Journal of Molecular Structure 919 (2009) 26–33

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Theoretical investigation on the molecular structure, Infrared, Raman and NMR spectra of *para*-halogen benzenesulfonamides, 4-X-$C_6H_4SO_2NH_2$ (X = Cl, Br or F)

Mehmet Karabacak [a,*], Mehmet Çınar [a], Ali Çoruh [b], Mustafa Kurt [c]

[a] Department of Physics, Afyon Kocatepe University, 03040 Afyonkarahisar, Turkey
[b] Department of Physics, Sakarya University, 54100 Sakarya, Turkey
[c] Department of Physics, Ahi Evran University, 40100 Kırşehir, Turkey

ARTICLE INFO

Article history:
Received 26 June 2008
Received in revised form 30 July 2008
Accepted 12 August 2008
Available online 22 August 2008

Keywords:
4-Chlorobenzenesulfonamide
4-Bromobenzenesulfonamide
4-Fluorobenzenesulfonamide
HF and DFT
Vibrational frequencies
IR, Raman and NMR spectra

ABSTRACT

In the present study, the structural properties of *para*-halogen benzenesulfonamides, 4-X$C_6H_4SO_2NH_2$ (4-chlorobenzenesulfonamide (I), 4-bromobenzenesulfonamide (II) and 4-fluorobenzenesulfonamide (III)) have been studied extensively utilizing ab initio Hartree–Fock (HF) and density functional theory (DFT) employing B3LYP exchange correlation. The vibrational frequencies were calculated and scaled values were compared with experimental values. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The effects of the halogen substituent on the characteristic benzenesulfonamides bands in the spectra are discussed. The ^1H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of the molecules were calculated using the Gauge-Invariant Atomic Orbital (GIAO) method. Finally, geometric parameters, vibrational bands and chemical shifts were compared with available experimental data of the molecules. The fully optimized geometries of the molecules were found to be consistent with the X-ray crystal structures. The observed and calculated frequencies and chemical shifts were found to be in very good agreement.

1. Introduction

Amide, sulfonamide and its derivatives have been the subject of investigation for many reasons. The amide is an important constituent of many biologically significant compounds. The chemistry of sulfonamides is of interest as they show distinct physical, chemical and biological properties. The sulfonamide derivatives are known for their numerous pharmacological activities, antibacterial, antitumor, insulin-release stimulation and antithyroid properties [1]. In addition, the unsubstituted aromatic/heterocyclic sulfonamides act as carbonic anhydrase inhibitors [2,3] whereas other types of derivatives show diuretic activity (high-ceiling diuretics or thiadiazine diuretics), hypoglycemic activity and anticancer properties [4]. Due to their significant pharmacology applications and widespread use in medicine, these compounds have gained attention in bio-inorganic and metal-based drug chemistry.

Gowda et al. [5] reported Infrared and NMR spectra of 4-chlorobenzenesulfonamide (I), 4-$ClC_6H_4SO_2NH_2$, 4-bromobenzenesulfonamide (II), 4-$BrC_6H_4SO_2NH_2$, and 4-fluorobenzenesulfonamide (III), 4-$FC_6H_4SO_2NH_2$, and they have also analyzed X-ray crystallographic structure of these arylsulfonamides [6]. However, no ab initio Hartree–Fock (HF) and density functional theory (DFT) studies have been made on the conformation, vibrational and NMR spectra of the title compounds yet. The purpose of this work is the detailed investigation of the substituent effects on the vibrational and NMR spectra of 4-X-$C_6H_4SO_2NH_2$ (X = F, Cl or Br). Therefore, we have carried out ab initio Hartree–Fock and DFT calculations with the combined Becke's three-parameter exchange functional in combination with the Lee, Yang, and Parr correlation functional (B3LYP) exchange-correlation energy functions. The geometric structure, vibrational frequencies, ^1H and ^{13}C NMR chemical shifts of title molecules were studied.

Electronic structure methods, such as HF self consistent field method and DFT, are used for modeling molecular properties. DFT calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity effects [7–12]. In order to take into account correlation effects, post-HF calculations of organic molecules have been performed using Møller–Plesset (MP) perturbation and/or DFT methods. MP perturbation methods are very time consuming and hence applicable only to small molecular systems. In this regard, DFT methods are preferred in the study of large organic molecules, metal complexes, organometallic compounds and for gauge-including atomic orbital (GIAO) ^{13}C chemical shifts calculations [13–15].

* Corresponding author. Tel.: +90 272 2281311; fax: +90 272 2281235.
E-mail address: karabacak@aku.edu.tr (M. Karabacak).

0022-2860/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.molstruc.2008.08.007

2. Quantum chemical calculations

Geometry optimization was started from the X-ray experimental atomic position [6]. The molecular structure of three molecules in the ground state (in vacuo) was optimized. The optimized structural parameters were used in the vibrational frequencies and isotropic chemical shifts calculations. The Hartree–Fock and Becke's three-parameter hybrid density functional (B3LYP) [16,17] were used to calculate harmonic vibrational wavenumbers with the 6-311++G(d,p) basis set. These values were scaled by corresponding scaling factors. The scale factors of 0.9051 and 0.9614 were used for HF and B3LYP with 6-311++G(d,p) basis set, respectively [18]. The total energy distribution (TED) was calculated by using the SQM program [19] and the fundamental vibrational modes were characterized by their TED.

For NMR calculations, the title molecules were firstly optimized at 6-311++G(d,p) level. After optimization, ^{1}H and ^{13}C NMR chemical shifts (δH and δC) were calculated using the GIAO method in Dimethylsulfoxide (DMSO) at HF and B3LYP methods with 6-311++G(d,p) basis set [20].

The theoretical results have enabled us to make the detailed assignments of spectra of title molecules. All calculations are performed by using *GAUSSIAN 03* and *GaussView* program package on the personal computer [21].

3. Results and discussion

The title molecules consist of 17 atoms, so they have 45 normal vibrational modes. According to the theoretical calculations, all molecules have assumed to posses a planar structure of C_s point group symmetry. On the assumption of a C_s symmetry the numbers of vibration modes of the 45 fundamental vibrations of molecules are 25A' + 20A". The vibrations of the A' species are in plane and those of the A" species are out of plane. All fundamental vibrations are active in both IR and Raman. Optimized ground-state geometries and vibrational modes, ^{1}H and ^{13}C NMR chemical shifts for studied molecular structures were obtained by HF and DFT (B3LYP), and compared with the available experimental crystal geometry (bond lengths and bond angles), frequencies and NMR data.

