Spectroscopic Properties of Novel Bis {4-[3-Methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethine]yhenyl} Biphenyl-4,4'-disulfonate Molecule

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ABSTRACT:

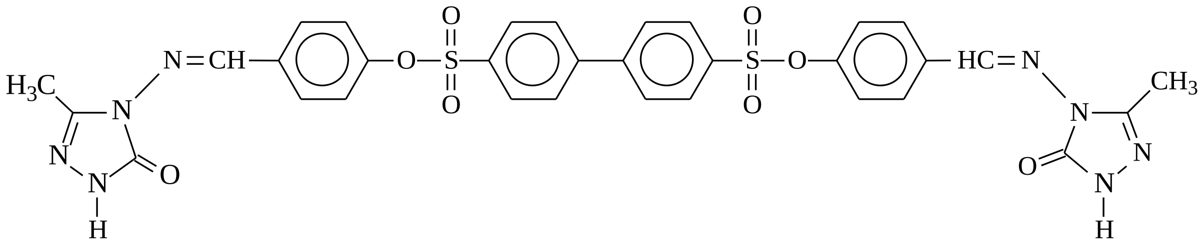
In this study, bis{4-[3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one-4-yl)-azomethine]phenyl} biphenyl-4,4'-disulfonate was optimized by using the B3LYP/631G (d) and HF/631G (d) basis sets. IR absorption frequencies of analysed molecule were calculated by two methods. Theoretically calculated IR data are multiplied with appropriate adjustment factors and the data obtained according to HF and DFT method are formed using theoretical infrared spectrum. Then, they were compared with experimental data, which are shown to be accurate. The veda4f program, was used in defining IR data, which were calculated theoretically. In addition to, molecule's theoretical bond lengths, UV-Vis values, dipole moments, formal charges, HOMO-LUMO energies, total energy of the molecule, ionization potential, electron affinity and calculated thermodynamic properties for both methods were calculated.

Key words: 4,5-dihydro-1*H*-1,2,4-triazol-5-on, Gaussian 09W, GIAO, B3LYP, HF, 631G(d)

1. Introduction

Triazole is an unsymmetrical heterocyclic organic compound having three nitrogen atoms in the five-membered ring. 1,2,4-Triazole and 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives are reported to possess a broad spectrum of biological activities such as antimicrobial, antifungal, antitumor, anti-HIV, antiviral, anticancer, anti-inflammatory, analgesic and antioxidant properties [1-5]. In addition, several articles reporting the synthesis of some *N*-arylidenamino-4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives have been published [6-10]. A number of papers have recently appeared in the literature concerning the calculation of spectroscopic properties by quantum-chemistry methods. For example; 4,5-dihydro-1H-1,2,4-triazol-5-one have been investigated spectroscopic (IR, NMR and UV–vis) and electronic properties using ab initio Hartree-Fock (HF) and density functional theory (B3LYP) [11-14].

In this paper, bis{4-[3-methyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethine]phenyl} biphenyl-4,4'-disulfonate (**1**) was synthesized according to literature [15]. The starting compound 3–ethyl–4–amino–4,5–dihydro–1*H*–1,2,4–triazol–5–one **(1)** was prepared from the reaction of ethyl acetate ethoxycarbonylhydrazone with an aqueous solution of hydrazine hydrate as described in the literature [16, 17].



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2. EXPERIMENTAL

2.1. Computational details

The molecular structure of the title compound in the ground state (in vacuo) is computed by performing both Hartree-Fock (HF) and the density functional theory (DFT) by a hydrid functional B3LYP functional (Becke’s three parameter hybrid functional using the LYP correlation functional) methods [18, 19] at 6-31G(d) level. Density functionals for all studies reported in this paper have been in the following form.

$$E_{XC} = (1-a_0)E_X^{LSDA} + a_0 E_X^{HF} + a_X \Delta E_X^{B88} + a_C E_C^{LYP} + (1-a_C)E_C^{VWN} \quad (1)$$

Where the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke’s exchange functional correction, the gradient corrected correlation functional of Lee, Yang and Parr, and the local correlation functional of Vosko, Wilk and Nusair [20]. The theoretical geometric structure of the title compound is given in Figure 1. Molecular geometry is restricted and the optimized geometrical parameters, of the title compound in this study are carried out by using Gaussian 09W program package [21] and the visualization parts were done with GaussView program [23] on personal computer employing 6-31G(d) basis set. Additionally, harmonic vibrational frequencies for the title compound are calculated with these selected methods and then scaled by 0.9516 and 0.9905, respectively [23] and these results were compared with the experimental data.

