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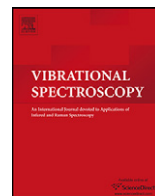


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Conformational analysis and vibrational study of sulfanilamide

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ABSTRACT

The possible stable conformers of sulfanilamide molecule were searched by potential energy surface scan at both semi-empirical PM3 and DFT/B3LYP-3-21G levels of theory. Both the harmonic and anharmonic vibrational modes, the corresponding wavenumbers and IR and Raman intensities of the conformers were calculated by DFT method at B3LYP/6-31++G(d,p) level. The assignments of the fundamentals were proposed on the basis of total energy distribution (TED) calculations. The IR and Raman spectra of solid sulfanilamide were recorded and compared with the calculated ones. The dimer of the title compound were studied at DFT/B3LYP/6-31++G(d,p) level to investigate the intermolecular hydrogen bonding interactions of sulfanilamide molecule.

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1. Introduction

Sulfanilamide is the parent compound of a group of pharmaceuticals known as sulfa drugs, which are synthetic antimicrobial agents that contain the sulfonamide group. Sulfanilamides were widely used as effective chemotherapeutic agents for the prevention and cure of bacterial infections in humans [1]. It is used in treatment of meningitis, tonsillitis, gonorrhea, pneumonia and sinus infections [2]. Since the study of polymorphism is an important issue in the pharmaceutical industry, the crystal structure of sulfanilamide has been widely investigated by many researchers so far and various polymorphs were determined [3–9]. X-ray diffraction studies of three most common polymorphs of sulfanilamide (α , β and γ) have been studied and crystal structure parameters were determined [3–6]. Lin et al. characterized the physical properties of four (α , β , γ and δ) polymorphs of sulfanilamide by X-ray diffraction measurements [8]. Although the polymorphic behaviour of the title compound has been extensively studied, there had been confusion about the stability of the polymorphs in the older studies. In the recent study of Portieri et al., β -sulfanilamide was found to be the stable form at room temperature and the α and γ forms to revert to β form on storage. The δ form was also determined by these workers but they were not able to produce sufficient amount of that form for spectroscopic characterization [7]. In a very recent

study of Gelbrich et al., the δ form was determined to be another stable form in addition to the β form [9].

Also, experimental and theoretical vibrational analysis of sulfanilamide has been reported in some studies. Varghese et al. [10] studied the molecular structure and vibrational frequencies of free sulfanilamide at HF level using 6-21G* basis set together with experimental FT-Raman and FT-IR spectra. Topaccli and Topaccli [11–14] performed IR analysis and computed the molecular structure and vibrational frequencies of free sulfanilamide and its metal complexes by both ab-initio methods employing 3-21G basis set and PM3, AM1, MINDO, MINDO3 semi-empirical methods. The RAMAN spectra of sulfathiazole and sulfanilamide were recorded by Lopez-Sanchez et al. [15].

Another vibrational study was done by Popova et al. [16] at DFT/B3LYP/6-31G++G(d,p) level of theory in which two stable conformers of sulfanilamide molecule were determined. Up to now, no systematic conformational analysis studies have been reported. In previous studies, assignments of the fundamentals were based on approximations rather than TED calculations. Furthermore, there were no theoretical vibrational studies reported on dimer and hydrogen bonding interactions of sulfanilamide molecule.

Since the differences between the polymorphic forms are associated with the existence of different conformers of the sulfanilamide molecule in the crystal lattice, the complete theoretical conformational analysis of free sulfanilamide molecule was done and four conformers were obtained. The effects of conformational changes were investigated through the optimized structure and the vibrational spectra of each conformer were obtained by DFT calculations. Since the crystal structure of α , γ and δ sulfanilamide is formed

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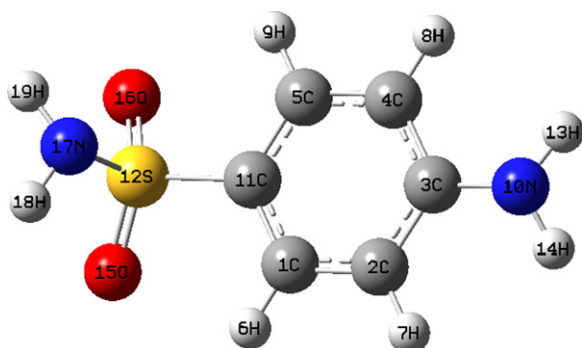


Fig. 1. Molecular model and numbering of atoms of free sulfanilamide molecule.

by joining of dimers together [9], in order to model H-bonding between the sulfanilamide molecules in the crystal structure, the dimer of the title compound is studied.

2. Methods and calculations

2.1. Experimental

The FT-Raman spectrum of the sulfanilamide was obtained from powdered sample placed in a Pyrex tube using the Bruker RFS 100/S spectrometer in the 4000–20 cm^{-1} range. The 1064 nm line, provided by a near infrared Nd:YAG air-cooled laser was used as excitation line. The output laser power was set to 100–120 mW.

