Impact of non-covalent interactions on FT-IR spectrum and properties of 4-methylbenzylammonium nitrate. A DFT and molecular docking study

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ABSTRACT

In this research, the impact of non-covalent interactions on the FT-IR spectrum and structural, electronic, topological and vibrational properties of hybrid 4-methylbenzylammonium nitrate (4MBN) have been studied combining B3LYP/CC-PVTZ calculations with molecular docking. 4MBN was synthesized and characterized by using the FT-IR spectrum while the optimized structures in gas phase and in ethanol and aqueous solutions have evidenced monodentate coordination between the nitrate and methylbenzylammonium groups, in agreement with that experimentally determined for this species by X-ray diffraction. Here, non-covalent interactions were deeply analyzed in terms of topological parameters (AIM), electron localization function (ELF), localized orbital locator (LOL), Hirshfeld surface and reduced density gradient (RDG) method. Weak interactions such as H-bonds, VDW and steric effect in 4MBN were visualized and quantified by the independent gradient density (IGM) based on the promolecular density. The hyper-conjugative and the delocalization of charge in 4MBN have been elucidated by natural bonding orbital (NBO) while its chemical reactivity was studied and discussed by using molecular electrostatic potential surface (MESP), frontier molecular orbital (FMOs), density of state (DOS) and partial density of state (PDOS). The complete vibrational assignments of 69 vibration modes expected for 4MBN are reported together with the scaled force constants while the electronic transitions were evaluated by TD-DFT calculations in ethanol solution. Thermal analysis (DTA and DSC) was also determined. Molecular docking calculations have suggested that 4MBN presents biological activity and could act as a good inhibitor against schizophrenia disease.

1. Introduction

In recent years, molecular modelling has become a widely used tool for research and modelling new chemical compounds because it is a handy technical to reconstruct the structures of molecules from experimental data. Numerous experimental and theoretical studies have been carried out for a better prediction and understanding of the structures, molecular interactions and various properties of chemical species [1]. Thus, many studies on the most important inter and intra-molecular interactions have allowed describing, measure and comprehending their nature [1, 2]. In particular, the weak interactions are well known in various physical, chemical and biological fields [2] while the non-covalent interactions exist in the crystal structure of hybrids to ensure maintain the geometry of large molecules. In fact, the concept of "hybrid material" is utilized in many applications because it combines both organic and inorganic entities. In this research work, we have studied the hybrid material, 4-4-methylbenzylammonium nitrate (4MBN) whose structure was already determined by X-ray diffraction [3]. This material consists of an organic unit which is 4-methylbenzylammonium nitramine and an inorganic unit which is nitric acid. This type of material which combines the nitrate anion with the organic molecule has attracted attention due to their many uses in different fields, such as...
Figure 1. ORTEP representation of 4-methylbenzylammonium nitrate.

Figure 2. Graphical representation of hydrogen bonds: N-H…O and C-H…O.
biomolecular science, liquid crystals, catalysts and fuel cells [4]. So far, the vibrational study, complete vibrational assignments and properties of 4MBN even not were reported yet. Hence, one of aim of this work is the vibrational study of 4MBN by using the FT-IR spectrum, the normal internal coordinates and the SQMFF methodology in order to analyze the coordination mode between inorganic and organic species based on the corresponding vibration modes and taking into account assignments for similar species [5, 6, 7, 8]. To achieve this purpose, DFT calculations were employed to study the structure and physico-chemical properties in order to reproduce with great precision the experimental structure and the FT-IR spectrum of 4MBN. Other of the objectives is to study the non-covalent interactions from a theoretical point of view using atoms in molecule (AIM) approach, electron localization function (ELF) and localized orbital locator (LOL). Hirshfeld surface have been used in order to analyze intra and intermolecular interactions in the crystal structure 4MBN. Reduced density gradient (RDG) and independent gradient density (IGM) were performed also to reveal the weak interactions. Natural bonding orbitals (NBO) analysis was used to determine the different donor-acceptor interactions presents in 4MBN while the molecular electrostatic potential surface (MESP) was displayed to identify its electrophilic and nucleophilic sites. The reactive sites were evaluated by using the frontier molecular orbital (FMOs) while the character of the molecular orbitals (MO) and the contribution of each group in 4MBN were illustrated by means of graphics of density of state (DOS) and partial density of state (PDOS). The UV-Visible absorption spectroscopy computes the major absorption features: excitation energy (E), Absorption wavelength (\( \lambda \)), oscillator force (f) and major contribution of the electronic transitions using TD-DFT method. Further, thermal analysis was reported here. In the pharmaceutical field, the 4MBN has promising use, as an intermediate pharmaceutical compound. It is popularly used to treat anxiety disorders as Schizophrenia diseases. Because of this, and because of the very important properties of this compound, we were encouraged to study the biological activities of our compound. Thus, by using the molecular docking method to assess the activity of quarter ligands (4MBN, BEZ, FAD and 98B) described in the literature as potential inhibitors of DAO protein. The objective of this method is to understand the mechanisms of action of this protein (DAO) and its role in the treatment of schizophrenia disease.

2. Experimental and computational details

2.1. Physical measurements

Reagents were purchased from Sigma Aldrich Company. The IR spectrum was obtained on a Perkin-Elmer Spectrum BX II FT-IR spectrometer using a sample dispersed in a spectroscopically pure KBr
pellet in the 400–4000 cm⁻¹ region. The spectral resolution was 4 cm⁻¹. UV-Vis spectrum was recorded on a Perkin Elmer Lambda 19 spectrophotometer using quartz cuvettes with 1 cm optical path in the 200–800 nm range. This technique involves adding to the cuvette a solution of the sample in 2 mL of ethanol with a concentration of 2.10⁻³ mol.L⁻¹. The spectral resolution was 2 nm.

The thermal analysis of the synthesized compound is carried out using a multimodule 92 Setaram analyzer under argon. The mass of product was 10.2 mg for DTA-TG and 11.21 mg for DSC placed in a platinum crucible from room temperature up to 880 K for DTA-TG and in the range temperature [298–535 K] for DSC with a heating rate of 5 K.min⁻¹.

2.2. X-ray diffraction analysis

The experimental structure of 4MBN was determined by X-ray diffraction at room temperature (293 K) [3]. This analysis revealed that 4MBN belongs to the monoclinic crystal system with the space group P2₁/c and their lattice parameters are as follows: a = 15.097 (2) Å, b = 5.812 (10) Å, c = 10.486 (2) Å and β = 99.75 (2)° [3]. Figure 1 shows an ORTEP plot of 4MBN with displacement ellipsoids drawn at the 30% probability level. The molecular structure consists of an organic cation which is 4-methylbenzylammonium and an inorganic anion NO₃⁻. In the crystal structure, molecules develop in parallel layers along the b axis and along the c axis are described by a succession of cationic and anionic layers (Figure 2). In addition Figures 3 and 4 indicates that the crystal cohesion and stability between cationic and anionic entities is ensured by two types of weak hydrogen bonds: C-H…O and N-H…O. These two interactions were evaluated by different computational and experimental methods, as we will see later.

2.3. Computational details

In the present study, all calculations were performed by using Gaussian 09 [9] program and GaussView 6.0 [10] as interface visualization. The molecular geometry structure has been optimized with density functional theory (DFT) using the hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) [11, 12] with CC-PVTZ basis set. The non-covalent interactions were
examined in detail with AIM, ELF, LOL, RDG and IGM analysis using Multiwfn program [13] and the isosurfaces are visualized via VMD software package [14]. Also, the Hirshfeld surface has been generated using Crystal Explorer 3.1 program [15]. A natural orbital bond (NBO) analysis was carried out to study the transfer of electronic charge (donor-acceptor) in the molecule and the bond orders. The molecular electrostatic potential surface (MESP) was mapped to identify the electrophilic and nucleophilic sites which promote the formation of hydrogen bonds in 4MBN. The complete vibrational assignments of all bands observed in the experimental FT-IR spectrum of 4MBN in gas phase were performed with the calculated harmonic force fields by using the scaled quantum mechanical force field (SQMFF) methodology and taking into account the normal internal coordinates, transferable scaling factors and the Molvib program [16, 17, 18]. The experimental structure has evidenced that NH2 group is coordinate to H atom of OH of acid and, hence, it is as NH3 group, for which this group was considered with C3V symmetry because it group was optimized with two double bonds character and the other one as simple bond, as was observed in similar species [5, 6, 7, 8]. Also, UV-Vis spectra and electronic properties such as frontier molecular orbital analysis (HOMO–LUMO) were computed with the help of time-dependent DFT (TD-DFT) method. Plots of state density (DOS) and partial state electron (HOMO and LUMO) were obtained using GaussSum software [19]. Finally, the molecular docking has been performed for the determination of biological activity and to analyze various ligand-receptor interactions. In addition, the structures ligands and protein are extracted from the PDB data bank (Protein Data Bank) [20]. The docking calculations were carried out by using iGEMDOCK program [21] and the results obtained were visualized using discovery studio software [22].

3. Results and discussion

3.1. Optimized geometry of the molecule studied

The optimized structure of 4MBN obtained with the B3LYP/CC-PVTZ method is depicted in Figure 5. Table 1 presents the effect of dispersion on the values of minimum energies and dipolar moment (μ) in the gas phase and in the presence of a solvent (water). The examination of this table shows that the optimization in the gas without dispersion is the most stable because it has the minimum energy value (E = -647.440 a.u). The dipole moment is high in water (μ (dispersion) = 15 D and μ (without dispersion) = 14.2 D) compared to gas (μ (dispersion) = 4.6 D and μ (without dispersion) = 5.7 D), which indicate the increase of the polar character and charge separation in water.

