Experimental IR and Raman Spectroscopy and DFT Methods Based Material Characterization and Data Analysis of 2- Nitrophenol

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Abstract

Vibrational characteristics of 2- nitrophenol have been investigated using experimental IR and Raman data and computational data using DFT method employing the 6-311++G** basis set available on Gaussian-09 software for the most stableconformer C-1. Complete vibrational assignments of the experimental IR and Raman bands have been proposed in light of the results obtained from the DFT computations and the PEDs computed using GAR2PED software. The optimized geometrical parameters suggest that the overall symmetry of the most stablemolecule is Cs. The molecule is expected to have three conformers. In the present article all the characterizations and the analyses of the lowest energy conformer of 2-NP have been studied. The charge transfer occurring in the molecule has been shown by HOMO–LUMO energy orbitals the energy gap of HOMO LUMO orbitals have been found 4.03eV. The mappings of electron density iso-surface with the electrostatic potential (ESP), has been carried out to get the information about the size, shape, charge density distribution and site of chemical reactivity of 2-NP. Current density and magnetic shielding of C-1 have been investigated. Some essential thermo molecular characteristics, namely, enthalpy, Gibb’s free energy, thermal energy, entropy, heat capacity, internal energy and the partition functions of the molecule have also been analyzed.

Keywords: Optimized structure; Conformers; Entropy; MESP; Magnetic shielding; 2-nitro-phenol

Introduction

Nitro phenols constitute a class of volatile organic compounds that is increasingly presented in urban as well as in natural environments [1-3]. These are important and versatile compounds in the industrial, agricultural and defence applications [4] and are frequently used as intermediates in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, rubber chemicals, lumper preservatives, photographic chemicals, etc. [5-8]. 2- Nitro-phenols (2-NP), in particular, poses significant health risks since it is a toxic to mammals, microorganisms and anaerobic bacteria. Its toxicity is thought to be due to the nitro group being easily reduced by the enzymes into nitro anion radical, nitroso and hydroxylamine derivatives [4]. Although extensive experimental and theoretical studies are reported on the structural and vibrational studies of mono-substituted phenols [9,10] dealing with their structural features, intra-molecular H-bonding parameters and the vibrational spectra [11-14], only few works of this kind exist on phenols [15-18]. In the present study we report the results of our probing into the application of the DFT based SQM method [19] to the vibrational analysis of hydrogen bonded systems. The main difficulty in such investigations is that the vibrational spectra of these compounds have not been completely analyzed even now and generally only rough assignments are available. Therefore, an investigation of the performance of the DFT-based SQM method has to be carried out simultaneously with a complete vibrational analysis of the molecule. This process was done successfully in the case of 2 6-difluorophenol earlier [20].

The 2-NP molecule, contains a strong intra-molecular (O) H......O(N) hydrogen bonding interaction which has been analyzed by various experimental and theoretical studies [21-31]. The extensive investigations corresponding to the vibrational description of 2-NP is not complete. Most of the numerous spectroscopic studies [24,31-33] focused on the vibrations from which the information can be carried out about the hydrogen bonding interaction, first of all on the OH stretching and OH torsion.

In the present work calculations have been made for the optimized molecular geometries, APT and Mulliken atomic charges and the fundamental vibrational wave numbers along with their intensities in the IR spectrum, Raman activities and the depolarization ratios of the Raman lines using the DFT (B3LYP) method employing the 6-311++G** basis set [34-38] available with Gaussian-09 software [39] for the lowest energy conformer C-1 of 2-NP. The experimental IR and Raman spectral data have been analyzed in the light of the computed fundamentals and the corresponding PEDs calculated, using the GAR2PED software [40]. For the calculation of the PEDs the vibrational problem was set up in terms of the internal coordinates for the GAR2PED software. HOMO-LUMO, total density plots, electrostatic potential (ESP) surface and their arrays have been investigated. The essential NLO as well as thermo molecular parameters have been investigated and using NMR analysis employing Continuous Set of Gauge Transformation (CSGT) method electro-magnetic characteristics of 2-NP have been investigated.

Experimental Detail

One to two milligrams of the pure (98%), a yellow crystalline solid in powdered form, 2-nitro phenol, purchased from Sigma Aldrich Chemical Co. (USA), was used to record the Raman spectra using a home assembled micro-Raman spectrometer: Horiba Jobin-Yvon Spectrometer (iHR-320) system with an inverted microscope (Nikon Eclipse Ti-U, Japan). A Diode laser (Star bright Diode Laser, Torsana Laser Tech, Denmark) of λ=785 nm used as source to illuminate the

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sample sandwiched between quartz cover slip and borosilicate glass slide. The sample was mounted on the microscope stage and a 60X microscope objective have been used to focus the laser beam and to record the Raman signals. A liquid Nitrogen cooled Symphony CCD detector have been utilized to collect the Raman scattered radiation. The spectral range of the micro-Raman have been kept 200-3100 cm\(^{-1}\) with resolution 5 cm\(^{-1}\), accuracy 2 cm\(^{-1}\) at spectrometer slit width 100 µm. In order to record a better Raman spectrum, data were obtained using a laser power of 47mW with the acquisition times of 5 min.

FTIR spectrum of 2-NP sample was recorded using KBr pellet. The 10 mg of the 2-NP sample was weighed and properly mixed with 990 mg KBr. This mixture was then pelleted using KBr pellet maker by applying pressure using 8 tons weight for half an hour. FTIR spectrum was recorded using the above mentioned pellet at room temperature, using an FTIR spectrometer (Jasco 6300) with a standard source. The spectra have been recorded in the range of 400-4000 cm\(^{-1}\). The 200 scans have been taken with 2 cm\(^{-1}\) spectral resolution for all the three samples.

### Computational Details

To optimize the structure of 2- NP the following procedure was adopted. Initially the benzene ring (including H atoms only) was optimized. After this an OH group was added to a carbon atom of benzene ring and the structure was optimized. With this structure a nitro group was added to the ortho position of phenolic group (Figure 1). This structure was further optimized. In the optimized structure if hydrogen atom of the OH group faces the NO\(_2\) group the structure remains planar. However, if the hydrogen atom of the OH group is

The bond lengths of C1-C2, C3-O11, C4-N13 and C5-C6 respectively are found to be larger in the most stable conformer than both the C-1 and C-2 conformers. Also, angle \(\alpha\) (C4-C3-O11) is found to be larger while angle \(\alpha\) (O11-N13-O12) is found to be shorter in the most stable conformer than the other two (Table 2). These conformational discrepancies may be due to intra-molecular hydrogen bonding in the most stable conformer and also due to instability of conformers C-2 and C-3 respectively.