The IR spectrum of solid sulfanilamide was recorded by KBr disc technique in the range 4000–400 cm^{-1} with 2 cm^{-1} resolution on a Jasco 300 FT-IR spectrometer by accumulating 200 scans.

2.2. Computational details

The theoretical conformational analysis of free sulfanilamide was done by single point energy calculations at both semi-empirical PM3 and DFT/B3LYP/3-21G theory levels. The dihedral angles around the 17N-12S, 12S-11C and 3C-10N bonds (see in Fig. 1) were altered by 30° in each iteration. The obtained structures were optimized at the same level of theory used in single point energy calculations to check the structures that correspond to local minima. The structures corresponding to real minima are reoptimized, their harmonic and anharmonic force fields, vibrational frequencies and IR and Raman intensities were calculated at DFT/B3LYP/6-31G++(d,p) theory levels. The calculations were performed by means of the Gaussian 03 software package [17]. The molecular model of free sulfanilamide is given in Fig. 1. The total energy distribution (TED %) calculations were done by the scaled quantum mechanical (SQM) force field method using the Parallel Quantum Solutions (PQS) program [18]. In order to investigate the hydrogen bonding interactions in the crystal structure, dimer of the title compound were formed and studied at DFT/B3LYP/6-31++G(d,p) level of theory.

3. Results and discussion

3.1. Conformational changes and polymorphism

The theoretical conformational analysis shows that the free sulfanilamide molecule has four conformers, two of them stable at room temperature (see in Fig. 2). Considering the energy differences between the global minimum (lowest energy) conformer and the other three conformers (see Table 1), it is seen that the energy of the first two conformers are less than kT energy (0.6 kcal/mol at room temperature and 1 atm pressure) indicating that these

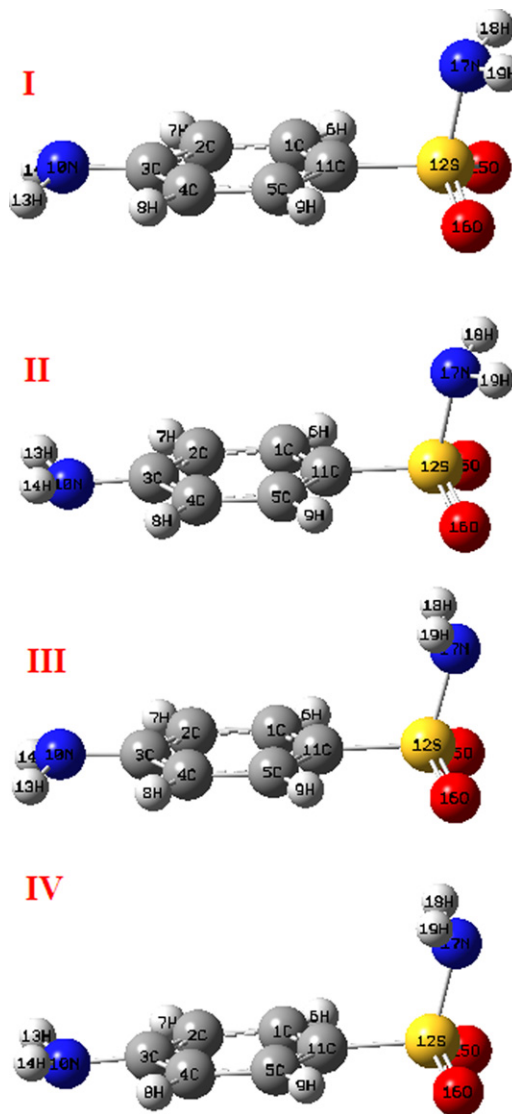


Fig. 2. The four low energy stable conformers of free sulfanilamide molecule: Global minimum conformer (I), second (II), third (III) and fourth (IV) lowest energy conformers.

two conformers have considerable population at room temperature. The energy difference of the third and fourth conformer with respect to the lowest energy conformer is calculated as 0.92 and 1.03 kcal/mol, respectively, which shows that these conformers are energetically less favourable than the first two conformers at room temperature. The optimized geometrical parameters of the global minimum conformer (I) and four stable conformers (I–IV) of sulfanilamide molecule and the optimized dihedral angles of

Table 1

The SCF energies of four conformers of free sulfanilamide molecule.

Conformers	Calculated SCF energies ^a		Relative energies ^c	
	(hartree)	(hartree) ^b	(hartree)	(kcal/mol)
Conf. I	–891.572888	–891.429399	0	0
Conf. II	–891.572733	–891.429266	0.000133	0.08346
Conf. III	–891.571868	–891.427939	0.001460	0.91616
Conf. IV	–891.571588	–891.427756	0.001643	1.03100

^a Calculated at DFT/6-31G++(d,p) level.

^b Corrected for zero-point vibrational energy.

^c The relative energies of the conformers are given with respect to the global minimum conformer (Conf. I).