To see how well the theoretical model represents reality, an RMSD (Root Mean Square Deviation) calculation was performed to compare between the experimental and theoretical values. RMSD values (Table 2) shows that the dispersion has a weak effect on the calculated bond lengths in the gas phase unlike the solvent (water). For bond angles, the dispersion shows a small change in gas phase and solvent. The lowest RMSD values are noted for bond lengths (0.012 Å) and 0.965° for angles in water with and without dispersion, respectively. The graphs of correlations between theoretical and experimental distances and bond angles in gas phase and in solvent with and without dispersion are shown in Figures 6, 7, 8, and 9. The values of R2 (Table 2) are very close to 1, so we can say that all the parameters calculated are agreeing well with the experiment. The geometric parameters such as the bond length and bond angle are compared with the experimental results as presented in Table 2. The bond angle of intramolecular hydrogen bonding interaction (N-H⋯O) has found to be 106.550°. 4MBN has eight C-C bond lengths, three O-N bond lengths, a single C-N bond and hydrogen bonds. Theoretically, the C-C intermolecular bond lengths of the benzene group are: C9-C14 (1.392 Å), C9-C12 (1.391 Å), C11-C20 (1.398 Å), C11-C12 (1.392 Å), C15-C20 (1.386 Å) and C14–C15 (1.397 Å). It is noticed that the values of the computed geometric parameters are slightly different compared to the experimental ones. This difference is explained by the fact that the experimental results are obtained from a solid state where the packing forces were not considered because the calculations were performed in the gaseous state for the molecules isolated. These differences also are observed in the broad band observed in the FT-IR spectrum in the 4000-2000 cm⁻¹ region.

| Method | DFT/B3LYP/CC-PVTZ |
|--------|-------------------|
|        | Gas without dispersion | Gas with dispersion |
|        | Energy (a.u)      | μ (D)      |
| Energy (a.u) | -647.440 | -647.413 |
| Dipolar moment (D) | 15 | 4.6 |

Table 1. Energies and dipole moment values in gas and solvent phase with/without dispersion effect.
### Table 2. Comparison between experimental and calculated geometric parameters of 4MBN compound.

| Geometric parameters | Exp without dispersion | water without dispersion | water with dispersion |
|----------------------|------------------------|--------------------------|-----------------------|
| **Bond lengths (Å)** |                        |                          |                       |
| O1-N2                | 1.368                  | 1.268                    | 1.240 (2)             |
| O1-H4                | 1.038                  | 1.763                    | 1.748 (2)             |
| N2-O2                | 1.201                  | 1.245                    | 1.244 (2)             |
| N2-O4                | 1.220                  | 1.249                    | 1.248 (2)             |
| N2-H6                | 1.014                  | 1.020                    | 0.890 (2)             |
| N2-H7                | 1.015                  | 1.020                    | 0.19 (2)              |
| N2-H8                | 1.620                  | 1.045                    | 1.044 (2)             |
| C15-C14             | 1.484                  | 1.507                    | 1.508 (2)             |
| C14-H13             | 1.083                  | 1.083                    | 0.930 (2)             |
| C15-C14             | 1.391                  | 1.388                    | 1.388 (2)             |
| C14-C17             | 1.507                  | 1.502                    | 1.502 (3)             |
| C16-H17             | 1.082                  | 1.083                    | 0.930 (2)             |
| C14-C17             | 1.397                  | 1.394                    | 1.394 (2)             |
| C17-H18             | 1.092                  | 1.086                    | 1.086 (2)             |
| C17-H18             | 1.083                  | 1.083                    | 0.970 (2)             |
| C17-H19             | 1.089                  | 1.090                    | 0.961 (2)             |
| C16-H15             | 1.090                  | 1.090                    | 1.09 (2)              |
| C11-C22             | 1.113                  | 1.106                    | 1.097 (2)             |
| C11-C22             | 1.119                  | 1.106                    | 1.108 (2)             |
| C11-C22             | 1.113                  | 1.106                    | 1.108 (2)             |
| C11-C22             | 1.119                  | 1.106                    | 1.108 (2)             |
| RMSD                | 0.138                  | 0.105                    | 0.083 (2)             |
| R²                 | 0.969                  | 0.983                    | 0.954 (2)             |

### Table 2 (continued)

| Geometric parameters | Exp without dispersion | water without dispersion | water with dispersion |
|----------------------|------------------------|--------------------------|-----------------------|
| N6-C21-H23           | 106.998                | 107.251                  | 106.345 (2)           |
| N6-C21-H24           | 111.300                | 111.431                  | 106.837 (2)           |
| C14-C17-H18          | 110.635                | 110.473                  | 111.639 (2)           |
| C14-C17-H19          | 109.298                | 110.107                  | 111.529 (2)           |
| C14-C17-H20          | 107.262                | 107.594                  | 108.929 (2)           |
| C11-C20-C15          | 121.251                | 121.058                  | 121.166 (2)           |
| C11-C22-H21          | 119.448                | 119.486                  | 119.461 (2)           |
| C11-C22-H22          | 119.300                | 119.452                  | 119.432 (2)           |
| C11-C22-H23          | 111.441                | 111.601                  | 111.362 (2)           |
| C11-C22-H24          | 111.341                | 110.455                  | 111.311 (2)           |
| RMSD                | 1.535                  | 1.635                    | 0.965 (2)             |
| R²                 | 0.993                  | 0.995                    | 0.959 (2)             |

### 3.2. Non-covalent interaction analysis

#### 3.2.1. Topological analysis

**3.2.1.1. Quantum theory of atoms in molecules AIM.** Quantum theory of atoms in molecules (QTAIM) theory is broadly used to study non-covalent interactions and it is initially developed by Bader [23, 24]. This approach has extensively been applied to identify the nature of bond critical points (BCPs) and to evaluate their energies. Generally, topological analysis has been used to classify hydrogen bond (weak, moderate, strong) and analyze the nature of interactions in terms of electron density ρ (r) and its Laplacian $\nabla^2 \rho (r)$ inside the molecular systems [25].

The - (G(r)/V(r)) ratio in AIM analysis which describes the nature of the hydrogen bond [26]. In fact, when - (G(r)/V(r)) > 1, the hydrogen bond has a character non-covalent, whereas for 0.5 < - (G(r)/V(r)) < 1, the hydrogen bond is covalent. Further, the topological properties are handy tool to characterize the strength of hydrogen bond such as: electron density ρ (r), and its Laplacian $\nabla^2 \rho (r)$, kinetic energy density G (r), potential V (r), total energy H (r) and the bond energy $E_{HB} = V (r)/2$ (proposed by Espinosa and his collaborators [27]) are also the efficient parameters to characterize the hydrogen bonding. The various bond critical points (BCPs), new ring critical points (NRCPs) and ring critical points (RCPs) were identified as shown in Figure 10. Their corresponded topological parameters are provided in Tables 3 and 4. Inspection of the table shows that the low values of the ellipticity at the RCP points confirm that there is delocalization of electrons in the aromatic nucleus.

In addition, the high value of ellipticity suggests that there is a strong delocalization in NRCP structures. As shown in Figure 3, the interactions between the monomer, dimer, around organic cation and around inorganic anion are mainly ensured by two types of hydrogen bonds: N···H-O and C···H-O. Basing on the values of $\nabla^2 \rho (r)$ and G(r) + V(r) are all positive in various cases as well as $E_{interaction}$ is less than 12.0 kcal/mol (50 kJ/mol). These results confirm that the hydrogen bonds forming within our compound are considered weak. The ratio 0.5 < - (G(r)/V(r)) < 1, indicating also that low hydrogen bonds existing in our compound are non-covalent nature. Moreover, the interactions of hydrogen bonds can be characterized by various important aspects, including the energy of ΔE bonds in the case of charged and neutral complexes [28]. In this context, the values of ΔE < 2.5 kcal/mol, therefore the hydrogen bonds of our compound are weak and dominated by dispersions and electrostatic interactions.
3.2.1.2. Electron localization function analysis (ELF). The topological analysis of the ELF [29, 30] is a powerful tool for determining the localization of electron pairs probability. It also helps to understand the behavior of electrons in multielectronic systems. This approach was generated by Silvi and Savin [30], it allows to decide if the electrons are localized. In fact, when the electrons are perfect localized the value of ELF varies in the range [0.5, 1], whereas an ELF $\leq 1/2$ shows the delocalized electronic region [31]. Furthermore, ELF furnishes some local measure of Pauli repulsion which is associated directly with the kinetic energy of electrons. Usually, the ELF value is close to 1 for the regions with the highest Pauling repulsion and is close to 0 for the regions with the lowest Pauling repulsion. The Figure 11 illustrates the ELF map of the title compound 4MBN on the plane C22, N5, N2 atoms. A color code is represented with the ELF map varies from blue to red which show the scale range from 0 to 1. We can see from the 2D carte that the areas presented by a blue color around some carbon such as C22, C14, C11 and oxygen atoms (O3) represent the delocalized electron. Whereas, the red and orange color around the hydrogen atoms of the organic group C8H12N+ have comparatively large ELF values. Therefore, this region can be associated with a covalent bond character which is characterized by an appreciable electron density (a region of maximum Pauli repulsion). Generally, the elevated ELF regions are indicated a high localization of electrons, and may be identified with presence of a covalent bond, a lone pair of electrons, or a nuclear shell in that region. The visualization of the ELF can also indicate the non-covalent interactions (hydrogen bonds). Here, we noted that the ELF value is high around N5-H8 bond of the organic group (red region) and low around the O1 atom of the inorganic group (blue circle). In addition, the blue region between the hydrogen atom H8 and oxygen O1 gave evidence for occurrence of interaction in this region, leading to a hydrogen bond of N-H $\cdots$ O type. Not only, the other types of hydrogen bonds can be displayed in the crystal structure of our compound. Therefore, we can conclude that this method is in agreement with the AIM approach.

