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Vibrational spectra, crystal structure, DFT quantum chemical calculations and conformation of the hydrazo – bond in 6-methyl-3-nitro-2-(2-phenylhydrazinyl)pyridine

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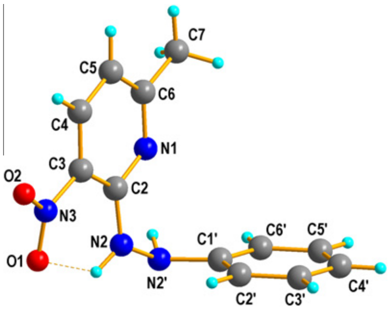
HIGHLIGHTS

- ▶ The crystal structure of 6-methyl-3-nitro-2-(2-phenylhydrazinyl)pyridine was studied.
- ▶ The IR and Raman wavenumbers have been calculated from the optimized geometry of monomer and dimer.
- ▶ X-ray, IR, Raman and DFT methods confirm the existence of an intramolecular N—H···O bond.

GRAPHICAL ABSTRACT



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ABSTRACT

The crystal and molecular structures of 6-methyl-3-nitro-2-(2-phenylhydrazinyl)pyridine (6-methyl-3-nitro-2-phenylhydrazopyridine) have been determined by X-ray diffraction and quantum chemical DFT analysis. The crystal is monoclinic, space group *C2/c*, with $Z = 8$ formula units in the elementary unit cell of dimensions $a = 16.791(4)$, $b = 6.635(2)$, $c = 21.704(7)$ Å, $\beta = 100.54(3)^\circ$. The molecule consists of two nearly planar pyridine subunits. A conformation of the linking hydrazo-bridge C—NH—NH—C is bend and the dihedral angle between the planes of the phenyl and pyridine rings is 88.2(5)°. The hydrogen bonding of the type N—H···N and possibly also C—H···O favors a dimer formation in the crystal structure. The dimers are further linked by a N—H···O hydrogen bond, so forming a layer parallel to the ***ab*** plane. The molecular structure of the studied compound has been determined using the DFT B3LYP/6-311G(2d,2p) approach and compared to that derived from X-ray studies. The IR and Raman wavenumbers have been calculated for the optimized geometry of a possible monomer structural model but the possibility of the dimer formation through the N—H···N hydrogen bond has also been considered. The structural and vibrational properties of the intra-molecular N—H···O interaction are described.

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Introduction

The pyridine derivatives are widely used in the syntheses of various compounds i.e. hydrazone Schift bases [1] and complexes [2,3].

The basic reaction of hydrazo compounds synthesis is reduction of nitro compounds in an alkaline medium. Their aromatic derivatives are also produced as intermediate products in the syntheses of benzidine and its derivatives (tolidine, dianisidine, etc.). Aromatic hydrazo derivatives isomerize to diaminodiphenyls, important ligands in the complex compounds synthesis. Due to their specific electron properties hydrazo compounds are easily oxidized to azo derivatives in the reaction R—NH—NH—R′ → RN=NR′ [4].

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Hydrazo compounds also can be used to syntheses of polymers (polyimides). It can be proved successful in applications where severe conditions, like elevated temperatures and solvent resistance, will be required [5]. Surprisingly, this class of compounds has not often been examined using the X-ray method. An analysis of Cambridge Structural Database (CSD version 5.33 updates (May 2012); ConQuest Version 1.14) identified only several structures that contain the 1,2-diphenylhydrazine; two metal complexes [6,7], four hydrazino phosphines [8], two hydrazobenzene polymorphs [9–11]. Although, the CSD search on pyridines with ArNH—NHAr substitutes in the 2-position of the ring showed one structure, namely 2-(2-phenylhydrazinyl)pyridine [12].

Azo dyes are important class of pyridine derivatives that are extensively employed as color materials and used for their unusual electronic properties as well as their wide color range [13–15]. These dyes exhibit azo-hydrazo tautomerism that has been widely studied using IR and Raman [16], resonance Raman [17] and electron absorption and emission spectroscopies [4].

The present paper is a continuation of our earlier work on azo and hydrazo derivatives of pyridine [18–21]. The new structural study of 6-methyl-3-nitro-2-(2-phenylhydrazinyl)pyridine (MNPHP) was undertaken to confirm the chemical formula and to determine the preferred configuration of the title molecule. It consists of the phenyl ring and 6-methyl-3-nitropyridine interconnected through the dihydrazo bonding. This information is correlated with the results of studies of the chemical and spectroscopic properties.

Experimental

Synthesis

6-Methyl-3-nitro-2-(2-phenylhydrazinyl)pyridine (MNPHP) was synthesized from 2-fluoro-3-nitro-6-methylpyridine. 2.5 g (0.01 mol) of 2-fluoro-3-nitro-6-methylpyridine was dissolved in 10 cm^3 of methanol and 0.02 mol of phenylhydrazine was added. The mixture was heated at 60 °C for 1–2 min and then stored at ambient conditions for 24 h. The solvent was distilled under low pressure and the residue was extracted with the warm chloroform (50 °C). Non-soluble phenylhydrazine fluorohydrat was filtered off and washed with warm chloroform. The chloroformic extract was vaporized to dryness and the residue was dissolved in a small amount of pharmaceutical petrol to remove the remnants of the phenylhydrazine. Non-soluble product in a form of yellow crystals was filtered off, dried and re-crystallized twice from ethanol.