Table 2

The optimized dihedral angles ($^{\circ}$) of the four stable conformers (I, II, III, IV) of sulfanilamide molecule obtained at DFT-B3LYP/6-31G++(d,p) level.^a

Dihedral angle	Conformers			
	I	II	III	IV
D(1,2,3,10)	178.0	−177.8	178.1	−177.6
D(7,2,3,10)	−2.2	1.4	−2.5	1.2
D(10,3,4,5)	−178.1	177.8	−178.0	177.6
D(10,3,4,8)	2.2	−1.4	2.5	−1.6
D(2,3,10,13)	159.7	−21.9	159.8	−21.9
D(2,3,10,14)	22.0	−160.5	22.1	−161.1
D(4,3,10,13)	−22.2	160.8	−22.0	161.0
D(4,3,10,14)	−160.0	22.2	−159.7	21.7
D(11,12,17,18)	−105.8	−106.1	−67.1	−67.2
D(11,12,17,19)	126.7	126.7	67.2	67.3
D(15,12,17,18)	8.8	8.5	47.6	47.6
D(15,12,17,19)	−118.7	−118.8	−178.1	−178.0
D(16,12,17,18)	139.6	139.3	178.2	178.1
D(16,12,17,19)	12.1	12.1	−47.6	−47.4
D(1,11,12,17)	96.0	95.5	89.7	89.7
D(5,11,12,16)	27.9	27.6	23.0	23.1
D(1,11,12,15)	−18.2	−18.6	−23.1	−23.1

the four stable conformers that differ from each other are given in Table S1 (see Supplementary material) and Table 2, respectively. The conformers differ from each other according to the orientation of amino groups both in the sulfon and aniline side of the molecule with respect to the phenyl ring. Despite the change in the dihedral angles around the 17N–12S, 12S–11C and 3C–10N bonds, calculations show that the bond length and bond angle parameters are only slightly affected by it.

When the molecular model and the total energies of the calculated conformers are compared to the structures obtained by Popova et al. [16], it is seen that conformers I and IV correspond to their structures 1a and 1b, respectively.

The crystal structure parameters of the four polymorphic forms of sulfanilamide are given as a Supplementary material (see Table S2) [3–6,9]. The dihedral angle parameters for these polymorphs are not given in those published papers. The bond distance (*R*) and bond angle (*A*) parameters of each polymorph are slightly different from each other.

The three dihedral angles (C1–C11–S12–N17, C5–C11–S12–O16, C1–C11–S12–O15) of the α , β , γ and δ forms of sulfanilamide obtained from the unpublished results by Portieri et al. and Hursthouse et al. were given in the recent study of Portieri et al. [7]. These three dihedral angle parameters of α , β , γ and δ forms of sulfanilamide [7] are given together with the calculated parameters of the four conformers (I–IV) in Table 3. In the study of Portieri et al., the main difference in the crystal structures of these polymorphs are said to be associated with the dihedral angle C1–C11–S12–N17 [7]. It can be seen from Table 3 that the dihedral angles of conformers I and II correspond to the angles of δ -sulfanilamide. In the present study, conformers I and II are found to be stable at room temperature. Since δ form is determined as a stable polymorph at room temperature in the previous studies [7,9], this finding is in agreement with this result. Table 3 also indicates that the dihedral angles of conformers III and IV correspond to the angles of γ -sulfanilamide that is not known as a stable polymorph [7–9]. Since the conformers III and IV are calculated as energetically less favourable conformers at room

temperature, we suggest that these conformers correspond to the unstable γ -form.

The experimentally obtained wavenumbers in solid phase, the calculated and scaled harmonic and anharmonic vibrational wavenumbers of the dimer and four conformers (I–IV) ([16] and this work), and TED of the modes are given in Table 4. The vibrational motions examined by means of GaussView were also considered during the assignment procedure.

The scaled theoretical IR spectra of the four conformers (I–IV) are given in Fig. 3. The experimentally obtained FT-IR and FT-Raman spectra of solid sulfanilamide are given in Fig. 4. While the scaled harmonic wavenumbers are closer to the experimental ones than the anharmonic corrections, the wavenumbers obtained for the dimer of the title compound gave the best fit to the experimental values.

In each conformer, the difference in the orientation of amino groups with respect to the phenyl ring results in a significant change in ν_2 , ν_{18} , ν_{28} , ν_{33} (NH, SO, NS, CS stretching), ν_{34} , ν_{42} (NH, NCC bending), and ν_{39} , ν_{49} , ν_{51} (NC, NS, SC torsional) frequencies. The ν_2 , ν_{18} , ν_{28} , ν_{33} stretching, ν_{42} bending and ν_{49} , ν_{51} torsional modes in conformers III and IV show upward shift in comparison to I and II. The ν_{28} stretching and ν_{34} bending modes show downward shift in conformers III and IV compared to I and II. The ν_{39} bending frequency also decreases in conformers II and IV in comparison to I and III (see Table 4). The CS stretching mode is observed at 636 cm^{-1} and 625 cm^{-1} in IR and Raman spectra, respectively, and calculated with strong intensity at 635 cm^{-1} and 637 cm^{-1} for the conformers I and II, and 669 cm^{-1} for the conformers III and IV. While the NC stretching mode is observed at 1304 cm^{-1} and 1300 cm^{-1} in IR and Raman spectra, it is calculated with strong intensity at 1283 cm^{-1} and 1284 cm^{-1} for conformers I and II, respectively, this mode cannot be observed in the calculated spectra of conformers III and IV. Also the SO_2 asymmetric stretching mode observed at 1314 cm^{-1} in the measured IR spectra, was calculated as 1339 , 1339 , 1354 , and 1355 cm^{-1} for the conformers I, II, III, and IV, respectively. The NS stretching mode observed at 837 cm^{-1} and 844 cm^{-1} in the IR and Raman spectra, respectively, were calculated at 832 cm^{-1} for I, 833 cm^{-1} for II, and 785 cm^{-1} for III and IV.