3.1. Molecular geometries

The first task for the computational work was to determine the optimized geometry of the compounds. The optimized structure of compounds is shown in Fig. 1(a) with numbering of the atoms and Fig. 1(b) shows the obtained crystal structure of the compounds [6] where X can be chlorine, bromine or fluorine. The optimized structure parameters of 4-chloro, 4-bromo and 4-fluoro-benzenesulfonamide (I, II and III) calculated by HF and B3LYP with the 6-311++G(d,p) basis set are listed in Table 1, in accordance with the atom numbering scheme given in Fig. 1(a). The available experimental data [6] obtained by the X-ray study for three compounds are also given in Table 1. However, the N–H bond lengths and bond angles between H and other two atoms were not given for 4-fluorobenzenesulfonamide in X-ray study [6].

From the theoretical values one can find that most of the optimized bond lengths are larger than the experimental values. This overestimation can be explained that the theoretical calculations belong to isolated molecule in gaseous phase and the experimental results belong to molecule in solid state. The changes for bond length of the C–H bond on substitution, the substituents may be of the electron withdrawing type (Cl, F, Br, etc.), due to a change in the charge distribution on the carbon atom of the benzene ring were explained by many authors [22–25]. The carbon and

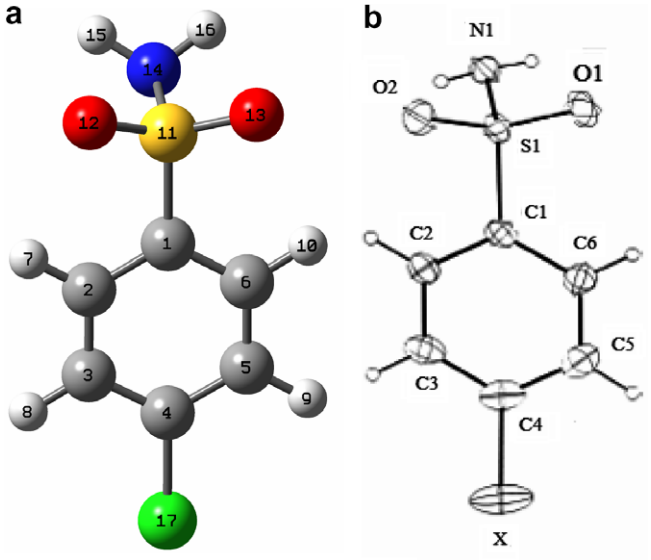

Fig. 1. (a) The theoretical geometric structure and atoms numbering of the title compounds. (b) Molecular geometry of compounds with numbering of atoms [6].

Table 1
Comparison of the theoretical and experimental geometric parameters of I, II and III, bond lengths in Angstrom (Å) and bond angles in degrees (°)

Parameters	X-Ray[a]			6-311++G(d,p)/B3LYP			6-311++G(d,p)/HF		
	I	II	III	I	II	III	I	II	III
Bond length									
C(1)–(2)	1.381	1.375	1.394	1.392	1.392	1.393	1.384	1.384	1.385
C(1)–(6)	1.382	1.379	1.384	1.392	1.392	1.393	1.384	1.384	1.385
C(1)–(11)	1.767	1.768	1.601	1.797	1.798	1.796	1.769	1.770	1.766
C(2)–(3)	1.378	1.373	1.390	1.391	1.392	1.391	1.383	1.384	1.382
C(3)–(4)	1.371	1.373	1.377	1.393	1.393	1.388	1.383	1.384	1.378
C(4)–(5)	1.375	1.376	1.372	1.393	1.393	1.388	1.383	1.384	1.378
C(4)–(17)[b]	1.738	1.896	1.359	1.753	1.913	1.350	1.739	1.896	1.321
C(5)–(6)	1.387	1.391	1.379	1.391	1.392	1.391	1.383	1.384	1.382
S(11)–(12)	1.430	1.432	1.437	1.461	1.461	1.461	1.424	1.424	1.424
S(11)–(13)	1.430	1.426	1.431	1.461	1.461	1.461	1.424	1.424	1.424
S(11)–(14)	1.595	1.599	1.601	1.693	1.692	1.694	1.643	1.643	1.645
Bond angle									
C(2)–(1)–(6)	121.1	121.6	123.8	121.4	121.4	121.5	121.0	121.0	121.0
C(2)–(1)–(11)	118.1	120.7	119.2	119.3	119.3	119.3	119.5	119.5	119.5
C(6)–(1)–(11)	120.9	118.1	119.5	119.3	119.3	119.3	119.5	119.5	119.5
C(1)–(2)–(3)	119.5	119.0	119.4	119.4	119.4	119.4	119.6	119.6	119.7
C(1)–(2)–(7)	120.3	120.5	–	120.1	120.2	120.1	120.2	120.2	120.1
C(3)–(2)–(7)	120.3	120.5	–	120.5	120.5	120.6	120.2	120.2	120.2
C(2)–(3)–(4)	119.4	119.3	118.0	119.2	119.2	118.5	119.2	119.2	118.5
C(2)–(3)–(8)	120.3	120.5	–	120.6	120.3	121.6	120.6	120.3	121.6
C(4)–(3)–(8)	120.3	120.5	–	120.2	120.5	119.9	120.2	120.5	119.9
C(3)–(4)–(5)	121.8	121.3	121.3	121.5	121.5	122.8	121.5	121.4	122.7
C(3)–(4)–(17)[b]	118.6	120.0	118.2	119.3	119.3	118.6	119.2	119.3	118.7
C(5)–(4)–(17)[b]	119.6	118.3	118.2	119.3	119.3	118.6	119.2	119.3	118.7
C(4)–(5)–(6)	119.1	119.0	118.0	119.2	119.2	118.5	119.2	119.2	118.5
C(4)–(5)–(9)	120.5	120.3	–	120.2	120.5	119.9	120.2	120.5	119.9
C(6)–(5)–(9)	120.5	120.3	–	120.6	120.3	121.6	120.6	120.3	121.6
C(1)–(6)–(5)	119.2	119.8	119.5	119.4	119.4	119.4	119.6	119.6	119.7
C(1)–(6)–(10)	120.4	120.1	–	120.1	120.2	120.1	120.2	120.2	120.1
C(5)–(6)–(10)	120.4	120.1	–	120.5	120.5	120.6	120.2	120.2	120.2
C(1)–(11)–(12)	106.7	106.5	107.4	107.5	107.5	107.5	107.6	107.6	107.6
C(1)–(11)–(13)	107.9	108.3	107.7	107.5	107.5	107.5	107.6	107.6	107.6
C(1)–(11)–(14)	109.2	108.9	109.5	103.5	103.5	103.6	104.7	104.6	104.9
O(12)–(11)–(13)	119.5	119.6	119.0	122.6	122.7	122.6	121.7	121.7	121.7
O(12)–(11)–(14)	106.7	107.0	106.5	107.1	107.1	107.0	107.1	107.1	107.0
O(13)–(11)–(14)	106.6	106.2	106.5	107.1	107.1	107.0	107.1	107.1	107.0
S(11)–(14)–(15)	111.9	114.0	–	110.3	110.4	110.3	112.1	112.1	112.0
S(11)–(14)–(16)	113.6	116.0	–	110.3	110.4	110.3	112.1	112.1	112.0
H(15)–(14)–(16)	119.0	117.0	–	111.8	112.0	111.8	113.1	113.2	113.0

