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Structural and Theoretical Investigation of N'-[(E)-(4-Bromophenyl)(Phenyl)Methylidene]-4-Methyl benzene sulfonohydrazide Crystal Prepared by Slow Evaporation Method

V. MOHAN [1,2], P. MAADESWARAN[3,*], B. BABU[4] and J. CHANDRASEKARAN[4]

[1]Research and Development Center, Bharathiar University, Coimbatore - 641 046, Tamil Nadu, India.
[2]Department of Physics, K.S.Rangasamy College of Technology, Tiruchengode-637215, Tamil Nadu, India.
[3]Department of Energy Studies, Periyar University, Salem-636011, Tamil Nadu, India.
[4]Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore - 641 020, Tamil Nadu, India.
*Corresponding author E-mail: maadesphysics@gmail.com

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ABSTRACT

The N'-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules were synthesized by condensation method. The synthesized N'-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4- methyl benzene sulfonohydrazide crystal geometric parameters were characterized by single crystal X-ray diffraction analysis. The crystal structure and optimized geometry parameter of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecules were obtained by the B3LYP STO-3gG level of basis set. The Mulliken charges, Highest Occupied Molecular Orbits (HOMO) and Lowest Unoccupied Molecular Orbits (LUMO) analyses have been done in order to calculate the energy gap, Ionization potential, Electron affinity; Global hardness, Chemical potential, global electrophilicity and Molecular electrostatic potential properties for N'-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4-methylbenzenesulfonohydrazid molecules were found out. The calculated HOMO and LUMO energies show that the charge transfer occurs in the N'-[(E)- (4-Bromophenyl)(phenyl)methylidene]-4- methyl benzene sulfonohydrazid molecules for B3LYP STO-3gG basis set.

Keywords: Crystal structure, X-ray diffraction, HOMO LUMO

INTRODUCTION

Benzophenone can be used as a photo initiator in UV-curing applications[1] such as inks, imaging, and clear coatings in the printing industry. Benzophenone prevents ultraviolet (UV) light from damaging scents and colors in products such as perfumes and soaps. This can also be added to plastic packaging as a UV blocker to prevent photo-degradation of the packaging polymers or its contents. Its use allows manufacturers to package the product in clear glass or plastic (such as a PETE water bottle). Without it, opaque or dark packaging would be required. Its derivatives have been investigated extensively for their biological activities such as anti-fungal and anti-inammatory [2-7].

In present study, Molecular geometry, Optimized parameters, Atomic charges, Mulliken charges, HOMO (highest occupied molecular orbital) and LUMO (Lowest unoccupied molecular orbital) energies, Frontier orbital energy gap, Molecular electrostatic potential**,** properties are experimental and computed the performance of the computational methods for ab initio B3LYP STO-3gG basis set are compared.

EXPERIMENTAL

Synthesis

The 4-Bromoobenzophenone (1 mmol) and tosylhydrazide (1mmol) were dissolved in ethanol (50 ml). The reaction mixture was heated under reflux for 3 hr and cooled gradually to room temperature[8]. The reaction mechanism is shown in Fig. 1. Crystals suitable for X-ray diffraction analysis were obtained by slow room temperature evaporation of the solution containing the compound. The as grown crystals of N-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide is depicted in Fig. 2.

Computational details

The quantum chemical calculation of N-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4-methyl benzene sulfonohydrazide has been performed using the B3LYP STO-3gG level of basis set, using the Gaussian 09 Program. The optimized geometries corresponding to the minimum on the potential energy surface have been obtained by solving self-consistent field equation iteratively. The B3LYP STO-3gG level of basis set was used for HOMO-LUMO analysis, Electrostatic potential (MESP) properties were calculated by Gaussian 09 Program[9].

Characterization techniques

Characterization: Single crystal X-ray intensity data of sucrose was collected at room temperature (T = 296 K) on a Bruker X8 KAPPA APEX-II CCD diffractometer equipped with graphite mono chromated Mo Kα radiation. Initial unit cell parameters were obtained from SMART V5.05 software for CCD detector system; Bruker Analytical X-ray Systems, Madison, WI, 1998. Data integration, correction for Lorentz polarization effects and final cell refinement were performed by SAINTPLUS, V5.00 Software for the CCD detector system; Bruker Analytical X-Ray System, Inc.: Madison, WI, 1998. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using SADABS, Program for absorption correction using SMART CCD based on the method of Blessing. Structure was obtained by a combination of the direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F2 using the SHELXTL.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction

N-[(E)-(4-Bromophenyl)(phenyl) methylidene]-4-methylbenzenesulfonohydrazide optimized geometric crystal structure is shown in the Fig. 3, belongs to the noncentro symmetric monoclinic space group $P2_1/c$ and the cell dimensions are a=8.4480Å, b=19.7198 Å, c=12.9679 Å; $\alpha=\gamma=90^{o}$and β=120.046; and V=1870.06 Å^3. The packing diagram in N-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecule and crystal structure view along the (a) *a*-axis (b) *b*-axis, and (c) *c*-axis is presented in Fig. 4(a-c) and 5(a-c). The powder XRD pattern is shown in the Fig. 6.

