Research Article

Vibrational Spectroscopic Study of (E)-4-(Benzylideneamino)-N-Carbamimidoyl Benzenesulfonamide

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The Fourier transform infrared and Fourier transform Raman spectra of (E)-4-(benzylideneamino)-N-carbamimidoyl benzenesulfonamide were recorded and analyzed. Geometry and harmonic vibrational wavenumbers were calculated theoretically using Gaussian 03 set of quantum chemistry codes. Calculations were performed at the Hartree-Fock (HF) and density functional theory (DFT; B3PW91, B3LYP) levels of theory. The calculated wavenumbers (B3LYP) agree well with the observed wavenumbers. Potential energy distribution is done using GAR2PED program. The red shift of the N-H stretching band in the infrared spectrum indicates the weakening of the N-H bond. The geometrical parameters of the title compound are in agreement with that of reported similar derivatives. The calculated first hyperpolarizability is comparable with the reported value of similar derivative and may be an attractive object for further studies of nonlinear optics. Potential energy surface scan studies have been carried out to understand the stability of planar and nonplanar structures of the molecule.

1. Introduction

Benzenesulfonamide derivatives find wide applications for the synthesis of pharmaceutical products which have bactericidal properties and of various bioactive agents, artificial fibers, dyes, and plasticizers, and the synthesis of high molecular weight substances. Sulfonamides are chemotherapeutics most commonly used in veterinary practices because of their inexpensiveness and wide spectrum antimicrobial activity [1]. Sulfonamides represent one of the classical chemotypes associated with potent CA inhibition [2–5]. The chemistry of sulfonamides has been known as synths in the preparation of various valuable biologically active compounds [6, 7] used as an antibacterial [8], protease inhibitor [9], diuretic [10], antitumor [11], and hypoglycaemic [12]. Singh et al. [13] reported the synthesis and antimicrobial activity of Schiff’s and N-Mannich bases of Isatin and its derivatives with 4-amino-N-carbamimidoyl benzene sulfonamide. There has been growing interest in using organic materials for nonlinear optical (NLO) devices, functioning as second harmonic generators, frequency converters, electro-optical modulators, and so forth because of the large second order electric susceptibilities of organic materials. The organic compound showing high hyperpolarizability are those containing an electron-donating group and an electron-withdrawing group interacting through a system of conjugated double bonds. In the case of sulfonamides, the electron-withdrawing group is the sulfonyl group [14, 15]. To our knowledge, no theoretical
with a total registration time of about 30 min. The spectral emission wavelength 1064 nm, maximal power 150 mW, measures the emission of an Nd:YAG laser was used, excitation on a BRUKER RFS 100/S, Germany. For excitation of the spectrometer in KBr pellets, number of scans 16, resolution 4.59/4.63; N 18.40/18.50; S 10.58/10.59. The FT-IR spectrum, 1360, 1133 cm\(^{-1}\) in the Raman spectrum, and 1371, 1148 cm\(^{-1}\) theoretically are assigned as SO\(_2\) stretching modes. These modes are not pure, but contain significant contributions from other modes also. Although the region of SO\(_2\) scissoring (560 ± 40 cm\(^{-1}\)) and that of SO\(_2\) wagging (500 ± 55 cm\(^{-1}\)) partly overlap, the two vibrations appear separately [21]. These deformation bands of SO\(_2\) are assigned at 515, 469 cm\(^{-1}\) in the IR spectrum and at 510, 457 cm\(^{-1}\) theoretically. Chohan et al. [22] reported the SO\(_2\) stretching vibrations at 1345, 1110 cm\(^{-1}\) and SN and CS stretching modes at 833 cm\(^{-1}\) for sulfonamide derivatives. Hangen et al. [23] reported SO\(_2\) modes at 1314, 1308, 1274, 1157, 1147, and 1133 cm\(^{-1}\) and SN stretching modes at 917, 920, 932, and 948 cm\(^{-1}\) for sulfonamide derivatives. The twisting mode of SO\(_2\) is expected at around 350 cm\(^{-1}\) [21]. The calculated bands (B3LYP) at 365, 298 cm\(^{-1}\) are assigned as the twisting and rocking modes of SO\(_2\). The NS stretching vibration is expected [21] in the region 905 ± 30 cm\(^{-1}\) and the band observed at 841 cm\(^{-1}\) in the IR spectrum and at 831 cm\(^{-1}\) theoretically are assigned as vSN. The C–S stretching vibration is assigned at 692 cm\(^{-1}\) (IR) and at 679 cm\(^{-1}\) (DFT) cm\(^{-1}\) [21].

The C=N stretching bands [24] are observed in the region 1550–1700 cm\(^{-1}\) and for the title compound, the B3LYP calculation give these bands at 1687(C12–N14), 1641 cm\(^{-1}\) (C30–N13). The CN stretching vibrations [21] are moderately to strongly active in the region 1275 ± 55 cm\(^{-1}\). Primary aromatic amines with nitrogen directly on the ring absorb at 1330–1200 cm\(^{-1}\) because of the stretching of the phenyl

HF or density functional theory (DFT) calculations or detailed vibrational infrared or Raman analyses have been performed on the title compound.