[a] Taken from Ref. [6].
[b] X can be Cl, Br or F.

hydrogen atoms are bonded with σ-bond in benzene ring, and the substitution of halogen reduces the electron density at C atom. Therefore, the substitution with the Cl, Br or F at the C(4) atom which shares its p electron with the ring leads to some changes of the bond lengths and bond angles in the aromatic ring.

It is well-known that DFT methods predict bond lengths which are systematically too long, particularly the C–H and N–H bond lengths [26]. Since the large deviation from experimental C–H and N–H bond lengths may arise from the low scattering factors of hydrogen atoms in the X-ray diffraction experiment we didn't include lack of C–H experimental bond lengths. This overestimation is also verified in our calculation as represented in Table 1. The experimentally value of C–H bond lengths is 0.93 Å [6] while the value in the theoretical result is bigger than 1 Å. Likewise the calculated N–H values are bigger than observed values [6]. The obtained bond lengths of C=C fall in the range from 1.371 to 1.394 Å [6] for three compounds. For benzenesulfonamide molecule these bond lengths were found in the range 1.339–1.407 Å [27]. B3LYP method predicted these bonds at ca. 1.392 Å and HF ca. 1.384 Å. Calculated values of C=C with both B3LYP and HF are longer than experimental bond lengths. As seen in Table 1, the S–N bonds for three compounds are predicted longer than according to the other bond lengths. On the contrary, the computed C–S bond lengths by HF method show excellent agreement with experimental data [6]. The computational method, B3LYP, which include electron correlation effects, overestimate strongly all bond lengths around sulphur, while the HF approximation reproduces these bond lengths correctly [28–30]. Similarly, in this study, the S–O bond lengths are predicted well with experiment using HF method.

Substitution with the halogen atom and SO_2 leads to some changes of the bond angles in the aromatic ring. The C(2)–C(1)–C(6) angle at the position of the SO_2 substituent and C(3)–C(4)–C(5) angle at the position of the halogen substituent are bigger (121.1° and 121.8°, respectively) and the others are smaller than typical hexagonal angle of 120°. The calculated angles of benzene ring are more reliable with experimental data than the sulfonamide group.

Table 2
Comparison of the calculated and experimental vibrational spectra of 4-chlorobenzenesulfonamide

Mode No	HF/6311++G(d,p)		B3LYP/6311++G(d,p)		Experimental Infrared [5]	TED[b] (%)
	Unscaled freq.	Scaled freq.[a]	Unscaled freq.	Scaled freq.[a]		
1	35	31	19	18		τCCSO (58) + τCCSN (39)
2	81	74	71	69		τCCCS (33) + τCCCCl (17) + τHCCS (13)
3	154	139	132	127		tNH_2 (90) (τHNSC)
4	174	157	154	148		τHNSO (50) + δCCS (38) + δCCCl (12)
5	214	194	190	183		δCSN (30) + τCCCCl (24) + τHCCCl (11) + τCCSO (10)
6	279	252	252	242		νCS (38) + δCCC (14) + νCCl (10)
7	322	292	295	283		δCCCl (57) + τHNSO (26) + δCSO (17)
8	382	345	337	324		δCSN (28) + τCCCCl (15) + τCCCS (12) + τHCCCl (10)
9	415	376	366	352		δNSO (34) + τCSNH (25) + δCSO (13) + δCCCl (11)
10	456	413	416	400	453 m (γCC)	τCCCC (55) + τCCCH (24) + τCCCCl (10) + τCCCS (10)
11	493	446	440	423		δCCS (21) + τCSNH (20) + δCSO (12) + δCCCl (10)
12	518	469	461	443		τCCSO (23) + τCCCC (15) + δOSO (17)
13	527	477	470	452		νCCl (35) + νCS (10) + δCCC (10)
14	603	546	534	514		τCCCH (28) + τCCSO (23) + τCCCC (13) + νSN (10)
15	639	579	586	563		τHNSO (32) + νCCl (14) + νCS (14) + δCSO(12)
16	686	621	631	607		νSN (31) + τHNSO (29) + δHNS (14) + τCSNH (12)
17	712	645	639	614		δCCC (56) + δCCH (17)
18	819	741	749	720		τCCCC (30) + νCCl (11) + νCS (10)
19	825	747	753	724		τCCCC (25) + δCCC (11) + νCCl (10)
20	936	847	836	804	746 m (γCH)	γCH (68) + τHCCCl (18) + τHCCS (14)
21	937	848	837	805	767 s (γCH)	γCH(60) + τHCCCl (23) + τHCCS (13)
22	961	869	849	816	913 w (νSN)	νSN (24) + δHNS (10) + τHNSO (10) + τHCCCl (10)
23	1081	978	968	930		γCH(80)
24	1105	1000	983	945		γCH(85)
25	1105	1000	1028	988		Trigonal ring breathing δCCC (40) + δCH (24) + νCC(13)
26	1173	1062	1078	1036		νSO_2 (47) sym. + νCC (32)
27	1185	1072	1090	1048		tNH_2 (85) + νSO_2 (12) asym.
28	1199	1085	1097	1055	1010 s (νCCl)	νCC (61) + νCCl (20)
29	1202	1088	1127	1083	1157 s (νSO_2 sym.)	νSO_2 (42) sym. + νCS (15) + νCC (15)
30	1256	1137	1129	1085	1069 s (δCH)	δCH (60) + νCC (31)
31	1271	1150	1199	1153	1089 s (δCH)	δCH (75) + νCC (20)
32	1290	1168	1309	1258		νSO_2 (43) asym. + νCC (28) + δCH (10)
33	1431	1295	1322	1271		δCH (70) + νCC (20)
34	1463	1324	1329	1278	1329 s (νSO_2 asym.)	νSO_2 (40) asym. + νCC (35)
35	1532	1387	1420	1365	1396 s (νCC)	νCC (37) + δCH (34)
36	1643	1487	1506	1448	1474 s (νCC)	δCH (65) + νCC (27)
37	1735	1571	1587	1526		ρNH_2 (89)
38	1753	1586	1614	1551		νCC (80)
39	1773	1605	1616	1553	1583 s (νCC)	νCC (70) + δCH (16)
40	3360	3041	3197	3073		νCH (100) asym
41	3361	3042	3198	3075		νCH (100) asym
42	3375	3055	3209	3085		νCH (100) asym
43	3376	3056	3211	3087	3094 w (νCH sym.)	νCH (100) sym
44	3754	3398	3511	3375	3266 s (νNH_2 sym.)	νNH_2 (100) sym.
45	3864	3498	3618	3478	3353 s (νNH_2 asym.)	νNH_2 (100) asym.

