An insight into the conformal flexibility and vibrational behavior of 2-nitroso-1-naphthol: A density functional theory approach

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ABSTRACT
The conformational stability of 2-nitrosol-1-naphthol (2N1N) was elucidated using potential energy surface scan studies. In order to carry out a detailed vibrational spectroscopic analysis of 2N1N, Fourier transform infrared and Fourier transform Raman spectra have been recorded in condensed phase. To determine the optimized geometry and vibrational wavenumber, density functional theory calculations in the B3LYP/6-31G** level have been carried out followed by scaling using the scaled quantum mechanical methodology. A root mean square deviation of 9.69 cm\(^{-1}\) has resulted from the scaled quantum mechanical treatment. Substitution of nitroso group into the 1-naphthol has produced remarkable changes in the structural parameters. The ultraviolet-visible spectra of the title compound dissolved in various solvents were recorded in the range of 300–500 nm. The natural bond orbital analysis, frontier molecular orbital analysis, and thermodynamic features were also performed using B3LYP/6-31G** method.

Introduction
Nitroso-naphthols have greater ability to form metal chelates, and it is sensitive for fluorimetric determinations of tyrosine residues in proteins and peptides.\cite{1,2} Biological monitoring is the best way in assessing the organic contaminant present in human blood, urine, and biological tissues. Naphthol has an enhanced solubility in nature due to the presence of hydroxyl group. 1-Naphthol is found to be an urinary metabolite of both carbaryl and naphthalene. In recent days, 1-naphthol is used as an urinary biomarker since the half-life of carbaryl present in it is of order of days. The conformational equilibrium of the monooximes of 1,2-naphthoquinone and their nuclear magnetic resonance (NMR) reports have been extensively carried out previously.\cite{3,4} The density functional studies on 1-naphthol have been extensively carried out by Raja et al.\cite{5} The hyperpolarizability studies on the 1-naphthol compounds reveal its nonlinear optical property.\cite{3-7} The nitroso-oxime tautomerism of 2-nitroso-1-naphthol (2N1N) has been treated in several reports.\cite{1,2,6-14} The existence of both tautomeric forms of naphthol derivatives in different solvents was suggested based on \(^1\)H NMR data. The existence of oxime tautomeric form of naphthols was confirmed using NMR spectroscopy by Galya Ivanova et al.\cite{6} The separation and preconcentration of trace cadmium and its determination by differential pulse photography were studied by Mohammad Ali Taher et al.\cite{7} The nitroso-oxime tautomeric forms have been investigated using ultraviolet-visible (UV-vis) and NMR techniques by Gonewar et al.\cite{14} employing Hatree–Fock (HF) and \textit{ab initio} calculations. The effect of inclusion of electron correlation into the calculations on tautomerization barrier of the molecule was studied extensively by Galya Ivanova et al.\cite{6} In the present study, the analysis of Fourier transform infrared (FTIR), Fourier transform Raman (FT-Raman), UV-vis spectra, and Density functional theory (DFT) analysis of 2N1N is presented.

Methods

Experimental details
A fine sample of 2N1N was obtained from M/s. Sigma Aldrich chemical company, USA and used without any further purifications for spectral measurements. The FTIR of the title compound was recorded in the region 4000–400 cm\(^{-1}\) using Perkin–Elmer spectrum RX1 spectrophotometer equipped with Helium–Neon laser source, potassium bromide (KBr) beam splitter, and LiTaO\(_3\) detector. The sample was prepared by pressing 2N1N with KBr into pellet form.

The FT-Raman spectrum of 2N1N was recorded in 3500–50 cm\(^{-1}\) range with a Nicolet model 950 FT-Raman spectrometer at 4 cm\(^{-1}\) spectral resolution using the 1064 nm line of a Nd:YAG laser for excitation at a 200 mW output power. The UV-vis absorption spectrum of the title compound was recorded in the range 500–300 cm\(^{-1}\) using Analytik Specord Plus UV-vis spectrophotometer.