2. Experimental

All the chemicals were procured from Sigma-Aldrich, USA. 0.5 mg of sulphaguanidine and 0.3 mL of benzaldehyde in 20 mL ethyl alcohol were refluxed for 3 hrs. The white precipitate was filtered off, washed with ethanol, and dried. Elemental analysis: found/calculated (%): C 55.50/55.63; H 4.59/4.63; N 18.40/18.50; S 10.58/10.59. The FT-IR spectrum (Figure 1) was recorded on a DR/Jasco FT-IR 6300 spectrometer in KBr pellets, number of scans 16, resolution 2 cm\(^{-1}\). The FT-Raman spectrum (Figure 2) was obtained on a BRUKER RFS 100/S, Germany. For excitation of the spectrum the emission of an Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, measurement of solid sample. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2 cm\(^{-1}\).

3. Computational Details

Calculations of the title compound were carried out with Gaussin 03 program [16] using the HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. The wavenumber values computed contain known systematic errors [17] and we, therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets. Parameters corresponding to optimized geometry (B3LYP) of the title compound (Figure 3) are given in Table 1. The absence of imaginary values of wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. Potential energy distribution is done using GAR2PED program [18]. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes [19, 20]. Potential energy surface scan studies have been carried out to understand the stability of planar and non planar structures of the molecule. The profiles of potential energy surface for torsion angles C15–N14–C12–C3, N28–S25–C22–C20, N31–C30–N28–S25 and N32–C30–N33–S25 are given in Figures 4–7. The energy is minimum for −177.0 (−1309.42093 Hartree), 86.0 (−1309.41690 Hartree), 12.6 (−1309.42098 Hartree), and −169.9 (−1309.42070 Hartree) for the above torsion angles.

4. Results and Discussion

4.1. IR and Raman Spectra. The observed IR, Raman bands, and calculated (scaled) wavenumbers, and assignments are given in Table 2.

The asymmetric and symmetric stretching modes of SO\(_2\) group appear in the region 1360–1310 and 1165–1135 cm\(^{-1}\) [21]. The observed bands at 1358, 1130 cm\(^{-1}\) in the IR spectrum, 1360, 1133 cm\(^{-1}\) in the Raman spectrum, and 1371, 1148 cm\(^{-1}\) theoretically are assigned as SO\(_2\) stretching modes. These modes are not pure, but contain significant contributions from other modes also. Although the region of SO\(_2\) scissoring (560 ± 40 cm\(^{-1}\)) and that of SO\(_2\) wagging (500 ± 55 cm\(^{-1}\)) partly overlap, the two vibrations appear separately [21]. These deformation bands of SO\(_2\) are assigned at 515, 469 cm\(^{-1}\) in the IR spectrum and at 510, 457 cm\(^{-1}\) theoretically. Chohan et al. [22] reported the SO\(_2\) stretching vibrations at 1345, 1110 cm\(^{-1}\) and SN and CS stretching modes at 833 cm\(^{-1}\) for sulfonamide derivatives. Hangen et al. [23] reported SO\(_2\) modes at 1314, 1308, 1274, 1157, 1147, and 1133 cm\(^{-1}\) and SN stretching modes at 917, 920, 932, and 948 cm\(^{-1}\) for sulfonamide derivatives. The twisting mode of SO\(_2\) is expected at around 350 cm\(^{-1}\) [21]. The calculated bands (B3LYP) at 365, 298 cm\(^{-1}\) are assigned as the twisting and rocking modes of SO\(_2\). The NS stretching vibration is expected [21] in the region 905 ± 30 cm\(^{-1}\) and the band observed at 841 cm\(^{-1}\) in the IR spectrum and at 831 cm\(^{-1}\) theoretically are assigned as vSN. The C–S stretching vibration is assigned at 692 cm\(^{-1}\) (IR) and at 679 cm\(^{-1}\) (DFT) cm\(^{-1}\) [21].

The C=N stretching bands [24] are observed in the region 1550–1700 cm\(^{-1}\) and for the title compound, the B3LYP calculation give these bands at 1687(C12–N14), 1641 cm\(^{-1}\) (C30–N13). The CN stretching vibrations [21] are moderately to strongly active in the region 1275 ± 55 cm\(^{-1}\). Primary aromatic amines with nitrogen directly on the ring absorb at 1330–1200 cm\(^{-1}\) because of the stretching of the phenyl
The NH deformation band of guanidine structural motif is expected in the region 1395 ± 25 cm\(^{-1}\) [21, 25]. The DFT calculations give these modes at 1442 and 1485 cm\(^{-1}\). The bands observed at 1500, 1450 cm\(^{-1}\) in the IR spectrum and at 1486, 1446 cm\(^{-1}\) in the Raman spectrum are assigned as the deformation bands of NH group. The out-of-plane NH deformation is expected in the region 650 ± 50 cm\(^{-1}\) [21] and bands at 727 (IR), 729 (Raman) and 706, 608 cm\(^{-1}\) (DFT) are assigned as these modes.

Since the identification of all the normal modes of vibration of large molecules is not trivial, we tried to simplify the problem by considering each molecule as a substituted benzene. Such an idea has already been successfully utilized by several workers for the vibrational assignments of molecules containing homo- and heteroaromatic rings [30–32]. In the following discussion, mono- and parasubstituted phenyl rings are designated as PhI and PhII, respectively. The modes in the phenyl rings will differ in wavenumber and the magnitude of splitting will depend on the strength of the interactions between different parts (internal coordinates) of the two rings. For some modes, this splitting is so small that they may be considered as quasidegenerate, and for some other modes a significant amount of splitting is observed. Such observations have already been reported [33, 34].