s, strong; m, medium; w, weak; ν, stretching; δ, in-plane bending; γ, out-of-plane bending; ρ, scissoring; τ, torsion; t, twisting.
[a] Scale factor of 0.9050 and 0.9614 were used for HF and B3LYP with 6-311++G(d,p) basis set [18].
[b] Total energy distribution.

3.2. Vibrational analysis

The fundamental frequencies of I, II and III as calculated by HF and DFT (B3LYP) using 6-311++G(d,p) basis set, are given in Tables 2–4. The resulting vibrational frequencies for the optimized geometries, the proposed vibrational assignments and available experimental Infrared frequencies [5] are also given in Tables 2–4. Vibrational modes are numbered from smallest to largest frequency. In the last columns are given a detailed description of the normal modes based on the total energy distribution (TED). The discussions are similar to compounds in general. The calculated IR and Raman spectra are shown in Fig. 2 for comparative purposes, where the calculated intensity and activity is plotted against the harmonic vibrational frequencies. It should be noted that calculations were made for a free molecule in vacuum, while experiments were performed for solid samples. Furthermore, the anharmonicity is neglected in real system for calculated vibrations. Thus, there are disagreements between calculated and observed vibrational wavenumbers, as seen in Tables 2–4.

The heteroaromatic structure shows the presence of C–H and N–H stretching vibrations above 3000 cm^{-1} which is the characteristic region for ready identification of this structure [31,32]. These are usual range of appearance for NH_2, CH_3 and ring C–H stretching vibrations. The investigated molecules have only one NH_2 group and hence one symmetric and one asymmetric N–H stretching vibrations in NH_2 group are expected. It is stated that the N–H stretching vibrations occur in the region 3300–3500 cm^{-1} [33]. The asymmetric NH_2 stretching vibration appears from 3420 to 3500 cm^{-1} and the symmetric NH_2 stretching is observed in the range 3340–3420 cm^{-1} [33]. Álvareza assigned two strong bands in the IR spectrum of the liquid sulfamoil fluoride and sulfamoil chloride substances at 3418 cm^{-1}, 3312 cm^{-1} and 3386 cm^{-1}, 3282 cm^{-1} [28,34]. They were assigned to the NH_2 antisymmetric and symmetric fundamental stretching modes, respectively. With reference to these, the vibrational frequencies described by modes 44 and 45 assigned to the N–H symmetric and asymmetric stretching modes, respectively. As expected these two modes are pure stretching modes as it is evident from TED column, they are almost

Table 3
Comparison of the calculated and experimental vibrational spectra of 4-Bromobenzenesulfonamide

Mode No	HF/6311++G(d,p)		B3LYP/6311++G(d,p)		Experimental Infrared [5]	TED[b] (%)
	Unscaled freq.	Scaled freq.[a]	Unscaled freq.	Scaled freq.[a]		
1	36	33	27	26		τCCSO (55) + τCCSN (40)
2	71	65	63	60		τCCCS (30) + τCCCBr (22) + τHCCS (11)
3	147	133	125	120		tNH_2 (90) (τHNSC)
4	166	150	139	133		τHNSO (53) + δCCS (37) + δCCBr (10)
5	202	183	180	173		δCSN (29) + τCCCBr (22) + τHCCBr (11) + τOSCC (10)
6	231	209	209	201		νCBr (25) + νCS (24) + δCCC (13)
7	290	263	263	253		δCCBr (56) + τHNSO (27) + δCSO (15)
8	373	337	329	317		δCSN (30) + τCCCBr (13) + τCCCS (12) + τHCCBr (10)
9	412	373	363	349		δNSO (33) + τCSNH (32) + δCSO (17) + τCCSN (10)
10	453	410	406	391		νCBr (40) + νCS (25) + τHNSO (10)
11	453	410	416	400	419 m (γCC)	τCCCC (55) + τCCCH (24) + τCCCBr (10) + τCCCS (10)
12	491	445	438	421		δCCS (20) + τCSNH (20) + δOSN (13) + δCSO (12)
13	521	472	457	439		τCCSO (27) + τCCCC (15) + τCCCH (15) + δOSO (14)
14	595	539	528	508		τCCCH (25) + τCCSO (22) + τCCCC (15) + νSN (10)
15	630	570	572	550	518 s (νCBr)	τCSNH (35) + δCSO(15) + νCBr (10)
16	685	620	627	603		τHNSO (30) + νSN (29) + δHNS (15) + τCSNH (12)
17	707	639	637	612		δCCC (52) + δCCH (22)
18	804	727	735	707		δCCC (30) + νCS (15) + νCBr (13) + δCCBr (10)
19	820	742	745	717		τCCCC (55) + τCCCH (15)
20	933	845	835	803	742 s (γCH)	γCH (69) + τHCCBr (19) + τHCCS (12)
21	938	849	839	807	819 s (γCH)	γCH (68) + τHCCBr (18) + τHCCS (14)
22	960	869	848	815	910 s (νSN)	νSN (45) + τHNSO (17) + δHNS (12)
23	1085	982	973	935		γCH(80)
24	1101	997	988	950		γCH(82)
25	1105	1000	1024	984		Trigonal ring breathing δCCC (53) + δCH(20) + νCC (10)
26	1163	1053	1076	1034		νCC (64) + νSO_2 (23) sym.
27	1172	1061	1080	1038		νCC (35) + νSO_2 (25) sym. + δCH (20)
28	1195	1082	1089	1047		tNH_2 (85) + νSO_2 (11) asym.
29	1202	1088	1126	1083	1147 s (νSO_2 sym.)	νSO_2 (44) sym. + νCS (15) + νCC (15)
30	1255	1136	1129	1085	1011 s (δCH)	δCH (59) + νCC (32)
31	1269	1149	1202	1155	1092 s (δCH)	δCH (71) + νCC (19)
32	1294	1171	1308	1258		νSO_2 (40) asym. + νCC (40) + δCH (10)
33	1433	1297	1323	1272		δCH (71) + νCC (22)
34	1464	1325	1328	1277	1328 s (νSO_2 asym.)	νSO_2 (48) asym. + νCC (30)
35	1529	1384	1416	1361	1390 s (νCC)	νCC (36) + δCH (34)
36	1639	1484	1502	1444	1469 s (νCC)	δCH (67) + νCC (26)
37	1735	1570	1586	1525		ρNH_2 (89)
38	1749	1583	1609	1547		νCC (80) + δCH (15)
39	1769	1601	1610	1548	1575 s (νCC)	νCC (79)
40	3360	3041	3197	3073		νCH (100) asym
41	3361	3042	3198	3074		νCH (100) asym
42	3375	3055	3209	3085		νCH (100) asym
43	3376	3056	3210	3086	3021 w (νCH sym.)	νCH (100) sym
44	3754	3397	3510	3374	3240 s (νNH_2 sym.)	νNH_2 (100) sym.
45	3864	3498	3617	3478	3330 s (νNH_2 asym.)	νNH_2 (100) asym.