3.2.1.3. Localized orbital locator (LOL) theory. Electron localization descriptor such as localized orbital locator (LOL) is widely used to describe the molecular bonding, reactivity and chemical structure. This tool is similar to the ELF as both depend on the kinetic energy density [32]. LOL analysis was introduced by Silvi and Savin [30] and carried out by using Multiwfn software. Also, the LOL map is a simpler and clearer picture than ELF. Moreover, ELF explains the electron pair density and LOL illustrates highest localized orbitals overlapping owing to the gradients of orbitals. Color filled map of the LOL for the atoms of the title compound is summarized in the Figure 12. According to this figure, we observed that the high limit for LOL is 0.8 (red) and the lower limit is 0 (blue). LOL achieves in high regions (superior in 0.5) when the electron density is dominated by electron localization. It is seen in the Figure 11 that the region represented by the blue color around the carbon and nitrogen atoms provides LOL values $\leq 0.5$ (region where the electron
density is considerably depleted). Therefore the bonds could be classified in this region as weakly covalent bond or van der Waals bonds. Furthermore, the red color region near carbon atoms of the benzene ring with strong LOL values are due covalent bonds between the atoms (region where the electron density is much concentrated). As a result of the presence of a covalent bond in that area results in high localization of electrons, which proves great value in that region [32]. Also the small white circles present at the central part of the hydrogen atoms with maximum range caused to electron density (a region exceeds the high limit 0.8). As it is shown also in the figure of LOL that the low blue region between hydrogen H8 and nitrogen N5 displays the formation of a weak hydrogen bond of the N-H⋯O type. Similar to ELF, LOL confirms also the results found in AIM analysis.

3.2.2. Hirshfeld surfaces analyses (HS)

3D Hirshfeld surfaces (HS) and 2D fingerprint maps are unique for every molecule in the asymmetric unit of crystal structures. Indeed, (HS) provide a three-dimensional image of intermolecular interactions in crystals, while two-dimensional plots obtained by analysis of (HS) can identify each type of intermolecular interaction. The d_{norm} molecular (HS), “d_n”, Shape index and “Curvedness” of (C₈H₁₂N) NO₃ are respectively shown in Figure 13. These surfaces are shown transparent to highlight the visualization of the orientation and conformation of functional groups in the crystal. The normalized contact distance (d_{norm}) of the produced compound displays a surface with a color scheme (red, blue, white), where the red spots highlight the shortest intermolecular contacts which are attributed to the N-H⋯O and C-H interactions. … O. The blue areas indicate the most linguistic intermolecular contacts in the structure and the white areas represent the contacts around the van der Waals separation. The latter correspond respectively to the interactions H⋯H, N⋯H and C⋯H [33, 34, 35, 36]. These contacts have been observed on the d_n map where the large orange spots attributed to the N-H⋯O hydrogen bonds, while the small blue spots correspond to the H⋯H, C⋯H and N⋯H contact. The absence of red and blue triangles on the Shape index map and the small flat segments delimited by blue outlines on the curvedness map exclude the presence of π-π and C-H⋯π interactions in our crystal structure [36].

Electrostatic potential plays a key role in molecular recognition processes, including interactions with drug receptors. Again it exhibits important properties for the evaluation of lattice energy in crystals [37, 38]. The electrostatic potentials of (C₈H₁₂N) NO₃ were mapped on the (HS) using the STO-3G base fixed at the level of Hartree-Fock theory over a range of ±0.20 AU. Indeed, the presence of interactions and hydrogen bonds C-H⋯O and N-H⋯O between anions and cationic groups are observed through their (HS) mapped to the electrostatic potential (Figure 13 c). This map shows donor atoms (Nitrogen and Carbon of C₈H₁₂N⁺) in blue regions with positive potential and acceptor atoms (Oxygen of NO₃⁻) with negative potential in red regions [39, 40, 41].

The overall two-dimensional fingerprint plot as well as the percentages of the various contacts existing in the (C₈H₁₂N) NO₃ compound is
shown in Figure 13. d. In addition, Figure 14 represents the different contact which contributes in our molecule. H...H intercontacts (45.5%) have the greatest contribution on the (HS) with a maximum sum de ~ 2.3 Å. H⋯O/O...H contacts comprise 37% of the entire (HS) and represented by two narrow, symmetrical pointed tips with de ~ 1.9 Å. The C...H/C...C contacts show on its 2D graph the presence of two wings centred around a sum de + di ~ 2.79 Å. comparing the sum of the components of the pairs (de, di) of these contacts with the sum of the van der Waals radii of the atoms involved, we find that only the contacts O...H/H...O and C...H/H...C are considered to be close contacts with a sum de + di less than or equal to the sum of the van der Waals radii of the atoms involved (H: 1.09 Å, O: 1.52 Å, C: 1.70 Å).

Table 3. Topological parameters of critical points in monomer and dimer from.

| Interaction   | \(V^2\rho(r)\) (u. a) | \(\rho(r)\) (u. a) | \(G(r)\) (u. a) | \(V(r)\) (u. a) | \(H(r)\) (u. a) | \(\epsilon\) | \(E_{\text{interaction}}\) (kJ/mol) |
|---------------|------------------------|---------------------|----------------|----------------|----------------|----------|-----------------------------|
| **Monomer**   |                        |                     |                |                |                |          |                             |
| RCP           | 0.025                  | 0.159               | 0.036          | -0.033         | 0.004          | -1.233   |                             |
| NRCP1         | 0.005                  | 0.016               | 0.003          | -0.002         | 0.001          | -3.957   |                             |
| NRCP2         | 0.003                  | -0.002              | 0.002          | -0.002         | 0.001          | 2.777    |                             |
| O1...H8-N5    | 0.025                  | 0.074               | 0.018          | -0.018         | 0.002          | 0.045    | -23.498                     |
| **Dimer**     |                        |                     |                |                |                |          |                             |
| RCP1          | 0.025                  | 0.159               | 0.036          | -0.033         | 0.004          | -1.231   |                             |
| RCP2          | 0.025                  | 0.159               | 0.036          | -0.033         | 0.004          | -1.231   |                             |
| NRCP1         | 0.005                  | 0.016               | 0.003          | -0.002         | 0.001          | -3.075   |                             |
| NRCP2         | 0.002                  | 0.0072              | 0.001          | -0.001         | 0.001          | -3.397   |                             |
| NRCP3         | 0.005                  | 0.016               | 0.003          | -0.002         | 0.001          | -3.075   |                             |
| NRCP4         | 0.003                  | 0.011               | 0.002          | -0.002         | 0.001          | -2.487   |                             |
| NRCP5         | 0.003                  | 0.011               | 0.002          | -0.002         | 0.001          | -2.487   |                             |
| O1...H8-N5    | 0.024                  | 0.078               | 0.019          | -0.018         | 0.001          | 0.046    | -23.63                      |
| O27...H26-N26 | 0.017                  | 0.067               | 0.014          | -0.012         | 0.003          | 0.106    | -41.36                      |
| O2...C14-H16  | 0.005                  | 0.015               | 0.003          | -0.002         | 0.001          | 2.352    | -5.51                       |
| O2...C14-C9   | 0.033                  | -0.011              | 0.111          | -0.498         | -0.387         | 0.261    | -653.75                     |
| O27...C90-H27 | 0.005                  | 0.015               | 0.003          | -0.002         | 0.001          | 2.352    | -2.76                       |
| O270...C90-C3 | 0.003                  | 0.010               | 0.002          | -0.002         | 0.001          | 2.270    | -1.84                       |

Figure 10. Graphic representation of critical points in: (a) monomer, (b) dimer, (c) around organic cations and (d) around inorganic anions.
Table 4. Topological parameters of critical points around organic cation and around inorganic anion.