In order to find the most optimized geometric parameters (bond length, bond angle and dihedral angles), the energy calculation are carried out for N'-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4-methylbenzenesulfonohydrazide, using B3LYP STO-3gG basis set value is given in the Table (1-3). The hydrazones molecules are attracted considerable

attention due to their biological activities and crystal structures of these compounds were reported[2-7]. Benzophenone and its derivatives have also been extensively investigated for their biological activities such as anti-fungal and anti-inflammatory. In present work, the title compound, $C_{20}H_{17}BrN_2O_2S$, was

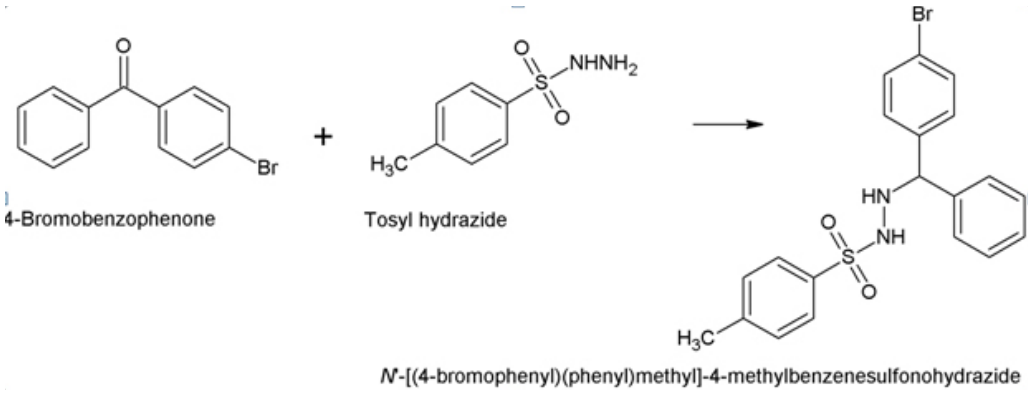

Fig. 1: N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules synthesis reaction

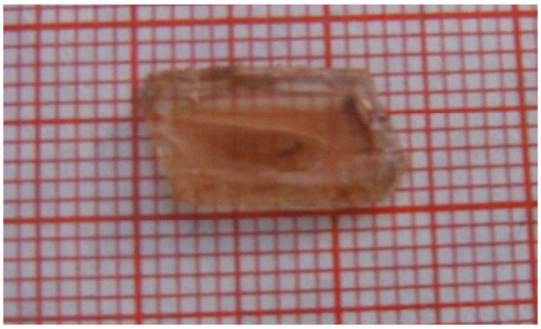

Fig. 2: As grown crystals of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide

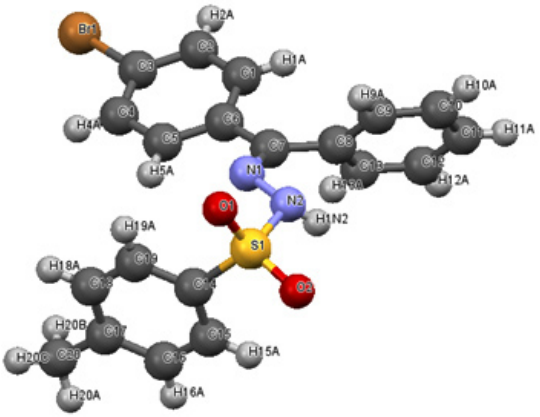

Fig. 3: Geometric structures of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide

synthesized by Schiff base condensation reaction between 4-bromobenzophenone and tosyl hydrazine were used synthesized by N'-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4-methyl benzene sulfono hydrazide molecules. The optimized geometric structure of molecule (Fig. 3) the bromo substituted with benzene ring (Br1-C3) forms bond length 1.8986Åand 1.8973 Å for experimental and B3LYP STO-3gG basis set values respectively. The bromo benzophenone linked bridge tosyl hydrazine group (N1-N2) bond length is 1.4014 Å and 1.4519 Å experimental and theoretical values. The bond length of benzene ring carbon and hydrogen bond of (C2-H2A), (C10-H10A), (C12-H12A), (C13-H13A) and (C20-H20C) values at 0.9499 Å, 0.9493 Å, 0.9509 Å, 0.9506 Å, 0.9497 Å & 0.9800 Å and 1.0977 Å, 1.0984 Å, 1.0984 Å, 1.0985 Å, 1.0985 Å & 1.1008 Å for experimental and theoretical values. Experimental values as compare to those theoretical values, more or less equal values are get. The N'-[(E)-(4- Bromophenyl)(phenyl) methylidene]-4-methyl benzene sulfonohydrazide molecules hydro-carbon of benzene ring are (H1A-C1-C2), (H1A-C1-C6), (C8-C9-H9A), (H9A-C9-C10), (C8-C13-H13A), (C12-C13-H13A) (H16A-C16-C17) (H18A-C18-C19) (C14-C19-H19A) and (C18-C19-H19A) bond angle values at 119.50 °, 119.52 °, 119.94 °, 119.87 °, 119.82 °, 119.86 °, 119.24 °, 119.73 °, 120.16 ° & 120.10 ° and 119.3254 °, 119.6576 °, 119.3914 °, 119.9437 °, 119.3903 °, 119.9368 °, 119.6115 °, 119.5452 °, 120.7595 ° &