3. RESULTS AND DISCUSSION

3.1. Molecular Structure

The optimized molecular structures and chemical structure of the compound **1** was given in Fig. 1. Similarly, the optimized molecular geometric parameter (bond lenghts) of the compound 3 by using B3LYP/6–31G(d) and HF/6–31G(d) levels are listed in Table 1

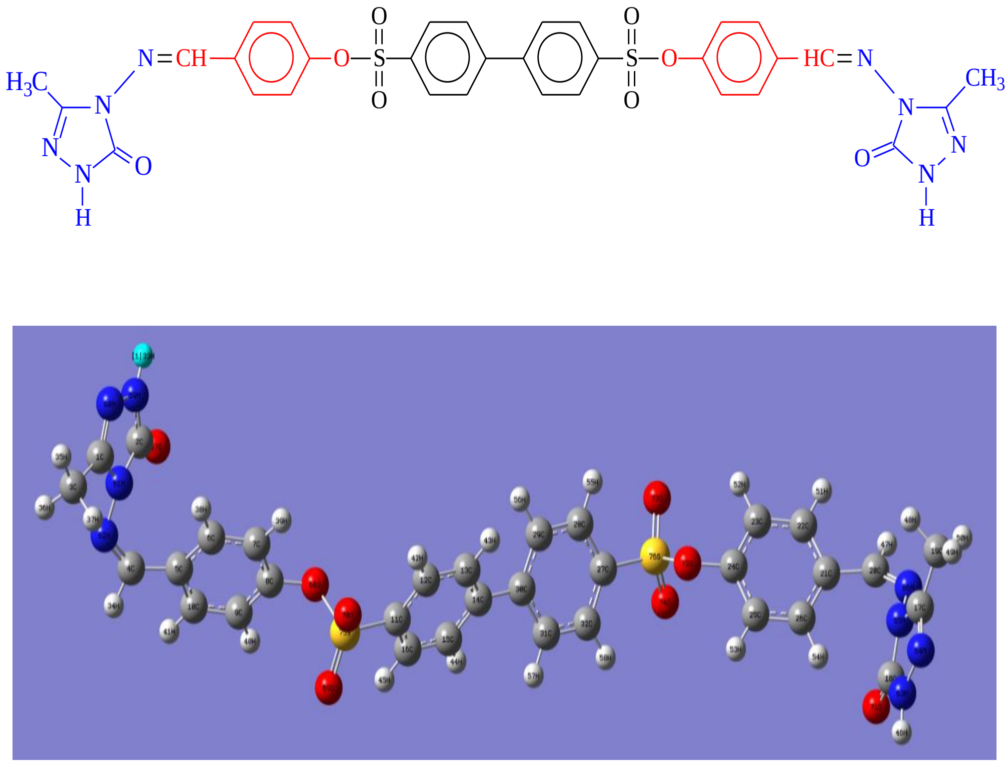


Fig. 1. The chemical structure (top) and optimized molecular structure (bottom) of compound **1** with DFT/B3LYP/6–31G(d) level.

Table 1. The calculated bond lengths of compound **3**.

	Bond Lenghts	B3LYP	HF		Bond Lenghts	B3LYP	HF
1	C(1)-N(61)	1.390	1.380	**42**	C(17)-N(65)	1.400	1.380
2	C(1)-N(60)	1.301	1.268	**43**	C(17)-N(64)	1.301	1.269
3	C(1)-C(3)	1.487	1.489	**44**	C(17)-C(19)	1.487	1.489
4	C(3)-H(35)	1.092	1.081	**45**	C(17)-H(48)	1.092	1.081
5	C(3)-H(36)	1.095	1.083	**46**	C(17)-H(49)	1.096	1.084
6	C(3)-C(37)	1.096	1.084	**47**	C(17)-C(50)	1.096	1.084
7	N(60)-N(59)	1.383	1.374	**48**	N(64)-N(63)	1.380	1.371
8	N(59)-H(33)	1.008	0.992	**49**	N(63)-H(46)	1.008	0.992
9	N(59)-C(2)	1.374	1.352	**50**	N(63)-C(18)	1.372	1.349
10	C(2)-O(67)	1.218	1.196	**51**	C(18)-O(71)	1.222	1.200
11	C(2)-N(61)	1.422	1.390	**52**	C(18)-N(65)	1.414	1.383
12	N(61)-N(62)	1.389	1.384	**53**	N(65)-N(66)	1.408	1.398
13	N(62)-C(4)	1289	1.260	**54**	N(66)-C(20	1.286	1.259
14	C(4)-H(34)	1.092	1.078	**55**	C(20)-H(47)	1.092	1.079
15	C(4)-C(5)	1.471	1.483	**56**	C(20)-C(21)	1.474	1.486
16	C(5)-C(6)	1.407	1.391	**57**	C(21)-C(22)	1.409	1.392
17	C(6)-H(38)	1.083	1.073	**58**	C(22)-H(51)	1.087	1.076
18	C(6)-C(7)	1.390	1.382	**59**	C(22)-C(23)	1.390	1.382
19	C(7)-H(39)	1.084	1.073	**60**	C(23)-H(52)	1.084	1.072
20	C(7)-C(8)	1.394	1.380	**61**	C(23)-C(24)	1.396	1.380
21	C(8)-O(68)	1.402	1.392	**62**	C(24)-O(72)	1.400	1.391
22	C(8)-C(9)	1.392	1.378	**63**	C(24)-C(25)	1.393	1.379
23	C(9)-H(40)	1.084	1.073	**64**	C(25)-H(53)	1.085	1.073
24	C(9)-C(10)	1.391	1.383	**65**	C(25)-C(26)	1.392	1.385
25	C(9)-H(41)	1.087	1.075	**66**	C(26)-H(54)	1.083	1.072
26	C(5)-C(9)	1.406	1.389	**67**	C(21)-C(26)	1.405	1.390
27	O(68)-S(75)	1.676	1.598	**68**	O(72)-S(76)	1.677	1.600
28	S(75)-O(69)	1.460	1.424	**69**	S(76)-O(73)	1.461	1.424
29	S(75)-O(70)	1.460	1.424	**70**	S(76)-O(74)	1.459	1.423
30	S(75)-C(11)	1.783	1.758	**71**	S(76)-C(27)	1.782	1.758
31	C(11)-C(12)	1.395	1.385	**72**	C(27)-C(28)	1.395	1.385
32	C(12)-H(42)	1.084	1.073	**73**	C(28)-H(55)	1.084	1.073
33	C(12)-C(13)	1.392	1.382	**74**	C(28)-C(29)	1.392	1.382
34	C(13)-H(43)	1.086	1.074	**75**	C(29)-H(56)	1.086	1.074
35	C(13)-C(14)	1.406	1.393	**76**	C(29)-C(30)	1.406	1.393
36	C(14)-C(30)	1.485	1.491	**77**	C(30)-C(14)	1.485	1.491
37	C(14)-C(15)	1.406	1.393	**78**	C(30)-C(31)	1.406	1.393
38	C(15)-H(44)	1.086	1.074	**79**	C(31)-H(57)	1.086	1.074
39	C(14)-C(15)	1.392	1.382	**80**	C(31)-C(32)	1.391	1.382
40	C(16)-H(45)	1.085	1.073	**81**	C(32)-H(58)	1.085	1.073
41	C(11)-C(16)	1.395	1.385	**82**	C(27)-C(32)	1.395	1.385