| Interactions   | $\rho(r)$ (a.u) | $\rho(r)$ (a.u) | $G(r)$ (a.u) | $V(r)$ (a.u) | $H(r)$ (a.u) | $\varepsilon$ | $E$ interactions (kJ/mol) |
|----------------|-----------------|-----------------|-------------|-------------|-------------|-------------|-----------------------------|
| **Around organic cation** | | | | | | | |
| RCP | 0.026 | 0.160 | 0.036 | -0.033 | 0.004 | -1.229 | - |
| NRCP | 0.003 | 0.010 | 0.002 | -0.001 | 0.001 | -2.718 | - |
| NRCP | 0.004 | 0.016 | 0.003 | -0.002 | 0.001 | -2.464 | - |
| NRCP | 0.003 | 0.014 | 0.003 | -0.003 | -0.002 | -1.219 | - |
| O1...H8-N5 | 0.023 | 0.080 | 0.019 | -0.017 | 0.001 | 0.024 | -22.56 |
| O30...H17-N5 | 0.016 | 0.068 | 0.0140 | -0.011 | 0.003 | 0.077 | -14.57 |
| O28...H10-C9 | 0.005 | 0.17 | 0.346 | -0.003 | 0.001 | 0.161 | -3.28 |
| O28...H6-N5 | 0.020 | 0.073 | 0.016 | -0.014 | 0.002 | 0.017 | -18.50 |
| C14...O24-N2 | 0.031 | 0.010 | 0.002 | -0.013 | 0.001 | 2.449 | -17.07 |
| **Around inorganic anion** | | | | | | | |
| RCP | 0.026 | 0.159 | 0.036 | -0.033 | 0.004 | -1.232 | - |
| RCP | 0.026 | 0.159 | 0.036 | -0.033 | 0.004 | -1.232 | - |
| RCP | 0.025 | 0.159 | 0.036 | -0.033 | 0.004 | -1.232 | - |
| RCP | 0.026 | 0.159 | 0.036 | -0.033 | 0.004 | -1.232 | - |
| NRCP | 0.005 | 0.016 | 0.003 | -0.002 | 0.001 | -3.855 | - |
| NRCP | 0.002 | 0.010 | 0.002 | -0.005 | -0.001 | -1.404 | - |
| NRCP | 0.002 | 0.009 | 0.002 | -0.001 | 0.001 | -1.351 | - |
| NRCP | 0.002 | 0.0010 | 0.002 | -0.001 | 0.001 | -1.419 | - |
| NRCP | 0.002 | 0.009 | 0.002 | -0.001 | 0.001 | -1.339 | - |
| NRCP | 0.002 | 0.008 | 0.001 | -0.001 | 0.002 | -1.335 | - |
| NRCP | 0.005 | 0.016 | 0.003 | -0.002 | 0.001 | -2.536 | - |
| NRCP | 0.002 | 0.007 | 0.001 | -0.001 | 0.002 | -1.393 | - |
| NRCP | 0.005 | 0.016 | 0.003 | -0.002 | 0.001 | -3.660 | - |
| NRCP | 0.004 | 0.005 | 0.001 | -0.002 | -0.002 | -2.183 | - |
| NRCP | 0.003 | 0.014 | 0.003 | -0.0017 | 0.001 | -1.237 | - |
| NRCP | 0.003 | 0.015 | 0.003 | -0.0018 | 0.001 | -1.241 | - |
| O31...H33-C32 | 0.006 | 0.023 | 0.005 | -0.0034 | 0.001 | 2.730 | - |
| O31...H4-C46 | 0.006 | 0.020 | 0.004 | -0.0032 | 0.001 | 1.406 | -4.20 |
| O31...C15-C16 | 0.005 | 0.015 | 0.030 | -0.0022 | 0.001 | 1.771 | -2.89 |
| O31...H6-N5 | 0.024 | 0.081 | 0.019 | -0.0179 | 0.001 | 0.048 | -23.50 |
| O31...H20-N35 | 0.017 | 0.068 | 0.014 | -0.0117 | 0.003 | 0.133 | -15.36 |
| O31...C14-C44 | 0.003 | 0.010 | 0.002 | -0.0013 | 0.001 | 2.513 | -1.71 |
| O30...H32-N43 | 0.017 | 0.069 | 0.014 | -0.0118 | 0.003 | 0.112 | -15.49 |
| O30...H32-N34 | 0.024 | 0.081 | 0.019 | -0.0179 | 0.001 | 0.048 | -23.50 |
| O30...C49-N68 | 0.005 | 0.002 | 0.003 | -0.0022 | 0.001 | 2.498 | -2.89 |
| O30...H4-C49 | 0.006 | 0.021 | 0.004 | -0.0033 | 0.001 | 5.286 | -4.33 |
| O29...H27-N40 | 0.021 | 0.073 | 0.017 | -0.0148 | 0.002 | 0.039 | -38.86 |
| O29...H4-C40 | 0.005 | 0.018 | 0.004 | -0.0026 | 0.001 | 0.193 | -3.41 |
| O28...H4-C48 | 0.003 | 0.011 | 0.002 | -0.0012 | 0.001 | 2.355 | -1.56 |
| H71...H81-C80 | 0.044 | 0.014 | 0.003 | -0.0017 | 0.001 | 1.378 | -2.23 |
| H72...H82-N54 | 0.004 | 0.002 | 0.001 | -0.001 | -0.001 | 1.231 | -1.58 |
| C14...H33-C32 | 0.003 | 0.010 | 0.002 | -0.001 | 0.001 | 3.170 | -2.89 |
| C12...H116-C114 | 0.003 | 0.010 | 0.002 | -0.001 | 0.001 | 2.269 | -2.89 |
| H109...H112-C112 | 0.004 | 0.014 | 0.003 | -0.002 | 0.001 | 1.387 | -4.20 |
| C107...H18-C77 | 0.003 | 0.011 | 0.002 | -0.001 | 0.001 | 2.655 | -1.58 |
| O22...H30-C9 | 0.374 | -0.017 | 0.125 | -0.680 | -0.555 | 0.023 | -892.80 |
| O22...H6-N5 | 0.021 | 0.073 | 0.016 | -0.015 | 0.002 | 0.038 | -38.59 |

(continued on next page)
The ERXY enrichment ratio of a chemical element pair (X, Y) is defined as the ratio of the percentage of actual contacts in the crystal to the theoretical percentage of random contacts. The enrichment ratios (ER) of the intermolecular contacts existing in the asymmetric unit are calculated and given in Table 5. The list of enrichment ratios highlights the O…H/H…O contacts (EROH = 1.2) which appear to be favored in the crystal packaging with the formation of N-H…O and C-H type hydrogen bonds. H...H contacts appear with an enrichment ratio close to unity (0.90), this value agrees well with Jiech’s expectation [34]. Indeed these contacts necessarily occupy almost half of the (SH) with a percentage in SH > 70%. On the other hand, C...H/H...C contacts are slightly favored in a sample that contains aromatic molecules with an average ERCH value = 1.41. On the other hand, C...C contacts are in most cases very disadvantaged with RECC < 0.5 [42].

### 3.2.3. Reduced density gradient method (RDG)

The reduced density gradient method (RDG) is also a most efficient technique for analyzing non-covalent interactions (NCI) [43]. This approach was developed by Johnson et al. [44] and it enables to identify and visualize zones of weak interactions in a molecular system, such as the van der Waals (VDW) interaction, hydrogen bonds (H-B) and steric effect. His expression is a dimensionless quantity coming from the density and its first derivative [43]:

\[
RDG(r) = \frac{1}{2(3\pi^{2})^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{5/3}}
\]  

The RDG represents a color code to examine the interaction within the systems molecular. Blue zone indicates the presence of strong attractive interactions (p > 0, \(\lambda_2 < 0\)), such as hydrogen bond, red zone indicates the presence of strong repulsive interactions (p > 0, \(\lambda_2 > 0\)), such as steric effect and green zone shows the presence of weak interaction. In three dimensional spaces (3D), the values of sign (\(\lambda_2\)) allow to determine the nature of interactions. In fact, hydrogen bond (H-B) was located between -0.035 a.u < sign (\(\lambda_2\)) < -0.020 a.u. The force between hydrogen atoms and NO3 group is the VDW interaction (green isosurface). This region located between -0.015 a.u < sign (\(\lambda_2\)) < -0.010 a.u. While, red color indicates the steric effect which is found in center aromatic rings (strong repulsion). These repulsive interactions were observed within 0.020 a.u < sign (\(\lambda_2\)) < 0.035 a.u.

### 3.2.3.1. Independent gradient model (IGM) analysis

To visualize and quantify inter-intramolecular interactions a novel visible method independent gradient model (IGM) was carried out. This approach is based on promolecular density to identify the hydrogen bonding and van der...
Waals interaction presents in chemical systems. It also defined the independent gradient function ($\delta g$), the inter-fragment ($\delta g_{\text{inter}}$) and intra-fragment ($\delta g_{\text{intra}}$) to show interaction regions in the IGM. The multiwfn program was used to carry out the IGM analysis to reveal the non-covalent interactions (Figure 16) of our compound 4MBN [45]. This figure shows the range of $\delta g$ values with an upper limit 0.2 (red color) and a lower limit is 0 (blue color). From this figure we see that the blue color around the carbon atoms indicates the charge depletion zone. Red color round hydrogen atoms present high electron density and the green color around the nitrogen atoms indicate the neuter zone. In addition, the white color indicates all chemical interactions that have bigger values of $\delta g$ (a region with $\delta g > 0.2$). The plots which are presented by $\delta g_{\text{intra}}$, $\delta g_{\text{inter}}$ and $\delta g$ versus sign ($\lambda_2$) $\rho$ values are depicted in Figure 17. Figure 17.a associated for inter-fragment ($\delta g_{\text{inter}}$) interactions indicates the presence of remarkable peak about 0.393 a.u with sign ($\lambda_2$) $\rho$ is equal to -0.025.

The negative sign ($\lambda_2$) $\rho$ implies attraction interaction (H-bond). The $\delta g_{\text{inter}}$ shows also another low intensity peak about 0.098 a.u with sign ($\lambda_2$) $\rho$ is equal to 0.035 a.u which indicates the presence of a repulsive interaction correspond to a steric effect. From the scattering plots of intra-fragment interaction (Figure 17.b), when sign ($\lambda_2$) $\rho$ is equal to -0.035 a.u, the $\delta g_{\text{intra}}$ has an intense peak which implies the presence of hydrogen bonds in our compound 4MBN. Two weak peaks are equal to 0.080 a.u and 0.050 a.u which are associated to sign ($\lambda_2$) $\rho$ $\approx$ 0 essentially corresponding to VDW interactions.

3.2.4. Natural orbital bond (NBO) analysis

NBO analysis is considered the most useful technique to describe and determine the different donor-acceptor interactions between the atoms of the studied molecular system. Its applies to study electronic transitions, charge transfer or hyper-conjugative interactions. It is also enables

![Figure 13. (a) "dnorm", (b) “Shape index”, (c) electrostatic potential, (d) “Curvedness” and percentages of the various contacts of (C$_8$H$_{12}$N) NO$_3$ mapped to the Hirshfeld surfaces.](image-url)
to identify the possible interactions between filled Lewis-type NBOs (donors) and Lewis unfilled NBOs (acceptors) for a molecule [46]. The stabilization energy of second order \(E(2)\) related from any donor \((i)\) and acceptor \((j)\), can be estimated by the following equation [47].

\[
E(2) = \Delta E_{ij} = q_i F_{ij}/(\epsilon_j - \epsilon_i)
\]

where \(q_i\) is the donor occupancy, \(F_{ij}\) is the Fock matrix element, \(\epsilon_i, \epsilon_j\) are the diagonal elements of the orbital energies.

