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2-Amino-3,5-dichlorobenzonitrile: DFT calculations in the monomer and dimer forms, FT-IR and FT-Raman spectra, molecular geometry, atomic charges and thermodynamical parameters

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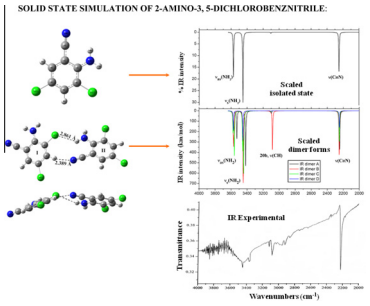
HIGHLIGHTS

- The Raman and IR spectra of 2-amino-3,5-dichlorobenzonitrile in the solid state were simulated.
- The simulation was carried out with four dimer forms.
- An accurate scaling procedure was used to improve the calculated wavenumbers.
- Dimer B is the expected form in the crystal with wavenumbers close to the experimental.
- The NH_2 group produces higher change on the geometry than the chlorine atoms.

GRAPHICAL ABSTRACT



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ABSTRACT

The experimental IR and Raman spectra of 2-amino-3,5-dichlorobenzonitrile molecule were recorded, and the results compared with theoretical values. Molecular geometry, vibrational wavenumbers and thermodynamic parameters were calculated using MP2 and DFT quantum chemical methods. With the help of specific scaling procedures for the computed wavenumbers, the experimentally observed FTIR and FT-Raman bands were analyzed and assigned to different normal modes of vibrations of the molecule. Simulations in the dimer form were carried out to improve the assignment of the bands in the solid state experimental spectra. The error obtained was in general very low. Using PED's were determined the contributions of the different modes to each wavenumber. Several general conclusions were also deduced.

Introduction

Benzonitrile (BN) is a mono-substituted benzene derivative. It is an aprotic polar solvent with a large dipole moment (4.18 D), and for this reason it has been extensively used in chemistry as a solvent and as a chemical intermediate for the synthesis of pharmaceuticals, dyestuffs and rubber chemicals [1–5]. BN and its derivatives also have several other important applications [7–9] that have been well reviewed recently [6], e.g. 3-ethyl-BN is used for the treatment of Urge Urinary Incontinence (UUI) [10], and as well vamicamide (a new anti-cholinergic agent synthesized from BN) is also used for the treatment of UUI [11], while *p*-hydroxy BN has alpha blocker properties on the cardiovascular system of rats [12].

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From the spectroscopic point of view the vibrational spectra of BN and its mono- and di- substituted derivatives have been extensively studied [13–18]. However, only the halogenated derivatives with fluorine and chlorine atoms offered more interest, and several studies have been published [19–23]. Theoretical vibrational analysis using force field calculations [19], as well as using Hartree–Fock (HF) *ab initio* methods and density functional (DFT) methods [8,9,24–29] have been also reported. Previously, we have studied the geometry, vibrational wavenumbers and thermodynamical parameters of a series of six difluoroBN [30], as well as a detailed analysis of the vibrational spectra of 2,3-difluoroBN [24], 2,4-difluoroBN [25], 2,4-dichloroBN [23], 2,5-difluoroBN [31] and 2,5-dichloroBN [32,33].

Amino benzonitrile derivatives have also been studied by IR and Raman spectroscopy. However, the special interest of these molecules has been centered in the fast excited state intramolecular charge Transfer (ICT) and dual fluorescence [26]. As amino-BN derivatives also offer great interest, therefore, we also have analyzed the vibrational spectra of *ortho*-, *meta*-, and *para*-, aminoBNs in different matrices, as well as the geometry, vibrational wavenumbers and several thermodynamical parameters of 3-aminoBN and 4-amino BN using *ab initio* quantum chemical methods [26,27].

However, neither a theoretical nor a complete experimental vibrational analysis of 2-amino-3,5-dichlorobenzonitrile molecule (in short 2A-3,5-DCBN) has been reported yet, therefore, the present manuscript undertakes this task with full identification of all the normal modes of the molecule. With the help of specific scaling procedures the observed FT-IR and FT-Raman bands were analyzed and accurately assigned to different modes. Moreover, using the PED's contributions of the different modes to each wavenumber were determined.

Experimental

The sample of 2-amino-3,5-dichlorobenzonitrile (solid powder) with spectroscopic purity was obtained from M/s Sigma Chemical Co., St. Louis, MO, USA) and used as such without any further purification.