3.2. Analysis of vibrational modes

Investigation of vibrational wavenumbers of the chemical compounds plays a primary role in the spectral analysis. In spectroscopic field, the vibrational spectra of substituted benzene derivatives have been greatly investigated by various spectroscopic, since the single substitution can have a tendency to put greater changes in vibrational wavenumbers of benzene [24-26]. In other words, molecular system of benzene is greatly affected by the nature of substituents. The number of potentially active fundamentals of non-linear molecule which have N atoms is equal to (3N-6) apart from three translational and three rotational degrees of freedom. The title molecule contains 76 atoms and 222 normal vibration modes have C1 symmetry. Experimentally, the investigated bis{4-[3-methyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethine]phenyl} biphenyl-4,4'-disulfonate (**3**), as expected the IR spectra data, the N-H stretching vibration at 3187 cm^{-1} and C=O peak at 1699 cm^{-1} was observed. In addition, C=C stretching vibrations at 1628 cm^{-1}, C=N stretching vibration at 1596 cm^{-1} and SO_2 peak at 1347 cm^{-1} and 1151 cm^{-1} are occurred. Theoretically, the calculated vibrational frequencies for the compound **1** are summarized in Table 2. Furthermore the experimental IR and simulated spectra by using B3LYP/6–31G(d) and HF/6–31G(d) levels of the compound **3** under investigation are given in Fig. 2.

Table 2. The calculated frequencies values of compound **1**.

Comp. 1	Vibration Types	Experimental	scaled DFT	scaled HF
1	τ CCSS(28), τ OSCC(11), τ SOCC(11)		3	3
2	τ COSC(25), τ CSOC(22)		3	5
3	τ CCOS(15), τ CCCC(10), τ COSC(18)		6	6
4	τ CCCS(12), τ CCCC(12), τ CSOC(14), τ SOCC(16)		8	9
5	τ CCCS(23)		14	13
6	τ NCCC(13), τ CCSO(21), τ CSOC(13), τ OSCC(13)		16	19
7	δ NCC(17), τ NCCC(18), τ CCOS(13)		22	22
8	δ CCN(11), τ NCCN(11)		26	26
9	τ NCCC(14), τ CCOS(10), τ OSCC(23)		30	29
10	τ CCSO(14), τ CCCC(10), τ CSOC(12)		32	33
11	τ CCSO(12), τ CCCC(14)		39	36
12	τ CCNN(10), τ SOCC(30)		41	40
13	δ SOC(13), τ CNNC(16), τ CCCC(16), τ OCCC(11)		52	49
14	τ CCOS(18), τ CNNC(11)		56	52
15	δ COS(13), τ NCNN(18), τ CCCC(10)		66	62
16	τ CCCC(30)		71	65
17	τ CCCC(10)		72	68
18	τ CNNC(29)		83	77
19	δ CSO(12)		91	92
20	τ NCCN(19)		109	105
21	τ NCNN(16)		113	111
22	δ CCC(11), τ CCNN(13)		122	119
23	τ CNNC(13)		136	131
24	τ HCCN(18)		142	138
25	δ CCS(20), δ SCC(26)		148	154
26	τ HCCN(35), τ CNNC(21)		151	156
27	τ CNNC(31)		159	161
28	τ HCCN(54)		168	164
29	τ CNNC(13)		178	170
30	δ SCC(10)		183	183
31	δ CNN(11)		198	209
32	δ CNN(13), τ NCCN(17)		206	217
33	τ NCCN(10)		213	225
34	δ CCN(13)		223	231
35	δ CCN(20)		236	239
36	δ CCN(20)		247	249
37	τ HNNC(10), τ NCNN(15)		272	280
38	τ HNNC(10), τ NCNN(15), τ CNNC(21)		273	280
39	δ CCN(12), δ OSO(17),		274	284
40	τ CNNC(19)		280	288
41	δ CCO(11), δ OSO(19)		285	295
42	τ OCCC(11)		286	302