Computational details
DFT calculations of 2N1N were performed by using Gaussian 09 software package\cite{15} at B3LYP functional\cite{16,17} combined...
with 6-31G** basis set to obtain the optimized geometry and energy of the title compound. Further, in order to express the normal modes in a molecular fixed coordinate system, a set of local symmetry coordinates for the title compound was defined as recommended by Pulay et al.[18] The defined local symmetry coordinates is listed in Table S1 (supplementary information) and the optimized geometry of 2N1N with atoms numbered are shown in Fig. 1c. The DFT force field was transformed from Cartesian to local symmetry coordinates and then scaled empirically according to the scaled quantum mechanical (SQM) procedure.[19]

\[
F_{ij}^{scaled} = (C_i C_j)^{1/2} F_{ij}^{B3LYP}
\]

where \(C_i\) is the scale factor of coordinate \(i\), \(F_{ij}^{B3LYP}\) is the B3LYP/6-31G** force constant in the local internal coordinates, and \(F_{ij}^{scaled}\) is the scaled force constant. The force field transformation from Cartesian to internal coordinates followed by the subsequent normal coordinate analysis (NCA) including the least-square fit refinement of the scale factors, calculation of potential energy distribution (PED), and prediction of IR and Raman intensities were done with the MOLVIB 7.0 program written by Sundius.[20,21] For the plots of simulated IR and Raman spectra of the title compound, pure Lorentzian band shapes were used with a bandwidth (full width half maximum) of 10 cm\(^{-1}\).

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities \(S_i\) calculated by the Gaussian 09 program and adjusted during scaling procedure with MOLVIB were converted to relative Raman intensities \(I_i\) using the following relationship derived from the basic theory of Raman scattering:[22–24]

\[
I_i = \frac{f (\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp \left(-\frac{hc\nu_i}{kT}\right)]}
\]

where \(\nu_0\) is the exciting frequency (in cm\(^{-1}\) units); \(\nu_i\) is the vibrational wavenumber of the \(i\)th normal mode; \(h\), \(c\), and \(k\) are the universal constants; and \(f\) is the suitably chosen common normalization factor for all the peak intensities. For the plot of spectra, digital version of the observed and simulated spectra of the title compound was used.

The natural bonding orbital (NBO) calculation was performed using NBO 5.1 program[25] as implemented in the Gaussian 09 package. The interaction energy and the hyperconjugation within the molecule were deduced from the second-order perturbation approach.[26–28]

**Results and discussion**

**Conformer stability and PES scan analysis**

The 2N1N molecule can adopt different conformers by spatially orienting the nitroso group with respect to the naphthol group. The initial assumption was that for the title compound there may exist four possible conformers which belong to rotameric forms of 2N1N as supported by literature.[6,7,14] The four conformers are given names as conformer1, conformer2, conformer3, and conformer4 and their structures are given in Fig. 1a–d. The results from the literature references[6,7,14] reveal that, conformer2 and conformer4 possess much higher energy than conformer1 and conformer3. The same has been verified by the authors from the optimization done on all the

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**Figure 1.** Conformers of 2-nitroso-1-naphthol.
four conformers, and the results from literature were validated. The conformers showing their optimized energies were tabulated and the same is shown in Table 1. Hence, conformer1 and conformer3 alone were considered for further investigation. Of the two minimum energy conformers of nearly equal energy, the conformer1 was found to have higher energy when compared to that of conformer3. Hence, conformer3 was chosen for further investigation and is also supported by the literature.\(^{[6,7,14]}\)

In order to confirm the choice of the most stable conformer of the title molecule, a potential energy scan (PES) scan using B3LYP level at 6-31G** basis set was carried out. The PES scan has been performed on the assumed geometry by rotating the nitroso group (N=O) between 0° and 360° with an increment of 10°. The PES curve is shown in Fig. 2. From the PES scan, the most stable conformer with minimum energy was obtained at a dihedral angle of 180° for C2–C3–N13–O14. This angle along with other geometrical parameters matches exactly with conformer3 obtained earlier. This confirms the correct choice of conformer for the title compound. The other two local minima were found at 170° and 190°.