An NBO analysis was performed at the DFT level on the 4MBN structure optimized with the B3LYP/CC-PVTZ method. Table 6 enumerated the various interactions between Lewis (donor), non-Lewis (acceptor) orbits and second-order interaction energy \(E(2)\) corresponding to monomer and dimer. The greater \(E(2)\) values representing the high intensive interaction between electron donors and electron acceptors [48]. Referring to the results summarized in Table 6, it has noted the presence of strong interactions between electron-donors in the monomer and dimer. These interactions are formed by the orbital overlap between \(\text{LP}_3(\text{O}4) \rightarrow \Pi^*(\text{N}2-\text{O}3)\) and \(\text{LP}_2(\text{O}1) \rightarrow \Pi^*(\text{N}2-\text{O}3)\), of stabilizing energies \(E(2)\) equal to 151.79 kcal/mol and 41.01 kcal/mol respectively. In case of dimer, all interactions between \(\Pi^*(\text{C}36-\text{C}41) \rightarrow \Pi^*(\text{C}32-\text{C}33)\) and \(\Pi^*(\text{C}30-\text{C}35) \rightarrow \Pi^*(\text{C}32-\text{C}33)\) have high energy values equal to 261.74 kcal/mol and 158.28 kcal/mol respectively. The NBO analysis of 4MBN can clearly show the existence of hydrogen bonded interaction \((\text{N-H} \cdots \text{O})\) between nitrogen lone electron pairs \((\text{LP}(\text{N}))\) and \(\sigma^*(\text{O-H})\) anti-bonding orbital. The hyper-conjugated interaction energy between \(\text{LP}_1(\text{N}5)\) donor and \(\sigma^*(\text{O}1-\text{H}8)\) acceptor is 45.70 kcal/mol. This hydrogen bonded interaction promotes the charge transfer in 4MBN and conserve the molecular stability. Hence, the monodentate coordination is clearly justified by this analysis. On the other hand, the study of bond orders, expressed as Wiberg bond index matrix in the NAO basis shows that of the two predicted hydrogen C15-H16-\cdots-O1 and N5-H8-\cdots-O1 bonds, suggested by AIM and Hirshfeld surfaces analyses, only one of them (N5-H8-\cdots-O1) has a higher bond order value (0.5873), as compared with the other one C15-H16-\cdots-O1 (0.0019) justifying this way, the monodentate coordination by means of the N5-H8-\cdots-O1 bond.

### 3.3. Electronic properties

#### 3.3.1. Molecular electrostatic potential surface (MESP) analysis

In this part, surface of molecular electrostatic potential (MESP) is created to predict and analyzed the molecular reactive behaviour of a studied molecule. It is related to the electronic density and is a very useful to study hydrogen bonding interactions and for determining electrophilic and nucleophilic attack sites [49, 50]. The MESP map of 4MBN was constructed by using B3LYP/CC-PVTZ method and it mapped in Figure 18. The image of MESP was represented with color code located between two extremes: -4,671 10^-2 (red indicates strongest repulsion) to 4,671 10^-2 (blue indicates strongest attraction). Red regions represent the most appropriate sites for nucleophilic attack and green color corresponds to a neutral zone. Positive electrostatic potential (blue region) in 4MBN is found around \(\text{NH}_3^+\) of the methylbenzylammouim cation group. Whereas, negative electrostatic potential (red and yellow regions) is localized around oxygen and nitrogen atoms of the \(\text{NO}_3^-\) group. In addition, the electrophilic and nucleophilic sites explain the formation

### Table 5. Enrichment ratio (RE) of the various contacts in (C8H12N) NO3.

| ER | H   | C   | N   | O   |
|----|-----|-----|-----|-----|
| H  | 0.90| 1.41| 0.86| 1.2 |
| C  | 1.79|     |     |     |
| N  |     |     |     | 0.66|
| O  |     | 21.75| 0.9 |

% Surface | 70.95 | 6.4   | 0.9   | 21.75 |
of hydrogen bonds between the nitrate groups and the methyl-
benzylammouim and its importance in the stability of 4MBN.

3.3.2. Frontier molecular orbitals (HOMO-LUMO) analysis

Theory of frontier molecular orbital (FMOs) is an invaluable tool to
discuss the energy transition of the charge density because these FMOs
play a key role in optical, electrical and chemical properties of comp-
ounds [51, 52]. Thus, HOMO (electron donor) represents the highest
occupied molecular orbital, while lowest unoccupied orbital LUMO
(electron acceptor) that takes part in chemical stability [53]. These two
bands describe the capacity of a molecule to offer an electron and to gain
an electron respectively. Furthermore, HOMO-LUMO are energetically

Figure 15. 2D (left) and 3D (right) RDG plots of: (a), (b) monomer, (c), (d) dimer, (e), (f) around organic interaction, (g), (h) around inorganic interaction.
separated by an energy gap, also they play an important role to characterize the chemical reactivity and chemical hardness-softness as well as optical polarizability of 4MBN [54]. Hence, the HOMO-LUMO plots of 4MBN were carried out in gas phase and in solvent effect (ethanol and water) which are given in Figure 19. As seen in this figure, two important molecular orbital (MO) was examined which presented by two colors: green color represents negatively charged surfaces (nucleophilic sites), while red color indicates positively charged surfaces (electrophilic sites).

It is clear that the HOMO iso-density plots are located on \((C_8H_{12}N^+)_\text{gas}\), while the LUMO iso-density plots are located on \((NO_3^-)\). In addition, the global reactivity descriptors: global hardness \((\eta)\), maximum load transfer index \((\Delta N_{\text{max}})\), electronegativity \(\chi\) and moment dipolar \(\mu\) were defined by Parr R.G and colleagues [55]. Table 7 summarized these values, and indicates that the gap energies of 4MBN are equal to: 5.59 eV (gas), 4.04 (water) and 4.98 eV (ethanol). Since a compound with a higher-gap energy value is more polarizable, associated with high chemical reactivity, indicates low kinetic stability and is also called a soft molecule [56]. \(\Delta N_{\text{max}} = 2.36\) eV is maximum in presence of water, which means that 4MBN acquires a maximum of charges in its structure unlike gas and ethanol. To examine the character of the molecular orbitals (MO) of our compound we have calculated the density of states (DOS) (Figure 20). It can be clearly seen from this figure that DOS spectrum shows two peaks in the presence of ethanol: one is very intense and well localized on LUMO orbital with energy equal to -0.89 eV, and other less intense localized on HOMO orbital with \(E_{\text{HOMO}} = -6.2\) eV. In the gas phase, the two peaks HOMO and LUMO are less intense such that the energies \(E_{\text{HOMO}} = -6.99\) eV and \(E_{\text{LUMO}} = -1.41\) eV. In water, the band HOMO is located at \(E_{\text{HOMO}} = -6.98\) eV and the band LUMO is located at \(E_{\text{LUMO}} = -1.42\) eV. As well as their energy differences in ultimate value are equal to 5.91 eV, 5.61 eV, and 5.56 eV respectively in gas, ethanol and water. To know the contribution of each group, we have calculated the partial density of state (PDOS) as illustrated in the Figure 21. It can be observed from PDOS that in gas phase the two organic and nitrate groups are contributed to the bands HOMO and LUMO with \(E_{\text{HOMO}} = -4.90\) eV and \(E_{\text{LUMO}} = -1.10\) eV. Furthermore, the PDOS shows that under the effect of the solvent (water and ethanol) the two groups are assigned in the contribution of the HOMO-LUMO orbitals. The HOMO-LUMO energy is \(E_{\text{HOMO}} \text{ (ethanol)} = -6.22\) eV, \(E_{\text{LUMO}} \text{ (ethanol)} = -0.51\) eV and \(E_{\text{HOMO}} \text{ (water)} = -6.22\) eV, \(E_{\text{LUMO}} \text{ (water)} = -0.51\) eV.
Table 6. Orbital analysis (NBO) of monomer and dimer from of 4-methylbenzyllammonium nitrate compound.

| Donor (i) | Acceptor (j) | E (2 kcal/mol) | E(j)-E(i) a.u. | F (i, j) a.u. |
|-----------|--------------|----------------|---------------|--------------|
| π (N2-O2) | π* (N2-O2)   | 9.69           | 0.34          | 0.061        |
| LPf(O1)   | σ*(N2-O4)    | 6.17           | 1.07          | 0.073        |
| LPf(O1)   | π* (N2-O4)   | 41.01          | 0.20          | 0.093        |
| LPf(O2)   | σ2(O2-N2)    | 30.45          | 0.45          | 0.105        |
| LPf(O2)   | σ1(O2-N2)    | 18.55          | 0.70          | 0.104        |
| LPf(O4)   | σ1(O2-N2)    | 27.45          | 0.46          | 0.101        |
| LP2(O2)   | σ1(O2-N2)    | 16.37          | 0.75          | 0.100        |
| LPf(O3)   | π* (N2-O2)   | 151.76         | 0.15          | 0.141        |
| LP3(O4)   | σ*(O1-H3)    | 45.70          | 0.70          | 0.160        |

E(2) energy of hyperconjugative interaction.