### APT charges

Atomic polarizability tensor (APT) charge is interpreted as the sum of charge tensor and charge flux tensor, leading to a charge-flux charge model [43,44]. The APT atomic charges (in unit of e) at various atomic sites of 2-NP are collected in Table 3. The carbon atoms belonging to the ring have alternately positive and negative APT charges with different magnitudes. All the H and N atoms have positive APT charges with different magnitudes, while the O atoms possess negative and different magnitudes of APT charges. The N atom possesses the highest magnitude which is connected directly to the ring and the two O atoms. It is also noticeable that the magnitude of the APT charge on

![Figure 1: Optimized structure of 2-Nitro phenol (C-I).](image-url)
Cᵢ attached to the OH group is the largest of all the C atoms. Also, it is interesting to note that the N atom possesses positive APT charge. The magnitude of the APT charge on Hᵢ is the largest of all the H atoms. The O atoms possess almost equal APT charges.

**Mulliken atomic charges**

Mulliken atomic charge calculation plays an important role in the application of quantum chemical calculation to molecular systems, because the atomic charges affect the dipole moment, polarizability, electronic structure, and much more properties of the molecular systems. Mulliken atomic charges (in unit of e) at various atomic sites of 2-NP are collected in Table 3 from which it can be noticed that all the carbon atoms except Cᵢ and Cₒ have negative Mulliken atomic charges. One of the O atoms attached to the N atom with a single bond possesses positive Mulliken atomic charge. However, it is an electronegative atom like N and O atoms. The H atoms possess positive Mulliken atomic charge. The Mulliken atomic charge at the C atom attached to the OH group is the largest of all the C atoms and the H atom of the OH group possesses the largest Mulliken atomic charge of all the H atoms in the C-1 conformation.

**ESP charges**

The studies of effective atomic charges play a crucial role in the application of quantum mechanical computations to the molecular systems. Despite the conceptual problems associated with the dividing up overall molecular charge density in atomic contributions, and all the conventional problems related to the finding of convenient and robust algorithm applicable to a wide range of the systems [45]. The beauty of effective atomic charges as the parameters for the calculation of electrostatic interactions in a various molecular mechanics simulation packages is certainly one essential area of application. Partial atomic charges play a different, but even more important, role in the qualitative rationalization of organic and inorganic reactivity [46]. The molecular electrostatic potential (ESP) derived charges are those of effective atomic charges as the parameters for the calculation of molecular electrostatic potential (MEP) at a number of points around the molecule at a (large) number of grid points using Mergen-Singh-Kollman (MK) scheme [47].

The molecular ESP derived charges at various atomic sites of 2-NP have been contained in the Table 3. Clearly, the ESP charges at all the C atoms except Cᵢ, have negative and small but different value while Cᵢ atom, attached to OH group of 2-NP, have positive and largest value amongst all the C atoms of 2-NP. All the H atoms on the ring possess smaller but positive ESP charges while H atom of OH group attains positive and largest value of all the H atoms in the molecule. The O atoms possess negative ESP charges. The O atom of OH group attains largest negative value (-0.590398 e) while N atom of NO₂ group attains largest positive value (0.681548 e) of ESP charges in 2-NP.

**Vibrational assignments**

The 2-NP molecule is a 15 atomic molecule with 39 normal modes of vibration in which 30 modes are associated with the benzene ring which are 12 stretching modes - 3 planar ring deformation modes, 3 non planar ring deformation -Φ(R), 6 planar deformation modes -β(C-H) and 6 non-planar deformation modes -ν(κ(C-H)) out of which 2 of each i.e. β(C-H) and γ(C-H) become β(C-N), β(C-O) and γ(C-N), γ(C-O) respectively. The three normal modes of OH group are: OH stretching -ν(OH), OH torsion -τ(OH) and C-O-H angle bending. The six normal modes of the nitro group are: anti-symmetric NO₂ stretching -ν(NO₂), symmetric NO₂ stretching -ν(NO₂), NO₂ rocking -ρ(NO₂), NO₂ wagging -ω(NO₂), NO₂ scissoring -δ(NO₂) and NO₂ torsion -τ(NO₂).

The calculated and observed vibrational frequencies along with the corresponding PEDs and vibrational assignments are collected in Table 4. The experimental and calculated IR and Raman spectra are reproduced in Figure 3-6. The normal mode assignments have been discussed under the following sections: (i) The phenyl ring modes (30), (ii) The OH group modes (3) and (iii) The NO₂ group modes (6).

**Phenyl ring modes (30)**: The four C-H stretching modes ν(C-H) are assigned to the frequencies 3034 (ν(ν₁)), 3181 (ν(ν₂)), 3186 (ν(ν₃)) and 3205 (ν(ν₄)) cm⁻¹ which correspond dominantly to the modes ν(C₁-H₇), ν(C₆-H₁₀), ν(C₃-H₈) and ν(C₅-H₉) respectively. The C-H stretching modes -ν(R) (C₁-H₇), -ν(R) (C₆-H₁₀), -ψ(R), -ψ(R) (C₃-H₈), -ψ(R) (C₅-H₉) and -ψ(R) (C₁-H₇) were assigned to the frequencies 3070, 3088, 3096 and 3117 cm⁻¹ [41] and also to the frequencies 3208, 3229 and 3245 cm⁻¹ [48]. The C-H stretching vibrations are pure and highly localized modes. There are 6 C-C stretching modes ν(R) due to the phenyl ring which are identified as the computed frequencies 1002 (ν(ν₁)), 1051 (ν(ν₂)), 1056 (ν(ν₃)), 1420 (ν(ν₄)), 1547 (ν(ν₅)), 1586 (ν(ν₆)) cm⁻¹. These modes are strongly coupled with many other modes. These modes were assigned to the frequencies 1020, 1581 and 1620 cm⁻¹ [41] and also to the frequencies 1369, 1551, 1584 and 1612 cm⁻¹ [48]. The C-N and O-C stretching modes occur at frequencies 667 (ν(ν₁)), 1442 (ν(ν₂)) cm⁻¹ corresponding to the modes ν(C₆-N₁₅) and ν(C₃-N₈) respectively. These modes are also coupled with many other modes. The C-O stretching mode in the literature was found to be corresponding to the frequency 1269 [41] and 1464 cm⁻¹ [48].

