer (I) was distilled off and condensed as a pure compound (obtained after drving 10 g), while residual 5-nitro isomer (III) was filtered off and crystallized from water (with H₂SO₄ and active carbon added initially for dissolving the compound and removing impurities). After neutralization, filtering off and drying, about 15 g of 5-nitro isomer (III) was obtained.

The 2-amino-4-methyl-3,5-dinitropyridine (II) was obtained from 2-amino-4-methyl-5-nitropyridine (III) by a similar procedure (nitration and rearrangement to dinitropyridines).

The residues were purified by crystallization from water to give 2-amino-4-methyl-3-nitropyridine, **I** (Yield: (27% (10 g), m.p. 134(1) °C), 2-amino-4-methyl-3,5-dinitropyridine, **II** (Yield: 80% (10.4 g), m.p. 197(1) °C) and 2-amino-4-methyl-5-nitropyridine, **III** (Yield: 40% (15 g), m.p. 218(1) °C), respectively. Melting points were determined using a Köfler apparatus. The chemical composition of the obtained compounds was checked using the Carlo Erba Analyser, Model 1104.

X-ray data collection

Details of the data collections, analyses and refinements for the studied compounds are given in Supplementary Table S1. X-ray measurements of the **I–III** derivatives were performed at 120, 90 and 100 K, respectively, using graphite-monochromated CuK α (λ = 1.5418 Å) for I and MoK α (λ = 0.71073 Å) radiation for II and III, respectively. The instrument was equipped with Oxford Cryosystems low-temperature devices. Lattice parameters were determined from least-squares analysis, and reflection data were integrated using the CrysAlis software [30]. For I, an empirical absorption correction determined with the CrysAlis RED 1.171 was applied to the data using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm [30]. A correction for extinction was applied for crystal I. For II and III, no absorption correction was applied; only Lorentz and polarization effects were taken into account.

The structures were solved by direct methods using SHELXS-97 program [31] and refined on F^2 by full-matrix least squares with anisotropic thermal parameters for all non H-atoms using SHEL-XL-97 [31]. The H atoms bound to C atoms were included in the geometrically calculated positions, with the C–H distances of 0.95–0.98 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C_{aryl})$ and $U_{iso}(H_{methyl}) = 1.5U_{eq}(C)$. The H atoms bounded to N and O atoms were located from difference Fourier maps and were freely refined with $U_{iso}(H) = 1.2U_{eq}(N)$ and 1.5 $U_{eq}(O)$, respectively.

Full crystallographic details, including structures have been deposited at the Cambridge Crystallographic Data Centre; CCDC Reference Nos. 858904–858906. These data can be obtained free of charge via <<u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.uk).

Spectroscopic measurements

IR spectra were recorded at room temperature in Nujol suspension in the 4000–50 cm⁻¹ range and potassium bromide pellet in the 4000–400 cm⁻¹ range. The spectra were measured using a FTIR Biorad 575C spectrometer with the resolution of 2.0 cm⁻¹.

Raman spectra were measured in back scattering geometry in the 4000–80 cm⁻¹ range using a FTRaman Bruker 110/S spectrometer. The resolution was 2.0 cm⁻¹. The YAG:Nd (excitation wavelength 1064 nm) laser was used as an excitation source.

Quantum chemical calculations

The geometry optimisation of the molecular structures of the studied compounds was performed for both the monomeric and dimeric units with the use of Gaussian 03 programme package [32]. All calculations were performed using density functional three-parameters hybrid (B3LYP) methods [33–35] with the 6-311G(d,p) [36,37] basis set starting from the X-ray geometry. The calculated and experimental values were compared using scaling factors to correct the evaluated wavenumbers for vibrational anharmonicity and deficiencies inherent to the used computational level. The Potential Energy Distribution (PED) of the normal modes among the respective internal coordinates has been calcu-







Fig. 2. The dimer of **I** formed by N–H…N hydrogen bonds. Dashed lines indicate intra- and intermolecular hydrogen bonds (symmetry code as in Table 2).

lated for **I–III** using the BALGA [38] program. As the input data the atomic coordinates from the X-ray studies were applied. The dimers are built from two molecular units coupled *via* two hydrogen bonds between them. In this case the eight-atomic ring system was formed (see Figs. 1 and 2).

The vector displacements of the atoms from their equilibrium positions during the vibration and the graphical pictures of these displacements were prepared using ANIMOL program that also visualizes particular modes in animated way [39].

Linear correlation was used for scaling the theoretical wavenumbers to compare them with the experimental values [40]. The mean square deviation between the experimental and calculated unscaled wavenumbers for I was 5.5 and 5.2 cm⁻¹, for II was 6.01 and 5.7 cm⁻¹ and for III was 7.4 and 5.7 cm⁻¹, for the IR and the Raman spectra, respectively. The scaling of the calculated wavenumbers improves this result to 2.0 cm⁻¹ for the IR and 1.7 cm⁻¹ for the Raman spectra – for I, 2.8 cm⁻¹ for the IR and 2.7 cm⁻¹ – for II, 4.4 cm⁻¹ for the IR and 3.3 cm⁻¹ – for III. 0.960, 0.957, 0.972 scaling factors were used for the 3600– 2900 cm⁻¹ range and 0.974, 0.979, 0.978 were used for the 1700–0 cm⁻¹ range of the monomers and the dimers of I–III, respectively.

The theoretical Raman intensities were calculated using the RAINT computer program [41] reported in [42].

Results and discussion

Structures description

The structure determinations of **I–III** revealed that the three studied compounds crystallize in centrosymmetric space groups,

 $P2_1/n$, $P\overline{1}$ and C2/c, respectively. Atom numbering schemes and molecular structures of the studied compounds are depicted in Fig. 1(a)–(c). Selected geometric parameters are presented in Table 1. The pyridine ring is slightly distorted from planarity; the largest deviation (0.022(2) Å) from an aromatic ring plane occurs for C3 atom. The amino N2 and methyl C7 atoms lie approximately in the pyridine ring plane. The intramolecular N-H-O hydrogen bond exists between the amino and nitro groups in I and II. Nevertheless, the nitro group is twisted with respect to the pyridine ring, the dihedral angle between these planes is 16° in I, 40° and 26° in **II**; probably as the result of the steric hindrance of the neighboring nitro and methyl groups in the aromatic ring. For instance, the twisting angle of the NO₂ group is <10° in 2-amino-3-nitropyridine compounds [13,14,43-46], and as large as 55° in 2-amino-4methyl-3-nitropyridininium trifluoroacetate [25]. The other geometrical parameters for I-III may be regarded as normal and are comparable with the values observed for 2-amino-3-nitropyridine polymorphs [43,44] and also 2-amino-4-methyl-3-nitropyridine [28].

The main features of the crystal structures are the centrosymmetric dimers formed by two identical N–H…N hydrogen bonds (Tables 2–4) involving one H atom of NH₂ group as a donor and the pyridine N-atom as an acceptor. In such a way, the dimer and two HBs form eight-membered ring denoted as $R_2^2(8)$ graph set motif (Fig. 2, Table 2) [47]. Similar dimers appear in crystals of 2-aminopyridine and its nitro derivatives [43,44,48].