s, strong; m, medium; w, weak; ν, stretching; δ, in-plane bending; γ, out-of-plane bending; ρ, scissoring; τ, torsion; t, twisting.
[a] Scale factor of 0.9050 and 0.9614 were used for HF and B3LYP with 6-311++G(d,p) basis set [18].
[b] Total energy distribution.

Table 4
Comparison of the calculated and experimental vibrational spectra of 4-Fluorobenzenesulfonamide

Mode No	HF/6311++G(d,p)		B3LYP/6311++G(d,p)		Experimental Infrared [5]	TED[b] (%)
	Unscaled freq.	Scaled freq.[a]	Unscaled freq.	Scaled freq.[a]		
1	31	28	27	26		τCCSO (56) + τCCSN (40)
2	99	89	86	83		τCCCS (37) + τHCCS (15) + τCCCF (10)
3	149	135	131	126		tNH_2 (93) (τHNSC)
4	190	172	170	163		δCCS (55) + τHNSO (45)
5	241	218	214	206		δCSN (34) + τCCCF (20) + τCCCC (10) + τHCCF (10)
6	308	279	277	266		νCS (45) + δCCC (14)
7	388	351	344	331		τHNSO (44) + δCSO (30) + δNSO (15) + δCCF (11)
8	407	369	360	346		δCSN (23) + τCCCF (28) + τCCCS (11) + δOSO (10)
9	445	402	396	381		δCCF (34) + δNSO (24) + τCCSN (13) + τCSNH (12)
10	463	419	423	407	485 m (γCC)	τCCCC (55) + τCCCH (24) + τCCCS (10) + τCCCF (10)
11	504	456	455	438		δCCF (30) + δCCS (18) + τCSNH (11) + δCSO (10)
12	540	489	472	454		τCCSO (18) + δOSO (14) + νSN (10)
13	580	525	527	506		τHNSO (30) + τCCCH (10)
14	616	558	545	524		τCCCH (24) + τCCSO (19) + νSN (10) + τCCCC (10)
15	678	614	631	606		τHNSO (27) + νSN (21) + δSNH (18) + τHNSC (13)
16	689	624	641	616		δCCC (52) + δCCH (18) + νCC (10)
17	736	666	642	618		νCS (25) + δCCC (15) + νNS (11) + νCF (10) + δCCF (10)
18	800	724	724	696		τCCCC (54) + τCCCH (15) + τCCSO (10)
19	896	811	825	793		νCC (20) + νCF (18) + νNS (15) + δCCC (10)
20	924	837	828	796	815 m (γCH)	γCH (68) + τHCCF (19) + τHCCS (13)
21	949	859	852	819	841 s (γCH)	γCH (60) + τHCCF (15)
22	962	870	855	822	914 s (νSN)	νSN (30) + τHNSO (10) + τHCCF (10) + δHNS (10)
23	1071	969	957	921		γCH (80)
24	1103	998	981	943		γCH (85)
25	1104	999	1029	989	1013 m (δCH)	Trigonal ring breathing δCCC (34) + δCH (32) + νCC (27)
26	1172	1060	1075	1034		νSO_2 (49) sym. + νCC (25)
27	1191	1078	1091	1049		tNH_2 (85) + νSO_2 (11) asym.
28	1203	1089	1119	1076	1092 s (δCH)	δCH (65) + νCC (28)
29	1251	1132	1124	1081	1150 s (νSO_2 sym.)	νSO_2 (44) sym. + νCS (17) + νCC (17)
30	1270	1150	1177	1131		δCH (75) + νCC (10)
31	1284	1162	1246	1198	1238 s (νCF)	νCF (48) + νCC (21) + δCH (10)
32	1371	1241	1308	1258		δCH (43) + νSO_2 (40) asym.
33	1425	1290	1323	1268		δCH (44) + νSO_2 (35) asym. + νCC (14)
34	1462	1323	1328	1289	1332 s (νSO_2 asym.)	νCC (77) + νSO_2 (13) asym.
35	1545	1398	1416	1376	1409 m (νCC)	νCC (39) + δCH (32)
36	1664	1506	1502	1463	1494 s (νCC)	δCH (60) + νCC (28)
37	1735	1571	1586	1526		ρNH_2 (89)
38	1774	1606	1609	1567		νCC (72) + δCH (15)
39	1786	1617	1610	1571	1587 s (νCC)	νCC (78)
40	3359	3040	3197	3074	3075 w (νCH sym.)	νCH (100) asym
41	3361	3042	3198	3076		νCH (100) asym
42	3375	3055	3209	3086		νCH (100) asym
43	3376	3056	3210	3087		νCH (100) sym
44	3753	3397	3510	3374	3261 s (νNH_2 sym.)	νNH_2 (100) sym.
45	3863	3497	3617	3477	3361 s (νNH_2 asym.)	νNH_2 (100) asym.

s, strong; m, medium; w, weak; ν, stretching; δ, in-plane bending; γ, out-of-plane bending; ρ, scissoring; τ, torsion; t, twisting.
[a] Scale factor of 0.9050 and 0.9614 were used for HF and B3LYP with 6-311++G(d,p) basis set [18].
[b] Total energy distribution.

contributing 100%. The corresponding symmetric mode occurs in the experiment at 3266, 3240 and 3261 cm^{-1} and asymmetric mode at 3353, 3330 and 3361 cm^{-1} for I, II and III. Other vibrations, the in-plane NH_2 deformation falls from 1580 to 1650 cm^{-1}. Therefore, the frequency No. 37 identified with NH_2 scissoring. This value deviates negatively by ca. 10 cm^{-1} (for HF) from expected characteristic value. Likewise, the twisting vibration (mode 3) is also in good agreement with literature values [28,34–37].