There are three ring planar deformation modes which we assign as the frequencies 865 (ν(ν₁)), 559 (ν(ν₂)) and 373 (ν(ν₃)) cm⁻¹. These modes are coupled with other modes as shown in the Table 4. The three ring non-planar deformation modes are correlated to the frequencies 657 (ν(ν₆)), 413 (ν(ν₈)) and 141 (ν(ν₉)) cm⁻¹ corresponding to modes 4 and 16(a,b) of the

### Table 1: Total and relative energies of all the possible conformers of 2-NP.

| Conformers | Point group | Total energy (Hartree) | Relative energy (Hartree) | Hartree | Temp. (K) | kcal/mol |
|------------|-------------|------------------------|--------------------------|---------|-----------|----------|
| C-1        | C₁          | -512.12911314          | 0                        | 0       | 0         | 0        |
| C-2        | C₀          | -512.11230617          | 0.01678697               | 5300.9405365 | 10.53984965 |        |
| C-3        | C₁          | -512.10755721          | 0.02155593               | 6806.88848 | 13.52655319 |        |

Figure 2: Front and side views of conformer C-2 {a(i)} & a(ii) and conformer C-3 {b(i)} & b(ii) of 2-NP.
| S.No. | Parameters | B3-LYP/6-311++G** | ED@ | MP2(FC) / 6-31G* |
|-------|------------|-------------------|------|------------------|
| 1     | r(C1-C2)   | 1.382             | 1.389| 1.389            |
| 2     | r(C1-C2)   | 1.404             | 1.396| 1.396            |
| 3     | r(C1-C3)   | 1.084             | 1.084| 1.084            |
| 4     | r(C1-C6)   | 1.404             | 1.400| 1.400            |
| 5     | r(C1-H7)   | 1.063             | 1.066| 1.066            |
| 6     | r(C2-C3)   | 1.415             | 1.405| 1.405            |
| 7     | r(C2-H8)   | 1.081             | 1.082| 1.082            |
| 8     | r(C3-C4)   | 1.380             | 1.387| 1.387            |
| 9     | r(C3-O11)  | 1.219             | 1.221| 1.221            |
| 10    | r(C4-C5)   | 1.248             | 1.228| 1.228            |
| 11    | r(C4-N13)  | 121.031           | 120.5| 120.5            |
| 12    | r(C5-C6)   | 119.217           | 119.3| 119.3            |
| 13    | r(C6-H10)  | 120.2             | 120.2| 120.2            |
| 14    | r(O11-H12) | 0.982             | 0.964| 0.969            |
| 15    | r(N13-O14) | 121.1             | 118.1| 118.1            |
| 16    | α(C2-C1-C6) | 119.741       | 120.0| 120.0            |
| 17    | α(C2-C1-H7) | 120.2         | 120.2| 120.2            |
| 18    | α(C3-C2-C3) | 117.659       | 117.8| 117.8            |
| 19    | α(C3-C2-H8) | 117.714       | 122.0| 122.0            |
| 20    | α(C3-C1-C6) | 124.600       | 120.2| 120.2            |
| 21    | α(C3-C1-C2) | 121.165       | 121.1| 121.1            |
| 22    | α(C3-C1-H7) | 120.816       | 121.5| 121.5            |
| 23    | α(C3-C2-C3) | 118.019       | 117.4| 117.4            |
| 24    | α(C3-C2-H8) | 119.999       | 120.3| 120.3            |
| 25    | α(C3-C1-C6) | 119.747       | 121.5| 121.5            |
| 26    | α(C3-C1-C2) | 119.360       | 119.2| 119.2            |
| 27    | α(C3-C1-H7) | 120.505       | 120.7| 120.7            |
| 28    | α(C3-C2-C3) | 120.135       | 120.1| 120.1            |
| 29    | α(C3-C2-H8) | 107.393       | 109.5| 109.5            |
| 30    | α(C3-C1-C6) | 119.320       | 118.1| 118.1            |
| 31    | α(C3-C1-C2) | 117.914       | 116.9| 116.9            |
| 32    | α(C3-C1-H7) | 122.766       | 124.9| 124.9            |
| 33    | α(C3-C2-C3) | 0.004         | 0.8  | -0.8             |
| 34    | α(C3-C2-H8) | 179.999       | -179.0| 179.0            |
| 35    | α(C3-C1-C6) | 179.997       | -179.6| 179.6            |
| 36    | α(C3-C1-C2) | -0.008        | 0.6  | -0.6             |
| 37    | α(C3-C2-C3) | -0.011        | 0.0  | -0.0             |
| 38    | α(C3-C2-H8) | 180.001       | 179.9| -179.9            |
| 39    | α(C3-C1-C6) | -180.004      | -179.7| 179.8            |
| 40    | α(C3-C1-C2) | 0.008         | 0.2  | -0.2             |
| 41    | α(C3-C2-C3) | -0.004        | -0.4 | 0.4              |
| 42    | α(C3-C2-H8) | -180.000      | -178.4| 178.4            |
| 43    | α(C3-C1-C6) | 179.999       | -179.4| 179.4            |
| 44    | α(C3-C1-C2) | 0.004         | 1.4  | -1.4             |
| 45    | α(C3-C2-C3) | 0.011         | -0.8 | 0.8              |
| 46    | α(C3-C2-H8) | 180.029       | 179.3| -179.3            |
| 47    | α(C3-C1-C6) | 180.007       | 177.3| -177.3            |
| 48    | α(C3-C1-C2) | -0.033        | -2.7 | 2.7              |
| 49    | α(C3-C2-C3) | 180.028       | 2.2  | -2.1             |
| 50    | α(C3-C2-H8) | 0.032         | -175.8| 175.9            |
| 51    | α(C3-C1-C6) | -0.018        | 1.5  | -1.5             |
| 52    | α(C3-C1-C2) | -180.007      | -178.6| 178.6            |
| 53    | α(C3-C2-C3) | 180.020       | 178.5| -178.5            |
| 54    | α(C3-C2-H8) | 0.031         | 1.4  | -1.4             |
Table 2: Computed and observed geometrical parameters of 2-NP (C-1).