Comp. 1	Vibration Types	Experimental	scaled DFT	scaled HF
43	ν SC(17)		298	309
44	δ CCN(15)		315	323
45	δ CCC(13), δ CCN(12)		326	331
46	τ CCCC(22)		347	358
47	δ CCO(10)		360	369
48	δ HCC(23), τ HCCC(18)		384	401
49	δ HCC(41), τ HCCC(10), τ CCCC(22), τ CCCS(18)		397	403
50	τ HCCC(20), τ CCCC(19), τ CCCS(16)		403	409
51	δ HCC(42), τ CCCC(52), τ CCCS(17)		405	409
52	τ HCCC(14), τ CCCC(16), τ OCCC(11)	410	407	412
53	τ HCCC(13), τ CCCC(36)	410	409	415
54	τ HCCC(14), τ HNNC(23)		419	429
55	τ HNNC(44)		431	435
56	τ HNNC(52)		434	437
57	τ HNNC(18)		435	446
58	τ OCOS(15)	444	439	450
59	δ OCN(11)		451	466
60	τ CCOC(14)		461	477
61	δ OSO(10)		471	495
62	δ OCN(11), δ OSO(16)		474	507
63	δ OSO (17), τ OCOS(18)		484	511
64	δ OSO (13), τ OCOS(12)		497	514
65	τ CCOC(16)		509	523
66	τ CSCC(21)	519	522	536
67	τ CSCC(12)		526	545
68	δ HCH(28), τ HCCN(17),	551	546	563
69	ν NN(14), ν CC(11), δ NCN(24)		559	568
70	τ CCOC(11)		562	570
71	δ OCN(21), τ CCOC(17)	580	575	589
72	ν CC(12), δ OCN(12), τ CCNN(14)		589	599
73	τ OCOS(10)		591	606
74	δ CCC(19)		611	614
75	δ CCC(24)		614	620
76	δ CCC(14)		615	622
77	δ CCC(12)		622	626
78	δ CCC(35)		625	632
79	τ NCNN(17), τ NNCC(11)		628	639
80	τ NCNN(23)		630	643
81	ν SO(30)	628	637	652
82	ν SO(20)	628	645	660
83	ν NN(14)		670	687
84	ν NN(16)		680	691
85	τ ONNC(12)		690	708
86	τ HCCC(11), τ CCCC(18)	689	696	716
87	τ CCCC(11)		698	724
88	τ HCCC(10)		701	732
89	τ HCCC(11), τ CCCC(26)		709	739
90	τ ONNC(53)		713	754
91	ν SO(13), τ ONNC(11)		717	756
92	ν SO(10), τ ONNC(21)		720	760
93	τ ONNC(50)	723	725	764
94	τ ONNC(38)	744	769	777

Comp. 1	Vibration Types	Experimental	scaled DFT	scaled HF
95	ν NC(16), δ CNN(23)		777	784
96	ν OC(10), ν NC(37), ν CC(10), δ NCN(18)	786	779	785
97	τ HCCC(18), τ HCCS(11)		804	837
98	τ HCCC(91)		805	837
99	τ HCCC(32)		810	840
100	τ HCCC(15)		812	843
101	τ HCCC(38), τ HCCS(12)	819	819	855
102	τ HCCC(14)		823	855
103	τ HCCC(39), τ HCCS(16)		825	857
104	τ HCCC(17)		828	858
105	ν SO(22), τ HCCC(13)		831	863
106	ν CC(14), ν SO(15), τ HCCC(31)		842	870
107	τ HCCC(30), τ HCCS(18), τ CCCC(11)		844	875
108	δ CNN(10), τ HCCC(26)		867	896
109	τ HCNN(45)	850	915	957
110	τ HCCC(37)		924	958
111	τ HCCC(30), τ CCCC(12)		935	976
112	δ NNC(12), δ HCH(12), τ HCCN(17)		938	980
113	δ CCC(13), τ HCNN(28)		942	981
114	ν CC(13), δ CCC(22), τ HCNN(10), τ HCCC(48)	948	943	981
115	τ HCCN(23)		946	983
116	τ HCCN(36)	948	947	984
117	τ HCCC(26), τ HCCS(19)		949	986
118	τ HCCC(29), τ HCCS(25)		964	990
119	δ CCC(21)		965	995
120	τ HCCC(45), τ HCCS(27)	982	968	998
121	δ CCC(28), δ CCO(16)		1010	999
122	HCCC(33), τ HCCS(29)	1008	1024	1000
123	δ CCC(33),	1008	1028	1000
124	ν CC(15), δ CCC(16)		1029	1005
125	τ HCCC(41)		1038	1024
126	δ HCH(23), τ HCCN(23), τ CNNC(12)		1066	1049
127	δ HCH(13), τ HCCN(54)	1066	1069	1049
128	ν NC(10), ν NN(11), δ NNC(12)		1073	1063
129	ν CC(45)	1093	1076	1065
130	ν CC(25)	1093	1086	1066
131	ν NN(11), δ NNC(16), τ HCNN(14)		1088	1069
132	ν CC(27), δ HCC(14)		1101	1069
133	ν CC(25)		1104	1074
134	ν CC(17), ν SO(14)		1132	1076
135	ν CC(14), ν SO(15)		1137	1078
136	ν NN(28), δ HNN(14)		1137	1090
137	ν NN(31), δ HNN(14), τ HCCN(17)		1139	1091
138	δ HCC(15), δ CCO(12)		1145	1142
139	ν CC(22), δ HCC(15), δ CCO(12)		1147	1142
140	ν CC(35)		1172	1143
141	ν SO(19)	1151	1178	1145
142	ν CC(10), ν OC(12), δ HCC(17)		1183	1145
143	ν CC(13), ν SO(24), δ HCC(13)	1151	1186	1157
144	ν SO(20), δ HCC(16)	1151	1206	1160
145	ν NC(10), δ HCC(10)		1210	1170
146	ν CC(11), ν NC(21), δ HCC(15)	1170	1215	1171