For all the aromatic compounds the carbon–hydrogen stretching vibrations are observed in the region 3000–3100 cm^{-1} [31,32,38]. Accordingly, in this range there is one observed vibration, which is 3094, 3021 and 3075 cm^{-1} for molecules of I, II and III, respectively [5]. In the present study, the four adjacent hydrogen atoms left around the ring the *para*-halogen benzene sulfonamide give rise four C–H stretching modes (40–43), four C–H in plane bending (30–33) and four C–H out-of-plane bending (20, 21, 23, 24) vibrations which corresponds to modes of C(2)–H(7), C(3)–H(8), C(5)–H(9), and C(6)–H(10) units. In our calculations, C–H stretching vibrations are predicted in the range 3073–3087 cm^{-1} (B3LYP), which are in agreement with experimental assignment [5]. They are very pure modes since their TED contribution are 100%. The C–H in-plane bending frequencies appear in the range of 1000–1300 cm^{-1} and C–H out-of-plane bending vibration in the range 750–1000 cm^{-1} in the aromatic compounds. The vibrations (30–33) are assigned the in plane C–H bending even though found to be contaminated by other stretching vibrations. The calculated four vibrations (modes 20, 21, 23 and 24 in Table 2) assigned out-of-plane C–H bending. The TED for both the in-plane and out-of-plane bending vibrations suggests that these are mixed modes. In general the aromatic C–H vibrations (stretching, in-plane and out-of-plane bending) calculated theoretically are in good agreement with experimentally accepted values [31,32,38–40]. The change in the frequencies of these deformations from the values in benzene is almost determined exclusively by the relative position of the substituents and is almost independent of their nature [41].

Empirical assignments of vibrational modes for peaks in the fingerprint region are difficult. In the wavenumber region of 600–

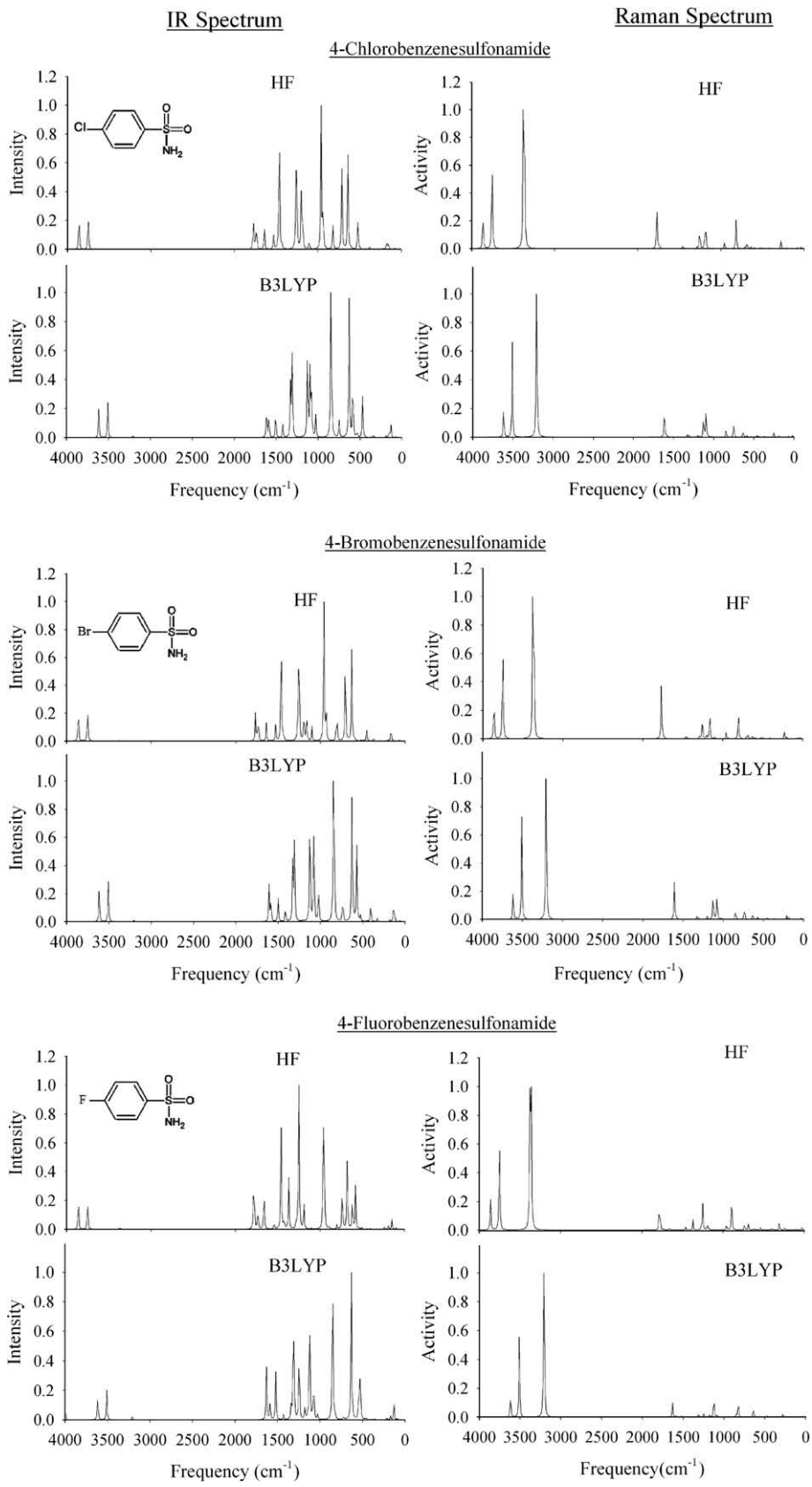

Fig. 2. Comparison of calculated frequencies in cm^{-1}, normalized IR intensities and Raman activities at each level of theory considered for I, II and III. These theoretical spectrum were obtained by using HF and DFT (B3LYP) methods with 6-311++G(d,p) basis set.

1660 cm^{-1}, the spectrum observed in the experiments closely resembles the calculated spectrum, except for differences in details. The ring carbon–carbon stretching vibrations occur in the region 1400–1650 cm^{-1} in benzene derivates. Varsanyi observed five

bands, 1625–1590, 1590–1575, 1540–1470, 1465–1430 and 1380–1280 cm^{-1}, in this region [38]. Here, the vibrations (modes 35, 36 and 39) have been assigned to C=C bond stretching vibration. Gowda et al. [5] observed C=C stretching vibration at 1583, 1575 and 1587 cm^{-1} for I, II and III. The theoretically calculated CCC out-of-plane bending modes have been found to be consistent with the recorded spectral values. According to TED results, mode 25 was assigned as trigonal ring breathing for I, II and III molecules.