120.8558 ° for experimental and B3LYP STO-3gG basis set values respectively. The bromine substituted benzene ring (Br1-C3-C4) 119.81 ° and 120.2469 ° for both values. The bond angle of crystal, molecules are linked through nitrogen and carbon (N1-C7-C6) values at 115.65 ° and 115.4307 ° for experimental and theoretical values. The molecules, bond angle between two benzene rings (C5-C6-C7) (C6-C7-C8) (C7-C8-C13) and (C11-C12-C13) values at 120.38 °, 119.60 °, 120.67 °& 119.80 ° and 119.8369 °, 119.3776 °, 120.3213 ° & 120.1798 ° for experimental

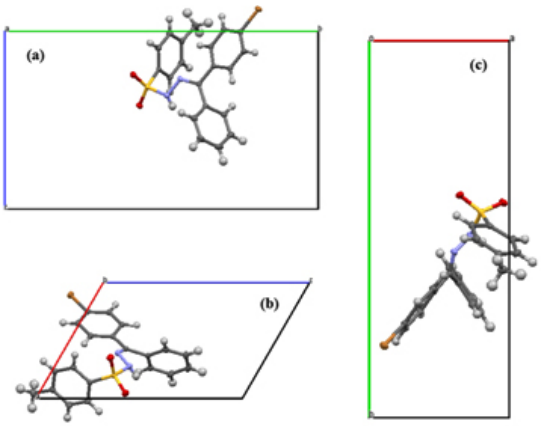

Fig. 4: The molecule packing diagram in N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide crystal and structure view along the (a) *a*-axis (b) *b*-axis (c) *c*-axis

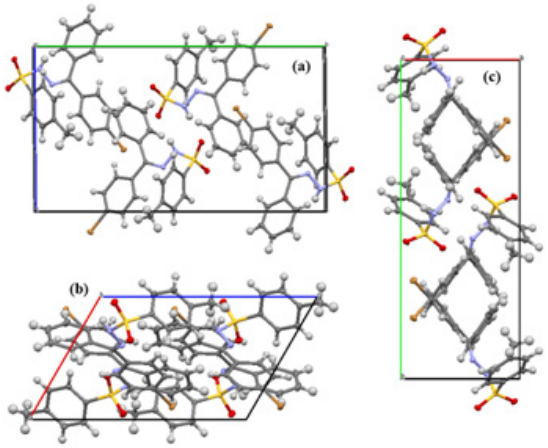

Fig. 5: The crystal packing diagram in N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide crystal and structure view along the (a) *a*-axis (b) *b*-axis (c) *c*-axis

Table 1: Optimized geometrical parameters for N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules bond length(Å)

S. No	Bond length	Experimental	B3LYP STO-3gG
1	Br1-C3	1.8986	1.8973
2	S1-O1	1.4335	1.627
3	S1-O2	1.4390	1.6281
4	S1-N2	1.6575	2.0742
5	S1-C14	1.7589	1.9287
6	N1-N2	1.4014	1.4519
7	N1-C7	1.2929	1.3502
8	N2-H1N2	0.8127	1.087
9	C1-H1A	0.9499	1.0977
10	C1-C2	1.3908	1.4057
11	C1-C6	1.3984	1.4204
12	C2-H2A	0.9493	1.0984
13	C2-C3	1.3869	1.4163
14	C3-C4	1.3877	1.4188
15	C4-H4A	0.9500	1.0983
16	C4-C5	1.3877	1.4024
17	C5-H5A	0.9505	1.0985
18	C5-C6	1.4009	1.4228
19	C6-C7	1.4844	1.5079
20	C7-C8	1.4899	1.5225
21	C8-C9	1.3974	1.4198
22	C8-C13	1.3909	1.4205
23	C9-H9A	0.9498	1.0988
24	C9-C10	1.3925	1.4083
25	C10-H10A	0.9509	1.0984
26	C10-C11	1.3843	1.4087
27	C11-H11A	0.9502	1.0984
28	C11-C12	1.3864	1.4103
29	C12-H12A	0.9506	1.0985
30	C12-C13	1.3933	1.4066
31	C13-H13A	0.9497	1.0985
32	C14-C15	1.3900	1.4021
33	C14-C19	1.3887	1.4037
34	C15-H15A	0.9502	1.1019
35	C15-C16	1.3970	1.4088
36	C16-H16A	0.9503	1.0989
37	C16-C17	1.3963	1.417
38	C17-C18	1.3965	1.4175
39	C17-C20	1.5057	1.5387
40	C18-H18A	0.9502	1.0989
41	C18-C19	1.3882	1.4097
42	C19-H19A	0.9498	1.0999
43	C20-H20A	0.9806	1.1005
44	C20-H20B	0.9801	1.1042
45	C20-H20C	0.9800	1.1008