| Atoms         | APT charges | Mulliken atomic charges | ESP charges | ESP Potentials |
|---------------|-------------|-------------------------|-------------|----------------|
| (C-1)         | (C-2/C-3)   | (C-1)                   | (C-2/C-3)   | C-1            |
| C_6           | 0.168082    | 0.109390                | -0.251868   | -0.187756      | 14.73524 -14.73734 |
| C_2           | -0.168431   | -0.166562               | -0.165953   | 0.112268       | -0.242264 -0.276459 |
| C_1           | 0.617390    | 0.569682                | -0.630033   | -0.280495      | 0.387901 0.311740 -14.66298 -14.66522 |
| C_5           | -0.369569   | -0.186726               | 0.559561    | -0.248181      | -0.069178 0.011254 -14.69304 -14.70101 |
| C_13          | 0.089874    | 0.070105                | 0.139598    | 0.278052       | -0.166961 -0.210985 -14.73417 -14.73785 |
| C_12          | -0.238821   | -0.186101               | -0.249269   | -0.259811      | -0.137599 -0.132966 -14.74581 -14.74815 |
| C_11          | 0.051609    | 0.049260                | 0.175404    | 0.172879       | 0.138456 0.134908 -1.07628 -1.07627 |
| C_10          | 0.067916    | 0.037818                | 0.205976    | 0.138330       | 0.181123 0.149018 -1.07645 -1.06388 |
| C_9           | 0.102578    | 0.094642                | 0.231910    | 0.231315       | 0.166648 0.166660 -1.07216 -1.07586 |
| C_8           | 0.049672    | 0.048614                | 0.185472    | 0.174964       | 0.136837 0.133989 -1.08086 -1.08272 |
| O_8           | -0.726207   | -0.645764               | -0.185498   | -0.177027      | -0.590398 -0.522159 -22.31645 -22.30600 |
| H_13          | 0.390488    | 0.297918                | 0.290132    | 0.270747       | 0.471626 0.47133 -0.95701 -0.94374 |
| N_14          | 1.350233    | 1.219919                | -0.296760   | -0.207132      | 0.681548 0.736291 -18.13866 -18.15683 |
| O_15          | -0.688553   | -0.677157               | 0.004856    | -0.034067      | -0.388638 -0.452560 -22.32424 -22.34426 |
| O_16          | -0.705060   | -0.635038               | -0.020819   | 0.016214       | -0.480781 -0.415470 -22.32304 -22.34320 |

*Charges are in the unit of e

Table 3: APT, Mulliken and ESP fitted (MK scheme) atomic charges and molecular electrostatic potentials at different atomic sites of 2-NP (C-1).
The four C-H planar deformations \( \gamma(\text{C-H}) \) and four C-H non-planar deformations \( \gamma(\text{C-N}) \) are assigned at the frequencies 1106(\( \nu_17 \)), 1158(\( \nu_15 \)), 1260(\( \nu_13 \)), 1131(\( \nu_16 \)) cm\(^{-1}\) respectively. These modes were found to occur at frequencies 667(\( \nu_8 \)), 683(\( \nu_7 \)) and 690 cm\(^{-1}\) corresponding to the modes \( \beta(\text{C}1-\text{H}7), \beta(\text{C}2-\text{H}8), \beta(\text{C}5-\text{H}9), \beta(\text{C}4-\text{H}10) \) respectively. These modes are strongly coupled with various vibrational modes. The modes were found to occur at frequencies 522(\( \nu_32 \)), 533(\( \nu_31 \)) and 542 cm\(^{-1}\) respectively. The NO\(_2\) group modes (6 modes): There are six modes of vibrations corresponding to the frequencies 1311(\( \nu_9 \)), 1377 cm\(^{-1}\) and is strongly coupled with other modes of vibrations. The C-C-H angle bending- \( \alpha(\text{C}3-\text{O}11-\text{H}12) \) mode is found to correspond to the frequency 1349(\( \nu_11 \)) cm\(^{-1}\) and also to the frequencies 1377 cm\(^{-1}\) and 1386(\( \nu_12 \)) cm\(^{-1}\). The NO\(_2\) torsion-\( \tau(\text{NO}_2) \) occurs at frequency 720(\( \nu_26 \)) cm\(^{-1}\) in our work and at the frequency 711 cm\(^{-1}\) in the literature. The benzene molecule. These modes were found to occur at frequencies 152, 297 and 565 cm\(^{-1}\). The four C-H planar deformations \( \beta(\text{C-H}) \) and four C-H non-planar deformations \( \gamma(\text{C-H}) \) are assigned at the frequencies 1160(\( \nu_6 \)), 1177(\( \nu_5 \)), 1260(\( \nu_4 \)), 1131(\( \nu_3 \)), 978(\( \nu_2 \)), 849(\( \nu_1 \)), 956(\( \nu_0 \)) and 760(\( \nu_{-1} \)) cm\(^{-1}\) corresponding to the modes \( \beta(\text{C}2-\text{H}_5), \beta(\text{C}3-\text{H}_5), \beta(\text{C}4-\text{H}_5), \beta(\text{C}5-\text{H}_5), \gamma(\text{C}-\text{H}_5), \gamma(\text{C}-\text{H}_6), \gamma(\text{C}-\text{H}_7) \) and \( \gamma(\text{C}-\text{H}_8) \) respectively. These modes are coupled with many other modes. The modes \( \beta(\text{C}-\text{N}), \gamma(\text{C}-\text{N}), \beta(\text{C-O}) \) and \( \gamma(\text{C-O}) \) correspond to the frequencies 285(\( \nu_2 \)), 240(\( \nu_1 \)), 240(\( \nu_0 \)) and 240 cm\(^{-1}\) respectively. These modes are strongly coupled modes. The modes \( \beta(\text{C}-\text{N}) \) and \( \beta(\text{C-O}) \) were assigned to the frequencies 298 and 432 cm\(^{-1}\). The four C-H planar deformations \( \beta(\text{C-H}) \) and four C-H non-planar deformations \( \gamma(\text{C-H}) \) are assigned at the frequencies 1160(\( \nu_6 \)), 1177(\( \nu_5 \)), 1260(\( \nu_4 \)), 1131(\( \nu_3 \)), 978(\( \nu_2 \)), 849(\( \nu_1 \)), 956(\( \nu_0 \)) and 760(\( \nu_{-1} \)) cm\(^{-1}\) corresponding to the modes \( \beta(\text{C}2-\text{H}_5), \beta(\text{C}3-\text{H}_5), \beta(\text{C}4-\text{H}_5), \beta(\text{C}5-\text{H}_5), \gamma(\text{C}-\text{H}_5), \gamma(\text{C}-\text{H}_6), \gamma(\text{C}-\text{H}_7) \) and \( \gamma(\text{C}-\text{H}_8) \) respectively. These modes are coupled with many other modes. The modes \( \beta(\text{C}-\text{N}), \gamma(\text{C}-\text{N}), \beta(\text{C-O}) \) and \( \gamma(\text{C-O}) \) correspond to the frequencies 285(\( \nu_2 \)), 240(\( \nu_1 \)), 240(\( \nu_0 \)) and 240 cm\(^{-1}\) respectively. These modes are strongly coupled modes. The modes \( \beta(\text{C}-\text{N}) \) and \( \beta(\text{C-O}) \) were assigned to the frequencies 298 and 432 cm\(^{-1}\).