The symmetric and asymmetric SO_2 stretching vibrations occur in the region 1125–1150 and 1295–1330 cm^{-1} [40]. The intense signals appearing at 1418 cm^{-1} and 1217 cm^{-1} (IR) and 1414 cm^{-1} and 1228 cm^{-1} (Ra) can be attributed to the SO_2 antisymmetric and symmetric stretching fundamental modes for sulfamoil fluoride substance [28]. For molecules of I, II and III asymmetric S=O stretching vibrations were recorded at 1329, 1328 and 1332 cm^{-1} and the symmetric S=O vibrations at 1157, 1147 and 1150 cm^{-1} [5]. The calculated frequencies for asymmetric vibrations with HF method give good agreement with observed values (1324, 1325 and 1323 cm^{-1}) while DFT method estimates lower than the typical values given in experimental study. These results indicate that the HF calculations approximate the observed frequencies much better than the B3LYP results for S=O stretching vibrations. For compounds I and III vibration No. 12 and for compound II vibration No. 13 are assigned O=S=O bending modes.

At 913, 910 and 914 cm^{-1} in the IR spectra for molecules of I, II and III, respectively, the S–N stretching fundamental mode can be observed. For the sulfamoil fluoride and sulfamoil chloride molecules, this vibration is assigned at 964, 966 cm^{-1} and 921, 920 cm^{-1} in the IR and Raman spectra, respectively [28,34]. According to TED results, mode 22 was assigned as the S–N stretching for I, II and III.

Mooney assigned vibrations of C–X group (X = Cl, Br and I) in the frequency range of 1129–480 cm^{-1} [42,43]. The theoretical wavenumbers of C–Cl stretching vibration are coupled with other group vibrations. Ring–Cl modes are partially C–Cl stretching and bending modes that have been reported in a frequency range of 200–800 cm^{-1} [38]. Here, C–Cl stretching vibration is presented mode 28 be contaminated by C–H in-plane bending. The heavier mass of bromine obviously makes the C–Br stretching mode to appear at longer wavelength region (200–480 cm^{-1}) as reported by Varsanyi [38]. The theoretically calculated value of 410 cm^{-1} (DFT) is good agreement with this range. The C–F stretching is observed in the region 1100–1350 cm^{-1} [33,44]. This vibration was also observed at 1238 cm^{-1} by Gowda et al. [5]. Sundaraganesan et al. [45] observed two strong bands at 1279 and 1331 cm^{-1} in FT-IR and at 1280 and 1332 cm^{-1} in FT-Raman were assigned to C–F stretching mode for 2,3-difluoro phenol molecule. In the present investigation we assigned the band at 1198 cm^{-1} (DFT) due to C–F stretching mode (mode 31). According to the calculated TED, our calculations show that there is no pure (C–halogen atom) band in this range. The remainder of the observed and calculated frequencies accounted in Tables 2–4.

3.3. NMR spectra

Initially, molecular structures of the mentioned compounds were optimized. Then, gauge-including atomic orbital (GIAO) ^{13}C and ^{1}H chemical shift calculations of the compounds were made by using HF and B3LYP method in conjunction with 6-311++G(d,p) basis set. The GIAO [46,47] method is one of the most common approaches for calculating nuclear magnetic shielding tensors. For the same basis set size GIAO method is often more accurate than those calculated with other approaches [48]. The NMR spectra calculations were performed by Gaussian 03 [21] program package. Dimethylsulfoxide (DMSO) was used as a solvent.

Relative chemical shifts were estimated by using the corresponding TMS shielding calculated in advance at the same theoretical level as the reference. ^{13}C and ^{1}H isotropic magnetic shielding (IMS) of any X carbon (or hydrogen) atom was made according to the value ^{13}C IMS of TMS: $CS_x = IMS_{TMS} - IMS_x$. Besides X-ray crystallography, NMR spectroscopy can provide the required structural data for the investigated compounds [5,6]. Theoretical and experimental chemical shifts [5] of I, II and III in ^{1}H and ^{13}C NMR spectra are gathered in Table 5. ^{1}H atom is the smallest of all atoms and mostly localized on periphery of molecules; therefore their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solutions as compared to that for other heavier atoms. Taking into account that the range of ^{13}C NMR chemical shifts for a typical organic molecule usually is >100 ppm [49,50], the accuracy ensures reliable interpretation of spectroscopic parameters. In the present paper, ^{13}C NMR chemical shifts in the ring for the title compound are >100 ppm, as they would be expected (in Table 5). The C(4) atom which bonded to halogen shows calculated ^{13}C chemical shifts that are too high. Fluorine atom has also more electronegative property than bromine and chlorine atom. Therefore, the chemical shifts value of the C(4) atom which bonded to fluorine is the highest. As seen in Table 5, the calculated chemical shifts for ^{1}H are more sensitive to that of ^{13}C. Isotropic ^{1}H chemical shifts for three molecules calculated by means of B3LYP method and ^{13}C shifts by means of HF method are closer to experimental data.

4. Conclusion

In the present study, the molecular structure, vibrational frequencies, proton and carbon GIAO NMR shielding of 4-chlorobenzenesulphonamide (I), 4-bromobenzenesulphonamide (II) and 4-fluorobenzenesulphonamide (III) have been studied using HF and DFT (B3LYP) calculations with the 6-311++G(d,p) basis set. On the basis of the calculated and experimental results; assignment of the fundamental vibrational frequencies were examined. The available experimental results were compared with theoretical data. Theoretical ^{13}C and ^{1}H chemical shift values (with respect to TMS) were reported and compared with experimental data, showing a very good agreement both for ^{13}C and ^{1}H.

Table 5
Theoretical and experimental ^{1}H and ^{13}C isotropic chemical shifts (with respect to TMS, all values in ppm) for I, II and III

Atom	4-Chlorobenzenesulfonamide (I)			4-Bromobenzenesulfonamide (II)			4-Fluorobenzenesulfonamide (III)		
	Exp.[a]	HF	B3LYP	Exp.[a]	HF	B3LYP	Exp.[a]	HF	B3LYP
H(7), H(10)	7.83	8.29	8.17	7.80	8.27	8.07	7.90	8.14	8.00
H(8), H(9)	7.45	7.87	7.80	7.67	7.94	7.98	7.14	7.10	7.13
C(1)	142	135.6	151.7	139.6	136.6	151.6	139.7	132.3	149.4
C(2), C(6)	127.6	126.2	132.3	128.4	125.7	131.6	128.8	129.2	133.7
C(3), C(5)	128.9	123.9	134.5	132.2	127.3	138.0	115.9	108.8	119.9
C(4)	137.8	142.3	153.2	127.3	140.2	152.6	166.1	161.5	174.3

[a] Taken from Ref.[5]. The atoms are numbered as in Fig. 1(a).

