



Structural, spectroscopic and NLO features of the 4-chloro-1-naphthol

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ABSTRACT

The IR and Raman spectra of the 4-chloro-1-naphthol (4C1N) recorded for a solid phase, in the range 4000–500 cm^{-1} and 4000–100 cm^{-1} respectively, are compared with the results of DFT B3LYP/6-311 + G(3d,2p) calculations. Theoretical spectra, after standard scaling procedure, fit the experimental ones very well – RMS are 7.61 cm^{-1} and 4.98 cm^{-1} . PED analysis allows to the description of the observed vibrations. A location and character of the particular deformations agree well with those reported for the similar aromatic compounds. A UV-VIS spectrum recorded for a 4C1N solution in tetrahydrofuran is perfectly reproduced by TD-DFT calculations results with the same functional and basis set as indicated above. On the other hand, MP2-CIS results work very badly. The calculated values of the components of the polarizability and two first hyperpolarizabilities (β , γ) tensors, significantly greater than these for urea, reveal that 4C1N may be considered as promising NLO material.

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1. Introduction

The naphthols are an important group of organic compounds which are not only widely used in organic synthesis but also often found in natural products and pharmaceuticals [1]. What is more, they are promising as charge conducting moieties. This is due to a π -stacking effect observed between neighboring layers of naphthols in solid state [2]. The big advantage of naphthols is a possibility to obtain their derivatives in simple, not expensive ways. An example may be a cyclization method. The reaction, for which ortho-iodoacetophenones and methyl ketone are the substrates, starts with arylation of ketones. Different functional groups may be connected with substrates what opens a possibility to obtain a variety of compounds useful in organic and medical chemistry [1]. Oxidising arylation of naphthols is one of the main ways in dyes production [3]. The substituents in positions 2 or 4 are of special importance for reactivity of naphthols. Unsubstituted naphthols are much less reactive [3]. In the case of monosubstituted 1-naphthols, a type of the substituent in considered position is important. It determines the overlapping of π orbitals of the molecules in the subsequent layers [2].

The structure of the 4-chloro-1-naphthol (4C1N) crystals was

resolved by Marciniak [4]. It occurred to belong to the orthorhombic system, crystallized in $Pna2_1$ space group; there are four molecules in a unit cell. The 4C1N molecules are connected with strong hydrogen bond O–H \cdots O, connecting O2 oxygen atom through H3 hydrogen with O2 oxygen in the next molecule (for atom numeration see Fig. 1). This bond is nearly linear, the O–H \cdots O angle is 160°, and stabilizes the relative positions of the molecules in adjacent layers. In this way, the interlayer carbon chains are obtained, what influences the conductivity properties of the crystal [4].

4C1N is also interesting due to its applications in chemical synthesis and for analytical purposes. An example of synthesis may be a preparation of antitumor active 2-amino-4-arylo-6-chloro-4H-benzo[h]chromene-3-carbonitrile which is obtained from 4C1N reaction with cyanocinnamates in ethanol solutions [5]. 4C1N enzymatically oxidized together with a 3,3'-diaminobenzidine derivatives are used for colorimetric detection of a horseradish peroxidase with DNA matrix technology [6]. 4C1N was also found to be very useful in immunological applications within the micro-matrix technique. This effective method is limited by a low signal level and a necessity of sophisticated and expensive detectors. It was demonstrated in the study of a *Lysteria monocytogenes*, the dangerous pathogen frequently found in food, that 4C1N is the substratum increasing chromatic signal from micro-matrix to a level recognizable with a not equipped eye [7].

Asymmetry of the 4C1N molecules makes them an interesting

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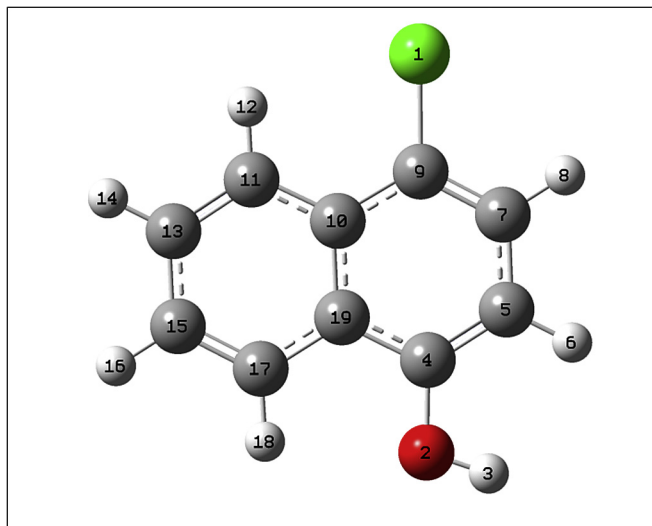


Fig. 1. Structure of the more stable 4-chloro-1-naphthol molecule with atoms numeration.

material for a nonlinear optical (NLO) devices. In practice, some problems have to be avoided due to poor durability of the material whereas as a part of composite it may work very good.