### O-H group modes (3 modes): The OH stretching \( \nu(\text{O}-\text{H}_) \) mode corresponds to the frequency 3453(\( \nu_1 \)) cm\(^{-1}\). The O-H stretching vibration is pure and highly localized mode. The O-H stretching mode was found to correspond to the frequency 3255(\( \nu_1 \)) cm\(^{-1}\) and to the frequency 3308 cm\(^{-1}\). The torsion of the OH group - \( \tau(\text{C}2-\text{O}1) \) occurs at frequency 720(\( \nu_4 \)) cm\(^{-1}\) in our work and at the frequency 711 cm\(^{-1}\) and is strongly coupled with other modes of vibrations. The C-O-H angle bending- \( \alpha(\text{C}2-\text{O}1-\text{H}_2) \) mode is found to correspond to the frequency 1349(\( \nu_1 \)) cm\(^{-1}\) and also to the frequencies 1377 cm\(^{-1}\) and 1386(\( \nu_12 \)) cm\(^{-1}\). The NO\(_2\) group modes (6 modes): There are six modes of vibrations due to the NO\(_2\) group, namely, asymmetric NO\(_2\) stretching- \( \nu(\text{NO}_2) \), symmetric NO\(_2\) stretching- \( \nu(\text{NO}_2) \), asymmetric NO\(_2\) stretching- \( \nu(\text{NO}_2) \), NO\(_2\) rocking- \( \nu(\text{NO}_2) \), NO\(_2\) wagging- \( \tau(\text{NO}_2) \), NO\(_2\) scissoring- \( \nu(\text{NO}_2) \) and NO\(_2\) torsion- \( \tau(\text{NO}_2) \) which correspond to the frequencies 1511(\( \nu_1 \)), 1226(\( \nu_4 \)), 542(\( \nu_1 \)), 683(\( \nu_0 \)), 819(\( \nu_0 \)) and 74(\( \nu_0 \)) cm\(^{-1}\) respectively. The NO\(_2\) torsion- \( \tau(\text{NO}_2) \) is slightly coupled with \( \tau(\text{C}2-\text{O}1) \) and the other five modes strongly coupled with various vibrational modes. The modes \( \nu(\text{O}-\text{N}_2) \),...
νs(NO$_2$), ω(NO$_2$), δ(NO$_2$) and τ(NO$_2$) were found to correspond to the frequencies 1560, 1294, 741, 818 and 75 cm$^{-1}$ [41] and also 1531, 1258, 702, 825 and 165 and also ρ(NO$_2$) corresponds to the frequency 505 cm$^{-1}$ [48].

Comparative study of vibrational modes for the three conformers: The computed vibrational fundamentals of the three conformers of 2-NP together with their respective differences have been collected in Supplementary material (Table-S1). It could be seen that the modes τ(C-OH) and ν(O-H) of the OH group show very large frequency differences (in the range 350-400 cm$^{-1}$). Also, the modes τ(C$_n$-N$_n$), β(C$_n$-O$_n$), ω(NO$_2$) α(C$_n$-O$_n$-H$_n$) and ν$_s$(NO$_2$) show frequency differences of the order of a few tens of a wave number. Clearly, major contribution for this frequency difference is expected to come from H bonding between H$_n$ and O$_n$ atoms in the conformer C-1 which is absent in the conformers C-2 / C-3. The phenyl ring modes Φ$_3$(R),α$_3$(R), Φ$_2$(R), γ(C$3$-H$_3$) and ν(C$3$-H$_3$) in the C-1 conformer have higher magnitudes than the corresponding modes in the conformers C-2 / C-3. However, the modes ω(NO$_2$), β(C$_n$-O$_n$), ν(O$_n$-H$_n$), Φ$_1$(R), ν$_s$(C$_n$-O$_n$), ν(R) and β(C$_n$-H$_n$) have higher frequencies in the conformers C-2 / C-3 than their corresponding modes in the most stableone.

The IR intensities and Raman activities for each of the three conformers are collected in Supplementary material (Table-S2). It is noticeable that the IR intensities for the C-1 conformer are much higher than those of the C-2/C-3 conformers for the modes ν(O$_1$-H$_1$), ν(C$_2$-O$_2$), vs(NO$_2$), β(C$_n$-H$_n$), β(C$_n$-H$_n$), ω(NO$_2$), δ(NO$_2$), ρ(NO$_2$) and ρ(C$_n$-N$_n$) (S$_2$).

The IR intensities for the modes α(C$_3$-O$_1$-H$_12$), vs(N$_1$3-O$_1$4), τ(C$_3$-O$_1$1), α(C$_3$-O$_1$1), ν(C$_n$-H$_n$), ν(C$_n$-H$_n$), vs(NO$_2$), α(R), γ(C$_n$-H$_n$),β(C$_n$-H$_n$),δ(NO$_2$) β(C$_n$-O$_n$), ν(C$_n$-H$_n$) and ν(C$_n$-N$_n$) for the conformers C-2/C-3 are much higher than the conformer C-1. One could see the major differences in the Raman activities for the modes vs(NO$_2$), ν(C$_n$-O$_n$), α(C$_n$-O$_n$-H$_n$), ν(C$_n$-H$_n$), ν(R) ν(C$_n$-H$_n$), α$_s$(NO$_2$), ν(C$_n$-O$_n$-H$_n$), ν(C$_n$-H$_n$), β(NO$_2$), β(C$_n$-H$_n$), β(C$_n$-H$_n$) and β(C$_n$-N$_n$). Such discrepancies could be due to the hydrogen bonding in the conformer C-1 and the non-planar geometry of the C-2/C-3 conformers of 2-NP. The highest IR intensity and Raman activity for C-1 occur for the modes ν(O$_1$-H$_1$) and ν(C$_2$-H$_2$) respectively and those for C-2/C-3 for vs(NO$_2$) and ν(C$_n$-H$_n$) respectively. From the above discussion it is clear that the intra-molecular H-bonding plays a crucial role in the molecular conformation.

HOMO–LUMO energy gap

The HOMO and LUMO studies are very important for quantum chemistry. These orbitals are also known by the name frontier orbitals, because they lie at the outermost boundaries of the electrons of the molecules. Both the HOMO and the LUMO are the main orbitals that take part in the chemical stability [49]. The kinetic stability of the molecule is measured in terms of energy gap DE [32,50] and the difference of the energies of the HOMO and LUMO is a measure of the excitability of the molecule, the smaller the energy, more easily it can be excited and vice versa. The lower HOMO and LUMO energy gap explains the eventual CT interaction taking place within the molecule, which is responsible for the bioactivity of the molecule. The larger the value of the energy gap the higher the kinetic stability and lower the chemical reactivity because it is energetically unfavorable to add electrons to a high lying LUMO, to remove electrons from a low lying HOMO and so to form the activated complex of any potential reaction [33]. The sketch of the atomic orbital compositions of the frontier MOs are shown in Figure 7. The green and red solid regions in Figure 7 represent the MOs with completely opposite phases. The present calculations predict that the energy gap (DE) of the 2-NP, i.e. the transition energy from HOMO to LUMO of the 2-NP is 0.148189 a.u. This electronic transition corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from HOMO to LUMO.
**Figure 6:** Calculated Raman spectra of 2-nitrophenol in two parts of Raman shifts.

