

# Substituent effects on vibrational and electronic excitation spectra of pyridone tautomers and ions: The case of the cyano group



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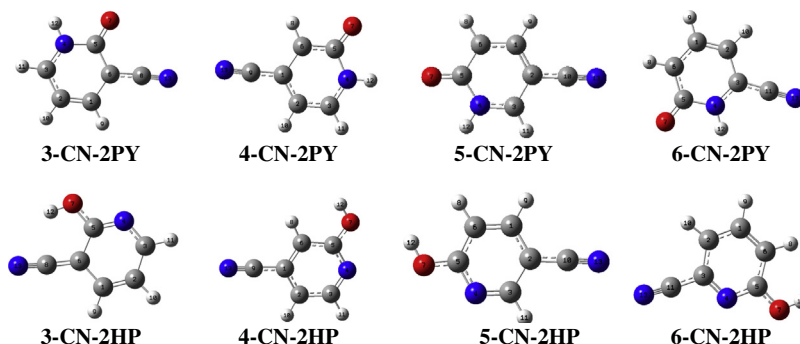
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## HIGHLIGHTS

- We computed the spectroscopic parameters for cyano substituted 2-pyridones.
- We examined the effect of tautomerism equilibrium on those systems.
- We showed that the cyano group strongly disturbs the molecular orbitals.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this theoretical work, we computed the equilibrium geometries and a set of rotational and vibrational spectroscopic parameters for cyano substituted 2-pyridones neutral or cationic and their tautomers (cyano 2-hydroxypyridines). We examined also the effect of tautomerism equilibrium on those systems. In our analysis, we mostly focused on the perturbations induced by the CN group on the electronic structure and on the spectroscopy of 2-pyridone/2-hydroxypyridine block. Moreover, we investigated the pattern of their low lying electronic states at both the PBE0/aug-cc-pVDZ Density Functional Theory (DFT) and the CASSCF/aug-cc-pVTZ levels of theory. Vertical excitation spectra and both adiabatic and vertical ionization energies were performed.

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## Introduction

2-Pyridone (2PY), its dimer and their charged species are model systems to study DNA bases, isolated or paired, as well as the hydrogen bonding in their complexes. Several experimental and theoretical studies on the neutral molecule have been reported [1–4]. Pyridone derivatives are also of great importance because

of their biological, pharmacological and industrial applications. This theoretical work treats the structure and the spectroscopy of cyano substituted 2-pyridones. It follows the continuous and increasing interest on studying substituted DNA basis and derivatives and analogues.

From a pharmacological point of view, pyridone derivatives are used as medicaments. Indeed, 4-pyridone derivatives were identified as potent specific inhibitors of FabI, the enoyl-acyl carrier protein reductase in *Escherichia coli* and *Staphylococcus aureus* [5]. Moreover, N-alkyl-3-cyano-2-pyridones and 3-cyano-2-alkoxy-pyridines are known to present an efficient anti-viral activity [6]

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as well as a confirmed phototoxicity and photogenotoxicity for nine pyridone derivatives as discussed by Gocke et al. [7].

In industry, 3-cyano-2-pyridones derivatives are used in the manufacturing of several practically useful materials such as dyes and pigments, stabilizers for varnishes and polymers, additives for fuels and lubricants, and acid–base indicators [8]. In the literature, numerous works describe the methods for the preparation of 2-pyridone derivatives [6,9,10]. For instance, Refs. [11–20] present a wide variety of procedures for the synthesis of 3-cyano-2-pyridones and using several precursors.

In this work, molecular structure of cyano substituted 2-pyridones were computed (denoted hereafter as xCN-2PY; x = 3–6), where x corresponds to the cyano group position (Fig. 1). 2-Hydroxypyridines derivatives (denoted xCN-2HP, Fig. 1), which are tautomer's forms of the previous molecules, were also studied as well as their cations. The equilibrium geometry optimizations were calculated at the PBE0/aug-cc-pVDZ Density Functional Theory (DFT) level. We deduced hence a set of spectroscopic properties for these compounds including their rotational constants at equilibrium and their vibrational frequencies. Furthermore, we used multi-configuration Self Consistent Field and Time Dependent Density Functional Theory (TD-DFT) approaches to compute the pattern of their lowest electronic excited states. Through the comparison of the results on xCN-2PY/xCN-2HP to 2-pyridone/2-hydroxypyridine, we scrutinize the possible induced cyano group perturbation on the electronic structure and on the spectroscopy of the 2-pyridone/2-hydroxypyridine blocks. Most of our data represent predictions. They should be helpful for the interpretation of the IR,  $\mu$ w and ionization spectra of these important class of 2-pyridone derivatives whenever measured.