and B3LYP STO-3gG basis set values respectively. The dihedral angle between three benzene ring of N'-[(E)-(4- Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecules in (C8-C9-C10-H10A), (C9-C10- C11-H11A), (H12A-C12-C13-C8), (C15-C14-C19-H19A), (H16A-C16-C17-C18), (C16-C17-C18-H18A) and (H18A-C18-C19-C14) values at 178.71 °, -178.91 °, 178.53 °, 177.79 °, 176.92 °, -177.25 ° & 179.84 ° and 179.6285 °, -179.7863 °, 179.644 °, 179.2793 °, 179.5913 °, -179.6164 ° & 179.9329 ° for experimental and B3LYP STO-3gG basis set values respectively.

Mulliken population analysis

The atomic charges in molecules are fundamental to chemistry. For instance, atomic

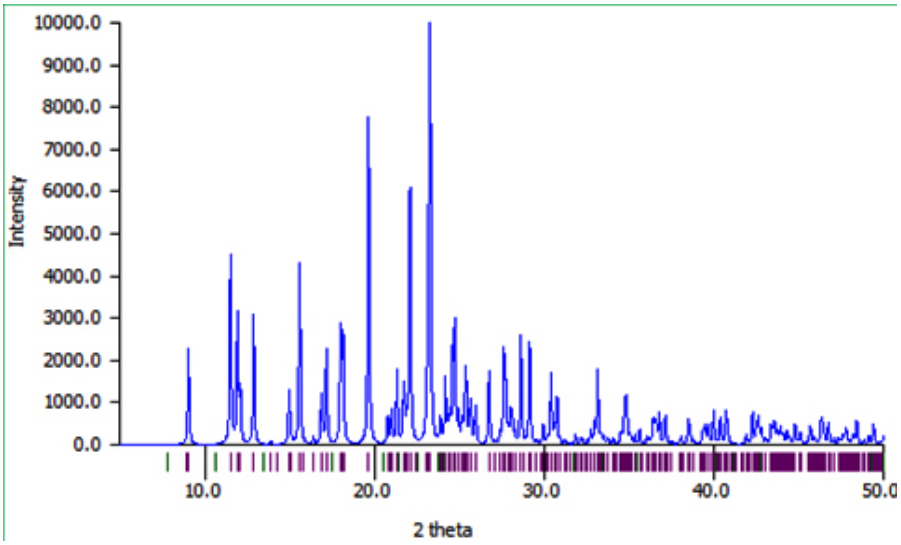

Fig. 6: X-ray diffraction pattern of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide crystal

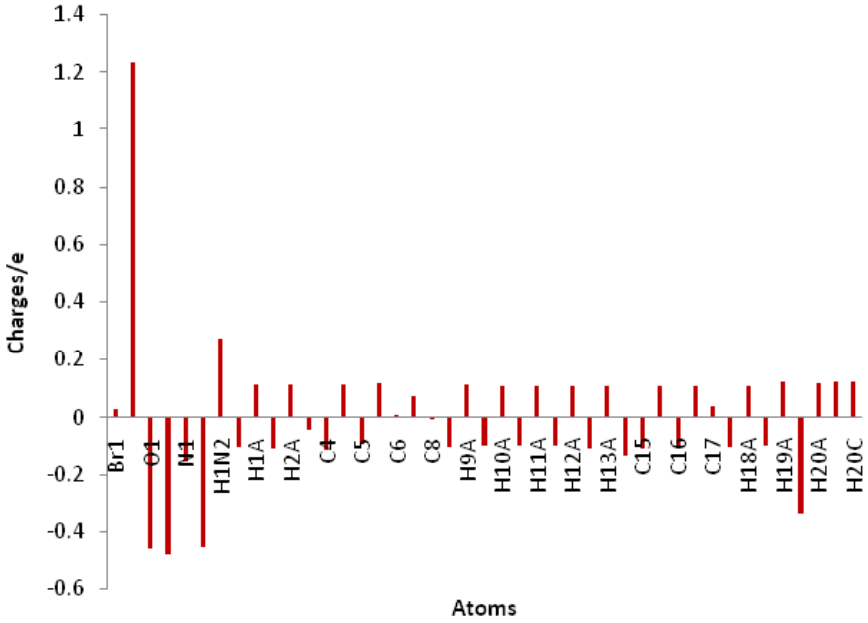

Fig. 7: The charge distribution calculated by the Mulliken method for N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules

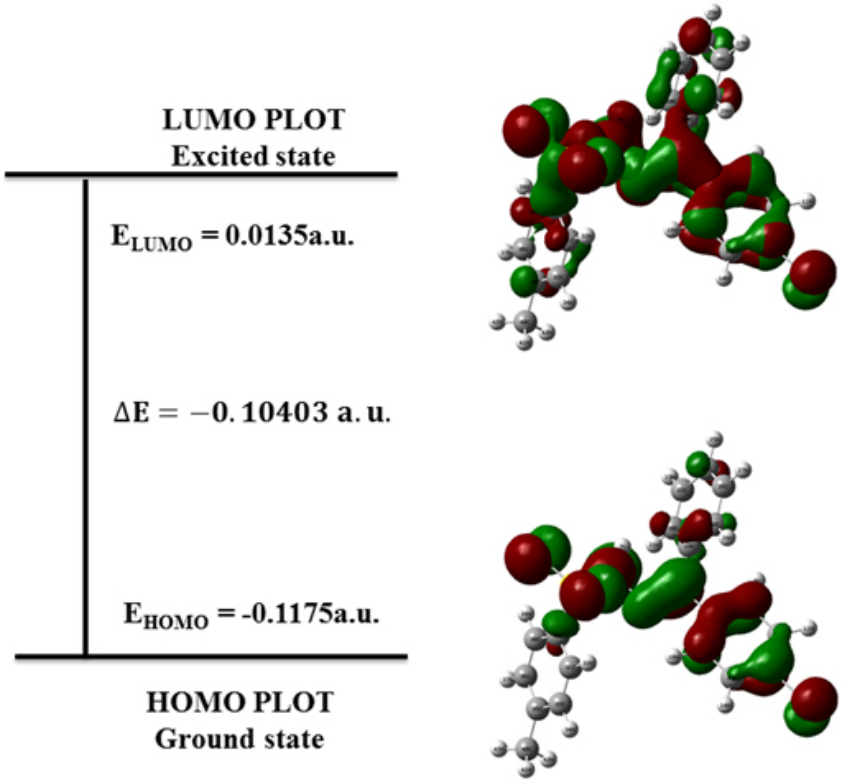

Fig. 8:The atomic orbital compositions of the frontier molecular orbital of N'-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules

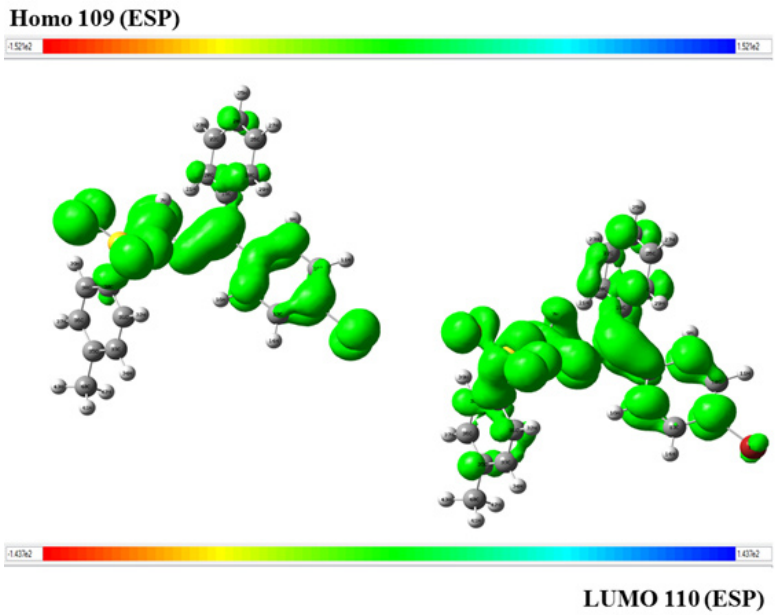

Fig. 9: The Electrostatic potential of diagram in N'-[(E)-(4-Bromophenyl) (phenyl) methylidene] -4-methylbenzenesulfonohydrazide

Table 2: Optimized geometrical parameters for N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules bond angle(˚)