Comp. 1	Vibration Types	Experimental	scaled DFT	scaled HF
147	δ HCC(23)		1216	1172
148	ν CC(10), ν NC(15), δ NCN(10)		1221	1173
149	δ HCC(29)	1199	1227	1176
150	ν CC(20), ν OC(28)	1238	1265	1190
151	ν CC(14)		1268	1193
152	ν OC(12)	1238	1299	1193
153	ν CC(11), δ HCC(12)		1304	1196
154	ν CC(41), δ HCC(11)		1323	1256
155	δ NCN(20), δ CNN(14)		1327	1281
156	ν NC(12), δ NCN(28), δ NNC(11)		1329	1287
157	δ HCC(41)	1293	1332	1296
158	δ HCC(22)	1293	1336	1297
159	δ HCC(42)	1293	1337	1302
160	δ HCC(21)	1293	1339	1303
161	ν SO(93)	1347	1340	1322
162	ν SO(92)	1347	1345	1324
163	δ HCN(60)		1386	1362
164	δ HCN(53), δ HCH(11)		1386	1369
165	ν CC(10), δ HCC(25)		1398	1375
166	δ HNN(16), δ HCH(32)		1402	1376
167	δ HNN(10), δ HCH(34)		1417	1378
168	ν NC(15), δ HNN(54)		1418	1387
169	ν NC(15), δ HNN(49)		1421	1389
170	ν CC(14), δ HCC(20)		1443	1404
171	ν CC(10), δ HCN(11)		1444	1406
172	ν CC(20), δ HCN(18)		1444	1408
173	ν CC(12), δ HCH(30)		1454	1419
174	ν NC(16), ν CC(12), δ HCH(38)		1454	1420
175	δ HCH(35), τ HCCN(19)		1485	1444
176	δ HCH(45), τ HCCN(19)		1490	1445
177	δ HCH(58)		1497	1455
178	δ HCH(38), δ HCCN(17)		1498	1455
179	δ HCC(34)		1516	1486
180	δ HCC(10)		1534	1506
181	δ HCC(10)		1535	1506
182	ν CC(12), δ CCC(14)		1537	1509
183	ν CC(20)	1596	1596	1562
184	ν CC(23)	1596	1612	1583
185	ν CC(18), δ CCC(10)		1614	1588
186	ν CC(24)		1616	1591
187	ν CC(11), δ HCC(11)		1637	1608
188	ν CC(21)		1638	1619
189	ν CC(51)		1639	1620
190	ν CC(23), δ HCC(11)		1641	1622
191	ν NC(37)	1628	1644	1678
192	ν NC(42)	1628	1647	1680
193	ν NC(43)	1628	1675	1713
194	ν NC(47)	1628	1676	1716
195	ν OC(70), ν NC(12)	1699	1808	1764
196	ν OC(73), ν NC(12)	1699	1824	1780
197	ν CH(85)		3032	2880
198	ν CH(93)		3034	2882

Comp. 1	Vibration Types	Experimental	scaled DFT	scaled HF
199	ν CH(92)		3088	2935
200	ν CH(61)		3090	2938
201	ν CH(58)		3108	2973
202	ν CH(86)		3114	2974
203	ν CH(98)		3136	2985
204	ν CH(30)		3137	2988
205	ν CH(37)		3161	3006
206	ν CH(28)		3165	3014
207	ν CH(27)		3176	3022
208	ν CH(31)		3177	3023
209	ν CH(23)		3182	3026
210	ν CH(21)		3182	3027
211	ν CH(50)		3193	3038
212	ν CH(42)		3201	3044
213	ν CH(62)		3203	3050
214	ν CH(37)		3204	3050
215	ν CH(51)		3204	3050
216	ν CH(88)		3205	3050
217	ν CH(51)		3205	3051
218	ν CH(36)		3211	3052
219	ν CH(50)		3218	3053
220	ν CH(44)		3220	3060
221	ν NH(100)	3187	3646	3515
222	ν NH(100)	3187	3648	3518