Despite such wide known applications and may be future ones, as an organic conductor or as NLO chromophore, there is lack of, up to our knowledge, the wider study of the electronic structure, IR and Raman spectra, components of polarizability tensors, etc. To complete this, joining some experimental results with data obtained from the calculations, is a goal of this study.

2. Experimental

For the measurements purposes 4C1N supplied by Sigma-Aldrich, >98% of purity, after recrystallization from ethyl acetate, was used. An Infrared spectrum was recorded with Ati Mattson Infinity FTIR 60 spectrometer, in KBr palettes, with a resolution of 4 cm^{-1} . An absorption spectrum in the range from 200 nm up to 1100 nm was obtained for a solution in tetrahydrofuran, with Ocean Optics HR 4000CG spectrometer, deuterium lamp (3.8 W) and tungsten-halogen lamp (1.2 W) were applied as the excitation sources. The resolution was 0.6 nm. Raman spectra, both for 4C1N powder and for its methanol solution, were recorded with Nicolet Omega XR dispersive spectrometer with 532 nm excitation from 24 mW Nd: YAG laser. Recordings were done in the $100\text{--}4000\text{ cm}^{-1}$ range with the resolution of 2.2 cm^{-1} .

2.1. Calculations

All the calculations were performed with the Gaussian09 package [8]. We used both Hartree-Fock method with MP2 perturbation correction and DFT with several different potentials. Namely, we made calculations with local type potential SVWN – Slater type exchange plus correlation functional as given by Vosko, Wilk and Nusair [9] and three component hybrid potential, B3LYP [10]. Each method or functional was combined with two different basis sets – one only with polarization functions on heavy atoms, 6-31G(d), and the second with polarization functions on both heavy atoms and hydrogens and diffusion functions only on heavy atoms, 6-311 + G(3d,2p). The course of the calculations was following: at the first stage minima on the potential energy surface (PES) were found with all the methods mentioned above. The character of the

extremal points was verified by checking if there are any imaginary frequencies among harmonic vibrations calculated for the considered structure. Afterwards, values of the geometrical parameters of the optimized structure, bond lengths, planar angles, representative torsion angles, were compared with these from crystal data [4]. The method leading to the smallest discrepancies between calculated and measured data was taken for further work. An absorption spectrum was simulated using CIS and TD-DFT calculations starting from the densities obtained in MP2/6-311 + G(3d,2p) and B3LYP with the same basis set.

Calculated vibrational spectrum was scaled separately in two frequency regions, according to the way proposed by Halls [11], normal modes energy distribution (PED) was calculated with VEDA4 software [12]. Polarizability and hyperpolarizability tensors were calculated in finite field approximation and dynamic values of this quantities with coupled perturbation HF scheme (CPHF) as they are implemented in Gaussian09.

3. Results and discussion

3.1. Structure

A starting geometry for molecule stationary point findings was extracted from the crystallographic data, from the *.cif file available in crystallographic data bases [4]. The view of the molecule together with the atoms numeration is given in Fig. 1. There were found two isomers, differing in hydroxyl group orientation. The one with lower energy, which may be considered to be a global minimum on molecule potential energy surface, (PES), has the hydroxyl group with the hydrogen atom oriented outside of the second aromatic ring. The molecule is flat, and both the substituents are also in the plane of the rings. The higher stationary point on PES, connected with the reverse orientation of –OH group hydrogen atom, is 2.38 kcal/mol over the previous one – see Fig. 2. The change of the –OH group orientation causes a slight deformation of the rings. The deviation from the planarity is not greater than two degrees – see insert in Fig. 2. This drawing illustrates the change of a dihedral angle between both rings planes, defined by C19, C10, C9 and C19, C10, C17 carbon atoms respectively when H3 atom rotate around the C4–O2 bond. This rotation is equivalent to a change of the dihedral angle between C4–O2–H3 and C19–C4–O2 planes. The values recalled above are from B3LYP/6-311 + G(3d,2p) calculations. The structures were optimized within a few calculation models – combination of method and basis set which was chosen. A part of the structural information, bonds lengths, and angles between bonds is collected in Table 1. The values obtained from calculations are compared with data from the experiment, despite the last are for solid phase, not for a single molecule. As the interactions between the molecules in a unit cell are not strong [4], we may assume it is an acceptable reference. As is seen from the data in Table 1, in all the applied models the agreement is on an acceptable level. The mean square deviation from the experimental values does not exceed 0.01 \AA for bonds and 0.3° for angles. The best agreement with the empirical data was obtained for B3LYP/6-311 + G(3d,2p) and, only slightly worse in reproducing the angles values, for MP2/6-311 + G(3d,2p) method.

3.2. Absorption spectra

An absorption spectrum of the 4C1N was recorded in tetrahydrofuran solution. It is given in Fig. 3. The considered compound is transparent in the visible region. The absorption is observed in ultraviolet with a maximum at 299 nm. The spectrum was also simulated both with TD-B3LYP/6-311 + G(3d,2p) and CIS following MP2/6-311 + G(3d,2p) calculations. Twenty excited states were

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