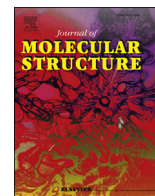




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Analysis of the structure and the FT-IR and Raman spectra of 2-(4-nitrophenyl)-4H-3,1-benzoxazin-4-one. Comparisons with the chlorinated and methylated derivatives

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ABSTRACT

In this work, the structural, topological and vibrational properties of the monomer and three dimers of the 2-(4-nitrophenyl)-4H-3,1-benzoxazin-4-one (NPB) derivative were studied combining the experimental FTIR and FT-Raman spectra in the solid phase with DFT calculations. Here, Natural Bond Orbital (NBO), Atoms in Molecules (AIM) and HOMO and LUMO calculations were performed by using the hybrid B3LYP/6-31G* and B3LYP/6-311++G** methods in order to compute those properties and to predict their reactivities. The comparisons with the properties reported for the chlorinated (Cl-PB) and methylated (CH₃-PB) derivatives at the same levels of theory can be clearly justified by the activating (CH₃) and deactivating (NO₂ and Cl) characteristics of the different groups linked to oxazin rings. The NBO and AIM studies evidence the following stability orders: Cl-PB > NO₂-PB > CH₃-PB in very good concordance with the $f(\nu_{C23-X26})$ force constants values. The frontier orbitals analyses reveal that the Cl-PB and NO₂-PB derivatives have good stabilities and high chemical hardness while CH₃-PB has a higher chemical reactivity. On the other hand, the complete vibrational assignments for monomer and dimers species of NPB were presented. The presence of the IR bands at 1574 and 1037 cm⁻¹ and, of the Raman bands at 1571 and 1038 cm⁻¹ support clearly the presence of the different dimeric species proposed for NPB.

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1. Introduction

As part of our investigations on heterocyclic derivatives containing different rings such as, isothiazoles, benzothiazole, oxadiazole, quinolin [1–5], in the present work, we have reported the structural and vibrational studies of the 2-(4-nitrophenyl)-4H-3,1-benzoxazin-4-one derivative by using their experimental infrared and Raman spectra in the solid phase and DFT calculations. Some 4H-3,1-benzoxazin-4-ones derivatives present a wide range of potential biological activities such as, antitumor, antimicrobial, antitubercular, antimalaria, anticonvulsant, anthelmintic, anti-inflammatory and analgesic among others [6–8]. Industrially, these derivatives are used in the preparation of soluble and processable polybenzoxazine precursors capable of forming high performance networks, as reported by Altinkok et al. [9] while, in

chemical synthesis these derivatives are also used to obtain novel quinazolinone derivatives of pharmacological interest [10,11]. Structurally, the 4H-3,1-benzoxazin-4-one derivatives have a benzene ring fused to an oxazin ring and with the incorporation of different groups in some of these rings or, in both, their chemical and pharmacological properties are modified. The 2-(4-nitrophenyl)-4H-3,1-benzoxazin-4-one (NPB) derivative was synthesized and characterized by Rai [12] by using the NMR and infrared spectra but, so far, its experimental structure was not reported and neither their Raman spectrum and only few IR bands were assigned. In this context, the aims of this work are: (i) to study the theoretical structures of NPB in gas phase by using the hybrid B3LYP method and the 6-31G* and 6-311++G** basis sets, (ii) to evaluate the atomic charges, molecular electrostatic potentials, bond orders, stabilization energies and the topological properties using both theory levels, (iii) to perform the vibrational analyses by using the IR and Raman spectra and compute the corresponding force fields in order to assign all the observed bands in those spectra, (iv) to predict the reactivities and behaviors by using the

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frontier orbitals and some reported descriptors at the same level of calculations and, finally, (v) to analyze the changes in all the properties when activating (CH₃) and deactivating groups (NO₂ and Cl) are incorporated to the benzene ring linked to the 4H-3,1-benzoxazin-4-one ring. In this way, the properties of NPB are compared with those reported for 2-(4-chlorophenyl)-4H-3,1-benzoxazin-4-one (CPB) and 2-(4-methylphenyl)-4H-3,1-benzoxazin-4-one (MPB) [13,14]. In this study, the presence of dimeric species of NPB were also considered because these species justify some bands observed in the vibrational spectra. This way, NPB could be easily identified by means of the vibrational spectroscopy and, in addition, this work constitutes a very important database to understand the connection that exists between the different groups present in the structure of a 4H-3,1-benzoxazin-4-one derivative in relation to their biological properties.