These results indicate that the calculated spectra of conformers I and II fit the measured spectra better than those of conformers III and IV. From these findings we can suggest that conformers I and II that are found to be stable at room temperature can be attributed to the structure that we have examined experimentally, which also correspond to the δ polymorph of sulfanilamide. And we can also suggest that the modification we have examined experimentally is the δ polymorph of sulfanilamide that is said to be one of the two stable polymorphs of the title compound.

3.2. The dimer of sulfanilamide

The molecular model of the dimer of the title compound is given in Fig. 5. In the dimer, one of the sulfon oxygens is bound to one of the amino hydrogens by H-bonds. In the crystal model of delta-sulfanilamide one of the sulfonyl oxygen atom is engaged in two $\text{NH}\cdots\text{O}$ bonds with hydrogens of the aniline NH_2 group of two neighboring molecules. The dimers are formed by the hydrogen bonds between one of the hydrogens of the aniline NH_2 group and one of the sulfonyl oxygens. And the dimers are joined together

Table 3

Dihedral angles ($^{\circ}$) for α , β , γ and δ forms of sulfanilamide crystals [7] and for optimized conformers I, II, III and IV of the free sulfanilamide molecule.

Dihedral angle	$\alpha^{[7]}$	$\beta^{[7]}$	$\gamma^{[7]}$	$\delta^{[7]}$	I	II	III	IV
C1–C11–S12–N17	124.2	108.2	91.4	97.1	96	95.5	89.7	89.7
C5–C11–S12–O16	54.8	42.4	29.4	30.7	27.9	27.6	23	23.1
C1–C11–S12–O15	8.2	−8.8	−24.2	−18.2	−18.2	−18.6	−23.1	−23.1

Table 4
Comparison of vibrational frequencies (cm^{-1}) of the conformers (I, II, III, IV) of free sulfanilamide and dimer of the molecule calculated at DFT-B3LYP/6-31G++(d,p) level of theory with the IR and Raman spectroscopic experimental data for solid sulfanilamide.