**Figure 7:** The atomic orbital compositions of the frontier MO of 2-NP (C-I).

**Volatility descriptors**

A molecule having high ionization potential ($V_p$) or electron affinity ($V_a$) loses or admits electron hardly [51,52]. By Koopmans’ approximation [53,54], the ionization potential and electron affinity of any molecule can be calculated using the relations,

$$V_p = -E_{HOMO}$$

$$V_a = -E_{LUMO}$$

Koopman’s theorem for closed-shell molecules [54] results in the hardness of the molecule;

$$\eta = (V_p - V_a) / 2$$

The chemical potential of the molecule;

$$\mu = -(V_p + V_a) / 2$$

The softness of the molecule;

$$S = 1 / 2 \eta$$

The electro negativity of the molecule;

$$\chi = (V_p + V_a) / 2$$

The electro-phlicity index of the molecule;

$$\omega = \mu^2 S$$

Using the above relations we find the electro molecular characteristics for 2-NP has been presented in Table-5.

**NLO characteristics:** Static polarizability and first order hyperpolarizability

Quantum chemical computational theory has been shown to be essential in the description of the relationship between the electronic structure of the systems and its NLO response [55]. The NLO activities provide the key functions for frequency shifting, optical switching, optical modulation and optical logic to develop the technologies for the communication, signal processing and optical interconnections [56].

The electric dipole moment ($\mu$), the polarizability ($\alpha$) and the hyper polarizability ($\beta$) of the 2-NP molecule have been calculated by finite field method using DFT-B3LYP method employing 6-311++G(d,p) basis set for the isolated molecule, the origin of the Cartesian coordinate system ($x, y, z$) = (0, 0, 0) was chosen at own centre of mass of 2-NP.

In the presence of an external electric field, the energy of a system is a function of the field and the first hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components using the Klein man symmetry [57]. The matrix can be given in the lower tetrahedral format. Clearly, the lower part of the 3x3x3 matrices is a tetrahedral. The components of $\beta$ are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. If the external field is weak and homogeneous, this expansion is as given below,

$$E = E^0 - \mu_i F_i - 1/2 (\alpha_{ij} F_i F_j - 1/6 (\beta_{ijk} F_i F_j F_k) + \ldots)$$

Here, $E^0$ is the energy of the unperturbed molecules, $F_i$ is the field at the origin, $\mu_i, \alpha_{ij}$ and $\beta_{ijk}$ are the components of dipole moment, polarizability and first hyperpolarizability, respectively.

The total static dipole moment $\mu$, the mean polarizability $\alpha_0$, the anisotropy of the polarizability $\Delta \alpha$ and the mean first hyperpolarizability $\beta_0$, using the $x, y$ and $z$ components are defined as;

- Dipole moment;
  $$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

- Static polarizability;
  $$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3$$

- The total polarizability;
  $$\Delta \alpha = (1/\sqrt{2}) \{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2] + 6(\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2)\}$$

- First order hyperpolarizability;
  $$\beta_0 = \left[ \frac{1}{3} \sum \beta_{ijk}^2 \right]^{1/2}$$

Where

- $\beta_{xx} = (\beta_{xxx} + \beta_{xxy} + \beta_{xxz})$
- $\beta_{yy} = (\beta_{yxx} + \beta_{yy} + \beta_{yyz})$
- $\beta_{zz} = (\beta_{zz} + \beta_{zxy} + \beta_{zzz})$

$$E_{LUMO} = -3.18 \text{ eV}$$

$$E_{HOMO} = 4.03 \text{ eV}$$

$$E_{SOMO} = -7.22 \text{ eV}$$
The static polarizability $\alpha_0$ (91.966 au) and total polarizability $\Delta \alpha$ (9483.787 au) of the 2-NP together with all its components and perturbation to all its components, first order hyperpolarizability ($\beta = 426.118$ au) and its components and the total as well as components of the dipole moment have been tabulated in the Table-5.

**Electrostatic potential**

The electrostatic potential (ESP) is the tool which is used to study the intermolecular association and molecular properties of small molecules, actions of drug molecules and their analogues, the biological function of haemoglobin and enzyme catalysis [33,58-61]. ESP is widely used as the reactivity map displaying most probable regions for the electrophilic attack of charged point-like reagents on organic molecules [62]. The values and spatial distribution of ESP are in fact responsible for the chemical behaviour of an agent in a chemical reaction. They strongly influence the binding of a substrate to its active site. ESP is typically visualized through mapping its values onto the molecular ED. The different values of the electrostatic potential at the surface are represented by different colors; the red represents regions of the most negative electrostatic potential, the blue represents regions of the most positive electrostatic potential and the green represents regions of zero potential. Potential increases in the order red, orange, yellow, green and blue. While the negative electrostatic potential corresponds to an attraction of the proton by the concentrated ED in the molecule (and is colored in shades of red), the positive electrostatic potential corresponds to the repulsion of the proton by atomic nuclei in regions where a low ED exists and the nuclear charge is incompletely shielded (and is colored in shades of blue). The total density plot and its array of the 2-NP are shown in the Figure 8. The molecular ESP values, corresponding to Merge-Singh-Koll man scheme [47], of the 2-NP molecule have been arranged in the Table 3. Also, the diagrammatic demonstration of the MEP via map and its contour has been shown in Figure 9. These Figs provide a visual representation of the chemically active sites and comparative reactivity of atoms. The ESP plots and the value arranged in the Table 3 predict that there are no regions of positive and zero potential present in the molecule. Also, the Figure 9 and the data in the Table 3 predict that the sites associated with the functional groups, namely, OH and NO$_2$ groups are most reactive sites for the nucleophilic reactions.