2. Experimental methods

The solid anhydrous commercial sample of 2-(4-nitrophenyl)-4H-3,1-benzoxazin-4-one in pure form was used to prepare KBr pellets. The infrared spectrum was recorded on a Fourier Transform Infrared (FT-IR) Perkin Elmer spectrophotometer in the wavenumbers range from 4000 to 400 cm⁻¹ provided with a Global source and DGTS detector. The Raman spectra of the compound in solid state was recorded between 4000 and 10 cm⁻¹ with a Bruker RF100/S spectrometer equipped with a Nd:YAG laser (excitation line of 1064 nm, 800 mW of laser power) and a Ge detector cooled at liquid nitrogen temperature. The IR and Raman spectra were recorded with 200 scans and a resolution of 1 cm⁻¹.

3. Computational details

Initially, the monomeric NPB structure was modeled with the GaussView program [15], after that, the hybrid B3LYP method [16,17] and the 6-31G* and 6-311++G** basis sets were used to optimize both structures with the Gaussian 09 program [18]. The theoretical monomeric structure can be seen in Fig. 1 together with the atoms numbering and identifications of the three six-membered rings. Hence, A1 is the phenyl ring fused with the

oxazin ring which is identified as A2 while A3 is the phenyl ring containing the NO₂ group. Then, three different dimeric species of NPB were also optimized by using the B3LYP/6-31G* method and, their structures are given in Fig. S1. The calculations of the atomic natural population (NPA) charges, bond orders and stabilization energies were computed by using the NBO program [19,20] while the molecular electrostatic potentials (MEP) were calculated from the Merz-Kollman charges [21]. The topological properties of the three rings of NPB were computed by using the atoms in molecules (AIM) calculations in accordance with the Bader's theory [22,23]. The harmonic frequencies were calculated from the optimized structures by using both approximation levels while the normal internal coordinates for NPB were defined in accordance to those reported for the CPB and MPB derivatives [13,14] and, for this reason, these coordinates for NPB were not presented here. The force fields were calculated by means of the Molvib program by using both basis sets [24] and the scaled quantum mechanical (SQM) methodology [25]. On the other hand, the reactivities and behaviors of NPB with the different basis sets were predicted by using the frontier orbitals, computing the energy band gap and some practical descriptors such as, chemical potential (μ), electronegativity (χ), global hardness (η), global softness (S) and global electrophilicity index (ω). The equations corresponding to these descriptors are widely known in the literature [1,2,26] and, therefore, they were presented in the Supporting material together with the calculated values for NPB with both basis sets and with those reported for the CPB and MPB derivatives [13,14].

4. Results and discussion

4.1. Geometry optimizations

A comparison of the dipole moment values for the two stable structures of NPB with those corresponding to CPB [13] and MPB [14] by using both methods are shown in Table 1. As it was expected, both methods predicted energy values in the following order: CPB > NPB > MPB. On the other hand, the dipole moment values present different values and directions according to the activating and deactivating characteristics of each group

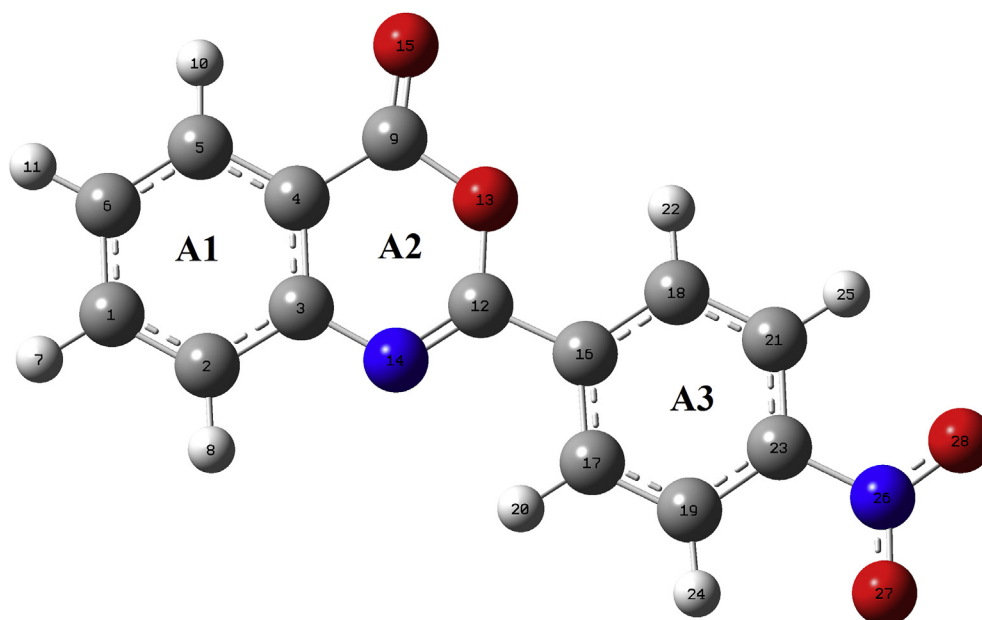


Fig. 1. Theoretical structure and atoms numbering of 2-(4-nitrophenyl)-4H-3,1-benzoxazin-4-one.

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