Modes	Ra ^a	IR ^a	DFT ^[16] har.	DFT ^a	DFT (harmonic) ^a				DFT (anharmonic) ^a				TED (total energy distribution) (%)
					Dimer ^{b,c}	I ^b	II ^b	III ^b	IV ^b	I	II	III	IV
ν_1, ν_{NH_2}	–	3478	3471	3485, 3489	3526	3530	3526	3534	3536	3560	3540	3555	ν_{NH_2} (100) ^{asym} (anilin)
ν_2, ν_{NH_2}	–	–	3401	3436, 3460	3453	3452	3468	3468	3458	3459	3474	3473	ν_{NH_2} (100) ^{asym} (sulfonamide)
ν_3, ν_{NH_2}	3376	3375	3368	3372, 3358	3418	3422	3420	3425	3443	3461	3445	3458	ν_{NH_2} (100) ^{sym} (anilin)
ν_4, ν_{NH_2}	3264	3266	3293	3327, 3343	3341	3341	3349	3349	3358	3357	3365	3364	ν_{NH_2} (100) ^{sym} (sulfonamide)
ν_5, ν_{CH}	–	–	3027	3066, 3064	3066	3066	3062	3062	3135	3030	3080	3083	ν_{CH} (98)
ν_6, ν_{CH}	3069	3068	3025	3063, 3062	3064	3064	3061	3061	3097	3031	3079	3082	ν_{CH} (98)
ν_7, ν_{CH}	3040	3037	2992	3044, 3048	3030	3032	3030	3030	3035	3013	3025	3027	ν_{CH} (96)
ν_8, ν_{CH}	–	–	2991	3033, 3030	3029	3030	3029	3029	3058	3023	3046	3049	ν_{CH} (97)
$\nu_9, \delta_{\text{HNNH}}$	1631	1629	1601	1640, 1637	1618	1620	1620	1619	1629	1625	1627	1629	δ_{HNNH} (48) ^{anilin} + δ_{HNC} (26)
$\nu_{10}, \nu_{\text{CC}}$	1594	1595	1608	1598, 1595	1598	1597	1596	1596	1604	1533	1605	1602	ν_{CC} (55) + δ_{HNNH} (12) ^{anilin} + δ_{CCH} (8) + δ_{CNH} (7)
$\nu_{11}, \nu_{\text{CC}}$	–	1572	1556	1565, 1564	1573	1572	1570	1569	1584	1578	1581	1580	ν_{CC} (72)
$\nu_{12}, \delta_{\text{HNNH}}$	1559	1550	1525	1542, 1543	1539	1539	1540	1540	1566	1559	1558	1558	δ_{HNNH} (53)sulfonamide + δ_{HNS} (33)
$\nu_{13}, \delta_{\text{CCH}}$	1505	1504	1479	1491, 1490	1491	1491	1489	1489	1482	1427	1501	1500	δ_{CCH} (53) + ν_{CC} (27) + ν_{NC} (9)
$\nu_{14}, \nu_{\text{CC}}$	–	1440	1416	1429, 1428	1424	1424	1423	1423	1447	1452	1437	1434	ν_{CC} (38) + δ_{CCH} (37)
$\nu_{15}, \nu_{\text{CC}}$	–	1338	1329	1341, 1340	1332	1332	1331	1330	1309	1300	1338	1338	ν_{CC} (73) + δ_{HNC} (12)
$\nu_{16}, \delta_{\text{CCH}}$	–	1294	1291	1293, 1293	1292	1292	1290	1290	1306	1307	1301	1305	δ_{CCH} (76) + ν_{CC} (19)
$\nu_{17}, \nu_{\text{NC}}$	1300	1304	1282	1301, 1299	1283	1284	1285	1285	1304	1213	1302	1299	ν_{NC} (51) + δ_{CCH} (17) + ν_{CC} (13)
$\nu_{18}, \nu_{\text{SO}_2}$ asym	1318	1314	1269	1314, 1324	1339	1339	1354	1355	1288	1286	1299	1304	ν_{SO} (85) + δ_{HNS} (8)
$\nu_{19}, \delta_{\text{CCH}}$	1189	1188	1177	1172, 1174	1172	1172	1171	1171	1190	1194	1190	1189	δ_{CCH} (75) + ν_{CC} (18)
$\nu_{20}, \delta_{\text{CCH}}$	1158	–	1126	1127, 1126	1118	1118	1117	1117	1135	1132	1136	1137	δ_{CCH} (63) + ν_{CC} (20) + δ_{HNC} (10)
$\nu_{21}, \nu_{\text{SO}_2}$ sym	1135	1147	1104	1157, 1167	1166	1166	1169	1069	1102	1001	1111	1110	ν_{SO} (33) + ν_{CC} (24) + ν_{SC} (17) + δ_{CCH} (11)
$\nu_{22}, \delta_{\text{HNS}}$	1095	1096	1066	1067, 1055	1055	1055	1051	1051	1044	1039	1053	1053	δ_{HNS} (73) + ν_{OS} (13)
$\nu_{23}, \nu_{\text{CC}}$	–	1067	1058	1047, 1034	1047	1047	1053	1053	1062	959	1066	1066	ν_{CC} (17) + ν_{OS} (54) + δ_{HNS} (9)
$\nu_{24}, \delta_{\text{HNC}}$	–	–	1052	1063, 1065	1041	1039	1039	1036	1042	1040	1042	1025	δ_{HNC} (59) + ν_{CC} (23)
$\nu_{25}, \delta_{\text{CCC}}$	1006	1003	1004	987, 987	989	989	988	988	1007	891	1003	1003	δ_{CCC} (37) + δ_{CCH} (26) + ν_{CC} (21)