The phenyl CH stretching modes occur above 3000 cm\(^{-1}\) and are typically exhibited as multiplicity of weak to moderate bands compared with the aliphatic CH stretching [35]. In the present case, the DFT calculations give \(\nu CH\) modes of the phenyl rings in the range 3132–3057 cm\(^{-1}\). The bands observed at 3026, 3073 cm\(^{-1}\) in the IR spectrum and at 3066 cm\(^{-1}\) in the Raman spectrum were assigned as CH stretching modes of the phenyl rings.

The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (occurring near 1600, 1580, 1490, and 1440 cm\(^{-1}\)) are good group vibrations. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers. In the absence of ring conjugation, the band at 1580 cm\(^{-1}\) is usually weaker than that at 1600 cm\(^{-1}\). In the case of C=O substitution, the band
Table 1: Geometrical (B3LYP) parameters of (E)-4-(benzylideneamino)-N-carbamimidoyl benzenesulfonamide, atom labeling according to Figure 3.

| Bond lengths (Å) | Bond angles (°) | Dihedral angles (°) |
|------------------|-----------------|--------------------|
| C1–C2           | 1.3901          | A(2,1,6)           | 120.2 | D(6,1,2,3) | −0.0 |
| C1–C6           | 1.4001          | A(2,1,7)           | 119.8 | D(6,1,2,8) | −180.0 |
| C1–H7           | 1.0866          | A(6,1,7)           | 119.9 | D(7,1,2,3) | 180.0 |
| C2–C3           | 1.4062          | A(1,2,3)           | 120.1 | D(7,1,2,8) | 0.0 |
| C2–H8           | 1.0852          | A(1,2,8)           | 121.3 | D(7,1,2,5) | 0.1 |
| C3–C4           | 1.4035          | A(3,2,8)           | 118.6 | D(7,1,6,11) | −180.0 |
| C3–C12          | 1.4666          | A(2,3,4)           | 119.2 | D(7,1,6,5) | −180.0 |
| C4–C5           | 1.3941          | A(2,3,12)          | 121.5 | D(7,1,6,11) | 0.0 |
| C4–H9           | 1.0878          | A(4,3,12)          | 119.3 | D(1,2,3,4) | −0.0 |
| C5–C6           | 1.3958          | A(3,4,5)           | 120.5 | D(1,2,3,12) | 180.0 |
| C5–H10          | 1.0864          | A(3,4,9)           | 119.4 | D(2,3,4,5) | 179.9 |
| C6–H11          | 1.0867          | A(4,5,6)           | 120.0 | D(2,3,4,12) | −0.2 |
| C12–H13         | 1.0906          | A(4,5,10)          | 120.2 | D(2,3,4,5) | 0.1 |
| C12–N14         | 1.2816          | A(4,5,11)          | 120.2 | D(2,3,4,5) | −179.9 |
| C13–N14         | 1.4020          | A(4,5,12)          | 120.2 | D(2,3,4,9) | −179.8 |
| C15–C16         | 1.4061          | A(1,6,5)           | 120.0 | D(12,3,4,5) | 0.2 |
| C15–C17         | 1.4078          | A(1,6,11)          | 120.0 | D(12,3,4,12) | −179.7 |
| C16–C18         | 1.3893          | A(5,6,11)          | 120.0 | D(12,3,4,13) | 1.1 |
| C16–H19         | 1.0854          | A(3,12,13)         | 115.6 | D(4,5,6,11) | 0.2 |
| C17–C20         | 1.3912          | A(3,12,14)         | 122.8 | D(4,5,6,12) | −179.9 |
| C17–H21         | 1.0859          | A(13,12,14)        | 121.6 | D(3,4,5,6) | −0.1 |
| C18–C22         | 1.3991          | A(12,14,15)        | 120.1 | D(3,4,5,10) | 180.0 |
| C18–H23         | 1.0845          | A(14,15,16)        | 117.8 | D(9,4,5,6) | 180.0 |
| C20–C22         | 1.3968          | A(14,15,17)        | 123.0 | D(9,4,5,10) | −0.0 |
| C20–H24         | 1.0827          | A(16,15,17)        | 119.2 | D(4,5,6,1) | −0.0 |
| C22–S25         | 1.7883          | A(15,16,18)        | 120.5 | D(4,5,6,11) | −180.0 |
| S25–O26         | 1.4658          | A(15,16,19)        | 118.6 | D(10,5,6,1) | 180.0 |
| S25–O27         | 1.4570          | A(18,16,19)        | 120.8 | D(10,5,6,11) | −0.0 |
| N31–H35         | 1.7054          | A(15,17,20)        | 120.7 | D(3,12,14,15) | −177.0 |
| N32–H39         | 1.0140          | A(15,17,21)        | 119.6 | D(13,12,14,15) | 3.8 |
| C30–N32         | 1.3990          | A(20,17,21)        | 119.7 | D(12,14,15,16) | −140.4 |
| C30–N31         | 1.2764          | A(16,18,22)        | 119.3 | D(12,14,15,17) | 42.1 |
| C30–N32         | 1.3990          | A(16,18,23)        | 120.9 | D(14,15,16,18) | −179.6 |
| N33–H35         | 1.0208          | A(22,18,23)        | 119.8 | D(14,15,16,19) | 1.7 |
| N32–H39         | 1.0149          | A(17,20,22)        | 119.1 | D(17,15,16,18) | −2.1 |
| N31–H35         | 1.0130          | A(17,20,24)        | 121.2 | D(17,15,16,19) | 179.2 |
| —               | —               | A(22,20,24)        | 119.7 | D(14,15,17,20) | 178.6 |
| —               | —               | A(18,22,20)        | 121.2 | D(14,15,17,21) | 0.6 |
| —               | —               | A(18,22,25)        | 118.7 | D(16,15,17,20) | 1.2 |
| —               | —               | A(20,22,25)        | 120.1 | D(16,15,17,21) | −176.8 |
| —               | —               | A(22,25,26)        | 107.7 | D(15,16,18,22) | 1.6 |
| —               | —               | A(22,25,27)        | 108.9 | D(15,16,18,23) | −177.7 |
| —               | —               | A(22,25,28)        | 107.7 | D(19,16,18,22) | −179.6 |
| —               | —               | A(26,25,27)        | 122.2 | D(19,16,18,23) | 1.0 |
| —               | —               | A(26,25,28)        | 101.5 | D(15,17,20,22) | −0.0 |
| —               | —               | A(27,25,28)        | 108.0 | D(15,17,20,24) | −178.6 |
| —               | —               | A(25,28,29)        | 112.2 | D(21,17,20,22) | 178.0 |
| —               | —               | A(25,28,30)        | 126.8 | D(21,17,20,24) | −0.5 |
| —               | —               | A(25,28,30)        | 117.8 | D(16,18,22,20) | −0.4 |
| —               | —               | A(28,30,31)        | 121.2 | D(16,18,22,25) | −179.4 |
Table 1: Continued.