**Molecular geometry**

The optimized structure of 2N1N along with numbering of atoms is shown in Fig. 1c. Different conformers were tried by changing the angles of nitroso group, and the most stable conformer (conformer3) was obtained when nitroso group turned away from the naphthol group (refer Table 1). This is also confirmed from the PES scan analysis. The global minimum energy obtained by DFT structure optimization and PES scan analysis of 2N1N was found to be \(-370,500.5\) kcal/mol. All the calculated vibrational wavenumber using the optimized geometry obtained were found to be positive for the title compound. The optimized parameters of 2N1N were compared with the 1-naphthol\(^{[5]}\) and are shown in Table 2. It was observed from the table that the substitution of nitroso group at the ortho position of 1-naphthol significantly influenced the parameters as mentioned below. Due to the presence of highly electronegative atoms nitrogen and oxygen of nitroso group, the bond lengths such as C2–C3, C4–C5, and C5–C6 were elongated. The bond angles C1–C2–C3 and C4–C5–C6 were shortened.\(^{[5]}\) The calculated C–H bond lengths of C2–H12 and C7–H17 was found to be 1.0843 Å and 1.0842 Å, respectively. These bond lengths deviate from their default values of 1.86 Å. This deviation observed in the C2–H12 and C7–H17 bond lengths may be due to the formation of the improper C2–H12…O14 hydrogen bonding. The distance between O14…H12 is found to be 2.25 Å, which is significantly less than that of van der Walls radii (2.72 Å) of oxygen and hydrogen atoms, which also further confirms the formation of hydrogen bonding.\(^{[29,30]}\)

**Molecular vibrations and simulated spectra**

The title compound 2N1N belongs to C\(_5\) point symmetry and its 54 fundamentals are distributed among the symmetry species as:

\[
\Gamma_{\text{vib}} = 37A'(\text{in-plane}) + 17A''(\text{out-of-plane}).
\]

For visual comparison, the observed and calculated FTIR and FT-Raman spectra of 2N1N are presented in Figs. 3 and 4, respectively. The results of the vibrational analysis, viz., calculated unscaled vibrational wavenumber, SQM wavenumber, PEDs, and assignment of the fundamentals, for the title compound 2N1N are collected in Table 3.

**Table 2.** Comparison of optimized geometrical parameters of 2-nitroso-1-naphthol with 1-naphthol obtained by B3LYP/6–31 G\(^*\) density functional calculations.

| Bond length | Value (Å)  | 2N1N  | 1-Naphthol
|-------------|------------|-------|------------------|
| C1–C2       | 1.364      | 1.375 | C1–C2–C3         | 1.198 | 120.7 |
| C2–C3       | 1.423      | 1.414 | C2–C3–C4         | 1.209 | 120.2 |
| C3–C4       | 1.402      | 1.379 | C3–C4–C5         | 1.210 | –     |
| C4–C5       | 1.427      | –     | C4–C5–C6         | 1.180 | –     |
| C5–C6       | 1.431      | –     | C5–C6–C7         | 1.201 | 120.5 |
| C5–C7       | 1.415      | 1.418 | C5–C7–C8         | 1.202 | –     |
| C7–C8       | 1.379      | 1.377 | C7–C8–C9         | 1.200 | 120.3 |
| C8–C9       | 1.411      | 1.415 | C8–C9–C10        | 1.206 | 120.3 |
| C9–C10      | 1.381      | 1.376 | C2–C1–C11        | 1.207 | 119.1 |
| C1–H1       | 1.086      | 1.086 | C2–H1–C12        | 1.227 | 120.3 |
| C2–H2       | 1.084      | 1.086 | C5–C7–H17        | 1.187 | 118.8 |
| C7–H7       | 1.084      | 1.084 | C7–H7–C8         | 1.201 | 120.0 |
| C8–H8       | 1.085      | 1.086 | C8–C9–H9         | 1.195 | 119.7 |
| C9–H9       | 1.086      | 1.086 | C9–H9–C10        | 1.202 | 120.4 |
| C10–H20     | 1.086      | 1.087 | C3–C4–O15        | 1.209 | 122.8 |
| C3–N13      | 1.399      | –     | C4–O15–H16       | 1.058 | 108.7 |
| N13–O14     | 1.231      | –     | C2–C3–N13        | 1.256 | 119.3 |
| C4–O15      | 1.340      | 1.368 | C3–N13–O14       | 1.172 | –     |
| O15–H16     | 0.980      | 0.969 |                     |