### Computational details

All electronic calculations were done using the MOLPRO [21] and the GAUSSIAN packages [22] in the  $C_1$  point group. We determined the equilibrium geometries, the rotational constants and the harmonic frequencies of the molecular compounds of interest using the PBE0 exchange–correlation functional [23] with the aug-cc-pVDZ basis set. These computations were done using the default options as implemented in GAUSSIAN. Here, the hydrogen, carbon, nitrogen and oxygen atoms were described using the aug-cc-pVXZ (X = D, T) basis set of Dunning [24,25] since it suited for PBE0 functional as established in Refs. [1,26]. To better describe the eventual diffuse nature of these electronic states, the used basis set was augmented by one s and one p gaussian type orbital (GTO) for C, N and O atoms (exponents: C: s 0.0155 and p 0.015; N: s

0.020 and p 0.06; O: s 0.0113 and p 0.011) and by one diffuse s orbital for H (exponent: s 0.077).

For electronic excited state computations, we used both an *ab initio* and a Time-Dependent Density Functional (TD-DFT) approaches. For each molecular species, we investigated their five lowest electronic states with either singlet/triplet or doublet/quartet spin-multiplicities whenever appropriate. For each molecular species, the excitation energies were computed at the equilibrium geometry of its electronic ground state optimized at the PBE0/aug-cc-pVDZ (cf. Figs. 2 and 3, and Supplementary material). TD-DFT calculations [27] were performed, as found in the GAUSSIAN package, using an ultra-fine grid for numerical integrals evaluation (99 radial shells and 590 angular points per shell) with a minimum of 40 excited states included in the Davidson diagonalization procedure of the TD-DFT excited state matrix. As discussed in Ref. [28], PBE0/aug-cc-pVDZ level is accurate enough to deduce the excitation energies of lowest excited states of pyridone derivatives.

In *ab initio* calculations, the electronic structure computations start with Restricted Hartree Fock (RHF) calculations of the neutral cyano 2-pyridone derivatives. Then, we used the full valence complete active space self-consistent field (CASSCF) approach [29,30] as implemented in MOLPRO [21]. In CASSCF, all electronic states having the same spin multiplicity were averaged together with equal weights using the MOLPRO state averaging procedure. An accurate description of these electronic states would require *a priori* the largest possible active space, which is computationally expensive. As an acceptable compromise between computation time and quality to reduce the cost of calculations without weakening the quality of the results, it is necessary to manage correctly a large number of active electrons with a reduced number of active molecular orbitals (MOs) or a reduced number of active electrons with a large number of active MOs. To choose this active space, a systematic study of the excitation energies for the lowest doublet electronic states of 5CN-2PY<sup>+</sup> cation were performed as benchmark system. The closed MOs are kept doubly occupied and frozen during the CASSCF calculations, and the active MOs are the next ones up to the highest included MO. The results are listed in Table 1. For example, the (26,37) active space of 5CN-2PY<sup>+</sup> is where we froze the lowest 26 MOs and considered the (27a) to (37a) MOs as active i.e. an active space where the molecular orbitals (MOs) HOMO–5 up to LUMO+6 are active. This ansatz corresponds to 11 active MOs and 9 active valence electrons. The resulting active spaces are build using all Configuration State Functions (CSFs) obtained by distributing all active valence electrons in these MOs. Table 1 gives also the number of CSFs, CPU time and disk used for a single point computation. As can be seen in Table 1, the (26,37) active space leads to a stabilized (converged) energies of the excited

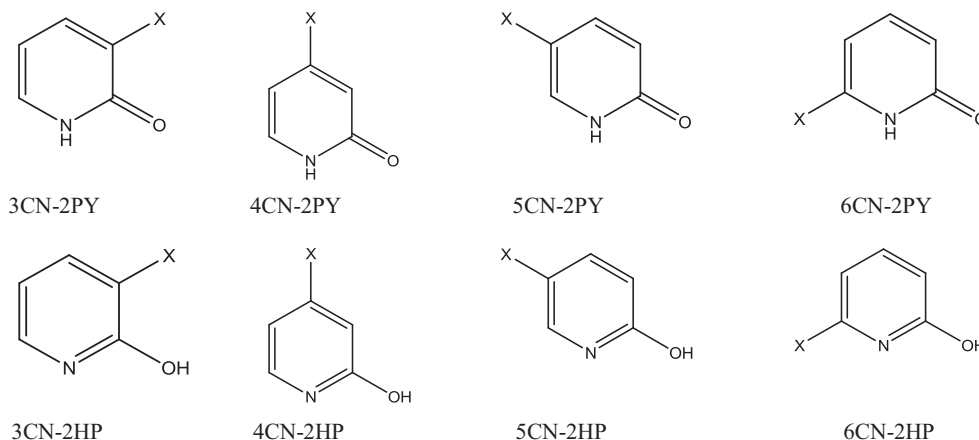


Fig. 1. Cyano 2-pyridone derivatives of interest on the present study and tautomers and their denomination. X = CN.

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