3.3.3. UV-visible spectroscopy

In order to understand the electronic transitions between the molecular orbitals HOMO-LUMO in 4MBN, a TD-DFT calculation in the solvent ethanol was affected. UV-Visible absorption spectroscopy is an analytical method used to characterize a molecule, to find the nature of electronic transitions and oscillatory strength. The simulated and experimental UV-Visible absorption spectra of our compound in ethanol are shown in Figure 22. The effect of the solvent (ethanol) was taken into account by using the polarizable continuum model of the integral equation formalism (IEFPCM). The major absorption features: excitation energy E (eV), oscillator strength (I), wavelength λ (nm) and major contributions (%) of the molecular orbitals involved in each transition are reported in Table 8. In comparison with experimental study, UV-visible spectrum shows two peaks: the first is the most intense, located at $\lambda_{max} = 277 \text{ nm} (E = 4.48 \text{ eV})$ and 274 nm for spectra theoretical and experimental respectively is due to HOMO-LUMO transition with (97%) contribution. This electronic transition can be carried out at the $\Pi-II*\sigma$ transition relative to the organic group, due to the presence of the benzene ring. The second peak, was observed at $\lambda_{max}$ (theoretical) = 235 nm (5.26 eV) and $\lambda_{max}$ (experimental) = 307 nm corresponding to H-1→L-1, H-1→L-2, HOMO→L-1, HOMO→L-2 with (27%), (12%), (20%), (41%) contributions respectively. All these transition appear to be due to n→$\Pi*$ of group nitrate.

3.4. Thermal behavior

The differential and thermogravimetric thermal analysis of 4-Methylbenzylammonium nitrate is carried out in a temperature range from ambient up to 880 K on a sample of mass equal to 10.2 mg with a heating rate of 5 K.min$^{-1}$ and under an argon atmosphere. The DTA curve given in Figure 23. a shows the presence of an endothermic peak located at 397 K without loss of mass observed by TG curve. To better understand the nature of this phenomenon or of this transformation, the starting product was heated to a temperature slightly below 397 K for a few minutes, which causes the melting of our product and the start of its decomposition. A second exothermic peak is observed at 497 K. This peak is accompanied, on the TG curve, by a great loss of mass which corresponds to the total decomposition during which our compound undergoes an ignition and an explosion which leads to the end of handling with nitrogen oxides [57, 58, 59]. The differential scanning calorimetry analysis (DSC) (Figure 23 b) of (4-CH$_3$C$_6$H$_4$CH$_2$N$_3$)NO$_3$ compound is carried out under a stream of nitrogen using a Setaram “multimodule 92” type thermo-analyzer. This analysis is carried out on 11.21 mg of product placed in an alumina crucible from room temperature up to 535 K with a heating rate of 5 K. min$^{-1}$. The DSC analysis shows the presence of two peaks one endothermic located at 416 K and the other exothermic at 507 K corresponding respectively to the melting and decomposition of our product; these two phenomena are also observed by DTA/TG.

3.5. Vibrational study

The optimization of 4MBN with the B3LYP/CC-PVTZ method and the previous studies for this species have clearly evidenced the presence of NH$_3$ group belonging to methylbenzylammonium cation and the NO$_3$ group where the coordination mode is clearly monodentate. The experimental FT-IR spectrum of 4MBN in the solid phase was compared in Figure 24 with the corresponding predicted for the compound in the gas phase and with the Raman spectrum also predicted in the same medium and level of theory. The Raman spectrum predicted in activities was transformed to intensities with suggested equations [61, 62]. The complete assignments of 69 vibration modes expected for the structure of 4MBN with $C_1$ symmetry were carried out with the calculated harmonic (water) = $-6.80 \text{ eV}$, $E_{\text{LUMO}}$ (water) = $-0.62 \text{ eV}$. From all these results we can conclude that our compound 4MBN is more reactive in water.
Figure 18. Molecular electrostatic potential map of the title compound.

Figure 19. HOMO and LUMO molecular orbitals of 4MBN in gas phase, water and ethanol.

Table 7. HOMO-LUMO energy and other electronic properties of 4MBN compound.

|                  | DFT/B3LYP/CC-PVTZ | Gas     | Water   | Ethanol |
|------------------|--------------------|---------|---------|---------|
| \( \varepsilon_{\text{HOMO}} \) (ev) | -6.98              | -6.78   | -6.78   |         |
| \( \varepsilon_{\text{LUMO}} \) (ev)  | -1.39              | -2.74   | -1.80   |         |
| \( \Delta \varepsilon_{\text{HOMO-LUMO}} \) (ev) | 5.59               | 4.04    | 4.98    |         |
| Electronic affinity A (ev)           | 1.39               | 2.74    | 1.80    |         |
| Ionization potential I (ev)           | 6.98               | 6.78    | 6.78    |         |
| Electronegativity \( \chi \) (ev)    | 4.19               | 4.76    | 4.29    |         |
| Chemical potential \( \mu \) (ev)    | -4.19              | -4.76   | -4.29   |         |
| Overall hardness \( \eta \) (ev)     | 2.79               | 2.02    | 2.49    |         |
| Maximum load transfer index \( \Delta N_{\text{max}} \) (ev) | 1.50               | 2.36    | 1.72    |         |
| Dipolar moment (Debye)               | 5.68               | 13.99   | 6.56    |         |
force field in the gas phase by using the scaled quantum mechanical force field (SQMFF) methodology and taking into account the normal internal coordinates, transferable scaling factors and the Molvib program [16, 17, 18]. In the construction of the normal internal coordinates, as detailed in computational section, the NH3 group was considered with C3V symmetry while the NO3 group with C2V symmetry. In the assignments of all vibrations modes were considered the SQM calculations performed here, potential energy distribution (PED) contributions ≥10 % and assignments reported for species with similar groups [5, 6, 7, 8]. Observed and
calculated wavenumbers for 4MBN in the gas phase by using B3LYP/CC-PVTZ calculations together with the corresponding assignments can be seen in Table 9. Note that the intense IR band predicted with the B3LYP/CC-PVTZ method at 2492 cm\(^{-1}\) and by SQM calculations at 2390 cm\(^{-1}\) is quickly assigned by its intensity to the N-O⋯H stretching mode of acid coordinate to NH\(_2\) group, as was reported for the p-xylylenediaminium bis(nitrate) at 2651 cm\(^{-1}\) [6]. Thus, the experimental IR bands between 2615 and 2346 cm\(^{-1}\) (with red circle in Figure 13) can be assigned to O1-H8 stretching mode although the intensity of band in the experimental spectrum is different from the theoretical one probably due to that the dimeric species is also present in the solid phase, as was reported for p-xylylenediaminium bis(nitrate) [6]. Discussions of some assignments for the most important groups are presented below.

### 3.5.1. Assignments

#### 3.5.1.1. NH\(_3^+\) groups.

In 4MBN, the N5-H8 bond is coordinate to OH group of acid and, for this reason, this bond present different

| E (eV) | \(\lambda\) (nm) | \(f\) (a. u.) | Major contribution (%) |
|-------|-----------------|--------------|------------------------|
| 4.475 | 277.016         | 0.0002       | HOMO\(\rightarrow\)LUMO (97%) |
| 4.677 | 265.048         | 0.0002       | HOMO-3\(\rightarrow\)LUMO (47%). HOMO-2\(\rightarrow\)LUMO (36%). HOMO-1\(\rightarrow\)LUMO (13%). |
| 4.828 | 256.781         | 0.0003       | HOMO-3\(\rightarrow\)LUMO (14%). HOMO-1\(\rightarrow\)LUMO (85%) |
| 5.167 | 239.949         | 0.0002       | HOMO-3\(\rightarrow\)LUMO (37%). HOMO-2\(\rightarrow\)LUMO (58%) |
| 5.257 | 235.810         | 0.0026       | HOMO-1\(\rightarrow\)LUMO+1 (27%). HOMO-1\(\rightarrow\)LUMO+2 (12%). HOMO\(\rightarrow\)LUMO+1 (20%). HOMO\(\rightarrow\)LUMO+2 (41%) |
| 5.814 | 213.247         | 0.1167       | HOMO-1\(\rightarrow\)LUMO+2 (16%). HOMO\(\rightarrow\)LUMO+1 (51%). HOMO\(\rightarrow\)LUMO+2 (22%). |
characteristic than the other two N5-H6 and N5-H7 ones. Many theoretical studies show that this mode are more sensitive to the presence of the hydrogen bond [63, 64, 65]. Hence, an anti-symmetric stretching mode of this group is predict at 3408 cm\(^{-1}\) while for the monomeric species these modes are predicted between 1672 and 1460 cm\(^{-1}\) [66, 67], in niobyl nitrate are assigned between 1763 and 1753 cm\(^{-1}\) [68] while in species containing NO\(_2\) groups these modes are assigned between 1584 and 1335 cm\(^{-1}\) [5, 69]. Here, due to the monodentate coordination the very strong band at 1305 cm\(^{-1}\) is clearly assigned to symmetric mode because the SQM calculations predict this mode at 1277 cm\(^{-1}\) while the anti-symmetric mode is assigned to the shoulder at 1652 cm\(^{-1}\) because this mode is

3.5.1.2. Nitrate groups. In 4MBN, two N=O and one N-O stretching modes are expected due to the monodentate coordination of N-O--H bond. In some inorganic nitrate salts, the N=O stretching modes are observed between 1672 and 1460 cm\(^{-1}\) [66,67], in niobyl nitrate are assigned between 1763 and 1753 cm\(^{-1}\) [68] while in species containing NO\(_2\) groups these modes are assigned between 1584 and 1335 cm\(^{-1}\) [5, 69]. Here, due to the monodentate coordination the very strong band at 1305 cm\(^{-1}\) is clearly assigned to symmetric mode because the SQM calculations predict this mode at 1277 cm\(^{-1}\) while the anti-symmetric mode is assigned to the shoulder at 1652 cm\(^{-1}\) because this mode is

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Table 9. Observed and calculated wavenumbers (cm\(^{-1}\)) and assignments for 4-methylbenzylammonium nitrate in gas phase by using the B3LYP/CC-PVTZ method.