Acknowledgement

We thank Dr. Tahir Güllüoğlu for SQM program Ahi Evran University, Kırşehir, Turkey.

References

[1] T.H. Maren, Annu. Rev. Pharmacol. Tox. 16 (1976) 309. and references cited therein.
[2] C.T. Supuran, A. Scozzafava, Curr. Med. Chem., Immunol., Endocrine Metabolic Agents 1 (2001) 61.
[3] C.T. Supuran, A. Scozzafava, A. Casini, Med. Res. Rev. 23 (2003) 146.
[4] C.T. Supuran, A. Scozzafava, Expert Opin. Ther. Patents 12 (2002) 217.
[5] B.T. Gowda, K. Jyothi, J.D.D. Souza, Z. Naturforsch. 57a (2002) 967.
[6] B.T. Gowda, K. Jyothi, J. Kozisek, H. Fuess, Z. Naturforsch. 58a (2003) 656.
[7] N.C. Handy, C.W. Murray, R.D. Amos, J. Phys. Chem. 97 (1993) 4392.
[8] P.J. Stephens, F.J. Devlin, C.F. Chavalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
[9] F.J. Devlin, J.W. Finley, P.J. Stephens, M.J. Frish, J. Phys. Chem. 99 (1995) 16883.
[10] S.Y. Lee, B.H. Boo, Bull. Korean Chem. Soc. 17 (1996) 754.
[11] S.Y. Lee, B.H. Boo, Bull. Korean Chem. Soc. 17 (1996) 760.
[12] G. Rauhut, P. Pulay, J. Phys. Chem. 99 (1995) 3093.
[13] P. Cimino, L. Gomez-Paloma, D. Duca, R. Riccio, G. Bifulco, Magn. Reson. Chem. 42 (2004) 26.
[14] R.A. Friesner, R.B. Murphy, M.D. Beachy, M.N. Ringnalda, W.T. Pollard, B.D. Dunietz, Y. Cao, J. Phys. Chem. A 103 (1999) 1913.
[15] L. Rulìsek, Z. Havlas, Int. J. Quantum Chem. 91 (2003) 504.
[16] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[17] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[18] D.C. Young, Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems (Electronic), John Wiley & Sons Inc., New York, 2001.
[19] J. Baker, A.A. Jarzecki, P. Pulay, J. Phys. Chem. A 102 (1998) 1412.
[20] K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.
[21] M.J. Frisch et al., Gaussian 03, Revision B 4, Gaussian Inc., Pittsburgh PA, 2003.
[22] J.V. Prasad, S.B. Rai, S.N. Thakuk, Chem. Phys. Lett. 164 (6) (1989) 629.
[23] K.M. Gough, B.R. Henry, J. Phys. Chem. 87 (1983) 3804.
[24] M.K. Ahmed, B.R. Henry, J. Phys. Chem. 90 (1986) 1737.
[25] M.S. Dewar, P.J. Grisdale, J. Am. Chem. Soc. 84 (1962) 3539.
[26] B.G. Johnson, P.M. Gill, J.A. Pople, J. Chem. Phys. 98 (1993) 5612.
[27] B.T. Gowda et al., Acta Cryst. E63 (2007) o2967.
[28] R.M.S. Álvareza, M.I.M. Valdeza, E.H. Cutin, C.O.D. Védova, J. Mol. Struct. 657 (2003) 291.
[29] M.F. Erben, C.O.D. Védova, R. Boese, H. Willner, C. Leibold, H. Oberhammer, Inorg. Chem. 42 (2003) 7297.
[30] M.E. Tuttolomondo, P.E. Argañaraz, E.L. Varetti, S.A. Hayes, D.A. Wann, H.E. Robertson, D.W.H. Rankin, A.B. Altabef, Eur. J. Inorg. Chem. (2007) 1381.
[31] M. Silverstein, G.C. Basseler, C. Morill, Spectrometric Identification of Organic Compounds, Wiley, New York, 1981.
[32] V. Krishnakumar, R. Ramasamy, Spectrochimica Acta Part A 62 (2005) 570.
[33] L.J. Bellamy, The Infrared Spectra of Complex Molecules, vol. 2, Chapman and Hall, London, 1980.
[34] R.M.S. Alvarez, E.H. Cutin, H.G. Mack, C.O.D. Védova, J. Mol. Struct. 440 (1998) 213.
[35] N. Puviarasan, V. Arjunan, S. Mohan, Turkish J. Chem. 28 (2004) 53.
[36] D.N. Singh, R. Shanker, R.A. Yadev, I.S. Singh, J. Raman Spectrosc. 27 (1996) 177.
[37] R.K. Gupta, R. Prasad, H.L. Bhatnagar, Indian J. Pure Appl. Phys. 28 (1990) 533.
[38] G. Varsanyi, Assignments of Vibrational Spectra of 700 Benzene Derivatives, Wiley, New York, 1974.
[39] M. Karabacak, M. Çınar, M. Kurt, J. Mol. Struct. 885 (2008) 28.
[40] D. Lin–Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Boston, Academic Press, MA, 1991.
[41] N. Sundaraganesan, H. Saleem, S. Mohan, Spectrochimica Acta A 59 (2003) 2511.
[42] E.F. Mooney, Spectrochimica Acta 20 (1964) 1021.
[43] E.F. Mooney, Spectrochimica Acta 19 (1963) 877.
[44] C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963.
[45] N. Sundaraganesan, B. Anand, C. Meganathan, B. Dominic Joshua, Spectrochimica Acta Part A 68 (3) (2007) 561.
[46] R. Ditchfield, J. Chem. Phys. 56 (1972) 5688.
[47] K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.
[48] J.R. Cheeseman, G.W. Trucks, T.A. Keith, M.J. Frisch, J. Chem. Phys. 104 (1996) 5497.
[49] H.O. Kalinowski, S. Berger, S. Braun, Carbon-13 NMR spectroscopy, John Wiley and Sons, Chichester, 1988.
[50] K. Pihlaja, E. Kleinpeter (Eds.), Carbon-13 chemical shifts in Structural and Stereochemical Analysis, VCH Publishers, Deerfield Beach, 1994.