**Thermo molecular characteristics**

The studies of some thermo molecular characteristics, namely, zero point vibrational energy, enthalpy, Gibb’s free energy, internal energy, entropy, heat capacity, thermal energy and the partition functions etc. have been found to play crucial role in the material characterization. We have presented some thermal parameters in Table 6. It can be noticed that all of the analysed thermodynamic parameters are increasing with the temperature but G is found to decrease with T [Figure 10(a)-10(h)] that all of the analysed thermodynamic parameters are increasing with temperature but G is found to decrease with T [Figure 10(a)-10(h)]

$$X_0 = \begin{bmatrix} \text{[Log}_{10}(r,c,v)_{\text{int. site}} = 23.9202 + (0.0388)T - (11.04)T^2} \end{bmatrix}$$

$$S_{\alpha} = 52.5299 + (0.1240)T - \left(2.8791 \times 10^{-5}\right)T^2 \quad \left(R^2 = 0.99999\right)$$

$$\epsilon_{p,\text{edt}} = -0.9985 + (0.1195)T - (5.4209)T^2 \quad \left(R^2 = 0.9999\right)$$

$$H_{\text{edt}} = 66.3212 + (0.0120)T + (3.3350)T^2 \quad \left(R^2 = 0.9993\right)$$

$$U_{\text{edt}} = 65.7785 + (0.0120)T + (3.3350)T^2 \quad \left(R^2 = 0.9993\right)$$

$$\Omega_{\text{edt}} = 66.3222 + (0.0100)T + (3.3335)T^2 \quad \left(R^2 = 0.9993\right)$$

$$G_{\text{edt}} = 68.2813 - (0.0586)T - (4.7655)T^2 \quad \left(R^2 = 0.9999\right)$$

All the thermo molecular data provide the crucial and helpful information for the further study on the 2-NP. They can be applied to compute the other thermodynamic characteristics according to relationships of thermo dynamical parameters and estimate directions of chemical reactions according to the second law of thermodynamics in thermo chemical fields. It should be noticeable that all calculations of thermo dynamical parameters have been done in gas phase and they could not be used in solution phase.

**NMR characterization: Magnetic susceptibility, shielding and current density tensors**

The NMR analysis plays an essential part in material characterization in presence of magnetic fields. This type investigation provides chemical shifts and magnetic shielding tensors to each atomic site of the molecule as well as magnetic susceptibility and the current density tensor for the material being investigated. We have applied Continuous Set Gauge of Transformation (CSGT) method for NMR investigation of the 2-NP molecule. The magnetic susceptibility tensor of 2-NP has been computed as

$$\lambda_1 = -111.7209, \lambda_2 = -44.2576 and \lambda_3 = -37.7896$$

Having the Eigen values $\lambda_1 = -111.7209, \lambda_2 = -44.2576 and \lambda_3 = -37.7896$ and the value of magnetic susceptibility $\chi$ is found to be -64589 cgs-ppm, the negative sign of $\chi$ shows the diamagnetic nature of the 2-NP molecule.

Also, the magnetic shielding tensors together with their corresponding Eigen values at different atomic sites can be depicted as below;

$$\sigma_i^j = \begin{bmatrix} 9.44 & 23.35 & 0.04 \\ 0.09 & -0.04 & 169.96 \\ \end{bmatrix}$$

$$\lambda_i = -72.25, \lambda_2 = 24.16 and \lambda_3 = 169.9$$

$$\lambda_1 = -26.67, \lambda_2 = 47.17 and \lambda_3 = 158.67$$

$$\lambda_1 = -21.45, \lambda_2 = 37.00 and \lambda_3 = 119.98$$

$$\lambda_1 = -9.20, \lambda_2 = 16.60 and \lambda_3 = 117.78$$

$$\lambda_1 = -21.47, \lambda_2 = 31.72 and \lambda_3 = 172.29$$

$$\lambda_1 = -39.76, \lambda_2 = 29.24 and \lambda_3 = 172.29$$

-64589 cgs-ppm, the negative sign of $\chi$ shows the diamagnetic nature of the 2-NP molecule.
Figure 8: (a) Total density (b) total density array of 2-NP (C-I).

Figure 9: (a) Electrostatic potential (ESP) of 2-NP (C-I). (b) Electrostatic potential array of 2-NP.

Figure 10: Graphical demonstration of essential thermodynamic parameters of 2-NP.

\[
H_i : \sigma_{ij} = \begin{bmatrix}
22.75 & 0.52 & 0 \\
0.74 & 24.26 & 0 \\
-0.002 & 0 & 21.83
\end{bmatrix}
\quad H_i : \sigma_{ij}^{\omega} = \begin{bmatrix}
27.52 & 1.41 & -0.001 \\
2.28 & 24.35 & -0.002 \\
-0.004 & 0.002 & 21.37
\end{bmatrix}
\]

\[
\lambda_i = 21.83, \lambda_j = 22.70 \text{ and } \lambda_k = 27.85 \\
\lambda_i = 21.57, \lambda_j = 23.50 \text{ and } \lambda_k = 28.37
\]

\[
H_i : \sigma_{ij} = \begin{bmatrix}
26.74 & 1.36 & 0 \\
0.74 & 24.26 & 0 \\
-0.001 & -0.003 & 20.34
\end{bmatrix}
\quad H_i : \sigma_{ij}^{\omega} = \begin{bmatrix}
27.07 & -1.38 & -0.002 \\
1.59 & 25.46 & 0 \\
-0.0004 & 0.003 & 22.21
\end{bmatrix}
\]

\[
\lambda_i = 20.34, \lambda_j = 23.87 \text{ and } \lambda_k = 27.12 \\
\lambda_i = 22.21, \lambda_j = 24.58 \text{ and } \lambda_k = 27.96
\]

\[
O_i : \sigma_{ij} = \begin{bmatrix}
98.07 & -1.38 & -0.002 \\
9.71 & 161.51 & -0.002 \\
0.16 & 0.12 & 286.79
\end{bmatrix}
\quad O_i : \sigma_{ij}^{\omega} = \begin{bmatrix}
33.34 & -1.38 & -0.002 \\
1.08 & 20.94 & -0.001 \\
0.82 & -0.06 & 10.39
\end{bmatrix}
\]

\[
\lambda_i = 85.06, \lambda_j = 174.53 \text{ and } \lambda_k = 286.79 \\
\lambda_i = 10.39, \lambda_j = 20.50 \text{ and } \lambda_k = 33.78
\]

\[
N_i : \sigma_{ij} = \begin{bmatrix}
-274.04 & -14.18 & -0.16 \\
-7.61 & -209.55 & -0.04 \\
-0.13 & -0.04 & 41.91
\end{bmatrix}
\quad O_i : \sigma_{ij}^{\omega} = \begin{bmatrix}
-450.67 & 153.53 & -0.28 \\
-0.51 & -682.72 & -0.49 \\
0.31 & 0.08 & 154.15
\end{bmatrix}
\]

\[
\lambda_i = -275.83, \lambda_j = -207.76 \text{ and } \lambda_k = -41.91 \\
\lambda_i = -705.87, \lambda_j = -427.72 \text{ and } \lambda_k = -154.15
\]

\[
\lambda_i = -511.64, \lambda_j = -393.18 \text{ and } \lambda_k = 113.76
\]

The magnetic shielding at the atomic sites, namely, C1, C2, C3, C4, C5, C6, H7, H8, H9, H10, O11, H12, N13, O14 and O15 have been computed as 40.625, 59.723, 20.510, 46.115, 53.924, 60.840, 20.340, 182.124, 21.558, -147.229, -326.418 and -263.685 ppm. It is noticeable that the shielding at every sites associated to NO2 group is negative and attaining higher values [Figure 11(a, b)]. From the Figure 11 it is obvious that the effect of the magnetic field is least nearby the NO2 group of 2-NP molecule.