In the crystal structure of **I**, another H atom of amino group is engaged in the intramolecular interaction with the O1 atom of the nitro group only (Table 2). In this compound the dimers are

 Table 1

 Selected geometric parameters (Å, °) in I–III.

| | I Exp. | Calc. | II Exp. | Calc. | III Exp. | Calc. |
|-------------|------------|-------|------------|-------|------------|-------|
| Distances | | | | | | |
| N1-C6 | 1.323(2) | 1.322 | 1.3216(14) | 1.316 | 1.3346(12) | 1.324 |
| N1-C2 | 1.357(2) | 1.355 | 1.3581(11) | 1.357 | 1.3593(12) | 1.353 |
| C2-N2 | 1.343(2) | 1.336 | 1.3316(14) | 1.332 | 1.3393(12) | 1.344 |
| C2-C3 | 1.432(2) | 1.437 | 1.4253(10) | 1.431 | 1.4169(13) | 1.413 |
| C3-C4 | 1.412(2) | 1.390 | 1.3912(14) | 1.404 | 1.3747(13) | 1.379 |
| C3-N3 | 1.448(2) | 1.450 | 1.4549(11) | 1.462 | - | - |
| N3-01 | 1.242(2) | 1.239 | 1.2287(12) | 1.235 | - | - |
| N3-02 | 1.226(2) | 1.227 | 1.2266(9) | 1.223 | - | - |
| C4-C5 | 1.386(2) | 1.390 | 1.4024(11) | 1.404 | 1.4212(12) | 1.416 |
| C4-C7 | 1.508(2) | 1.506 | 1.5042(11) | 1.505 | 1.5057(13) | 1.504 |
| C5-C6 | 1.387(2) | 1.387 | 1.3901(11) | 1.392 | 1.3921(13) | 1.390 |
| C5-N5 | - | - | 1.4496(15) | 1.462 | 1.4413(13) | 1.454 |
| N5-03 | - | - | 1.2294(9) | 1.226 | 1.2325(11) | 1.229 |
| N5-04 | - | - | 1.2316(9) | 1.227 | 1.2377(11) | 1.230 |
| | | | | | | |
| Bond angles | | | | | | |
| C6-N1-C2 | 118.5(2) | 118.9 | 118.36(7) | 118.8 | 116.97(8) | 117.6 |
| N2-C2-N1 | 114.5(2) | 115.5 | 115.77(8) | 116.0 | 117.19(8) | 117.0 |
| N2-C2-C3 | 125.8(2) | 124.5 | 124.66(7) | 124.3 | 120.98(8) | 121.7 |
| N1-C2-C3 | 119.7(2) | 120.1 | 119.56(7) | 119.7 | 121.82(8) | 121.3 |
| C4-C3-C2 | 120.8(2) | 120.1 | 123.00(6) | 121.9 | 121.69(8) | 121.6 |
| C4-C3-N3 | 119.9(2) | 120.2 | 119.27(7) | 119.7 | | - |
| C2-C3-N3 | 119.3(2) | 119.7 | 117.62(7) | 118.4 | - | - |
| 02-N3-01 | 121.2(2) | 122.0 | 123.72(7) | 123.4 | - | - |
| 01-N3-C3 | 119.0(2) | 119.0 | 118.02(7) | 118.2 | - | - |
| 02-N3-C3 | 119.8(2) | 118.9 | 118.22(7) | 118.3 | - | - |
| C3-C4-C5 | 116.4(2) | 116.9 | 113.97(7) | 114.9 | 115.31(8) | 115.7 |
| C3-C4-C7 | 125.5(2) | 125.3 | 122.59(7) | 122.7 | 118.79(8) | 119.0 |
| C5-C4-C7 | 118.1(2) | 117.8 | 123.24(7) | 122.3 | 125.90(8) | 125.3 |
| C6-C5-C4 | 119.60(14) | 119.7 | 121.28(7) | 120.6 | 120.31(8) | 119.5 |
| C6-C5-N5 | - | - | 116.06(7) | 116.0 | 117.03(7) | 116.9 |
| C4-C5-N5 | - | - | 122.59(7) | 123.5 | 122.65(8) | 123.6 |
| 03-N5-04 | - | - | 123.38(7) | 124.3 | 121.51(9) | 123.5 |
| 03-N5-C5 | - | - | 118.83(7) | 118.5 | 119.16(8) | 118.5 |
| 04-N5-C5 | - | - | 117.71(7) | 117.1 | 119.32(8) | 118.0 |
| N1-C6-C5 | 124.8(2) | 124.3 | 123.74(7) | 124.0 | 123.88(8) | 124.3 |

joined by C–H···O interactions involving one of the H atoms of the methyl group as a donor and the nitro O atom as an acceptor, forming a layer (Supplementary Fig. S1). Additionally, the appearance of aromatic π - π stacking and short N–O··· π contact are suggested by the X-ray data.

In the crystal structure of **II**, the H22 atom of amino group is involved in the intra- and intermolecular hydrogen bonds with three O atoms of two nitro groups (Table 3). The N–H…O bonds between the pyridine units form the ribbon as shown in Supplementary Fig. S2. The packing of the whole crystal is stabilized by C–H…O interactions and aromatic π – π stacking.

The crystal structure of **III** contains the dimers connected *via* N–H···O hydrogen bonds involving one of the H atoms of amino group as a donor and nitro O atoms as acceptors (Table 4). As a result of such interactions the layered structure is characteristic for the compound **III** (Supplementary Fig. S3).

Vibrational and DFT calculations

The IR and Raman spectra of the studied compounds are compared in Figs. 3 and 4. Experimental and calculated wavenumbers of **I–III** compounds are collected in Table 5, in which the assignment of the vibrational normal modes to the respective bands is proposed.

The IR spectrum of **I** measured in the present study was compared to the one that had been measured earlier and shown in the Spectral Database for Organic Compounds (SDBS) [27]. Both spectra of this compound are identical.

It should be noted that the majority of wavenumbers and PED contributions calculated for the dimers and monomers are nearly identical or very similar. They mainly differ by a few percent admixture of other internal co-ordinates in the normal modes. However, this does not influence the assignment of the normal modes to the respective IR and Raman bands that are based on the significant contribution of the definite internal co-ordinates.

Pyridine ring vibrations

The assignment of the pyridine ring vibrations for the studied compounds is based on the comparative spectra of pyridine [49], the results of DFT quantum chemical calculations reported by Urena et al. [50], as well as a number of our works on the IR and Raman spectra of several pyridine derivatives [16,19,22,23,51]. On that basis the following description of the lines observed in the spectra is proposed: v(CH): 3207–3109; $v(\phi)$: 1610–1521 and 1008–889; $v(\phi) + \delta(CH)$: 1280–1150; $\delta(\phi)$: 1158–1103, 791–750 and 679–529; $\gamma(CH) + \gamma(\phi)$: 1013–951, 849–782, 770–720 and 505–454; and $\gamma(\phi)$: 240–98 cm⁻¹. The detailed assignment of the observed bands to the respective normal modes is given in Table 5.