| Bond lengths (Å) | Bond angles (°) | Dihedral angles (°) |
|------------------|-----------------|---------------------|
| —                | —               | A(28,30,32) 110.2   | D(23,18,22,20) 178.9 |
| —                | —               | A(31,30,32) 128.6   | D(23,18,22,25) 0.0   |
| —                | —               | A(30,31,35) 111.1   | D(17,20,22,18) −0.4  |
| —                | —               | A(30,32,33) 114.6   | D(17,20,22,25) 178.5 |
| —                | —               | A(30,32,34) 113.9   | D(24,20,22,18) 178.2 |
| —                | —               | A(33,32,34) 111.9   | D(24,20,22,25) −2.9  |
| —                | —               | —                   | D(18,22,25,26) 13.7  |
| —                | —               | —                   | D(18,22,25,27) 148.1 |
| —                | —               | —                   | D(18,22,25,28) −95.1 |
| —                | —               | —                   | D(20,22,25,26) −165.2|
| —                | —               | —                   | D(20,22,25,27) −30.8 |
| —                | —               | —                   | D(20,22,25,28) 86.0  |
| —                | —               | —                   | D(22,25,28,29) 91.5  |
| —                | —               | —                   | D(22,25,28,30) −67.8 |
| —                | —               | —                   | D(26,25,28,29) −21.4 |
| —                | —               | —                   | D(26,25,28,30) 179.3 |
| —                | —               | —                   | D(27,25,28,29) −151.1|
| —                | —               | —                   | D(27,25,28,30) 49.6  |
| —                | —               | —                   | D(25,28,30,31) 12.6  |
| —                | —               | —                   | D(25,28,30,32) −169.9|
| —                | —               | —                   | D(29,28,30,31) −145.7|
| —                | —               | —                   | D(29,28,30,32) 31.8  |
| —                | —               | —                   | D(28,30,31,35) −173.1|
| —                | —               | —                   | D(32,30,31,35) 9.8   |
| —                | —               | —                   | D(28,30,32,33) 43.7  |
| —                | —               | —                   | D(28,30,32,34) 174.5 |
| —                | —               | —                   | D(31,30,32,33) −139.0|
| —                | —               | —                   | D(31,30,32,34) −8.2  |

Figure 4: Profile of potential energy scan for the torsion angle C₁₅–N₁₄–C₁₂–C₃.

near 1490 cm⁻¹ can be very weak. The fifth ring stretching vibration is active near 1315 ± 65 cm⁻¹, a region that overlaps strongly with that of the CH in-plane deformation. The sixth ring stretching vibration, or the ring breathing mode, appears as a weak band near 1000 cm⁻¹, in mono-, 1, 3-di-, and 1, 3, 5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the ring in-plane deformation [21, 36].

The υₚh modes are expected in the region 1285–1610 cm⁻¹ and 1280–1630 cm⁻¹ for PhI and PhII rings, respectively [21]. The DFT calculations give the Ph stretching modes in the range 1290–1598 cm⁻¹ and 1265–1578 cm⁻¹ for PhI and PhII, respectively. For the title compound the phenyl ring stretching modes are observed at 1567, 1500 (IR), 1581, 1486 cm⁻¹ (Raman), and 1587, 1528, 1403, 1130 cm⁻¹ (IR), 1133 cm⁻¹ (Raman), for PhI and PhII, respectively. Most of the modes are not pure but contain significant contributions from other modes also. The ring breathing mode of the para substituted benzenes with entirely different substituents [36] has been reported in the interval 780–880 cm⁻¹. For the title compound, the ring breathing mode PhII is observed at 757 cm⁻¹ in the IR spectrum which is supported by the computational result at 747 cm⁻¹. The ring breathing mode of PhI is observed at 1001 cm⁻¹ in the Raman spectrum and the theoretical calculated value is
The IR bands in the region 2882–1915 cm\(^{-1}\) and their large broadening support the intramolecular hydrogen bonding [37].