*Taken from the literature \([14]\).*
Analysis of vibrational spectra by SQM methodology and assignments

The well-known good performance of DFT for the estimation of vibrational spectra of organic compounds can be observed in the case of the title compound 2N1N also. The unscaled B3LYP/6–31G** vibrational wavenumber are generally some-what larger than the experimental value. This is true in the case of 2N1N also and is reflected in the values depicted in Table 3. The root mean square (RMS) error between unscaled and experimental wavenumber is 47.3 cm$^{-1}$ for 2N1N. However, for getting reliable information on the vibrational properties, the use of selective scaling is necessary. The calculated wavenumber was scaled using a set of transferable scale factors recommended by Rauhut and Pulay.[19,31] A comparison between observed and calculated wavenumbers have been made along with their RMS deviation, and the values are collected in Table S2 (supplementary information). The SQM treatment resulted in a RMS deviation of 9.69 cm$^{-1}$.

**CH vibrations**

2N1N gives rise to six C–H stretching mode. The aromatic C–H stretching vibrations appear in the region 3080–3010 cm$^{-1}$.[32,33] In 2N1N, the bands identified at 3123 cm$^{-1}$ in the IR spectrum and at 3068, 3089, 3097, 3105, 3137 cm$^{-1}$ in the Raman spectrum were assigned to C–H stretching vibrations. The aromatic C–H stretching vibrations are usually observed in the region 3080–3010 cm$^{-1}$.[34] The C2–H12 stretching vibration is observed at 3137 cm$^{-1}$ in IR spectrum. This blue-shifted C–H stretching wavenumber indicates the presence of improper C2–H12 ... O14 hydrogen bonding. This formation of hydrogen bonding is further confirmed from the NBO analysis section of the manuscript.

In naphthols, C–H in-plane bending vibrations are observed in the region 1300–1000 cm$^{-1}$ and are usually weak. The C–H out-of-plane bending modes arise in the region 900–600 cm$^{-1}$.[35] In the present study, the bands observed at 1076, 1107, 1167, and 1216 cm$^{-1}$ in the IR spectrum and the bands at 1033, 1106, 1158, 1178, 1211, and 1309 cm$^{-1}$ were assigned to C–H in-plane bending vibrations. The C–H out-of-plane bending modes of the title compound are observed in the IR spectrum at 968, 762, and 692 cm$^{-1}$ and in the Raman spectrum at 934, 847, and 693 cm$^{-1}$, respectively, and are presented in Table 3.

**C=O vibrations**

The C=O stretching vibrations generally occur in the region 1730–1450 cm$^{-1}$.[34,36] In the title compound, the band identified at 1621 cm$^{-1}$ in the IR spectrum and at 1610 cm$^{-1}$ in the Raman spectrum represents the C =O stretching vibrations. The two bands arising from C =O in-plane bending vibrations appear in the spectra near 505–480 cm$^{-1}$.[34,36] The C=O in-plane bending vibrations are observed at 500 cm$^{-1}$ in IR spectrum and 493 cm$^{-1}$ in Raman spectrum and the C=O out-of-plane bending vibrations of 2N1N are observed at 249 and 141 cm$^{-1}$.