It should be noted that the breathing $v_s(\phi)$ vibrations of the pyridine ring in the three studied compounds exhibit interesting conformity. These vibrations usually appear for benzene derivatives in the range 1000–900 cm⁻¹ [52,53]. For pyridine derivatives they usually appear in the range 900–750 cm⁻¹ depending on the number of substituents and their position at the heterocyclic ring [54]. For the studied here compounds **I–III** the DFT calculations predict the wavenumbers of these modes at 839, 814 and 813 cm⁻¹. The respective Raman lines appear as medium strong bands at 866, 836 and 841 cm⁻¹, respectively. This sequence shows a good agreement with the total dipole moments determined for the isolated **I–III** molecules in DFT calculations. They are 1.3840, 0.5843 and 1.2519 D, respectively.

As far as vibrational dynamics of the studied compounds is considered, the problem of the breathing vibrations of the pyridine ring in its derivatives can be also discussed taking into account the shift of the gravity point of the pyridine ring in the derivative according to its position in the unsubstituted pyridine. Supplemen-

Table 2

| מכטוווכנווכמו המומווכנכוה טו וועטוטצכוו הטווטה מווט הוטור ווונכומכנוטוה וטו | Geometrical | parameters of | of hydrogen | bonds and | short interac | tions f | ior |
|---|-------------|---------------|-------------|-----------|---------------|---------|-----|
|---|-------------|---------------|-------------|-----------|---------------|---------|-----|

| D–H…A | D-H | | H…A | H…A | | D····A | | D–H…A | |
|--|-----------------|--------------|-----------------|-------|----------------------|--------|---------------|-------|--|
| | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | |
| Intermolecular N2–H21…N1 ^a C7–H73…O1 ^b | 0.93(2) 0.98 | 1.02 1.09 | 2.09(2) 2.48 | 2.03 | 3.016(2) 3.457(2) | 3.046 | 173(2) 174 | 177 | |
| Intramolecular N2-H22…O1 | 0.94(2) | 1.00 | 1.98(2) | 1.88 | 2.614(2) | 2.615 | 124(2) | 127 | |

^a Symmetry codes: -x + 1, -y + 1, -z + 2;

^b -x + 1/2, y - 1/2, -z + 1/2.

Table 3

Geometrical parameters of hydrogen bonds and short interactions for ${\rm I\!I}.$

| D-H…A | D-H | D-H | | H…A | | | D-H···A | |
|-------------------------|---------|-------|---------|-------|----------|-------|-----------|-------|
| | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| Intermolecular | | | | | | | | |
| N2-H21N1 ^a | 0.88(2) | 1.02 | 2.18(2) | 2.03 | 3.057(2) | 3.045 | 176.9(10) | 177.6 |
| N2-H22… O3 ^b | 0.88(2) | 1.01 | 2.49(2) | - | 3.314(3) | - | 157.3(10) | - |
| N2−H22… O4 ^b | 0.88(2) | 1.01 | 2.65(2) | - | 3.082(2) | - | 111.9(9) | - |
| C6-H6…O2 ^c | 0.95 | 1.08 | 2.51 | - | 3.203(2) | - | 129.6 | - |
| Intramolecular | | | | | | | | |
| N2-H22…01 | 0.88(2) | 1.01 | 2.09(2) | 1.94 | 2.692(2) | 2.659 | 124.8(9) | 125.6 |
| C6-H6-O4 | 0.95 | 1.08 | 2.36 | 2.34 | 2.687(2) | 2.678 | 99.6 | 96.2 |
| C7-H71O3 | 0.98 | 1.08 | 2.42 | 2.30 | 2.783(2) | 2.764 | 101.0 | 103.4 |
| C7-H72…O2 | 0.98 | 1.08 | 2.42 | 2.30 | 2.799(2) | 2.741 | 102.6 | 101.9 |
| | | | | | | | | |

^a Symmetry codes: -x + 2, -y + 1, -z + 1;

^b x + 1, y + 1, z + 1;

^c *x*, *y*, *z*−1.

Table 4

Geometrical parameters of hydrogen bonds and short interactions for III.

| D-H…A | D-H…A D-H | | Н…А | | D····A | | <i>D</i> –H…A | |
|-------------------------|-----------|-------|---------|-------|----------|-------|---------------|-------|
| | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| Intermolecular | | | | | | | | |
| N2-H21…N1 ^a | 0.96(2) | 1.02 | 2.03(2) | 1.99 | 2.993(2) | 3.017 | 179.2(13) | 179.8 |
| N2-H22… O3 ^b | 0.87(2) | 1.00 | 2.52(2) | - | 3.062(2) | - | 121.6(12) | - |
| N2-H22… O4 ^b | 0.87(2) | 1.00 | 2.28(2) | - | 3.140(2) | - | 173.1(12) | - |
| Intramolecular | | | | | | | | |
| C6-H6…O4 | 0.95 | 1.08 | 2.33 | 2.29 | 2.685(2) | 2.665 | 101.1 | 97.8 |

^a Symmetry codes: -x + 1, -y + 1, -z + 1;

^b x + 1/2, -y + 3/2, z - 1/2.

tary Fig. S4 shows the position of these points in the analyzed molecules. The displacements of the gravity points are 0.9970, 0.8013 and 0.8392 Å for the compounds I–III, respectively. This sequence gives the order I > III > II that agrees with the sequence of Raman wavenumbers $v_I > v_{II} > v_{II}$: 866 > 841 > 836 cm⁻¹ for the breathing ring vibrations. It means, that the mass and place substitution simply influence the gravitation energy of this modes. In such a way, the effect of the substituents' mass and place of their substitution on the gravity centre position can be analyzed.

Methyl group vibrations

Three fundamental $v(CH_3)$ bands corresponding to one symmetric and two asymmetric vibrations are usually observed in the range between 2950 and 2990 cm⁻¹ [53,55]. Our DFT calculations locate these modes at the following bands: $v_{as}(CH_3)$ 2921–2884 (97–100% contribution) and $v_s(CH_3)$ 2836–2828 cm⁻¹ (100% contribution). They agree well with the experimental values found at 3107–2979 cm⁻¹ for $v_{as}(CH_3)$ and 2992–2932 cm⁻¹ for $v_s(CH_3)$. The other weak bands in this range arise from a Fermi resonance with the bending vibrations of these groups.

The asymmetric bending vibrations of the methyl groups should appear between 1410 and 1550 cm⁻¹ [53,55]. This is true for the compounds under study. $\delta_{as}(CH_3)$ vibration contributes to the bands observed in the range 1473–1429 cm⁻¹ giving a 20–99% contribution. The symmetric $\delta_s(CH_3)$ vibrations also appear in a typical range and are observed at 1436–1371 cm⁻¹ giving a 30– 99% contribution to the normal modes. The other bands involving the methyl groups are observed in the following regions: $\rho(CH_3)$: 1071–978, $\gamma(\phi$ -CH₃): 625–593, $\delta(\phi$ -CH₃): 407–395 and $\tau(CH_3)$: 221–202 cm⁻¹. The detailed assignment of the observed bands to the respective normal modes is given in Table 5.