4.2. Geometrical Parameters and First Hyperpolarizability. To the best of our knowledge, no X-ray crystallographic data of this molecule has yet been established. However, the theoretical results obtained are almost comparable with the reported structural parameters of the parent molecules.

Loughrey et al. [38] reported the bond lengths, \(S_{25–O_{27}} = 1.4337, S_{25–O_{26}} = 1.4256, S_{25–N_{28}} = 1.6051, S_{25–C_{22}} = 1.7737, C_{15–N_{14}} = 1.4212, C_{12–N_{14}} = 1.2712\), whereas the corresponding values for the title compound are 1.4570, 1.4658, 1.7054, 1.7883, 1.4020, and 1.2816 Å. For the title compound, the DFT calculations give the bond angles, \(C_{22–S_{25–O_{27}} = 108.9, C_{22–S_{25–O_{26}} = 107.7, S_{25–N_{28–H_{29}} = 112.2, O_{27–S_{25–O_{26}} = 122.2, O_{27–S_{25–N_{28}} = 108.0, O_{26–S_{25–N_{28}} = 101.5, N_{28–S_{25–C_{22}} = 107.7, C_{15–N_{14–C_{12} = 120.1, S_{25–C_{22–C_{18}} = 118.7, S_{25–C_{22–C_{20} = 120.1, C_{22–C_{18–C_{16} = 119.3, C_{18–C_{16–C_{15} = 120.5, C_{16–C_{15–C_{17} = 119.2, N_{14–C_{15–C_{17} = 123.0, N_{14–C_{15–C_{16} = 117.8, C_{15–C_{17–C_{20} = 120.7, N_{14–C_{12–C_{3} = 122.8°, whereas the corresponding reported values are 106.5, 107.4, 110.5, 107.7, 109.3, 118.8, 120.5, 119.1, 120.4, 119.9, 120.3, 119.3, 122.4, 118.2, 120.4, and 124.4° [38].

Loughrey et al. [38] reported the torsion angles, \(O_{27–S_{25–C_{22–C_{18} = −142.0, O_{27–S_{25–C_{22–C_{20} = 38.5, O_{26–S_{25–C_{22–C_{18} = −12.8, O_{26–S_{25–C_{22–C_{20} = 167.7, N_{28–S_{25–C_{22–C_{18} = 103.8, N_{28–S_{25–C_{22–C_{20} = −75.7, C_{12–N_{14–C_{15–C_{17} = 143.9, C_{12–N_{14–C_{15–C_{17} = −39.2, C_{15–N_{14–C_{12–C_{3} = 117.6, S_{25–C_{22–C_{18–C_{16} = −179.9, C_{20–C_{22–C_{18–C_{16} = −0.4, S_{25–C_{22–C_{20–C_{17} = 179.2, C_{18–C_{16–C_{15–N_{14 = 178.1, N_{14–C_{15–C_{17–C_{20} = −178.6, N_{14–C_{12–C_{3–C_{2} = 8.1, N_{14–C_{12–C_{3–C_{4} = −172.6°, For the title compound, the corresponding torsion angles are 148.1, −30.8, 13.7, −165.2, −95.1, 86.0, −140.4,

990 cm\(^{-1}\), as expected [21]. The in-plane and out-of-plane CH deformation bands of the phenyl ring are expected above and below 1000 cm\(^{-1}\) [21]. The in-plane CH deformation bands are assigned at 1319, 1160, 1156, 1096, 1076, and 1013 cm\(^{-1}\) for PhI and at 1317, 1230, 1103, and 1044 cm\(^{-1}\) for PhII theoretically. The strong γCH occurring at 840 ± 50 cm\(^{-1}\) is typical for 1, 4-disubstituted benzenes and the band observed at 804 cm\(^{-1}\) in the IR spectrum is assigned to this mode [21]. The in-plane and out-of-plane deformation modes of the phenyl ring are also identified and assigned (Table 2).
Table 2: Calculated vibrational wavenumbers (scaled), measured infrared and Raman band positions, and assignments of (E)-4-(benzylideneamino)-N-carbamimidoyl benzenesulfonamide.