**Hydroxy group vibrations**

For naphthol, O–H stretching vibration is expected in the region 3590–3400 cm$^{-1}$.[37] A strong band observed at 3439 cm$^{-1}$ in IR spectrum of 2N1N with PED 100% is assigned to O–H stretching vibration. Its Raman counterpart is observed at 3466 cm$^{-1}$. In general, free O–H stretching vibrations occur in the region 3700–3500 cm$^{-1}$.[34] A strong IR band observed at 3439 cm$^{-1}$ and a Raman band at 3466 cm$^{-1}$ correspond to the O15–H16 stretching mode. This red-shifted O15–H16 stretching wavenumber confirms the presence of O15–H16... N13 hydrogen bonding. The band observed at 1331 cm$^{-1}$ in IR is assigned to the O–H out-of-plane bending mode. The Raman band at 753 cm$^{-1}$ is assigned to the O–H out-of-plane bending mode.

**CN vibrations**

Generally, the C–N stretching vibrations in aromatic compounds form three or four bands in the region 1250–1160 cm$^{-1}$.[34] In 2N1N, the strong bands observed at 1269 cm$^{-1}$ in IR and 1265 cm$^{-1}$ in Raman were assigned to C–N stretching mode. The C–N out-of-plane bending modes

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Figure 3. Fourier transform infrared spectra of 2-nitroso-1-naphthol (a) observed and (b) calculated.

Figure 4. Fourier transform Raman spectra of 2-nitroso-1-naphthol (a) observed and (b) calculated.
of the title compound were observed at 343, 188, and 81 cm\(^{-1}\) in the Raman spectrum.

**Ring vibrations**

**Ring stretching vibrations**

The presence of double-bond conjugation with the ring makes the C–C stretching vibrations more interesting. The actual positions of the double bonds are determined by the substituent to the ring.\(^{[38–40]}\) Naphthols have several bands of various intensities in the range of 1660–1480 cm\(^{-1}\). For 2N1N, the IR bands at 1661, 1621, 1563, and 1527 cm\(^{-1}\) were assigned to C=C stretching vibrations and the Raman counterparts were at 1610 and 1454 cm\(^{-1}\). The IR bands observed at 1331 and 1216 cm\(^{-1}\) were assigned to C–C stretching vibrations. Their Raman counterparts were observed at 1321, 1235, and 1211 cm\(^{-1}\).

**In-plane bending vibrations**

The bands observed at 858, 719, 692, and 613 cm\(^{-1}\) in the IR spectrum of 2N1N are attributed to the ring in-plane bending vibrations.
vibrations. Their Raman counterparts were observed at 867, 723, and 693 cm\(^{-1}\).

**Out-of-plane bending vibrations**

In the aromatic rings, several ring modes were affected by the substitution.[5,34] Most monosubstituted naphthols have medium-intensity bands in the region 445–355 cm\(^{-1}\). For 2N1N, the bands observed at 482 cm\(^{-1}\) and 400 cm\(^{-1}\) were assigned to ring out-of-plane bending vibrations.

**Ring torsion vibrations**

In the present study, the vibrations observed at 770, 666, and 600 cm\(^{-1}\) in the IR spectrum and the Raman bands corresponding to 660, 435, and 134 cm\(^{-1}\) were attributed to the ring torsion modes of 2N1N. The inter-ring torsion mode (Butterfly) for 2N1N was Raman active at 279 cm\(^{-1}\).

**Nitroso vibrations**

The aromatic nitroso compounds absorb strongly at 1525–1480 cm\(^{-1}\).[34] The band position due to the N=O stretching vibration is affected by substituent groups in a very similar manner to that of carbonyl group. Nitroso compounds usually have a band at 1180–1000 cm\(^{-1}\) and another band at 865–750 cm\(^{-1}\) due to strong coupling of C–N stretching vibration and the vibration of carbon skeleton. The band observed at 1590 cm\(^{-1}\) in the IR spectrum and a strong band observed at 1559 cm\(^{-1}\) in Raman spectrum of 2N1N was assigned to N–O stretching vibration. The C–N=O in-plane bending was expected in the region 575 cm\(^{-1}\) and the vibration of carbon skeleton. The band observed at 1559 cm\(^{-1}\) for 2N1N it was observed at 534 cm\(^{-1}\) with medium-intensity peak in the IR spectrum. The C–N=O out-of-plane bending for the title compound was observed at 207 cm\(^{-1}\) in the Raman spectrum.