The infrared spectrum of the compound in the powder form in the range 400–4000 cm^{-1} was recorded with a Bruker IFS66 Fourier transform spectrometer equipped with a Global source, Ge/KBr beam splitter and a TGS detector. For the spectrum, 50 interferograms were collected at 1.0 cm^{-1} resolution.

The FT-Raman spectrum in the 50–4000 cm^{-1} range was recorded on a Bruker IFS 66 optical bench with an FRA 106 Raman module attachment interfaced to a microcomputer. The sample was mounted in the sample illuminator using optical mount and sample pretreatment of any kind was not undertaken. The NIR output (1064 nm) of an Nd:YAG laser was used to excite the spectrum. The laser power was set at 250 mW and the spectrum was recorded over 500 scans at a fixed temperature and a resolution of 1.0 cm^{-1}.

Computational methods

The adequate prediction of the vibrational spectra requires the use of quantum chemical methods. Therefore, the calculations were mainly carried out by using Density Functional methods (DFT) [34], because they provide a very good overall description of medium-size molecules. Moreover, for the wavenumber calculations [35–38] they appear more accurate than HF and MP2, and at lower computational cost. As DFT methods, we selected the Becke's three-parameter exchange functional (B3) [39] in combination with both the correlational functional of Lee, Yang and Parr (LYP) [40] and the Perdew and Wang's 1991 (PW91) [41]. Because results obtained with both correlation functionals are similar, and also for simplicity, only the B3LYP results are shown in the present manuscript. The default fine integration grid was employed. MP2 calculations were also carried out to confirm the geometry structure and atomic charges.

Several basis sets differing in size and contraction were used, but for simplicity and owing to the small improvement reached when the basis set increases, only the results with 6-31G** was discussed in the manuscript. Dimer simulations were also performed at this level. These procedures are implemented in the GAUSSIAN 03 [42] program package.

The optimum geometry was determined; with the keyword OPT, by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The full geometry optimization was done utilizing the Berny algorithm in redundant internal coordinates, and with the standard optimization convergence criteria. Different starting geometries were used in the optimizations to obtain the global minimum. The stability of the computed structures was checked by calculating the Hessian matrix. All the geometries determined belong to a true minimum proven by real wavenumbers in the vibrational analysis. Intramolecular vibrations were calculated in the harmonic approximation using analytical second derivatives. The natural NBO atomic charges [43,44] are one of the most accurate today to correlate properties, and they were determined in the present manuscript.

Results and discussion

Geometry optimization

The isolated state

The optimized bond lengths, bond angles and torsional angles in 2A-3,5-DCBN are listed in the 2nd and 3rd columns of Table 1, while the labeling of the atoms is plotted in Fig. 1. There are two possible orientations of the NH_2 group with respect to the C2—N bond axis, structures (a) and (b). Structure (a) with the C1—C2—N—H14 torsional angle of 12.76° is the only stable form and thus the final bond lengths and bond angles obtained in structure (a) are listed in Table 1. Structure (b) with the C1—C2—N—H14 torsional angle of 59.19° (58.72° by MP2) is a saddle point. At MP2 level it is 6.71 kcal/mol less stable than structure (a), and for this reason its geometrical parameters were not included in Table 1.

Perhaps one of the most interesting structural features of this molecule, and the most difficult to determine, is the degree of non-planarity of the amino group. The deformation from planarity (pyramidalization) of the amine nitrogen has been interpreted by one of us [45] as resulting from a balance between opposing forces: the stability gained by the molecule as a whole arising from p–π conjugation of the nitrogen lone pair with the aromatic system vs. that gained by the amine using highly directed sp^3 orbital for bond formation. As a measure of the pyramidalization is defined the inversion angle ω, supplement of the angle between the H—N—H plane and the C2—N bond. The value of ω is strongly dependent on the theoretical method and level used, and in 2A-3,5-DCBN is 22.07° by B3LYP and 38.27° by MP2. These values are remarkably lower than in aniline [45] 41.71° by B3LYP/6-31G**, 47.18° by MP2/6-31G**, and 43° by X-ray [46]. It can be interpreted as due to a weak interaction of the amine hydrogens with the neighboring chlorine atom Cl11, which reduces the pyramidalization of the amino group.

The nitrogen atom is slightly out-of-plane, with a torsional angle C4—C3—C2—N of −177.9° (−176.6° by MP2). As a measure of this displacement is defined the *tilt* angle ε between the nitrogen