Nitro-group vibrations

The nitro group bonded to the pyridine ring $(C_{\phi}-NO_2)$ gives rise to the eight vibrational normal modes. They are described as stretching $v_{as}(NO_2)$, $v_s(NO_2)$ and $v(C-NO_2)$ vibrations and five inplane vibrations: bending $\delta(NO_2)$, rocking $\omega(NO_2)$, bending $\delta(\phi-NO_2)$ and out-of-plane wagging $\rho(NO_2)$, twisting $\tau(NO_2)$ and torsional $\gamma(\phi-NO_2)$. Observed main IR and (RS) modes of the $C\phi-NO_2$ group have been identified and assigned to the following IR



Fig. 3. Experimental and calculated IR spectra of I-III in the range 3700-50 cm⁻¹.



Fig. 4. Experimental and calculated Raman spectra of I-III in the range 3600-80 cm⁻¹.

peaks for I–III, respectively: $v_{as}(NO_2)$ 1559; 1556; 1543; $v_s(NO_2)$ 1441; 1429; 1452 and the second range 1314; 1323; 1291; $\delta(NO_2)$ 866 (866), 835 (836); 841 (841), $\omega(NO_2)$ 786 (791); 785 (782); 765 (764) cm⁻¹. The respective theoretical wavenumbers of these vibrations calculated for the dimeric model are expected in the ranges 1613–1428, 1311–1215, 870–840, 778–704, 626–426, 400–365, 328–232 and 278–67 cm⁻¹. These modes involve the most significant PED contributions of the C–NO₂ and NO₂ coordinates into the normal modes. Some different modes also contain lower contribution of these atomic displacements and respective internal coordinates. This situation appears for the modes observed in the range 680–650, 635–600 and 480–460 cm⁻¹ (Table 5). The significant shifts to the higher wavenumbers are observed for the compound II for which the following vibrations are observed:

 $\upsilon_{as}(NO_2)$: 1596 (1597), $\upsilon_s(NO_2)$: 1348 (1348) and $\delta(NO_2)$: 894 (894) $cm^{-1}.$

Presented here results differ from the data reported earlier for 2-amino-5-nitropyridine [56], for which other assignment of bands were proposed: $v_{as}(NO_2)$: 1493 (1499), $v_s(NO_2)$: 1285 (1274) cm⁻¹. It probably follows from the differences of their crystallographic structures and other programs used in the DFT calculations.

Hydrogen bonds and short contacts vibrations

The series of the materials studied here creates a unique possibility to compare the structures and vibrational properties of the compounds with different substitution place of nitro groups. From the X-ray studies it follows that the position of this chromophore influences both the unit cell structure, space arrangement of the

| Table | 5 |
|-------|---|
|-------|---|

Experimental and calculated wavenumbers (cm⁻¹) and assignments of **I–III** compounds.