S. No.	Bond angle	Experimental	B3LYP STO-3gG
1	O1-S1-O2	119.55	122.0077
2	O1-S1-N2	107.91	105.7495
3	O1-S1-C14	107.62	111.4247
4	O2-S1-N2	104.08	111.3415
5	O2-S1-C14	111.01	107.7479
6	N2-S1-C14	105.77	95.3221
7	N2-N1-C7	117.06	116.4365
8	S1-N2-N1	111.23	104.0353
9	S1-N2-H1N2	111.79	102.2319
10	N1-N2-H1N2	117.59	107.2695
11	H1A-C1-C2	119.50	119.3254
12	H1A-C1-C6	119.52	119.6576
13	C2-C1-C6	120.98	121.0148
14	C1-C2-H2A	120.72	119.9058
15	C1-C2-C3	118.52	120.2135
16	H2A-C2-C3	120.75	119.88
17	Br1-C3-C2	118.19	120.3839
18	Br1-C3-C4	119.81	120.2469
19	C2-C3-C4	122.00	119.3691
20	C3-C4-H4A	120.60	119.8394
21	C3-C4-C5	118.81	120.0662
22	H4A-C4-C5	120.59	120.0943
23	C4-C5-H5A	119.66	120.5689
24	C4-C5-C6	120.76	121.1995
25	H5A-C5-C6	119.58	118.231
26	C1-C6-C5	118.90	118.1346
27	C1-C6-C7	120.72	122.0165
28	C5-C6-C7	120.38	119.8369
29	N1-C7-C6	115.65	115.4307
30	N1-C7-C8	124.75	125.1912
31	C6-C7-C8	119.60	119.3776
32	C7-C8-C9	119.94	121.1273
33	C7-C8-C13	120.67	120.3213
34	C9-C8-C13	119.36	118.5471
35	C8-C9-H9A	119.87	119.3914
36	C8-C9-C10	120.20	120.6594
37	H9A-C9-C10	119.94	119.9437
38	C9-C10-H10A	120.05	119.7477
39	C9-C10-C11	119.86	120.1663
40	H10A-C10-C11	120.08	120.086
41	C10-C11-H11A	119.77	120.1319
42	C10-C11-C12	120.42	119.7757
43	H11A-C11-C12	119.81	120.0925
44	C11-C12-H12A	120.07	120.0209
45	C11-C12-C13	119.80	120.1798
46	H12A-C12-C13	120.13	119.7992
47	C8-C13-C12	120.32	120.6705
48	C8-C13-H13A	119.82	119.3903
49	C12-C13-H13A	119.86	119.9368
50	S1-C14-C15	120.78	116.8293
51	S1-C14-C19	117.89	120.9216
52	C15-C14-C19	120.99	122.2344
53	C14-C15-H15A	120.72	119.2184
54	C14-C15-C16	118.49	118.8048
55	H15A-C15-C16	120.78	121.9758
56	C15-C16-H16A	119.26	119.7779
57	C15-C16-C17	121.50	120.6102
58	H16A-C16-C17	119.24	119.6115
59	C16-C17-C18	118.49	119.0239
60	C16-C17-C20	121.27	120.5254
61	C18-C17-C20	120.22	120.444
62	C17-C18-H18A	119.59	119.5142
63	C17-C18-C19	120.69	120.9404
64	H18A-C18-C19	119.73	119.5452
65	C14-C19-C18	119.74	118.3842
66	C14-C19-H19A	120.16	120.7595
67	C18-C19-H19A	120.10	120.8558
68	C17-C20-H20A	109.50	110.7846
69	C17-C20-H20B	109.52	110.3626
70	C17-C20-H20C	109.42	110.8128
71	H20A-C20-H20B	109.44	107.9849
72	H20A-C20-H20C	109.42	108.8753
73	H20B-C20-H20C	109.52	107.9249

charge transfers in the chemical reaction [10, 11]. We have examined the Mulliken atomic charges in solution (Methanol) in Table 5. The Mulliken atomic charges calculated at the B3LYP STO-3gG. It is worthy to mention that C6, C7, and C17 atoms of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecules exhibit positive charge, while C1, C2, C3, C4, C5, C8, C9, C10, C11, C12, C13, C14, C15, C16, C18, C19, and C20 atoms exhibits negative charges, Oxygen O1 and O2 has a maximum negative charges -0.46224 and -0.47788 for this values B3LYP STO-3gG basis set. The maximum positive atomic charges (1.235288) are obtained for S1 which is sulfonate present in the functional group SO_3^-. The positive atomic charges

Table 3: Optimized geometrical parameters for N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules dihedral angle(˚)