| HF $\nu$ (cm$^{-1}$) | B3PW91 $\nu$ (cm$^{-1}$) | B3LYP $\nu$ (cm$^{-1}$) | $\nu_{\text{IR}}$ | $\nu_{\text{Raman}}$ | Assignments |
|----------------------|---------------------------|--------------------------|-------------------|------------------------|--------------|
| 3563                 | 3532                      | 3501                     | —                 | —                      | $\nu_2$NH$_2$ (100) |
| 3450                 | 3476                      | 3453                     | 3459              | —                      | $\nu_{13}$H$_{35}$ (82) |
| 3443                 | 3426                      | 3399                     | 3421              | —                      | $\nu_4$NH$_2$ (82) |
| 3376                 | 3381                      | 3351                     | 3351, 3222        | —                      | $\nu_{18}$H$_{39}$ (100) |
| 3072                 | 3136                      | 3132                     | 3073              | —                      | $\nu_{\text{CH II}}$ (97) |
| 3052                 | 3115                      | 3109                     | —                 | —                      | $\nu_{\text{CH II}}$ (99) |
| 3042                 | 3107                      | 3100                     | —                 | —                      | $\nu_{\text{CH I}}$ (96) |
| 3037                 | 3098                      | 3090                     | —                 | —                      | $\nu_{\text{CH II}}$ (99) |
| 3027                 | 3098                      | 3087                     | —                 | —                      | $\nu_{\text{CH I}}$ (94) |
| 3025                 | 3089                      | 3082                     | —                 | —                      | $\nu_{\text{CH II}}$ (97) |
| 3014                 | 3087                      | 3076                     | —                 | —                      | $\nu_{\text{CH I}}$ (94) |
| 3001                 | 3076                      | 3066                     | 3066              | —                      | $\nu_{\text{CH I}}$ (93) |
| 2991                 | 3067                      | 3057                     | 3026              | —                      | $\nu_{\text{CH I}}$ (93) |
| 2895                 | 2923                      | 2915                     | —                 | —                      | $\nu_{\text{C}_{12}H_{13}}$ (99) |
| 1683                 | 1637                      | 1687                     | —                 | —                      | $\nu_{\text{C}_{12}N_{14}}$ (68) |
| 1676                 | 1655                      | 1641                     | —                 | —                      | $\nu_{\text{C}_{30}N_{31}}$ (60) |
| 1640                 | 1609                      | 1602                     | 1620              | 1625                   | $\delta$NH$_3$ (87) |
| 1617                 | 1603                      | 1598                     | —                 | —                      | $\nu_{\text{Ph I}}$ (53) |
| 1600                 | 1590                      | 1578                     | 1587              | —                      | $\nu_{\text{Ph II}}$ (58) |
| 1590                 | 1583                      | 1571                     | 1567              | 1581                   | $\nu_{\text{Ph I}}$ (63) |
| 1578                 | 1564                      | 1552                     | 1528              | —                      | $\nu_{\text{Ph II}}$ (68) |
| 1501                 | 1487                      | 1485                     | 1500              | 1486                   | $\nu_{\text{Ph I}}$ (42), $\delta$NH I (39) |
| 1495                 | 1473                      | 1472                     | —                 | —                      | $\nu_{\text{Ph II}}$ (60), $\delta$CH I (15), $\delta$CH II (20) |
| 1472                 | 1442                      | 1442                     | 1450              | 1446                   | $\delta$NH (65) |
| 1456                 | 1440                      | 1430                     | —                 | —                      | $\nu_{\text{Ph I}}$ (64), $\delta$CH I (34) |
| 1407                 | 1397                      | 1394                     | 1403              | —                      | $\nu_{\text{Ph II}}$ (57), $\delta$CH II (36) |
| 1387                 | 1370                      | 1371                     | 1358              | 1360                   | $\nu_6$SO$_2$ (60), $\delta$H$_{13}$ (28) |
| 1334                 | 1335                      | 1319                     | —                 | —                      | $\delta$CH I (68) |
| 1319                 | 1332                      | 1317                     | 1313              | 1310                   | $\delta$CH II (84) |
| 1310                 | 1314                      | 1299                     | —                 | —                      | $\delta$NH (56) |
| 1242                 | 1294                      | 1290                     | —                 | —                      | $\nu_{\text{Ph I}}$ (67), $\delta$CH I (17) |
| 1233                 | 1279                      | 1281                     | —                 | —                      | $\nu_{\text{Ph I}}$ (40), $\nu_{\text{C}_{15}N_{14}}$ (58) |
| 1215                 | 1272                      | 1265                     | —                 | —                      | $\nu_{\text{Ph II}}$ (82) |
| 1185                 | 1236                      | 1230                     | 1236              | 1234                   | $\nu_{\text{Ph II}}$ (14), $\delta$CH II (42) |
| 1181                 | 1187                      | 1181                     | 1182              | 1188                   | $\delta$CH I (36), $\delta$NH$_2$ (56) |
| 1172                 | 1159                      | 1160                     | 1170              | 1168                   | $\nu_{\text{C}_{15}N_{14}}$ (18), $\delta$CH II (14), $\delta$CH I (60) |
| 1148                 | 1156                      | 1156                     | —                 | —                      | $\delta$CH I (48), $\nu_{\text{Ph I}}$ (40) |
| 1107                 | 1147                      | 1148                     | 1130              | 1133                   | $\nu_6$SO$_2$ (46), $\nu_{\text{Ph II}}$ (46) |
| 1086                 | 1118                      | 1103                     | —                 | —                      | $\delta$CH II (61), $\delta$NH$_2$ (28) |
| 1078                 | 1097                      | 1100                     | —                 | —                      | $\nu_{\text{C}_{30}N_{29}}$ (45), $\delta$NH$_2$ (36) |
| 1074                 | 1095                      | 1096                     | 1087              | 1088                   | $\delta$CH I (61), $\nu_{\text{Ph I}}$ (38) |
| 1066                 | 1083                      | 1076                     | —                 | —                      | $\delta$CH I (73) |
| 1058                 | 1071                      | 1069                     | 1057              | 1065                   | $\nu_{\text{Ph II}}$ (46) |
| 1045                 | 1056                      | 1044                     | —                 | —                      | $\delta$CH II (70) |