| I | Ш | | | | | | Ш | | | | | |
|----------|-------------------|------------|------------|----|-------------------|--------------------|--------------------|----|-------|------------|------------|--|
| | Calc [*] | IR spectra | RS spectra | | Calc [*] | IR spectra | RS spectra | | Calc* | IR spectra | RS spectra | Assignment |
| 1 | 3371 | 3479 sh | - | 1 | 3354 | 3426 m | 3426 vw | 1 | 3418 | 3407 m | 3406 vw | $vNH_2 + vN - H \cdots N_{\phi}$ |
| 2 | 3370 | 3458 m | | 2 | 3354 | | | 2 | 3418 | | | 2 ψ |
| - | - | 3388 sh | - | - | - | 3392 sh | - | - | - | 3322 w | - | $vN-H\cdots N_{\phi}$ |
| 3 | 3112 | 3264 m | 3257 vw | 3 | 3099 | 3292 w | 3286 vw | 3 | 3055 | 3274 vw | - | $vN-H\cdots N_{\phi}^{\varphi}$ |
| 4 | 3085 | 3208 sh | | 4 | 3074 | 3235 sh | | 4 | 3021 | | | Ψ |
| 5 | 2963 | 3118 m | 3109 vw | 5 | 2945 | 3162 m | 3157 vw | 5 | 2964 | 3207 sh | - | vCH |
| 6 | 2963 | | | 6 | 2945 | | | 6 | 2964 | | | |
| - | - | 3068 vw | 3064 w | - | - | - | - | - | - | 3166 sh | - | Combination |
| - | - | - | 3048 sh | - | - | - | - | - | - | - | - | Combination |
| 7 | 2908 | 3031 vw | - | - | - | - | - | 7 | 2940 | 3120 m | 3112 vw | vCH |
| 8 | 2908 | | | | | | | 8 | 2940 | | | |
| 9 | 2891 | 2996 vw | 3005 w | 7 | 2921 | 3099 sh | 3099 vw | 9 | 2891 | 3107 sh | 3065 w | v _{as} CH ₃ |
| 10 | 2891 | 2981 vw | 2979 w | 8 | 2921 | 3045 sh | 3014 vw | 10 | 2891 | 3065 sh | 2991 vw | |
| 11 | 2885 | | | 9 | 2892 | | 2992 vw | 11 | 2884 | 2984 sh | | |
| 12 | 2885 | | | 10 | 2892 | | | 12 | 2884 | 2973 m | | |
| 13 | 2828 | 2932 vw | 2937 m | 11 | 2836 | 2992 vw | 2945 w | 13 | 2828 | 2945 sh | 2936 w | v _s CH ₃ |
| 14 | 2828 | | | 12 | 2836 | | | 14 | 2828 | | | 5 5 |
| - | _ | - | _ | - | _ | - | - | - | - | 2878 w | - | Combination |
| | | | | | | | | | | 2865 sh | | |
| - | _ | _ | - | _ | _ | - | _ | _ | - | 2844 w | - | Combination |
| _ | _ | 2736 vw | _ | _ | _ | _ | _ | _ | _ | 2719 vw | _ | Combination |
| _ | _ | _ | _ | - | - | _ | - | _ | _ | 2669 vw | _ | Combination |
| 15 | 1594 | 1618 vs | 1620 sh | 13 | 1613 | 1633 s | 1630 w | 15 | 1639 | 1668 sh | 1660 vw | $\delta\phi$ -NH _{2HP} |
| 16 | 1591 | | 1612 vw | 14 | 1611 | | | 16 | 1630 | 1654 m | | |
| 17 | 1561 | 1589 m | 1590 w | 15 | 1576 | 1596 m | 1597 m | 17 | 1568 | 1608 m | 1610 w | $v\phi \pm v_{rr}NO_{21}$ |
| 18 | 1550 | 1000 111 | 1000 11 | 16 | 1567 | 1000 111 | 1007 111 | 18 | 1562 | 1601 sh | 1010 11 | ϕ |
| 10 | 1000 | | | 10 | 1007 | | | 10 | 1002 | 1579 sh | | |
| 19 | 1519 | 1559 m | 1559 m | 17 | 1534 | 1556 m | 1552 w | 19 | 1501 | 1543m | 1538 w | $v\phi + v_{rr}NO_{2}uur + \delta CH_{1}$ |
| 20 | 1519 | 1555 11 | 1555 11 | 18 | 1534 | 1550 11 | 1352 W | 20 | 1498 | 1528 vw | 1521 vw | |
| 20 | 1498 | 1513 s | 1507 w | 19 | 1517 | 1536 m | 1523 m | 21 | 1463 | 1504 sh | 1499 m | $v = NO_{avar} + v\phi + \delta CH$ |
| 22 | 1490 | 1515 5 | 1507 W | 20 | 1514 | 1550 11 | 1525 11 | 21 | 1457 | 1493 vw | 1496 sh | |
| | - | _ | _ | 20 | 1485 | 1512 m | 1499 w | | - | - | - | $v NO_{ex} + v\phi$ |
| | | | | 21 | 1484 | 1505 sh | 1455 W | | | | | $v_{as} (0) = v \phi$ |
| 23 | 1435 | 1473 VW | 1459 sh | 22 | 1446 | 1480 w | 1473 sh | 23 | 1456 | 1475 sh | 1480 sh | $\delta_{\rm e}$ CH ₂ + $\nu \phi_{\rm e}$ NH ₂ up + $\nu_{\rm e}$ NO ₂ |
| 23 | 1433 | 1456 sh | 1455 511 | 23 | 1442 | 1400 W | 1475 311 | 23 | 1450 | 1475 311 | 1400 311 | |
| 25 | 1415 | 1441 m | 1445 w | 25 | 1433 | 1459 vw | 1462 sh | 25 | 1431 | 1470 sh | 1478 vw | δ. CH ₂ |
| 26 | 1414 | | 1115 W | 26 | 1432 | 1155 VW | 1 102 511 | 26 | 1430 | 11/0 511 | 11/0 / // | 0450113 |
| 27 | 1411 | | | 20 | 1412 | 1429 w | 1435 vw | 20 | 1417 | 1452 m | 1458 vw | $\delta_{\rm e}$ CH ₂ + ν NO ₂ |
| 27 | 1411 | | | 27 | 1412 | 1425 W | 1455 VW | 27 | 1417 | 1452 111 | 1450 VW | Vasenij · Všrtož |
| 20 | 1398 | 1424 sh | 1436 w | 20 | 1381 | 1414 w | 1413 vw | 20 | 1395 | 1431 sh | 1426 yw | $\delta CH_0 + v\phi + \delta NH_{out}$ |
| 30 | 1396 | 1424 3h | 1450 W | 30 | 1381 | 1414 W | 1415 000 | 30 | 1389 | 1426 sh | 1420 VW | σ _s en ₃ · νφ · σπη _{2HB} |
| 50 | 1550 | 1420 311 | | 50 | 1501 | | | 50 | 1505 | 1420 sh | | |
| 31 | 1356 | 1371 w | 1383 m | 31 | 1360 | 1375 w | 1384 vw | 31 | 1370 | 1372 w | 1372 vw | δ.CH ₂ |
| 32 | 1356 | 1571 W | 1505 11 | 32 | 1360 | 1375 W | 1304 000 | 32 | 1370 | 1372 W | 1572 VW | U _s eni ₃ |
| 32 | 1319 | 1350 w | 1346 w | 32 | 1326 | 1351 m | _ | 32 | 1300 | 1341 sh | 1352 sh | $\delta CH + \nu \phi + \delta NH_{out}$ |
| 3/ | 1315 | 1550 W | 1340 W | 34 | 1325 | 1551 11 | | 34 | 1207 | 1541 511 | 1552 511 | θCH · νψ · θAHI2HB |
| 35 | 1284 | 1314 m | 1312 vs | 35 | 1211 | 1348 m | 1348 m | 35 | 1286 | 1332 m | 1335 m | $v_{\rm NO_2} + v\phi$ |
| 36 | 1204 | 1302 ch | 1312 V3 | 36 | 1211 | 1372 vc | 1372 ve | 36 | 1285 | 1201 c | 1292 10 | vsito2 · vψ |
| 50 | 1204 | 1302 311 | | 37 | 1295 | 1323 VS 1311 ch | 1223 vs 1293 ch | 50 | 1205 | 1231 5 | 1232 13 | |
| | | | | 38 | 1295 | 1291 sh | 1233 311 | | | | | |
| 37 | 1225 | 1267 m | 1267 s | - | 1234 | - | _ | 37 | 1255 | 1274 ve | 1273 c | $v\phi + \delta CH + v NO_{ex}$ |
| 20 | 1255 | 1207 111 | 1207 5 | - | - | - | - | 20 | 1255 | 1274 VS | 12/3 5 | $v\psi + 0CII + v_{S}IVO_{2}$ |
| 30 | 1255 | 1230 c | 1734 10 | 20 | 1246 | 1280 cb | 1278 | 20 | 1233 | 1200 SH | | $v\phi + v NO_{-}$ |
| 40 59 | 1217 | 1233 S | 1234 VS | 40 | 1240 | 1200 511 | 12/0 W | 40 | 1244 | 1237 511 | | $v\psi + v_{s} w O_2$ |
| 40 | 1213 | 1150 511 | 1122 211 | 40 | 1244 | | | 40 | 1241 | | | |