The current density tensor (J) for the 2-NP have been computed and depicted in matrix form as;

\[
J_i = \begin{bmatrix}
0.0002 & 0.0001 & 0.0013 \\
0.0004 & 0 & 0.3173 \\
0.0084 & -0.2080 & 0.0001
\end{bmatrix}
\]

The two Eigen values of the current density tensor have been found imaginary while one Eigen value of J is \(\lambda = 0.0002\) for 2-NP molecule. The value of the J (~ 1.231x10 -5 a.u.) has been found to be negligibly small, which reveals that the electrical conductivity of 2-NP molecule is negligibly small. The mapping and corresponding contour of J for the title molecule have been demonstrated diagrammatically (Figure 12). Figure 12 also represents that the current density is extremely weak for the 2-NP molecule.

Conclusions

For the first time; complete material characterization, complete vibrational mode assignment, conformational analysis, HOMO - LUMO analysis, complete data analysis on thermo-dynamical parameters, data analysis on reactivity parameters and on NMR parameters, potential energy distribution and investigations of APT, Mulliken atomic charges and ESP derived charge of 2-NP has been carried out. The 2-NP molecule has been expected to possess three conformations out of which lowest energy conformer is planar possessing C, symmetry while other two are non-planar possessing
Some crucial molecular thermodynamic parameters of C-1 conformer of 2-NP.

Table 5: Molecular reactivity and NLO parameters of C-1 conformer of 2-NP.

| Parameter | Value (μ) | Polarizability (α) | 1st order Hyperpolarizability (β) |
|-----------|-----------|--------------------|-----------------------------------|
| Exact     | Perturbation to α |                         |                                   |
|                         | (a.u.) | esu *10^24 | (a.u.) | esu *10^24 |                         | (a.u.) | esu *10^24 |                         | (a.u.) | esu *10^24 |                         |
| \( V_a \) | 6.635 | (μ) | -3.951 | 123.434 | 18.268 | 74.308 | 10.998 | \( \beta_{ax} \) | 524.773 | 4534.563 |                         |                         |                         |                         |
| \( V_c \) | 0.881 | (μ) | -0.611 | -0.198 | -0.029 | -1.208 | -0.179 | \( \beta_{cy} \) | -125.223 | -581.160 |                         |                         |                         |                         |
| \( \eta \) | 2.877 | (μ) | -0.001 | 105.178 | 15.566 | 95.758 | 14.172 | \( \beta_{yz} \) | -102.311 | -884.069 |                         |                         |                         |                         |
| \( \mu \) | -3.758 | (μ) | 3.998 | 0.005 | -0.001 | -0.002 | -0.003 | \( \beta_{xy} \) | -95.389 | -824.256 |                         |                         |                         |                         |
| \( \chi \) | 0.174 | (μ) | -3.964 | 0.012 | 0.002 | 0.023 | 0.003 | \( \beta_{xz} \) | -0.080 | -0.691 |                         |                         |                         |                         |
| \( \omega \) | 3.758 | (μ) | -0.603 | 47.285 | 6.998 | 23.282 | 3.446 | \( \beta_{zz} \) | -0.023 | -0.199 |                         |                         |                         |                         |
| \( E_{ex} \) | 4.03 | (μ) | 4.010 | 9483.787 | 1403.600 | 8325.284 | 1232.142 | \( \beta_{xx} \) | -75.942 | -656.215 |                         |                         |                         |                         |
|                         |          | 0.001 | 47.285 | 6.998 | 23.282 | 3.446 | \( \beta_{yy} \) | -27.380 | -236.590 |                         |                         |                         |                         |
|                         |          | 0.003 | 91.966 | 13.612 | 64.449 | 9.538 | \( \beta_{zz} \) | -0.013 | -0.112 |                         |                         |                         |                         |
|                         |          | 4.010 | 9483.787 | 1403.600 | 8325.284 | 1232.142 | \( \beta_{zz} \) | 426.118 | 3681.229 |                         |                         |                         |                         |

* \( V_a \) = Ionization potential, \( V_c \) = Electron affinity, \( \eta \) = Hardness, \( \mu \) = Chemical potential, \( \chi \) = Softness, \( \omega \) = Electro-negativity, \( \chi \) = Electro-philicity of the molecules.

Table 6: Molecular reactivity and NLO parameters of C-1 conformer of 2-NP.

| T (K) | G Kcal/mol | H Kcal/mol | Q Kcal/mol | C cal/mol-K | S cal/mol-K | U Kcal/mol | ZPE Kcal/mol | LnQ_{eq} | LnQ_{a} |
|-------|------------|------------|------------|-------------|-------------|------------|-------------|---------|---------|
| 100   | 61.7744    | 68.2344    | 68.037     | 11.236      | 64.604      | 67.6911    | 67.226      | 27.427241 | -310.869495 |
| 200   | 54.7113    | 69.9739    | 69.578     | 19.973      | 76.312      | 69.4314    | 67.226      | 31.484367 | -137.662726 |
| 298.15| 46.7007    | 72.6006    | 72.010     | 29.552      | 86.670      | 72.0851    | 67.226      | 34.641248 | -78.823178 |
| 300   | 46.5394    | 72.6589    | 72.064     | 29.728      | 87.066      | 72.1164    | 67.226      | 34.697505 | -78.067224 |
| 400   | 37.3109    | 76.2864    | 75.493     | 38.613      | 97.440      | 75.7439    | 67.226      | 37.633424 | -46.901243 |
| 500   | 27.0689    | 80.7254    | 79.734     | 45.928      | 107.316     | 80.1829    | 67.226      | 40.415236 | -27.243602 |
| 600   | 15.8887    | 85.8181    | 84.628     | 51.726      | 116.585     | 85.2756    | 67.226      | 43.073074 | -13.309290 |
| 700   | 3.7721     | 91.4280    | 90.039     | 56.315      | 125.223     | 90.8855    | 67.226      | 45.615146 | -2.712595 |
| 800   | -9.1554    | 97.4488    | 95.861     | 60.001      | 133.258     | 96.9063    | 67.226      | 48.045839 | 5.759065  |
| 900   | -22.8595   | 103.8028   | 102.017    | 63.013      | 140.739     | 103.2603   | 67.226      |                     |                     |

* T = Temperature, G = Gibb's free energy, H = Enthalpy, Q = Thermal energy, C = Molar heat capacity, S = Entropy, U = Internal energy, ZPE = Zero point vibrational energy, Q_{a} = Total partition function taking reference 1 vibrational level, Q_{eq} = Total partition function taking reference at bottom of the well.
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