$\nu_{26}, \tau_{\text{HCCH}}$	969	969	963	948, 945	947	946	950	950	943	942	972	958	τ_{HCCH} (40) + τ_{CCCH} (25) + τ_{SCCH} (16)
$\nu_{27}, \tau_{\text{HCCH}}$	900	900	950	935, 931	933	937	939	939	1229	302	847	940	τ_{HCCH} (42) + τ_{CCCH} (23) + τ_{SCCH} (16)
$\nu_{28}, \nu_{\text{NS}}$	844	837	854	844, 792	832	833	785	785	968	686	760	757	ν_{NS} (28) + τ_{HNSO} (14) + δ_{HNS} (11) + ν_{CC} (13) + δ_{HNS} (11)
$\nu_{29}, \tau_{\text{CCCH}}$	821	824	837	817, 822	814	810	811	812	990	533	822	835	τ_{CCCH} (22) + τ_{NCCH} (21)
$\nu_{30}, \nu_{\text{CC}}$	–	–	827	810, 813	804	808	820	818	818	671	820	848	ν_{CC} (16) + ν_{CN} (10) + τ_{NCCH} (10) + ν_{NS} (9)
$\nu_{31}, \tau_{\text{CCCH}}$	–	–	822	801, 795	798	797	801	800	809	819	819	812	τ_{CCCH} (65) + τ_{NCCH} (21) + τ_{SCCH} (11)
$\nu_{32}, \tau_{\text{CCCC}}$	715	–	731	696, 690	701	708	698	700	1196	–646	522	671	τ_{CCCC} (46) + τ_{CCCH} (23)
$\nu_{33}, \nu_{\text{CS}}$	636	625	669	643, 631	635	637	669	669	632	547	632	635	ν_{SC} (27) + δ_{CCC} (24)
$\nu_{34}, \omega_{\text{NH}_2}$	688	683	668	674, 681	635	635	597	596	578	628	533	537	ω_{NH_2} (36) + τ_{HNSO} (20) + δ_{HNS} (14) + τ_{HNSC} (10)
$\nu_{35}, \delta_{\text{CCC}}$	–	–	661	625, 627	628	628	628	628	637	642	641	639	δ_{CCC} (52) + δ_{CCH} (16)
$\nu_{36}, \tau_{\text{OSCC}}$	564	563	561	514, 514	524	526	525	526	544	489	519	519	τ_{OSCC} (19) + τ_{CCCH} (19) + δ_{OSC} (12)
$\nu_{37}, \tau_{\text{HNSO}}$	541	541	554	509, 522	515	509	515	511	511	240	497	517	τ_{HNSO} (23) + τ_{HNCC} (11)
$\nu_{38}, \tau_{\text{OSCC}}$	–	495	504	476, 476	462	462	464	461	435	163	416	451	τ_{OSCC} (29) + δ_{OSO} (13) + τ_{HNCC} (10) + ν_{NS} (10)
$\nu_{39}, \tau_{\text{HNCC}}$	–	–	481	622, 598	440	421	441	398	288	95	239	70	τ_{HNCC} (60)
$\nu_{40}, \delta_{\text{NCC}}$	–	–	477	430, 441	434	435	440	440	432	430	447	446	δ_{NCC} (18) + δ_{SCC} (16) + τ_{HNSC} (11) + δ_{OSC} (9)
$\nu_{41}, \tau_{\text{CCCC}}$	–	448	452	406, 408	407	406	408	408	390	544	438	411	τ_{CCCC} (57) + τ_{CCCH} (23) + τ_{NCCC} (10) + τ_{SCCC} (9))
$\nu_{42}, \delta_{\text{NCC}}$	412	413	419	391, 391	372	372	402	402	384	377	401	402	δ_{NCC} (38) + δ_{OSN} (23) + τ_{NSCC} (11)
$\nu_{43}, \delta_{\text{NSC}}$	–	–	392	343, 353	344	342	348	348	345	8	354	360	δ_{NSC} (23) + τ_{NCCC} (11) + τ_{SCCC} (10) + δ_{OSN} (9)
$\nu_{44}, \tau_{\text{HNCC}}$	–	–	382	402, 422	333	333	335	333	363	377	334	332	τ_{HNCC} (81)
$\nu_{45}, \tau_{\text{HNSO}}$	–	–	372	320, 320	324	324	332	332	347	352	360	392	τ_{HNSO} (26) + τ_{HNCC} (18) + δ_{OSC} (22) + δ_{OSN} (13) + δ_{CCN} (13)
$\nu_{46}, \nu_{\text{SC}}$	–	–	326	278, 273	274	274	272	272	287	277	276	276	ν_{SC} (44) + δ_{CCC} (13)
$\nu_{47}, \delta_{\text{NSC}}$	298	–	257	242, 197	202	201	194	194	177	188	194	195	δ_{NSC} (26) + τ_{NCCC} (20) + τ_{CCCC} (11)
$\nu_{48}, \delta_{\text{SCC}}$	227	–	218	158, 161	160	160	157	157	159	162	162	161	δ_{SCC} (65) + τ_{HNSO} (31) + δ_{OSC} (11)
$\nu_{49}, \tau_{\text{HNSC}}$	–	–	173	178, 162	113	113	244	244	–36	–34	239	250	τ_{HNSC} (67)
$\nu_{50}, \tau_{\text{SCCC}}$	–	–	145	106, 96	83	83	83	83	89	60	76	83	τ_{SCCC} (34) + τ_{SCCH} (15)
$\nu_{51}, \tau_{\text{OSCC}}$	115	–	90	77, 83	22	23	47	46	–54	–80	60	52	τ_{OSCC} (51) + τ_{NSCC} (38)