| 41 | 1121 | 1150 w | 1153 w | 41 | 1203 | 1236 w | 1233 m | 41 | 1152 | 1188 w | 1189 m | $v\phi + \delta CH$ |
|----------|------|---------|----------|----|------|----------|----------|----|------|----------|----------|---|
| 42 | 1119 | | | 42 | 1202 | | | 42 | 1151 | | | |
| 43 | 1081 | 1120 w | 1121 w | 43 | 1112 | 1132 vw | 1139 w | 43 | 1081 | 1156 sh | 1158 vw | $\delta \phi + v \phi - NO_2 + \rho NH_{2HBI} + v(\phi - NH_2)_{HB}$ |
| 44 | 1079 | 1100 sh | 1103 sh | 44 | 1111 | | 1118 vw | 44 | 1080 | 1136 w | | , , 2, 200, (, 2000 |
| _ | _ | _ | _ | 45 | 1084 | 1109 w | 1093 vw | 45 | 1061 | 1109 m | 1110 m | $\rho NH_{august m} + v\phi$ |
| | | | | 46 | 1078 | 1105 W | 1083 104 | 46 | 1056 | 1002 ch | 1084 ch | $p_1 \dots p_{HBII,III} + \psi \psi$ |
| 45 | 1042 | 1069 | 1061 m | 40 | 1078 | | 1005 VW | 40 | 1050 | 1052 311 | 1004 311 | St L oCH |
| 45 | 1042 | 1008 W | 1001 111 | - | - | - | - | - | - | - | - | $\partial \phi + \rho C \Pi_3$ |
| 46 | 1041 | 1011 | 1001 | 47 | 1010 | 10.10 | 10.11 | 47 | 1007 | 1071 | 1011 | |
| 4/ | 1010 | 1044 w | 1031 W | 47 | 1016 | 1042 vw | 1041 w | 47 | 1027 | 1071 w | 1041 vw | $\rho CH_3 + v \phi$ |
| 48 | 1010 | 1009 w | 1027 sh | 48 | 1014 | 1030 vw | 1026 sh | 48 | 1026 | 1045 sh | 1031vw | |
| 49 | 993 | 997 sh | | 49 | 1010 | | | 49 | 998 | 1029 vw | | |
| 50 | 991 | | | 50 | 1010 | | | 50 | 998 | | | |
| 53 | 947 | 982 vw | 981 vw | 53 | 950 | 954 w | 951 w | 51 | 956 | 1013 vw | 1013 m | $\gamma CH + \gamma \phi$ |
| 54 | 947 | | | 54 | 949 | | | 52 | 956 | 998 sh | 975 vw | |
| | | | | | | | | | | 974 sh | | |
| 51 | 950 | 977 vw | 978 vw | 51 | 983 | 1002 vw | 1008 w | _ | _ | _ | - | $v\phi + \rho CH_2$ |
| 52 | 949 | 077 111 | 0/0/11 | 52 | 980 | 1002 111 | 1000 11 | | | | | , |
| 52 | 545 | | | 52 | 500 | | | 52 | 022 | 055 m | 052 m | ne |
| - | - | - | - | - | - | - | - | 55 | 922 | 900 sh | 9JZ III | $V\phi$ |
| | | | | | 070 | 004 | 005 | 54 | 921 | 889 511 | | |
| - | - | - | - | 55 | 870 | 894 w | 895 W | - | - | - | - | ∂NO_2 |
| | | | | 56 | 870 | | | | | | | |
| 55 | 839 | 866 m | 866 w | 57 | 814 | 835 m | 836 w | 57 | 813 | 849 sh | 841 m | $\delta NO_2 + \delta \phi$ |
| 56 | 838 | | | 58 | 814 | | | 58 | 813 | 841 m | | |
| 57 | 784 | 821 w | 819 vw | - | - | - | - | 55 | 840 | | | $\gamma CH + \gamma \phi$ |
| 58 | 783 | | | | | | | 56 | 840 | | | |
| 59 | 771 | 786 m | 791 m | 59 | 778 | 785 w | 782 m | _ | _ | _ | - | $v\phi + \omega NO_2$ |
| 60 | 771 | | | 60 | 778 | | | | | | | 77 |
| 61 | 769 | | | 61 | 764 | 770 | | 62 | 742 | 750 104 | | S = A + y A C H + S N O |
| C2 | 708 | | | 61 | 704 | 779 W | - | 02 | 743 | 750 VW | | $\delta \phi + v \phi - C \Pi_3 + \delta N O_{2I,II}$ |
| 62 | 767 | 750 | | 62 | 763 | 750 | 754 | 63 | 742 | 765 | 764 | |
| 63 | 751 | 756 W | - | 63 | /55 | 756 W | 754 W | 61 | 749 | 765 W | 764 m | $t\theta_{HB} + \omega NO_2$ |
| 64 | 717 | 721 w | 731 vw | 64 | 751 | 741 vw | | 59 | 763 | 770 w | | $\omega NO_2 + v \phi_{I,III} + \tau \theta_{HB}$ |
| 65 | 711 | | | 65 | 743 | | | 60 | 760 | | | |
| - | - | - | - | 66 | 710 | - | 721 vw | 64 | 725 | - | 735 vw | $\omega NO_2 + \gamma \phi + \gamma CH_{III}$ |
| - | - | - | - | 67 | 704 | - | | 65 | 709 | 720 w | | $\omega NO_2 + \gamma \phi$ |
| 66 | 699 | 707 sh | | 68 | 697 | 710 w | - | 66 | 693 | 681 sh | | $	au \theta_{HB}$ |
| 67 | 596 | 667 w | 606 m | 69 | 664 | 679 w | 679 w | 67 | 636 | 652 w | 645 vw | $\delta \phi + \delta NO_2 + breathing \theta_{HB}$ |
| 68 | 590 | 610 vw | | 70 | 661 | 668 vw | | 68 | 628 | | | , <u> </u> |
| _ | _ | - | _ | 71 | 626 | 638 w | 630 w | - | - | _ | _ | $\alpha N\Omega_{\alpha} + \delta \phi - NH_{\alpha \nu \mu}$ |
| | | | | 72 | 617 | 050 11 | 050 11 | | | | | pho2 + of hin2HB |
| <u> </u> | 570 | 502 | F02 | 72 | 500 | C01 | 500 | 60 | 507 | COE ah | | |
| 69 | 579 | 593 VW | 593 VW | 73 | 588 | 601 VW | 299 W | 69 | 587 | 625 SII | - | $\gamma \phi$ -CH ₃ + $\gamma \phi$ |
| 70 | 5/8 | | | 74 | 587 | | | 70 | 587 | 613 W | | |
| | | | | | | | | | | 600 w | | |
| 71 | 556 | 570 vw | 567 vw | - | - | - | - | 71 | 568 | 583 m | 588 w | $\rho NO_2 + \delta \phi - NH_{2HB} + \delta \phi$ |
| 72 | 550 | | | | | | | 72 | 567 | 568 sh | | |
| 73 | 522 | 544 m | 544 m | 75 | 548 | 559 w | 561 w | 73 | 520 | 532 m | 529 w | $\delta \phi + v \phi - CH_3$ |
| 74 | 522 | | | 76 | 548 | 566 sh | | 74 | 516 | | | |
| 75 | 501 | 526 m | 532 sh | 77 | 520 | 536 sh | - | - | - | - | - | $\omega NH_{2HB} + \gamma (N-HN_{\phi})$ |
| 76 | 488 | | | 78 | 511 | | | | | | | 2115 / (|
| 77 | 466 | 478 w | 481 w | 79 | 484 | 502 w | 505 vw | 75 | 458 | 454 sh | 452 vw | $y\phi + y\phi - CH_2 + y(N -$ |
| 78 | 462 | 170 W | 101 10 | 80 | 101 | 502 11 | 505 111 | 76 | 150 | 15 1 511 | 152 11 | $H_{\rm e}(N_{\rm e}) + aNO_{\rm em} + aNH_{\rm empth}$ |
| 78 | 402 | | | 80 | 479 | 467 | 465 m | 70 | 434 | 449 m | 440 | (1.11) |
| - | - | - | - | 81 | 403 | 407 W | 403 W | 77 | 436 | 440 111 | 440 VW | $\rho HO_2 + \delta \phi - HI_{2HB}$ |
| | | | | 82 | 462 | 120 | 400 | /8 | 426 | | | |
| - | - | - | - | 83 | 418 | 428 W | 423 VW | - | - | - | - | $\partial \phi - NH_{2HB} + \rho NU_2$ |
| | | | | 84 | 411 | | | | | | | |
| 79 | 411 | 419 w | 415 m | - | - | - | - | 79 | 378 | 379 vw | 376 w | $\omega NH_{2HB} + \gamma \phi_{HB}$ |
| 80 | 408 | | | | | | | 80 | 377 | | | |
| - | - | - | - | - | - | - | - | 81 | 356 | 369 vw | - | $\delta \phi + v \phi - NO_2$ |
| | | | | | | | | 82 | 352 | | | · · · |
| 81 | 382 | 396 sh | 395 w | 85 | 400 | 404 vw | 407 w | 83 | 32.8 | 336 vw | 336 vw | $\delta\phi$ -CH ₃ + $\delta\phi$ + $\nu\phi$ -NO ₂₁ |
| | | | | | | | | | | | | , |