The yield of MNPHP ($C_{12}H_{12}N_4O_2$) was 65.2% and its melting point was 128 °C. The chemical analysis: theoretical content: C 59.00%, N 22.94%, H 4.95%; found: C 59.30%, N 22.80% and H 4.79%.

Raman and IR measurements

IR spectra in the 40–4000 cm^{-1} range were recorded at room temperature in Nujol suspension, Fluorolube and KBr pellet with a FTIR Biorad 575C spectrometer. They were identical in the ranges where the bands of thinning agent are absent, so the IR spectra measured in KBr are shown in Fig. 3. The resolution was 2.0 cm^{-1}.

Raman spectra in the 80–4000 cm^{-1} range were measured in back scattering geometry with a FT Bruker 110/S spectrometer. The resolution was 2.0 cm^{-1}. The YAG:Nd^{3+} (excitation wavelength 1064 nm) laser was used as an excitation source.

X-ray diffraction

The crystallographic measurement for MNPHP ($C_{12}H_{12}N_4O_2$; yellow; 0.3 × 0.2 × 0.08 mm) was performed on a Xcalibur PX automated four-circle diffractometer with Ruby CCD camera. The intensity data were collected at 100(2) K using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Data collection, cell refinement, and data reduction and analysis were carried out with CrysAlisCCD and CrysAlisRED, respectively [22]. The structure was solved by direct methods using SHELXS-97 [23], and refined on F^2 by a full-matrix least-squares technique using SHELXL-97 [23] with anisotropic thermal parameters for non-H atoms. All H atoms were found in difference Fourier maps. In the final refinement cycles, the C-bonded H atoms were treated as riding atoms in geometrically optimized positions, with C—H = 0.95–1.00 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH or $1.5U_{eq}(C)$ for CH_3. The H atoms bonded to N atoms were freely refined with $U_{iso}(H) = 1.2U_{eq}(N)$. The figures were made using an XP program [24]. Crystal data for MNPHP: $C_{12}H_{12}N_4O_2$, $M = 244.26$, monoclinic, space group $C2/c$, $a = 16.791$ (4), $b = 6.635$ (2), $c = 21.704$ (7) Å, $\beta = 100.54$ (3)°, $V = 2377.2$ (12) $Å^3$, $Z = 8$, $T = 100(2)$ K, 5302 measured reflections, 2713 independent reflections, 2211 reflections with $I > 2\sigma(I)$, $S = 1.04$, $\theta_{min} = 3.31°$, $\theta_{max} = 28.78°$, $R[F^2 > 2\sigma(F^2)] = 0.041$, $wR(F^2) = 0.098$, $\Delta\rho_{max} = 0.28$ e $Å^{-3}$, $\Delta\rho_{min} = -0.23$ e $Å^{-3}$. CCDC-903660 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Quantum chemical calculations

The geometry optimisation of the molecular structure of the studied compound was performed for both the monomeric and dimeric units with the use of Gaussian 03 programme package [25]. All calculations were performed using density functional three-parameters hybrid (B3LYP) methods [26–28] with the 6-311G(d,p) [29,30] 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 was calculated for MNPHP using the BALGA [31] program. The atomic coordinates from the X-ray studies were used as the input data in the optimization procedure and the data from optimization were introduced to the BALGA program. The IR and Raman wavenumbers were calculated for a single molecule as well as for the dimer in which two molecules are joined through the N—H···N hydrogen bond.

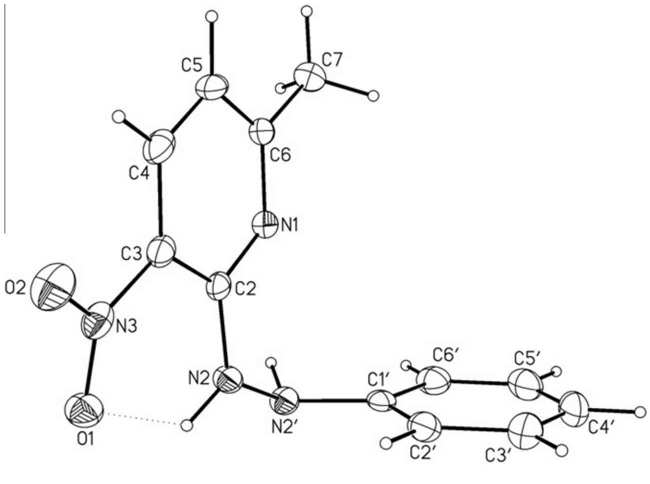

Fig. 1. Molecular structure of MNPHP, showing the atom numbering scheme. Displacements ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dotted line indicates the intramolecular N—H···O hydrogen bond.

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