| 1037                 | 1017                      | 1013                     | 1010              | 1015                   | $\delta$CH I (63) |
| 1035                 | 990                       | 990                      | —                 | 1001                   | $\nu_{\text{Ph I}}$ |
| 1029                 | 984                       | 980                      | —                 | —                      | $\gamma$CH II (69) |
| 1020                 | 980                       | 978                      | 971               | 974                    | $\gamma$CH I (82) |
| 1007                 | 977                       | 972                      | —                 | —                      | $\gamma$CH II (81) |
| HF $v$ (cm$^{-1}$) | B3PW91 $v$ (cm$^{-1}$) | B3LYP $v$ (cm$^{-1}$) | $\nu$(IR) | $\nu$(Raman) | Assignments |
|-------------------|------------------------|-----------------------|-----------|-------------|-------------|
| 994               | 966                    | 965                   | —         | —           | $\gamma$CH I (80) |
| 990               | 945                    | 942                   | 948       | —           | $\nu$C$_{35}$N$_{32}$ (68) |
| 975               | 940                    | 940                   | —         | —           | $\gamma$CH I (74) |
| 897               | 925                    | 926                   | 921       | 922         | $\gamma$CH II (79) |
| 887               | 902                    | 901                   | —         | —           | $\gamma$CH I (99) |
| 873               | 867                    | 865                   | 884       | 882         | $\gamma$CH II (89) |
| 859               | 831                    | 831                   | 841       | —           | $\nu$SN (67) |
| 847               | 830                    | 823                   | 829       | 820         | $\gamma$CH II (59), $\gamma$CH$_{13}$ (15) |
| 809               | 819                    | 819                   | —         | —           | $\gamma$CH II (57), rPh I (12) |
| 795               | 811                    | 806                   | —         | —           | $\delta$NH (82) |
| 798               | 800                    | 802                   | 796       | —           | $\gamma$CH I (63) |
| 782               | 776                    | 778                   | —         | —           | $\delta$NH$_2$ (61) |
| 748               | 745                    | 747                   | 757       | 751         | $\nu$Ph II (64) |
| 715               | 707                    | 706                   | 727       | 729         | $\gamma$NH (69) |
| 710               | 690                    | 689                   | 709       | 709         | $\gamma$CH I (25), $\delta$Ph I (64) |
| 694               | 678                    | 679                   | 692       | —           | rCS (58), $\delta$CN (23) |
| 656               | 673                    | 673                   | —         | —           | $\delta$SO$_2$ (40), $\delta$Ph II (18) |
| 636               | 619                    | 621                   | 633       | 629         | $\delta$Ph II (79) |
| 626               | 612                    | 610                   | 612       | 610         | $\delta$Ph I (85) |
| 602               | 605                    | 608                   | —         | —           | $\gamma$NH (65) |
| 570               | 590                    | 590                   | —         | —           | $\delta$Ph I (29), $\delta$Ph II (20), $\delta$CN (24) |
| 554               | 575                    | 579                   | —         | —           | rPhII (30), $\gamma$CS (17), $=CN$ (17) |
| 521               | 542                    | 541                   | 556       | 543         | rPhI (51), $\delta$CC$_{12}$ (31) |
| 510               | 530                    | 529                   | —         | —           | $\delta$NH (46), $\delta$NH$_2$ (32) |
| 478               | 509                    | 510                   | 515       | —           | $\delta$NH$_2$ (28), $\delta$SO$_2$ (47), $\delta$CN (14) |
| 468               | 497                    | 496                   | —         | —           | $\gamma$NH$_2$ (41), rPhI (20) |
| 442               | 455                    | 457                   | 469       | 460         | $\delta$SO$_2$ (41), $\gamma$NH (39) |
| 427               | 424                    | 419                   | 435       | —           | rPhII (84) |
| 419               | 405                    | 407                   | 408       | 415         | rPhI (84) |
| 413               | 399                    | 401                   | —         | —           | $\delta$SO$_2$ (40), rPhII (31) |
| 376               | 398                    | 397                   | —         | —           | $\delta$CN (35), rPhII (33) |
| 345               | 366                    | 365                   | —         | —           | $\delta$SO$_2$ (47), $\delta$CS (24) |
| 320               | 355                    | 353                   | —         | —           | $\delta$SO$_2$ (39), rCC (25) |
| 299               | 349                    | 347                   | —         | 343         | $\gamma$NH (64), SO$_2$ (15) |
| 275               | 342                    | 338                   | —         | —           | rNH (39), rPhI (36) |
| 270               | 299                    | 298                   | —         | 295         | $\delta$SO$_2$ (40), rNH (23) |
| 247               | 275                    | 275                   | —         | —           | $\delta$SO$_2$ (50), $\gamma$NH (28) |
| 243               | 253                    | 253                   | —         | 255         | rSO$_2$ (36), $\delta$CN (31) |
| 204               | 216                    | 217                   | —         | 209         | rSO$_2$ (48), rPhII (29) |
| 162               | 177                    | 179                   | —         | —           | $r$SO$_2$ (28), rNH (21), rCS (17) |
| 156               | 160                    | 160                   | —         | —           | $\delta$NH (47), $r$CN (26) |
| 133               | 138                    | 138                   | —         | —           | $\delta$NH (44), SO$_2$ (25) |
| 120               | 127                    | 128                   | —         | 120         | rCN (45), $\delta$SO$_2$ (38) |
| 108               | 107                    | 107                   | —         | —           | rCN (34), $r$CN (27) |
| 80                | 82                     | 81                     | —         | —           | $r$CN (38), $r$SO$_2$ |
| 59                | 55                     | 55                     | —         | —           | rCN (38), SO$_2$ (29) |
| 49                | 48                     | 48                     | —         | —           | rSO$_2$ (25), rCN (34) |
| 41                | 43                     | 42                     | —         | —           | rCN (53), SO$_2$ (12) |
| 25                | 24                     | 24                     | —         | —           | rPh II (63), rCN (56), $r$SO$_2$ (21) |
| 22                | 22                     | 23                     | —         | —           | rSO$_2$ (39), rCN (24), rNH (10) |