S. No.	Dihedral angle	Experimental	B3LYP STO-3gG
1	O1-S1-N2-N1	-70.31	175.4735
2	O1-S1-N2-H1N2	156.02	63.924
3	O2-S1-N2-N1	161.70	40.9306
4	O2-S1-N2-H1N2	28.03	-70.6188
5	C14-S1- N2-N1	44.64	-70.4822
6	C14-S1- N2-H1N2	-89.03	177.9683
7	O1-S1-C14-C15	-167.92	-142.9805
8	O1-S1-C14-C19	18.69	35.6574
9	O2-S1-C14-C15	-35.36	-6.6428
10	O2-S1-C14-C19	151.25	171.9951
11	N2-S1-C14-C15	76.93	107.7873
12	N2-S1-C14-C19	-96.46	-73.5748
13	C7-N1-N2-S1	-164.95	-137.9619
14	C7-N1-N2-H1N2	-34.23	-30.1186
15	N2-N1-C7-C6	173.73	-177.3678
16	N2-N1-C7-C8	-6.85	2.3895
17	H1A-C1-C2-H2A	0.38	0.4516
18	H1A-C1-C2-C3	-179.68	-179.2415
19	C6-C1-C2-H2A	-179.62	179.912
20	C6-C1-C2-C3	0.31	0.2188
21	H1A-C1-C6-C5	-178.81	178.9231
22	H1A-C1-C6-C7	1.98	0.1842
23	C2-C1-C6-C5	1.20	-0.5355
24	C2-C1-C6-C7	-178.01	-179.2744
25	C1-C2-C3-Br1	179.67	-179.9516
26	C1-C2-C3-C4	-1.09	0.1947
27	H2A-C2-C3-Br1	-0.40	0.3552
28	H2A-C2-C3-C4	178.85	-179.4986
29	Br1-C3-C4-H4A	-0.47	0.0194
30	Br1-C3-C4-C5	179.54	179.8679
31	C2-C3-C4-H4A	-179.70	179.8733
32	C2-C3-C4-C5	0.31	-0.2781
33	C3-C4-C5-H5A	-178.75	179.6607
34	C3-C4-C5-C6	1.26	-0.0499
35	H4-C4-C5-H5A	1.26	-0.4911
36	H4A-C4-C5-C6	-178.73	179.7983
37	C4-C5-C6-C1	-2.00	0.4515
38	C4-C5-C6-C7	177.21	179.2188
39	H5A-C5-C6-C1	178.01	-179.2656
40	H5A-C5-C6-C7	-2.78	-0.4983
41	C1-C6-C7-N1	157.08	164.5239
42	C1-C6-C7-C8	-22.38	-15.2485
43	C5-C6-C7-N1	-22.12	-14.194
44	C5-C6-C7-C8	158.43	166.0336
45	N1-C7-C8-C9	-58.22	-51.7809
46	N1-C7-C8-C13	123.45	127.4563
47	C6-C7-C8-C9	121.18	127.9675
48	C6-C7-C8-C13	-57.15	-52.7952
49	C7-C8-C9-H9A	1.75	-1.3717
50	C7-C8-C9-C10	-178.27	179.4752
51	C13-C8- C9-H9A	-179.90	179.3778
52	C13-C8- C9-C10	0.09	0.2248
53	C7-C8-C13-C12	179.65-	-179.1699
54	C7-C8-C13-H13A	-0.39	0.2613
55	C9-C8-C13-C12	1.31	0.0868
56	C9-C8-C13-H13A	-178.74	179.518
57	C8-C9-C10-H10A	178.71	179.6285
58	C8-C9-C10-C11	-1.30	-0.37
59	H9A-C9-C10-H10A	-1.31	0.4801
60	H9A-C9-C10-C11	178.69	-179.5184
61	C9-C10- C11-H11A	-178.91	-179.7863
62	C9-C10- C11-C12	1.11	0.2003
63	H10A-C10-C11-H11A	1.08	0.2151
64	H10A-C10-C11-C12	-178.89	-179.7982
65	C10-C11-C12-H12A	-179.75	-179.788
66	C10-C11-C12-C13	0.28	0.1101
67	H11A-C11-C12-H12A	0.27	0.1986
68	H11A-C11-C12-C13	-179.70	-179.9032
69	C11-C12-C13-C8	-1.50	-0.2544
70	C11-C12-C13-H13A	178.55	-179.6824
71	H12A-C12-C13-C8	178.53	179.644
72	H12A-C12-C13-H13A	-1.42	0.2159
73	S1-C14-C15-H15A	8.72	-0.528
74	S1-C14-C15-C16	-171.29	179.1197
75	C19-C14-C15-H15A	-178.10	-179.1466
76	C19-C14-C15-C16	1.89	0.5011
77	S1-C14-C19-C18	171.17	-179.033
78	S1-C14- C19-H19A	-8.83	0.7163
79	C15-C14-C19-C18	-2.21	-0.47
80	C15-C14-C19-H19A	177.79	179.2793
81	C14-C15-C16-H16A	-179.22	-179.9372

82	C14-C15-C16-C17	0.80	-0.1649
83	H15A-C15-C16-H16A	0.77	-0.2997
84	H15A-C15-C16-C17	-179.21	179.4726
85	C15-C16-C17-C18	-3.10	-0.1814
86	C15-C16-C17-C20	175.50	178.8862
87	H16A-C16-C17-C18	176.92	179.5913
88	H16A-C16-C17-C20	-4.48	-1.3411
89	C16-C17-C18-H18A	-177.25	-179.6164
90	C16-C17-C18-C19	2.78	0.2121
91	C20-C17-C18-H18A	4.14	1.3152
92	C20-C17-C18-C19	-175.84	-178.8563
93	C16-C17-C20-H20A	18.20	27.7399
94	C16-C17-C20-H20B	-101.81	-91.8077
95	C16-C17-C20-H20C	138.13	148.7013
96	C18-C17-C20-H20A	-163.22	-153.2058
97	C18-C17-C20-H20B	76.77	87.2466
98	C18-C17-C20-H20C	-43.29	-32.2444
99	C17-C18-C19-C14	-0.19	0.1045
100	C17-C18-C19-H19A	179.81	-179.6445
101	H18A-C18-C19-C14	179.84	179.9329
102	H18A-C18-C19-H19A	-0.16	0.1839