| IR Experimental\(^a\) | B3LYP/CC-PVTZ Method\(^a\) | Intensity\(^b\) | SQM\(^c\) | Assignments\(^d\) |
|----------------------|--------------------------|---------------|---------|-----------------|
| N2-O1 | 1498 | 12.0 | 1437 | sCH3 |
| C9-H10 | 1449 | 3.8 | 1403 | sCH3, wagCH2 |
| C12-H13 | 1418 | 16.7 | 1356 | sCH3 |
| C14-C17 | 1325 | 3.3 | 1293 | C11-C20 |
| C15-C20 | 1327 | 4.3 | 1297 | sNO2 |
| C12-H13 | 1290 | 5.1 | 1241 | pCH3 |
| C15-H16 | 1212 | 1.2 | 1212 | C14-C17 |
| C11-C22 | 1183 | 5.3 | 1153 | C11-C22 |
| C9-H10 | 1182 | 123.0 | 1144 | pNH3 |
| C12-H13 | 1146 | 1.5 | 1111 | C9-C12 \(\tau\)C12-H13 |
| C14-C17 | 1043 | 6.5 | 1043 | pCH3 |
| C11-C22 | 1032 | 3.0 | 1023 | pCH3 |
| C9-H10 | 1024 | 1.1 | 1002 | C12-H13 |
| C12-H13 | 987 | 4.4 | 987 | C15-H16 |
| C9-H10 | 997 | 1.3 | 981 | pCH3 |
| C9-H10 | 994 | 23.7 | 964 | C9-H10, \(\gamma\)C12-H13 |
| C9-H10 | 973 | 2.6 | 953 | \(\gamma\)C17-N5 |
| C9-H10 | 958 | 207.2 | 930 | sN2-O1 |
| C9-H10 | 905 | 45.4 | 852 | \(\gamma\)C20-H21 |
| C9-H10 | 863 | 3.7 | 851 | twCH3 |
| C9-H10 | 846 | 24.1 | 822 | \(\gamma\)C17-N5 |
| C9-H10 | 829 | 23.1 | 807 | pNH3 |
| C9-H10 | 804 | 11.2 | 794 | wagNO2 |
| C9-H10 | 759 | 4.5 | 739 | pNH3 |
| C9-H10 | 722 | 0.2 | 700 | pNH3 |
| C9-H10 | 693 | 3.7 | 681 | sNO2, \(\gamma\)NO2 |
| C9-H10 | 665 | 3.8 | 656 | sNO2 |
| C9-H10 | 659 | 0.5 | 653 | pNH3 |
| C9-H10 | 573 | 19.8 | 564 | sC14C17N5 |
| C9-H10 | 489 | 22.3 | 477 | \(\gamma\)C11-C22, twNH3 |

(continued on next page)
Table 9 (continued)

| 4-methylbenzylammonium nitrate | B3LYP/CC-PVTZ Methoda |
|---------------------------------|------------------------|
| **Experimental**                | **B3LYP/CC-PVTZ Methoda** |
| IR                              | Calculateda | Intensity | SQMa | Assignmentsa |
| 432sh                           | 449         | 16.5      | 435  | δ,NH3         |
| 403vw                           | 421         | 0.6       | 407  | τ(C=C)        |
|                                 | 388         | 1.0       | 384  | τ(C1-C22)     |
|                                 | 369         | 0.6       | 363  | τ(8H-N5,τO1-H8) |
|                                 | 291         | 1.8       | 287  | τ(C14-C17)    |
|                                 | 261         | 59.9      | 251  | τ(NH3)        |
|                                 | 218         | 1.7       | 213  | τ(8H-N5,τO1-H8) |
|                                 | 139         | 7.0       | 130  | τ(8H-N5)      |
|                                 | 109         | 1.6       | 105  | τ(8O1-H8,τN4H3) |
|                                 | 88          | 1.0       | 83   | τ(8H-N5,τO1-H8) |
|                                 | 54          | 0.2       | 51   | ρNH3,8NH5H8O1+τC14-C17.τvNO2 |
|                                 | 44          | 0.3       | 39   | τ(CH3)        |
|                                 | 36          | 0.6       | 33   | τ(8O1-H8,8H-N5) |
|                                 | 27          | 0.7       | 24   | τ(8O1-H8,8H-N5) |
|                                 | 23          | 1.3       | 21   | τ(8O1-H8)     |

Abbreviations: s, stretching; d, deformation in the plane; γ, deformation out of plane; τ, torsion; ρ, deformation ring τδ, torsion ring; ρ, rocking; τ, twisting; δ deformation; wag, wagging; a, antisymmetric; s, symmetric; (A1). Ring 1; *This work. aFrom B3LYP/CC-PVTZ method. aIntensities in KM/Mole; aFrom scaled quantum mechanics force field.

Table 10. Comparison of main scaled internal force constants for 4-methylbenzylammonium nitrate in gas phase by using the B3LYP/CC-PVTZ method with reported for monodentate coordinations of p-xylylenediaminium bis(nitrate) and chromyl nitrate with different basis set.

| B3LYP Method | 4-D-H-N | p-Xylylenediaminium bis(nitrate)a | Chromyl nitrateb |
|--------------|----------|----------------------------------|------------------|
| Force constant | CC-PVTZ | 6-311++G** | 6-311++G |
| f(N – O)     | 9.75     | 9.74                             | 15.83            |
| f(C-N)       | 4.29     | 4.25                             | 3.22             |
| f(C-O)       | 4.20     | 4.23                             | 2.77             |
| f(C-C)       | 4.30     | 4.27                             | 2.77             |
| f(C-Ca)      | 6.35     | 6.34                             | 4.23             |
| f(N-H)       | 4.37     | 4.36                             | 4.36             |
| f(N = N)     | 1.54     | 1.53                             | 1.58             |
| f(N = N- O)  | 1.60     | 1.58                             | 2.09             |
| f(N=O-H)     | 1.12     | 0.89                             | 0.18             |
| f(N-H-O)     | 0.18     | 0.19                             |                  |

Units are mdyn Å⁻¹ for stretching and mdyn Å rad⁻² for angle deformations. *This work. aFrom Ref. [6]. aFrom Ref. [63].

coupled with the τ(8H-N5) and τO1-H8 torsion modes. The stretching mode related to simple N2-O1 bond is predicted at 930 cm⁻¹ and, for this reason, the weak band at 923 cm⁻¹ is assigned to this vibration mode. The O=N-O deformation mode is predicted and assigned at 681 cm⁻¹, respectively. The τ torsion modes for the monodentate form of p-xylylenediaminium (nitrate) [6] are predicted at 76 cm⁻¹ while in 4MBN this mode is predicted at 51 cm⁻¹, as indicated in Table 9.

3.5.1.3. CH₃ and CH₂ groups. 4MBN has one CH₃ and CH₂ groups, later, the corresponding anti-symmetric and symmetric stretching modes are predicted between 2976 and 2896 cm⁻¹ and, for these reasons, the shoulders and group of IR bands in that region are assigned to these vibration modes, as is detailed in Table 9 [6, 7, 8, 69]. The symmetries of these modes cannot be verified because in this work the Raman spectrum was not recorded. The deformation modes of these groups are predicted between 1449 and 1356 cm⁻¹ while the wagging CH₃ and rocking CH₃ modes are predicted at 1403/1393 and 1043/981 cm⁻¹, respectively. The SQM calculations predicted the twisting CH₂ mode at 851 cm⁻¹ while the corresponding to CH₃ group at 39 cm⁻¹. This way, only the twisting CH₂ mode is assigned at 888 cm⁻¹.

3.5.1.4. Skeletal groups. The C=C stretching modes corresponding to the benzyl rings of p-xylylenediaminium at 1622 cm⁻¹, as reported in other similar compounds [5, 6, 8] while in 4MBN are predicted between 1605 and 1563 cm⁻¹. Hence, these modes are assigned to the IR bands at 1609 and 1522 cm⁻¹. On the other hand, the C-C stretching modes are predicted by SQM calculations between 1293 and 1111 cm⁻¹ while the C-N stretching mode is predicted at 953 cm⁻¹ and assigned to the shoulder at 966 cm⁻¹. The deformation and torsion of benzyl ring are assigned in the expected 1000-200 cm⁻¹ region, as predicted by SQM calculations [5, 6, 8, 69].

3.6. Force constants

The harmonic force constants are interesting and useful parameters to analyze the forces of different bonds and, especially when the molecule under study presents monodentate coordination as in 4MBN. These constants were calculated for 4MBN in the gas phase from the harmonic force field with the SQMFF methodology and by using B3LYP/CC-PVTZ method and the Molvib program [16, 17, 18]. The scaled force constants for 4MBN in the gas phase are compared in Table 10 with reported for species with monodentate coordinations, such as p-xylylenediaminium bis(nitrate) [6] and chromyl nitrate [67]. These comparisons are interesting because these compounds present the same coordination modes but different chemical characteristics, thus p-xylylenediaminium bis(nitrate) (nitrate) is a hybrid as 4MBN [6] while chromyl nitrate is an inorganic compound [67]. Comparing first the constants for both hybrid species we observed practically the same values for the two species and only slight changes in the f(N=O) force constants values are observed. Such differences could be attributed in part to the different basis sets used in the calculations. When the f(N – O) and f(N=O) force constants values for 4MBN are compared with the corresponding to chromyl nitrate we observed that the f(N – O) force constant value is lower in 4MBN while the other f(N=O) force constant is lower in chromyl nitrate [67]. Obviously, these differences are quickly associated to different nature of atoms linked to NO₃ group because in chromyl nitrate this group is coordinated to Cr while in 4MBN is coordinated to H. Hence, the Cr atom is most electropositive than H and, for this reason, the coordination is stronger between Cr and O (Cr – O) than H and O (H – O) [67].