**UV-visible spectral analysis**

The experimental UV-vis spectra of the title compound using water, dimethyl formamide (DMF), and ethanol solvents were presented in Fig. 5. The calculated electronic absorption spectra was obtained by using TD-DFT method based on the B3LYP/6–31G** level with the molecular orbital theory.[41] The excitation energies, oscillator strengths, and their corresponding excitation assignments were properly tabulated in Table S3 (supplementary information). A strong absorption occurs at 362 nm for DMF and at 376 nm for water and absorption band occurs for ethanol at 368 nm.

The DFT calculations were performed using water, ethanol, and DMF as solvents for the title compound using polarizable continuum model (PCM). The results of the PCM calculations show that the calculated absorption was observed in the water as a solvent at 313.28, 423.64, and 717.93 nm with excitation energies of 3.9576 eV, 2.9267 eV, and 1.7270 eV, respectively. For solvent of ethanol, the absorption wavelength was predicted at 313.17, 423.21, and 719.98 nm with excitation energies of 3.9590 eV, 2.9296 eV, and 1.7221 eV, respectively, and for DMF as solvent, the absorption peak was found at 311.77, 419.25, and 728.13 nm with optical energy of 3.9768 eV, 2.9573 eV, and 1.7028 eV as excitation energies, respectively.

We could observe a red shift of the experimental wavelength from that of calculated wavelength. This was observed in the excited state 3 for all the solvents.

**Frontier molecular orbital analysis**

The optical polarizability, chemical softness and hardness of a molecule, electrical properties, kinetic stability, and chemical reactivity of a molecule can be characterized with the help of spatial distribution of frontier molecular orbitals. The simplest way to calculate the excitation energy is by finding the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and is an excellent indicator of electronic transition absorption in the molecular systems.[42] The HOMO, LUMO energies, and the energy gap for 2N1N molecule were calculated using B3LYP level with 6-31G** basis set. Owing to the HOMO–LUMO orbital interaction, LP–π* and LP–LP type interactions were observed in the title compound consistent with the molecular orbital theory.[43,44] The position of HOMO–LUMO plots was shown in Fig. 6. The calculated HOMO, LUMO energies, and the energy gap are shown below.

\[
\text{HOMO energy} = -5.93\text{eV}
\]
\[
\text{LUMO energy} = -2.65\text{eV}
\]
\[
\text{HOMO} - \text{LUMO energy gap} = 3.27\text{eV}
\]

For the title compound 2N1N, a total of 45 occupied orbitals and 185 virtual orbitals were observed. The molecular orbital analyses for the title compound 2N1N based on its optimized geometry indicate that the frontier molecular orbitals for the title compound are mainly composed of p-atomic orbitals. The electronic transitions are predominantly LP–LP transition for the title compound. Moreover, the HOMO–LUMO energy gap clearly explains the eventual charge transfer interaction taking place within the molecule. The HOMO was
observed over the nitroso functional group attached to the naphthol ring. It is also observed from the electronic absorption spectra and also the LUMO of the title compound that the charge transfer is taking place in the compound from the nitroso group to the entire ring which shows that the LUMO spreads over the entire ring as observed from Fig. 6.