ν , bond stretching; δ , angle bending; τ , torsion; Ra, Raman; IR, infrared; asym, asymmetric; sym, symmetric.

^a This work.

^b Calculated frequencies were scaled using dual scale factors (0.952 and 0.97 above and below 2000 cm^{-1} , respectively) except for SO_2 stretching frequencies which were scaled by factor 1.033.

^c The two frequencies obtained in the dimer calculation for each internal mode are listed in the order as belonging predominantly to molecule 1 and 2, respectively.

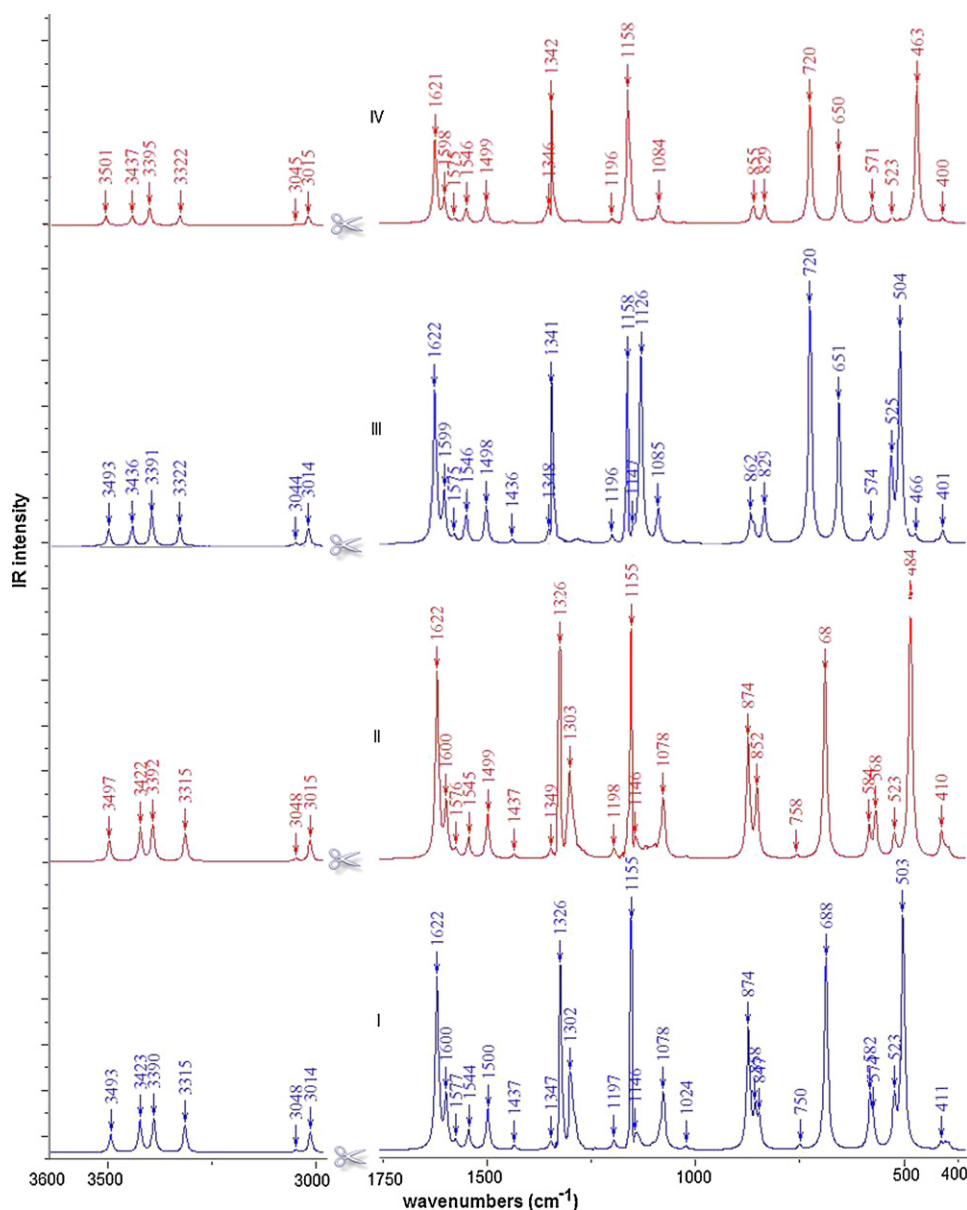


Fig. 3. Scaled theoretical IR spectra of global minimum conformer (I), second (II), third (III) and fourth (IV) lowest energy conformers.

with the same type of $\text{NH} \cdots \text{O}$ bond. The other hydrogen of the NH_2 group of sulfon side and the other oxygen are not participating in any further hydrogen bonds. The theoretical geometric model for the dimer given in Fig. 5 (this study) is similar to the dimer given in the crystal form of δ -sulfanilamide which is said to be a stable form.

The vibrational frequencies of the dimer calculated at DFT/B3LYP/6-31G++(d,p) level of theory are given in Table 4. The calculated frequencies for the dimer gave closer results to the experimental values than the free molecule, indicating the presence of intermolecular hydrogen bonding through dimerization. The NH_2 asymmetric (ν_1) and symmetric (ν_3) stretching, SO_2 asymmetric stretching (ν_{18}), and NH_2 bending (ν_9) and wagging (ν_{34}) frequencies observed at 3478, 3375, 1314, 1629, and 683 cm^{-1} in the IR spectra, were calculated as 3485/3489, 3372/3358, 1314/1324, 1640/1637 and 674/681 cm^{-1} for the dimer, and 3526, 3418, 1339, 1618 and 635 cm^{-1} for the isolated global minimum conformer (I) of the title molecule, respectively (see Table 4). The frequencies for ν_1 and ν_3 N–H stretching and ν_{18} , SO_2

stretching vibrations are downshifted in the dimer by 41/37, 46/60 and 15/25 cm^{-1} , respectively, while the ν_9 and ν_{34} NH_2 bending and wagging frequencies are upshifted by 22/19 and 39/46 cm^{-1} , respectively.