(continued on next page) 959

| Table 5 | (continued) |
|---------|-------------|
|---------|-------------|

| I | | | | II | | | | III | | | | | | |
|-----|-------|------------|------------|-----|----------|------------|------------|----------|----------|------------|------------|---|--|--|
| | Calc* | IR spectra | RS spectra | | Calc | IR spectra | RS spectra | | Calc* | IR spectra | RS spectra | Assignment | | |
| 82 | 381 | | | 86 | 399 | | | 84 | 326 | | | | | |
| 83 | 356 | 356 vw | 365 w | 87 | 369 | 361 vw | 362 vw | - | - | - | - | $\delta\phi + v\phi - NO_2 + \delta\phi - CH_{3I}$ | | |
| 84 | 353 | | | 88 | 365 | | | | | | | | | |
| 85 | 293 | 294 w | 294 w | 89 | 328 | 338 vw | 337 w | - | - | - | - | $\delta \phi - NO_2$ | | |
| 86 | 292 | | | 90 | 327 | 328 sh | 303 vw | | | | | | | |
| | | | | 91 | 311 | 292 sh | | | | | | | | |
| | | | | 92 | 305 | | | | | | | | | |
| - | - | - | - | 93 | 265 | 274 sh | 274 w | - | - | - | - | $\delta \phi - NO_2 + \gamma \phi - NH_{2HB}$ | | |
| | | | | 94 | 262 | | | | | | | | | |
| 87 | 245 | - | 264 w | 95 | 232 | - | 240 w | - | - | - | - | $\gamma\phi$ -NO ₂ + $\gamma\phi$ -CH ₃ + $\gamma\phi$ | | |
| 88 | 245 | | | | | | | 05 | 202 | 202 | 207 | | | |
| - | - | - | - | - | - | - | - | 85 | 282 | 280 VW | 287 VW | $\gamma \phi$ -CH ₃ | | |
| | | | | | | | | 86 | 281 | | | | | |
| - | - | - | - | - | - | - | - | 87 | 278 | | | $\gamma \phi$ -NO ₂ + $\gamma \phi$ -CH ₃ | | |
| | | | | | | | | 80 | 277 | | 261 | S + NO | | |
| - | - | - | - | - | - | - | - | 09 00 | 254 | - | 201 VW | $\partial \phi$ -INO ₂ | | |
| _ | _ | _ | _ | 96 | 225 | 226 sh | _ | 01 | 200 | 207 104 | 210 104 | ad + ad - CH | | |
| | | | | 50 | 225 | 220 311 | | 92 | 199 | 207 VW | 215 VW | $\gamma \psi \cdot \gamma \psi$ -eng | | |
| _ | _ | _ | _ | 97 | 206 | _ | 216 vw | - | - | _ | _ | $\delta \phi$ -NO ₂ | | |
| | | | | 98 | 203 | | 210 111 | | | | | 04 1102 | | |
| 89 | 237 | _ | 257 sh | 99 | 197 | 202 w | | _ | _ | _ | _ | τCH ₃ | | |
| 90 | 236 | | | 100 | 197 | | | | | | | | | |
| 91 | 196 | - | 221 w | 101 | 109 | - | 142 sh | - | - | - | - | $\tau NO_2 + \gamma \phi_1$ | | |
| 92 | 192 | | | 102 | 108 | | | | | | | - ,, . | | |
| 93 | 88 | 132 vw | 141 m | 103 | 97 | 133 sh | 126 sh | 94 | 108 | 130 vw | 132 sh | $\gamma \phi$ -NO ₂ + $\gamma \phi$ + $\gamma \phi$ -NH _{2II,IIIHB} | | |
| | | | | 104 | 92 | | | 95 | 102 | | 121 m | | | |
| 94 | 86 | | | | - | - | - | - | - | - | | $\delta \phi_{HB} + \rho NH_{2 HB} + \gamma \phi - NO_{2I}$ | | |
| 95 | 85 | | | | | | | | | | | | | |
| 96 | 74 | 120 vw | 110 m | 105 | 78 | - | 114 m | 93 | 114 | - | | $v NH \cdots N_{HB} + \delta \phi_{HB}$ | | |
| - | - | - | - | 107 | 63 | - | 98 sh | 96 | 80 | - | 99 m | $\gamma \phi$ -NO ₂ | | |
| | | | | | | | | 97 | 78 | | | | | |
| - | - | - | - | 106 | 67 | - | | - | _ | - | - | $\gamma \phi - NO_2 + \omega NH_{2HB}$ | | |
| - | - | - | - | 108 | 56 | 81 sh | 81 W | 99 | 58 | 69 vw | 68 w | $\delta \phi_{\rm HB} + \nu \rm NH \cdots \rm N_{HB}$ | | |
| 97 | 55 | - | 91 m | - | - | | | 98 | 62 | | | Waving ϕ HB | | |
| - | - | - | - | 109 | 52 | | | - | - | | | τNO_2 | | |
| 100 | 20 | 00 | 90 m | 110 | 52 | | | 101 | 52 | | | Waying to LaNO | | |
| 100 | 39 | õõ VW | 82 111 | 111 | 4ð 21 | | | 101 | 55 56 | | | Wagging $\phi = \phi + \pi NO$ | | |
| 90 | 45 | 00 511 | - | 112 | 21 | - | - | 100 | 00 | | | wagging φ , $\varphi \neq 0$ NO ₂ | | |
| 101 | 16 | _ | _ | 112 | 17 | _ | _ | 102 | 28 | _ | _ | Flanning ϕ | | |
| 102 | 11 | - | _ | 114 | 7 | _ | _ | 102 | 20 | _ | - | Twisting ϕ , ψ | | |
| 102 | 11 | - | - | 114 | 1 | - | - | - | - | - | - | ψ, ψ | | |

In-plane vibrations: v, stretching; δ , bending; ρ , rocking. Out-of-plane vibrations: γ , torsional; ω , wagging; τ , twisting. ϕ , pyridine ring; θ , eight-membered ring. * Scaling factor: f_{sc} = 0.963 (3600–2500 cm⁻¹), f_{sc} = 0.978 (2499–0 cm⁻¹) for **I–III** compounds.