### NBO analysis

NBO analysis has been performed on 2N1N, in order to investigate the intramolecular and intermolecular charge transfer (ICT) interactions, the stabilization energies, and delocalization of electrons. Further, it provides a convenient basis for investigating the interactions in both filled and virtual orbital spaces along with charge transfer and conjugative interactions in molecular system. The donor–acceptor interactions in the NBO analysis of the title compound were calculated by using second-order perturbation theory analysis.[45] The electron density (ED) changes in the antibonding orbitals (σ*, π*) and E(2) energies have been calculated by NBO analysis at B3LYP/6-31G* level to create a clear evidence for stabilization of energy originating from molecular interactions.[46]

The energy arising from hyperconjugative interactions was deduced from the second-order perturbation approach. The larger the amount of energy transferred (E(2)), more intensive is the interaction between electron donors and electron acceptors, i.e., more the donating tendency from electron donors to electron acceptors greater will be the extent of conjugation of the whole system.

The strength of the delocalization interaction can be estimated by the second-order energy lowering $E^{(2)}$;

$$E^{(2)} = \Delta E_{ij} = q_i F(i,j)^2 / E_j - E_i$$

where $E^{(2)}$ is the stabilization energy, $q_i$ is the donor orbital occupancy, $E_i$ and $E_j$ are the diagonal elements, and $F(i,j)$ is the off-diagonal NBO Fock matrix element reported.[47,48]

![Figure 6. HOMO and LUMO plots of 2-nitroso-1-naphthol.](image)

The possible interactions showing donors, acceptors, and their electron densities are given in Table S3. The interactions which are having $E^{(2)}$ greater than 4 (kcal/mol) were shown in Table 4. The energy density at the six conjugated π bonds (≈1.7856e) and π* bonds (≈0.3868e) of the phenyl rings clearly demonstrates strong delocalization, leading to stabilization of energy ≈ 40 kcal/mol. A strong intramolecular hyperconjugative interactions with greater energy contributions between π(C7–C8) → LP(1) C5 (41.01 kcal/mol), π(C9–C10) → LP(1) C6 (44.51 kcal/mol), and LP(1) C5 → π*(C3–C4) (79.96 kcal/mol) was observed in the naphthol ring. A strong hyperconjugative interaction observed due to LP(N13) → σ*(O15–H16) transition was found to be 6.84 kcal/mol which also leads to stability of the molecule. The strengthening of O15–H16 bonds is due to rehybridization (see vibration addition part), which is revealed by reduction in ED (0.03666e) in the σ*(O15–H16) orbital. This may be due to the formation of strong O15–H16…N13 intramolecular hydrogen bonding. Further, it reveals that the charge transfer from the lone pair to bond pair was found to be greater than bond pair to bond pair, and this contributes to the stabilization of the molecule.

### Mulliken population analysis

For the title compound 2N1N, the Mulliken population analysis[49] was performed using DFT method at B3LYP/6-31G* level to obtain the values of the atomic charges. The Mulliken atomic charges of 2N1N are listed in Table S4 (supplementary information). For visual comparison, the graphical representation of results is shown in Fig. 7. The large electropositive values observed on hydrogen atoms H19 (0.9775e) and H20 (0.9559e) may be due to the presence of neighboring large electronegative atoms N13, O14, and O15. Similarly, a less positive charge was observed on atom H16 (0.3373e) which may be due to its direct attachment with O15 which is an

| Table 4. Second-order perturbation theory analysis of Fock matrix in NBO basis. |
|----------------|----------------|----------------|----------------|----------------|
| Donor (i)      | ED (j) e        | Acceptor (j)   | ED (j) e        | $E^{(2)}$ (kcal/mol) |
| π (C1–C2)      | 1.78557         | LP*(1) C6      | 0.96890         | 37.79           |
| σ(C1–H11)      | 1.98091         | σ*(C2–C3)      | 0.03098         | 4.08            |
| π (C3–C4)      | 1.60445         | LP(1) C5       | 1.05176         | 34.07           |
| π (C7–C8)      | 1.70891         | LP(1) C5       | 1.05176         | 34.07           |
| π (C9–C10)     | 1.70540         | LP(1) C5       | 0.96890         | 44.51           |
| LP(1) C5       | 1.05176         | σ*(C3–C4)      | 0.38686         | 79.96           |
| LP*(1) C6      | 0.96890         | π*(C1–C2)      | 0.20150         | 57.20           |
| LP(2) O14      | 1.94809         | σ*(C3–N13)     | 0.04789         | 13.16           |
| LP(2) O15      | 1.81502         | π*(C3–C4)      | 0.38686         | 38.31           |
| σ*(C3–C4)      | 0.38668         | π*(C1–C2)      | 0.20150         | 44.14           |
| σ*(N13–O14)    | 0.26504         | π*(C1–C2)      | 0.20150         | 57.20           |