$\nu$: stretching, $\delta$: in-plane bending, $\gamma$: out-of-plane bending, $r$: torsion, PhI: monosubstituted phenyl ring, PhII: parasubstituted phenyl ring. Subscripts: as: asymmetric; s: symmetric.
42.1, −177.0, −179.4, −0.4, 178.5, −179.6, 178.6, 1.1, and −179.0°.

Petrov et al. [39] reported the molecular structure and conformations of benzenesulfonamide by gas electron diffraction and quantum chemical calculations and according to their results, the bond lengths, CS, SN, SO vary in the range 1.7756–1.7930, 1.6630–1.6925, 1.4284–1.4450 Å the bond angles, CNS, CSN, NOS, HNS, HNH vary in the range, 103.9–107.1, 107.6–107.8, 105.5–107.7, 111.0–113.7, 112.6–113.6 Å. These values are in agreement with the corresponding values for the title compound.

Lasbal et al. [40] reported the bond lengths SO = 1.4269–1.4291, SN = 1.6202, SC = 1.7582, N32–C30 = 1.4103, O31–C30 = 1.2723, N28–C30 = 1.3483 Å, whereas the corresponding values in the present case are 1.4658–1.4570, 1.7054, 1.7833, 1.3930, 1.2764, and 1.4033 Å. The values of bond angles O27–S25–O26 = 118.6, O26–S25–N28 = 108.9, O27–S25–N28 = 104.9, O27–S25–C22 = 107.9–108.3, N28–S25–C22 = 107.9, C30–N28–S25 = 123.0° reported by Lasbal et al. [40] are in agreement with our values.

At C3 position, the bond angles C4–C3–C2, C4–C3–C12, and C3–C1–C12 are 119.2, 119.3, and 121.5° respectively. This asymmetry in angles reveals the interaction between azomethane and the phenyl groups. At C15 position the angles C17–C15–N14 is increased by 3° and C16–C15–N14 is reduced by 2.2° from 120° which reveals the interaction between N14 and H21 atoms. At C22 position C20–C22–S25 = 120.1° and C20–C22–C18 = 121.2° which shows the interaction between SO2 group with H24 atom. At N28 position, S25–N28–H29 is reduced by 7.8° and S35–N35–C30 is increased by 6.8° from 120° which shows the interaction between H29 and O27. The C12 = N14 moiety is slightly tilted from monosubstituted phenyl ring as is evident from the torsion angles C3–C4–C3–C12 = −179.8, C4–C3–C12–N14 = −179.0°, C1–C2–C3–C12 = 179.9, C2–C3–C12–N14 = 177.4° and is more tilted from the para substituted phenyl ring as is evident from the torsion angles C20–C17–C15–N14 = 178.6, C17–C15–C14–C12 = 42.1, C18–C16–C15–N14 = 179.6, and C16–C15–N14–C12 = −140.4°. The torsion angle S25–N28–C30–N32 = −169.9 and S35–N28–C30–N31 = 12.6°, which shows that the N31 and N32 atoms are in different planes.

Nonlinear optics deal with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [41]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing [42, 43]. In this context, the dynamic first hyperpolarizability of the title compound is also calculated in the present study. The first hyperpolarizability (β0) of this novel molecular system is calculated using B3LYP method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [44]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

\[
E = E_0 - \sum_i \mu_i F_i - \frac{1}{2} \sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l + \cdots ,
\]

where \(E_0\) is the energy of the unperturbed molecule, \(F_i\) is the field at the origin, \(\mu_i, \alpha_{ij}, \beta_{ijk}\), and \(\gamma_{ijkl}\) are the components of dipole moment, polarizability, the first hyperpolarizabilities, and second hyperpolarizabilities, respectively. The calculated first hyperpolarizability of the title compound is \(6.25 \times 10^{-30}\) esu, which is comparable with the reported values of similar derivatives, but experimental evaluation of this data is not readily available. Kucharski et al. [45] reported the first hyperpolarizability of certain sulfonamide amphiphiles by calculation and hyper-Rayleigh scattering in the range 0.2156–0.189 × 10^{-30} esu. We conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

5. Conclusion

The FT-IR and FT-Raman spectrum of the title compound were recorded and analyzed. The molecular geometry and vibrational wavenumbers were calculated using HF and DFT methods, and the optimized geometrical parameters (B3LYP) are in agreement with that of reported similar derivatives. The red shift of the N–H stretching band in the infrared spectrum from the computed wavenumber indicates the weakening of the N–H bond. The calculated first hyperpolarizability is comparable with the reported value of similar derivative and may be an attractive object for further studies of non linear optics. Potential energy surface scan studies have been carried out to understand the stability of planar and non planar structures of the molecule.

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