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molecules in it, as well as the configuration and strength of the hydrogen bonds inside the unit cell. The studied compounds differ in the number and type of HBs appearing in their structure. The pyridine units of the compound I are joined via two types of HBs in which two hydrogen atoms of NH₂ group are involved: intermolecular NH…N_{ϕ} (ϕ = pyridine ring, N_{ϕ} - pyridine nitrogen) and intramolecular N-H-O_N (O_N - oxygen atom of the nitro group), see Supplementary Fig. S5. The compound III contains two HBs of the same type but both have inter-molecular nature joining two adjacent pyridine units. Finally, according to the X-ray data three types of HBs exist in III: two inter-molecular of the N–H...N_{ϕ} and N-H…O'_N types and the third of the N-H…O''_N type. The common feature of all these structures is the eight membered system built from two N2-H22...N1 hydrogen bonds that join two pyridine rings. This system strongly affects the structure and vibrational properties of the studied compounds. Such a ring contains weak bonds. It seems problematic to handle it as a relatively independent part (the whole unit) of an atomic system, like e.g., the benzene ring. Of course, it may be possible to define likely internal coordinates of the eight-atomic ring but this is not well established. The hydrogen bonds cannot compete with the covalent bonds. Parts of this ring belong to better-organized atomic systems, i.e., to molecules. The experimental and calculated geometrical parameters of all appearing HBs are collected in Tables 2-4. The X-ray data indicate that the length of the N–H…N_{ϕ} HB is 3.016(2) Å for I, 3.057(2) Å for II and 2.993(2) Å for III. On the other hand, the respective IR bands are observed at the wavenumbers 3458 and 3264 cm⁻¹ for I, 3426 and 3292 cm⁻¹ for II and 3407 and 3322 cm⁻¹ for III. It is clearly seen that good correlation exists between the X-ray parameters and the vibrational data. It means that other approach should be applied in the assignment of IR bands in which the eight-membered θ ring formed from the eight atoms N2-H22...N1-C2-N2-H22...N1-C2 should be considered as a whole unit. 18 normal modes characterize the vibrations of such system. Among them there are nine stretching modes: two v(N-H…N_{ϕ}), two v(C–N), two v(ϕ) describing the vibration of the C=N bonds of the pyridine ring, two $v(H \cdots N_{\phi})$ and one $v(\theta)$ breathing mode of the whole ring. Nine bending modes can be characterized as two in-plane $\delta(NH...N_{\phi})$, two out-of-plane $\gamma(NH...N_{\phi})$ and five torsions of the whole HB bridge ring $\tau(\theta)$. Because this ring has planar arrangement, the C_i symmetry can be adopted in the description of its vibrational normal modes described by the $9A_g + 9A_{ij}$ representation, where A_{g} modes are Raman active and A_{u} modes are IR active. Basing on the above consideration Table 6 lists the wavenumbers and their assignment to respective vibrations of the eight-membered θ ring. These data should be related to the structure of the ring for which the $N_{\phi(i)}$... $N_{\phi(ii)}$ distance is the most characteristic parameter. It is the closest distance between the adjacent pyridine rings. From the X-ray studies it follows that these distances are 3.609(3) Å for the compound I, 3.662(3) Å for the compound II and 3.765(3)Å for the compound III. This

Table 6

IR experimental wavenumbers [cm⁻¹] assigned to the vibrations of eight-membered ring built from to HBs.

| | I | II | III |
|---------------------------------------|---------------------|---------------------|------------------|
| $v(N-HN_{\phi})$ | 3458, 3264 | 3426, 3292 | 3407, 3322 |
| v(NH…N) | 120, – | -, 81 | -, 69 |
| $\rho(NH_2)_{HB} + v(\phi-NH_2)_{HB}$ | 1120, 1100 | 1109, – | 1109, 1092 |
| ν(φ) | 1473, 1456 | 1480, 1414 | 1475, 1431 |
| Breathing θ_{HB} | 667 | 679 | 652 |
| $\delta(N-HN_{\phi})$ | -, 1618 | 1633, - | 1668, 1654 |
| $\gamma(N-H\cdots N_{\phi})$ | 526, 478 | 536, 502 | 454, 379 |
| $\tau(\theta)_{HB}$ | 756, -, 721, 707, - | 756, 741, -, 710, - | 770, 765, –, 681 |

sequence fits well to the wavenumbers for the IR bands observed in the range 3460 – 3200 cm⁻¹. The bands at 3458, 3426, 3407 cm⁻¹ exhibit low-frequency shift, whereas the sequence 3264, 3292, 3322 cm⁻¹ shows high-frequency shift, respectively for the compounds **I–III**. It means that the splitting between respective bands Δv equals to 194, 134 and 85 cm⁻¹. Such an excellent fitting between the spectroscopic and X-ray data proves that two HBs appeared in the θ ring could not be considered separately in the discussion of the vibrational spectra. The agreement between the structural (N_{$\phi(ii)}...N_{<math>\phi(ii)$} distance) and spectroscopic (doublet of bands in the range 3460–3200 cm⁻¹) results could be obtained when the bridge θ ring is discussed as a whole unit. Table 6 presents the wavenumbers of other normal modes that in our opinion should be assigned to the vibrations of this intermolecular interaction.</sub>

The stretching vibration of the $\text{H}...\text{N}_{\phi}$ HB bonds, i.e., the $v(\text{H}...\text{N}_{\phi})$ mode, according to the results of the quantum chemical calculations should be observed in the range 114–74 cm⁻¹ (see Table 5). These values are in good agreement with the wavenumbers of IR bands observed in the range 200–68 cm⁻¹. The shapes of these broad contours are typical for those observed for other HB systems [57–61].

Apart from the bands in the region above 3200 cm^{-1} , the sequence of IR bands at 3118, 3162 and 3120 cm⁻¹ is observed. respectively. They are broad and multi-componential what probably arises from the participation of a few vibrations corresponding to different HBs appearing in the structure of the studied compounds. X-ray studies suggest the existence of the interactions between the CH₃ and NO₂ groups (intermolecular) as well as NH₂ and NO₂ groups (intramolecular) for the compound I. For the derivative **II** short contacts appear for the intermolecular interactions NH₂-...NO2 (3.082(2), 3.314(3) Å) and CH...NO2 (3.203(2) Å) as well as intramolecular interactions NH2···NO2 (2.692(2) Å), CH···NO2 (2.687(2) Å) and CH₃...NO₂ (2.783(2), 2.799(2) Å). Finally, in the compound III the short intermolecular contacts NH₂...NO₂ (3.062(2), 3.140(2) Å) and intramolecular CH...NO₂ (2.685(2) Å)are proposed (see Tables 2–4). These interactions seem to be weaker than those realized in the eight-membered bridge. Therefore the wavenumbers of respective bands should be red shifted. These interactions are probably reflected in the broad contour at about 3100 cm⁻¹. This problem should be answered when the IR and Raman spectra recorded at low temperature will be completed.

Conclusions

- (1) X-ray, IR and Raman studies as well as quantum chemical calculations performed for the studied compounds confirm the existence of intermolecular N-H…N hydrogen bonds in structures in which the NH₂ groups and pyridine nitrogen atoms are engaged. As a result, dimeric arrangement from adjacent pyridine units is formed consisting of eight-membered ring as a bridge system. The vibrations of this system are responsible for a characteristic sequence of bands observed in the defined ranges of the IR spectrum.
- (2) X-ray studies suggest the existence of the interactions between the CH_3 and NO_2 groups (intermolecular) as well as NH_2 and NO_2 groups (intramolecular) for the studied compounds. These interactions seem to be weaker than those realized in the eight membered bridge and therefore the broad contour at about 3100 cm⁻¹ probably corresponds to the vibrations of these HBs.
- (3) The quantum chemical calculations predict well the formation of the eight-membered bridge system built from hydrogen bonds but also exhibit good agreement between the theoretical and experimental wavenumbers of their normal

modes. It should be pointed out that the quantum chemical calculations refer to the molecules and their dimers in vacuum. However, the X-ray results refer to molecules in chemical environment. Therefore these results have to differ theoretically since the states of the molecules are different. Besides, the quantum chemical methods are approximations; they yield only approximate results. The scaling tries to equalize these deviations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.07.121.

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