$E^{(2)}$ means energy of hyperconjugative interactions (stabilization energy).
The atom O15 shows the largest electronegativity value of (0.5436e) and the atom C5 shows the largest electropositivity of (0.348e). This indicates the extensive charge delocalization in the molecule. The positive charges are localized on the hydrogen atoms. The atoms C3 and C4 show high positive charges of 0.2092e and 0.2871e when compared with other carbon atoms. This indicates that the conjugation between the substituent and the naphthol ring takes place through these atoms. In the naphthol ring, the carbon atoms C3, C4, C5, and C6 were having positive charges when compared to other carbons present in the ring. The reason may be due to their presence in the proximity of electronegative atoms. The hydrogen atoms H11, H12, H17, and H18 present in the naphthol ring show less positive (≈0.11e) charge, while the hydrogens H19 and H20 show more positive charge (>0.955e), which confirms the influence of electronegative atoms like nitrogen and oxygen atoms into the remote hydrogens. This indicates that the addition of nitroso functional group into the naphthol ring stimulates the charge transfer within the molecule and is evident from the above results.

**Thermodynamic properties**

For the title compound, thermodynamic functions like enthalpy changes (H), entropy (S), and heat capacity (C) were calculated by Thermo.pl using B3LYP/6-31G** method based on the vibrational analysis at different temperatures and are listed in Table S5 (supplementary information). It was observed from the table that the thermodynamic functions were increasing with 100 – 1000 Kelvin increase of temperature and is due to the fact that when temperature increases the molecular vibrational intensity increases. The equation connecting enthalpy changes (H), entropy (S), and heat capacity (C) changes and temperatures were fitted by quadratic formulas and the corresponding fit factors ($R^2$) for these thermodynamic properties are 0.99843, 0.9999, and 0.99926, respectively. The correlation graphs for the above-mentioned properties are shown in Fig. 8. The corresponding fitting equations were as given below.

$$
C = 15.02901 + 0.511467 - 2.24804 \times 10^{-4} T^2 \quad (R^2 = 0.99843)
$$

$$
S = 31.13706 + 0.58513T - 1.4852 \times 10^{-4} T^2 \quad (R^2 = 0.9999)
$$

$$
H = -5.87775 + 0.071617 + 1.33102 \times 10^{-4} T^2 \quad (R^2 = 0.99926)
$$

The thermodynamic data thus obtained provide the necessary information for further study on the title compound 2N1N. These data can be used to calculate other thermodynamic functions for estimation of a chemical reactions in thermochemical field to be done in gas phase.

**Conclusions**

The most stable conformer of 2N1N has been identified using DFT optimization procedure and PES analysis. A weighted RMS deviation of 9.6 cm$^{-1}$ between experimental and calculated wavenumber for the title compound has been achieved by employing the SQM methodology. Substitution of nitroso group into the 1-naphthol has produced remarkable changes in the structural parameters. A satisfactory assignment of most of the fundamentals was provided using the scaling procedure. The vibrational wavenumber, IR intensities, and Raman intensities were calculated using B3LYP/6-31G** method, and they were found to be in good agreement with the experimental values. The ED changes in the bonding and antibonding orbitals ($\sigma^*$, $\pi^*$) due to the charge transfer of electrons between various bonds have been investigated by NBO analysis. Further, it reveals that the charge transfer from the lone pair...
to bond pair was found to be greater than bond pair to bond pair, and this contributes to the stabilization of the molecule.

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