These results show that the downshifted NH_2 (in the aniline side) and SO_2 stretching modes and upshifted NH_2 bending modes are sensitive modes to dimerization and these noticeable frequency shifts show the affect of hydrogen bonding in the dimer. In addition to this, the calculated values for the modes mentioned above for the dimer fit the experimental values better than the results of the free molecule. Despite that, since the NH_2 group of the sulfonamide side of the molecule is not involved in hydrogen bonding through dimerization when the NH_2 asymmetric (ν_2) and symmetric (ν_4) stretching frequencies of the dimer and the free molecule are compared, no remarkable frequency shifts were observed for them.

Obviously, the dimer calculation cannot account for the additional hydrogen bonds present in the crystal between the aniline NH_2 group and the sulfonyl groups which are linking the dimers and

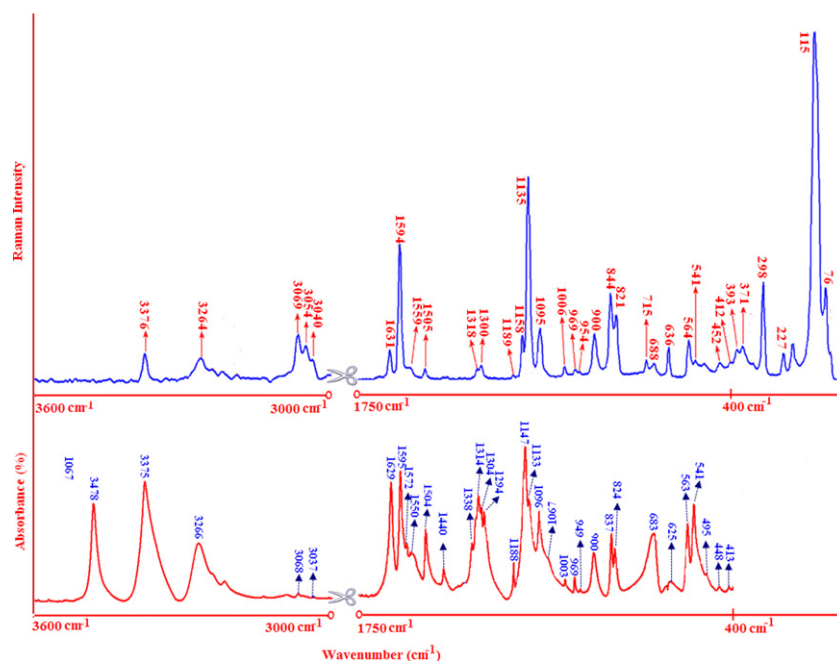


Fig. 4. Experimental FT-Raman (top) and FT-IR (bottom) spectra of solid sulfanilamide.

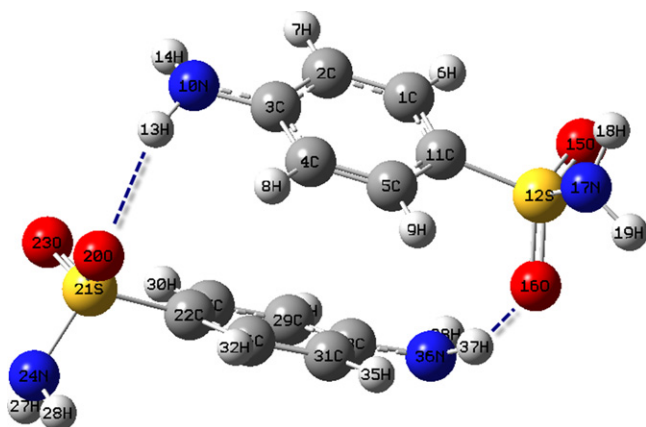


Fig. 5. Dimer of sulfanilamide molecule.

form an infinite 3D network. Therefore, further improvement in the calculations and better coincidence between the measured and calculated spectra could be expected only from a periodic calculation simulating the whole crystal lattice.

4. Conclusion

The possible stable conformers of sulfanilamide molecule were investigated via single point energy calculations at both semi-empirical PM3 and DFT/B3LYP-3-21G theory levels. The results show that the molecule has four conformers and the first two of them (I and II) are stable at room temperature. These conformers differ from each other according to the orientation of amino groups with respect to the phenyl ring. The expected dihedral angle and frequency shifts in each conformer prove that the geometry and frequency calculations are sensitive to conformational structures.

As seen from the calculated IR spectra presented in Fig. 3, while the conformational change of the amino group in the aniline part of the ring does not lead to a considerable change in the spectrum above 550 cm^{-1} , the conformational change of the NH_2 group of the sulfonamide part results in characteristic changes in the low

frequency region (below 880 cm^{-1}) and in the position and intensity of the νSO_2 asymmetric band near 1330 cm^{-1} .

The downward shifts of NH_2 and SO_2 stretching frequencies and the upward shifts of NH_2 and SO_2 bending frequencies shows that hydrogen bonding interactions via amino hydrogens and sulfon oxygens must be present and determine the measured vibrational frequencies to a great extent in the crystal structure. These results indicate that in order to obtain a better agreement between the measured solid-state vibrational spectra and the computational spectral simulations, the calculations should describe the intermolecular hydrogen bonded network in the crystalline environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.vibspec.2011.10.005](https://doi.org/10.1016/j.vibspec.2011.10.005).

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