ν, stretching; δ, bending; δ_s, scissoring; ρ, rocking; γ, out-of-plane bending; τ, torsion

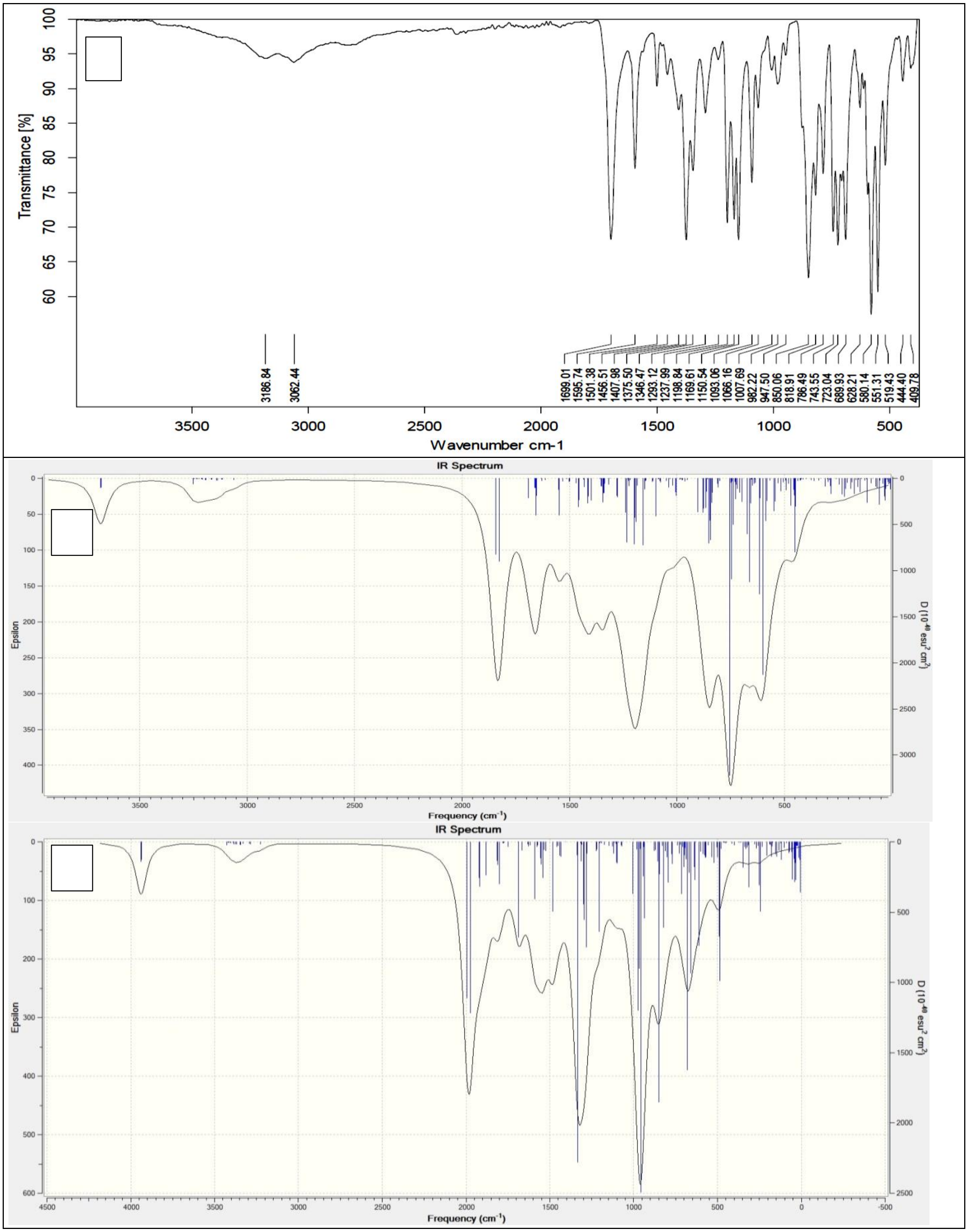


Fig. 2. IR spectra of (a) experimental and (b and c) simulated with DFT/B3LYP/6–31G(d) and HF/B3LYP/6–31G(d) levels of compound **1**.