3.7. Molecular docking

With the development of computer tools in the last 20 years, molecular docking is becoming a very efficient tool for the determination of biological activities. The docking study is a critical step in understanding biological reactions and in drug design [54, 55, 56, 57, 58, 59]. The objective of the computational molecular docking was performed to find out the orientations in space and bonding conformations between ligands with the target receptor [58]. A bibliographic study shows that the protein amino acid oxidase (DAO) is usually used in the treatment of mental disorder. In this study, docking calculations was effected for targeted protein related to the treatment of schizophrenia. The prototypical DAO inhibitor has been shown to be
effective in improving neurocognitive symptoms [60] and in the treatment of this disease [61, 62]. Molecular docking was used to evaluate the activity of quarter ligands: 4MBN, BEZ, FAD and 98B described in the literature as potential inhibitors of DAO. These ligands and protein structures are extracted from the PDB (Protein Data Bank) [14]. This database contains thousands of protein structures obtained either by crystallography (X-ray) or by NMR.

Figure 25 and Figure 26 show the best pose which corresponds to the minimum energies of the ligands in the DAO protein and 2D interactions between the different complexes gained from the docking of all studied ligands inside DAO. The total energy, VDW interactions, electronics and H-bond values obtained are indicated in Table 1. As reported clearly in this table that the predominant interaction is of VDW type. DAO-FAD complex showed the highest total energy (−304.288 Kcal/mol), with interaction energies of the order of: E_{VDW} = -232.615 kcal/mol, E_{H-bond} = -71.272 kcal/mol and E_{electronic} = -0.400 kcal/mol. The total energy scores of 4MBN, 98B and BEZ are respectively equal to: -76,828 kcal/mol, -65,111 kcal/mol and -61,792 kcal/mol, respectively. As depicted in Figure 25, all three ligands have almost the same positions in the protein. Their VDW interactions are of the order of -50.987 kcal/mol, -58.135 kcal/mol and -47.198 kcal/mol, as well as their hydrogen bond energies are equal to -25.841 kcal/mol, -6.976 kcal/mol and -14,594 kcal/mol, respectively. In another important steps Figure 10. C and Figure 27 show the presence of several types of interactions such as: Pi-alkyl, Pi-anion, hydrogen bonds and conventional hydrogen interactions which exist between the ligands and residues. In fact, electron acceptor-donor interactions promote the formation of these bonds. Therefore, these interactions mediate the stabilization of the complex with the residues (inhibitor stability).

Molecular docking studies have evidenced that 4MBN penetrates well into the active sites of the receptor while the interactions observed between the DAO protein and the 4MBN ligands prove a good degree of inhibition against schizophrenia disease.

4. Conclusions

In this research, the hybrid 4MBN compound has been synthesized in order to study the influence of non-covalent interactions on its experimental infrared spectrum and on its structural, electronic, topological and vibrational properties. For these purposes, the experimental IR spectrum and the structure previously determined by X-ray diffraction were employed in combination with B3LYP/CC-PVTZ level of theory to optimize 4MBN in gas phase and in ethanol and aqueous solutions. Then, the complete vibrational assignments of 69 vibration modes expected for the most stable structure of 4MBN was performed by using the SMMF methodology together with the normal internal coordinates and scaling factors. Different computational and analytical methods, such as AIM, RDG, Hirsfeld surface analysis, NBO, MEP surfaces were used to describe the non-covalent interactions in 4MBN. The AIM analysis of topological parameters and Hirsfeld surfaces have showed the presence of two weak hydrogen bonds (N-H⋅⋅⋅O and C-H⋅⋅⋅O) in 4MBN while the study of bond orders support the higher value of N-H⋅⋅⋅O interaction. Hence, the monodentate coordination between cation and anion is also supported by the predicted strong IR band assigned to the N-O-H stretching mode of acid coordinate to NH2 group of 4MBN. The RDG reduced density gradient method makes it possible to demonstrate, in addition to hydrogen bonds, the presence of van der Waals-type interactions and the steric effect. Natural orbital analysis (NBO) has shown that LP (O) → σ*(O-H) interactions (hydrogen bonds) stabilize the structure. Likewise, electronic properties were performed using the TD-DFT method. The nucelophilic and electrophilic sites were identified by calculating the Molecular Electrostatic Potential Surface (MESP). They clearly explain the monodentate coordination between nitrate and methylbenzylammonium groups and its importance in the stabilization of 4MBN. The Frontier Molecule Orbital Analysis (FMOs) of 4MBN in ethanol and aqueous solutions suggest that this species is most reactive in water. The UV-Visible spectra were studied.
Figure 26. Best pose of (a) BEZ, (b) 98B and (c) FAD in the DAO protein.

Table 11. Docking calculation in DAO protein.

| Protein | Ligand | Total energy | VDW | H-bond | Electronic |
|---------|--------|--------------|-----|--------|------------|
| DAO     | FAD    | -304.288     | -232.615 | -71.272 | -0.400     |
|         | 4MBN   | -76.828      | -50.987 | -25.841 | 0          |
|         | 98B    | -65.111      | -58.135 | -6.9759 | 0          |
|         | BEZ    | -61.792      | -47.198 | -14.594 | 0          |
by both experimental and DFT calculation in ethanol. Finally, molecular docking reveals that the title compound could act as an inhibitor against schizophrenia disease.

Declarations

Author contribution statement

Mouna Medimagh; Silvia Antonia Brandán: Analyzed and interpreted the data; Wrote the paper.

Noureddine Issaoui; Omar Al-Dossary: Conceived and designed the analysis.

Soфиан Gatfaoui: Performed the experiments; Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data. Houda Marouani: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data. Marek. J. Wojcik: Conceived and designed the experiments; Analyzed and interpreted the data.

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Data availability statement

The authors do not have permission to share data.

Declaration of interests statement

The authors declare no conflict of interest.

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References

[1] C. Kashyap, S.S. Ullah, L.J. Mazumder, A.K. Guha, Non-covalent interaction in benzene and substituted benzene: a theoretical study, Comput. Theor. Chem. 1130 (2018) 134–139.

[2] M. Vimala, S.S. Mary, R. Ramalakshmi, S. Muruth, A. Irfan, Computational prediction of polar and non-polar solvent effect on the electronic property of N-BOC-Piperidine-4-Carboxylic acid, J. Mol. Liq. 341 (2021) 117222.

[3] S. Gatfaoui, H. Marouani, M. Rzaigui, 4-Methylbenzylammonium nitrate, Acta Crystallogr. Sect. E: Struct. Rep. Online 69 (9) (2013) o1453-o1453.

[4] L.S. Eder, D.J. Watkin, A. Cousson, Richard Ian Cooperb, Werner Pauluc, CRYSTALS enhancements: refinement of atoms continuously disordered along a line, on a ring or on the surface of a sphere, J. Appl. Crystallogr. 37 (2004) 545–550.

[5] M.V. Castillo, R.A. Rudyk, L. Davies, S.A. Brandan, 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, J. Mol. Struct. 1140 (2017) 2–11.

[6] S. Gatfaoui, N. Issaoui, S.A. Brandán, H. Marouani, Synthesis and characterization of p-sulfonilidiaminomethionin(nitrate). Effects of the coordination modes of nitrate groups on their structural and vibrational properties, J. Mol. Struct. 1151 (2018) 152–168.

[7] J. Kauštėtis, V. Alekso, M.A. Iramain, S.A. Brandán, Cation-anion interactions in 1-butyryl-3-methyl imidazolium nitrate liquid and their effect on their structural and vibrational properties, J. Mol. Struct. 1164 (2018) 1–14.

[8] S. Gatfaoui, A. Saganam, N. Issaoui, T. Roisnel, H. Marouani, Synthesis, experimental, theoretical study and molecular docking of 1-ethylpiperazine-1,4-dium bis(nitrate), Solid State Sci. 106 (2020) 106326.
[63] N. Issaoui, N. Rekik, B. Oujia, M.J. Wojcik, Anharmonic effects on theoretical IR line shapes of medium strong H(D) bonds, Int. J. Quant. Chem. 109 (3) (2009) 483–499.

[64] N. Issaoui, N. Rekik, B. Oujia, M.J. Wojcik, Theoretical infrared line shapes of H-bonds within the strong anharmonic coupling theory and Fermi resonances effects, Int. J. Quant. Chem. 110 (14) (2010) 2583–2602.

[65] N. Rekik, N. Issaoui, H. Ghalla, B. Oujia, M.J. Wojcik, IR spectral density of H-bonds. Both intrinsic anharmonicity of the fast mode and the H-bond Bridge. Part I: anharmonic coupling parameter and temperature effects, J. Mol. Struct.: Theochem 821 (2007) 1–3, 9 – 211.

[66] S.A. Brandán (Ed.), Nitrate: Occurrence, Characteristics and Health Considerations, Nova Science Publishers, Inc, 2012. Edited Collection.

[67] S.A. Brandán, in: Ken Derham (Ed.), A Structural and Vibrational Study of the Chromyl Chlorosulfate, Fluorosulfate, and Nitrate Compounds, vol. 1, Springer Science, Business Media B.V., Van Godewijckstraat, 30, 2012, p. 3311. GZ Dordrecht, Netherlands.

[68] M.V. Castillo, E. Romano, H.E. Lanús, S.B. Díaz, A. Ben Altabef, S.A. Brandán, Theoretical structural and experimental vibrational study of niobyl nitrate, J. Mol. Struct. 994 (2011) 202–208.

[69] D. Romani, S.A. Brandán, Structural and spectroscopic studies of two 1,3-benzothiazole tautomers with potential antimicrobial activity in different media. Prediction of their reactivities, Comput. Theor. Chem. (Theochem) 1061 (2015) 89–99.