3.5. Mulliken's atomic charges

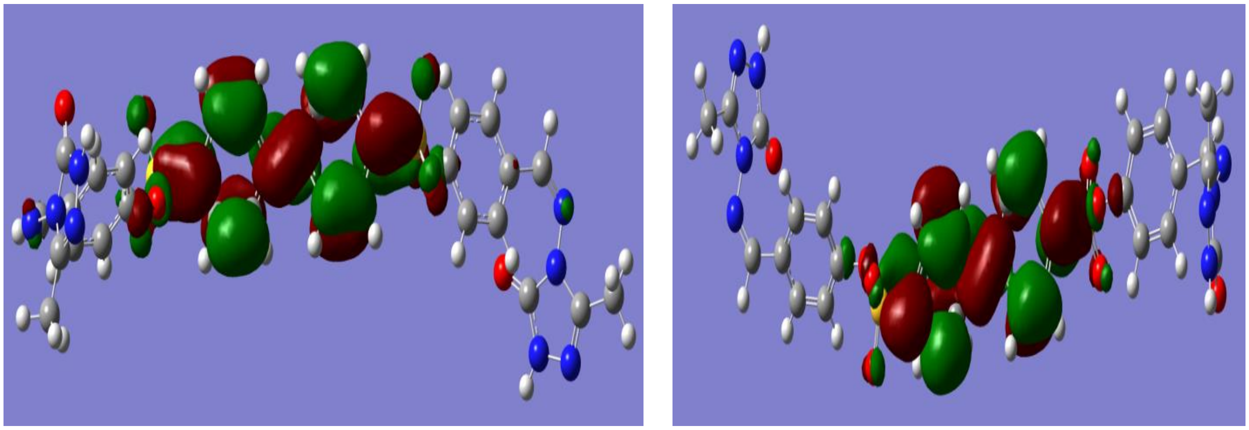
The Mulliken atomic charges at the HF/6-31 G(d) and B3LYP/6-31 G(d) level of compound 3 in gas phase are given in Table 3 [27]. The electronegative N59, N60, N61, N62, N63, N64, N65, N66, O67, O68, O69, O70, O71, O72, O73 and O74 atoms of compound **1** have negative atomic charge values. The Mulliken atomic charges (B3LYP/HF) of the mentioned atoms were calculated as -0.492/-0.639, -0.321/-0.342, -0.434/-0.635, -0.238/-0.256, -0.498/-0.640, -0.323/-0.337, -0.431/-0.634, -0.252/-0.246, -0.542/-0.632, -0.612/-0.764, -0.512/-0.658, -0.497/-0.657, -0.523/-0.654, -0.613/-0.765, -0.509/-0.659 and -0.509/-0.652 a.u., respectively. The C1, C2, C4, C8, C14, C18, C20, C24 and C30 carbon atoms bounded to the mentioned electronegative atoms in the molecule under study have positive atomic charge values. The values of the positive charges of the mentioned carbon atoms were found as 0.541/0.597, 0.781/1.012, 0.003/0.112, 0.336/0.360, 0.093/0.023, 0.538/0.600, 0.769/1.026, 0.320/0.365 and 0.093/0.023 a.u., respectively. Therefore the C1 atom surrounded with two electronegative N60 and N61 atoms, the C17 atom surrounded with two electronegative N64 and N65 atoms, the C2 atom surrounded with the electronegative N59, N61 and O67 atoms and the C18 atom surrounded with the electronegative N63, N65 and O71 atoms have the highest positive charge values. Because the carbon atoms π bonding have more positive charge density compared to ones having only σ bonding. In other words, the charge density of the carbon atoms with sp^2 hybrids is greater than those of the carbon atoms with sp^3 hybrids. Therefore the title molecule shows strong delocalization energy. In the compound **1** the atomic charges of all hydrogen atoms have positive values.

Table 3. Mulliken atomic charges of compound **1**.

	DFT	**HF**		**DFT**	**HF**		**DFT**	**HF**
Atoms	**Charges (a.u.)**		**Atoms**	**Charges (a.u.)**		**Atoms**	**Charges (a.u.)**	
C1	0.541	0.597	**C27**	-0.156	-0.324	**H52**	0.162	0.250
C2	0.781	1.012	**C28**	-0.135	-0.160	**H53**	0.161	0.245
C3	-0.520	-0.531	**C29**	-0.167	-0.215	**H54**	0.148	0.306
C4	0.003	0.112	**C30**	0.093	0.023	**H55**	0.188	0.265
C5	0.148	-0.008	**C31**	-0.167	-0.215	**H56**	0.155	0.231
C6	-0.186	-0.199	**C32**	-0.135	-0.160	**H57**	0.156	0.232
C7	-0.155	-0.196	**H33**	0.356	0.416	**H58**	0.187	0.266
C8	0.336	0.360	**H34**	0.168	0.222	**N59**	-0.492	-0.639
C9	-0.147	-0.197	**H35**	0.175	0.193	**N60**	-0.321	-0.342
C10	-0.195	-0.203	**H36**	0.187	0.213	**N61**	-0.434	-0.635
C11	-0.156	-0.324	**H37**	0.190	0.213	**N62**	-0.238	-0.256
C12	-0.136	-0.160	**H38**	0.208	0.233	**N63**	-0.498	-0.640
C13	-0.167	-0.215	**H39**	0.156	0.244	**N64**	-0.323	-0.337
C14	0.093	0.023	**H40**	0.183	0.244	**N65**	-0.431	-0.634
C15	-0.168	-0.215	**H41**	0.149	0.227	**N66**	-0.252	-0.246
C16	-0.135	-0.160	**H42**	0.190	0.265	**O67**	-0.542	-0.632
C17	0.538	0.600	**H43**	0.156	0.230	**O68**	-0.612	-0.764
C18	0.769	1.026	**H44**	0.156	0.232	**O69**	-0.512	-0.658
C19	-0.514	-0.537	**H45**	0.188	0.265	**O70**	-0.497	-0.657
C20	0.002	0.119	**H46**	0.355	0.418	**O71**	-0.523	-0.654
C21	0.204	-0.055	**H47**	0.162	0.226	**O72**	-0.613	-0.765
C22	-0.167	-0.214	**H48**	0.176	0.193	**O73**	-0.509	-0.659
C23	-0.130	-0.204	**H49**	0.185	0.210	**O74**	-0.509	-0.652
C24	0.320	0.365	**H50**	0.191	0.216	**S75**	1.250	1.688
C25	-0.129	-0.209	**H51**	0.159	0.223	**S76**	1.244	1.688
C26	-0.201	-0.221						

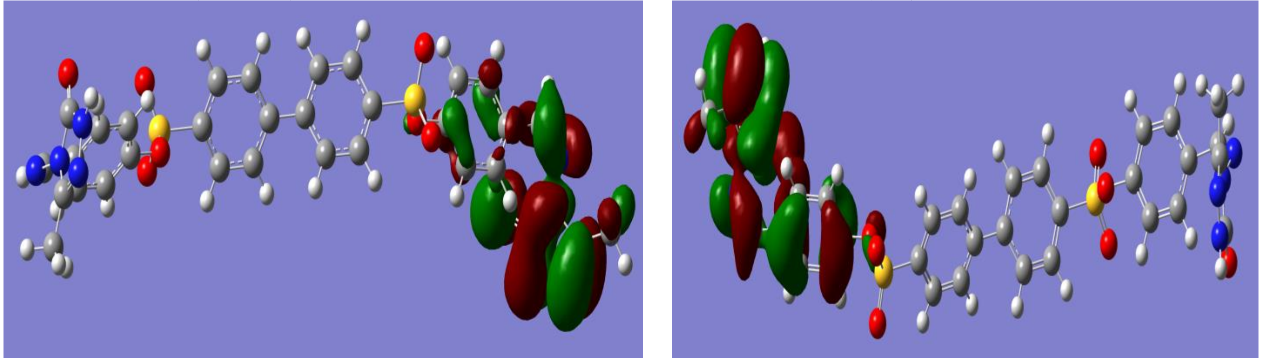
3.6. Frontier molecular orbital analysis

The energies of two important molecular orbitals of the title molecule; the second highest and highest occupied MO's (HOMO), the lowest and the second lowest unoccupied MO's (LUMO) were calculated by using DFT/B3LYP and HF methods with 6-31G(d) level and are presented in Figure 3. The energy gap of the title molecule was calculated at DFT/B3LYP and HF level, which reveals the chemical reactivity and proves the occurrence of eventual charge transfer. The HOMO is located almost over the carbon atoms, oxygen atoms and also slightly delocalized in hydrogen atom and the LUMO is mainly delocalized in carbon atoms of benzene ring. The energy gap (energy difference between HOMO and LUMO orbital) is a critical parameter in determining molecular electrical transport properties [28]. The HOMO-LUMO energy gap of the title molecule is found to 84,8895/240,7643 kcal/mol. obtained at DFT/HF method with 6-31G(d) levels.



E_{LUMO} (B3LYP) : -54,4177 kcal/mol

E_{LUMO} (HF) : 30,9049 kcal/mol



E_{HOMO} (B3LYP) :-139,3072 kcal/mol

E_{HOMO} (HF) : -209,8644 kcal/mol

Fig. 3. The calculated HOMO-LUMO energies of compound **1** according to DFT/B3LYP/6–31G(d) and HF/B3LYP/6–31G(d) levels

3.7. Dipole moment and total energy

The energetic behavior of title molecule was investigated in vacum. Dipol moments and total energy values of title molecule were calculated by using B3LYP/6-31G(d) and HF/6-31G(d) levels. The calculated dipole moments and total energy values are given in Table 4 and 5.

Table 4. The calculated dipole moment values of compound **1**.

Dipole Moment	B3LYP	HF
μ_x	-1.8364	-5.7657
μ_y	3.0225	-2.2041
μ_z	2.313	-2.9049
μ_{Toplam}	4.2263	6.8220

Table 5. The total energy of the of compound (1).

Energy	B3LYP	HF
(a.u.)	-3071.027	-3056.207

Table 6. The electron affinity of the of compound **1.**

compound	electron affinity	B3LYP	HF
1	kcal/mol	54,4177	-30,9049

Table 7. Ionisation potential of the of compound **1.**

compound	ionization potential	B3LYP	HF
1	kcal/mol	139,3072	209,8644

Table 8. Energies calculated using various theoretical models at 298,15 K, Kcal/mol (Compound 1).

	HF/6-31G(d)	B3LYP/6-31G(d)	ΔH
1 (Hatree)	-3070.422	-3088,244	
1 (Kcal/mol)	-1.926.720,539	-1.937.903,992	-11.183,45

4. CONCLUSION

The molecular structure, vibrational frequencies, HOMO and LUMO analyses and atomic charges of bis{4-[3-methyl-4,5-dihydro-1H-1,2,4-triazol-5-one-4-yl)-azomethine]phenyl} biphenyl-4,4'-disulfonate (**1**) has been calculated by using DFT/B3LYP and HF methods. By considering the results of experimental works it can be easily stated that the vibrational frequencies, ^{13}C and ^{1}H NMR chemical shifts and IR spectroscopic parameters obtained theoretically are in a very good agreement with the experimental data.

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