are observed (0.027547) for bromine atoms. The magnitude of hydrogen atomic charges is hydrogen atomic charges are found to be only positive and negative charges obtain, this listed given in the Table 5 for this B3LYP STO-3gG basis sets for the N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecules. The atomic charges plotted B3LYP STO-3gG basis set has been shown in Fig. 7. The nitrogen atoms presence of negative charges are N1 (-0.15703) and N2 (-0.45769) atoms. The above result shows that the natural atomic charges are more sensitive to the charges in the molecular structure the Mullikan's net charges.

Table 4: Comparison of HOMO, LUMO, energy gaps (e HOMO –LUMO), and related molecular properties of N'-[(E)-(4-Bromophenyl)(phenyl) methylidene]-4-methyl benzene sulfonohydrazide molecules (a.u.)

Molecular properties	B3LYP STO-3gG
EHOMO	-0.11757
ELUMO	0.01354
ΔEHOMO-LUMO gap (a.u.)	-0.10403
Ionisation Potential (I)	0.11757
Electron affinity(A)	-0.01354
Global Hardness (η)	-0.0646
Chemical potential (μ)	-0.0520
Global Electrophilicity (ω)	0.02089

HOMO-LUMO analysis

A deeper understand of chemical reactivity can be gained by this electronic absorption corresponds to the transition from the ground state to the first excited state and it is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)[12,13]. HOMO represents the ability to donate an electron and LUMO represent the ability to obtain an electron. The HOMO is delocalized over the Bromine substituted two benzene ring and bridge over the N-NH group. The LUMO is located on the Bromo benzophenone and tosylhydrazide group. Consequently, the HOMO-LUMO transition implies an electron density transfer from, the more aromatic part of the π-conjucated system including the electron donor group to its more quinonid side and mainly to the electron with drawing end the frontier molecular orbital's of

Table 5: The charge distribution calculated by the Mulliken method for N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules

Atoms	Charges
Br1	0.027547
S1	1.235288
O1	-0.46224
O2	-0.47788
N1	-0.15703
N2	-0.45769
H1N2	0.271619
C1	-0.10475
H1A	0.110807
C2	-0.11313
H2A	0.112495
C3	-0.04562
C4	-0.11412
H4A	0.111453
C5	-0.09862
H5A	0.117707
C6	0.010596
C7	0.070907
C8	-0.00651
C9	-0.10659
H9A	0.114875
C10	-0.10129
H10A	0.109164
C11	-0.10274
H11A	0.107332
C12	-0.10209
H12A	0.107313
C13	-0.11076
H13A	0.107218
C14	-0.13433
C15	-0.11229
H15A	0.10977
C16	-0.10761
H16A	0.106391
C17	0.039951
C18	-0.10834
H18A	0.10838
C19	-0.10236
H19A	0.123402
C20	-0.34109
H20A	0.11906
H20B	0.123953
H20C	0.121847

N'-[(E)-(4-Bromophenyl) (phenyl)methylidene]-4-methyl benzene sulfonohydrazide is shown in Fig. 8. The energy value of HOMO is computed -0.11757 a.u. and LUMO is 0.01354 a.u. The energy gap is -0.10403 a.u. in for N'-[(E)-(4-Bromophenyl)(phenyl) methylidene]-4-methyl benzene sulfonohydrazide molecules, respectively. Surface for the Frontier orbitals are drawn to understand the bonding scheme of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecules. We examine the two important molecular orbital's (MO) for N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecules: highest occupied MOs and lowest unoccupied and MOs which we denote HOMO and LUMO respectively.

The calculated Self Consistent Field (SCF) energy of N'-[(E)-(4-Bromophenyl)(phenyl) methylidene]-4-methylbenzenesulfonohydrazide is —3958.29016076 a.u. at B3LYP STO-3gG . The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecules.

HOMO-LUMO energy gap and related molecular properties

The HOMO, LUMO and HOMO-LUMO energy gap of N'-[(E)-(4-Bromophenyl)(phenyl) methylidene]-4-methyl benzene sulfonohydrazide molecules in the B3LYP STO-3gG basis set has been calculated. The HOMO–LUMO energy gap reveals that the energy gap reflects the chemical activity of the molecule. Associated within the framework of SCF MO theory the ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies as $I = -E_{HOMO}$ and $A = -E_{LUMO}$. The hardness corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO energy gaps the harder the molecules[14]. The global hardness, $\eta = 1/2(E_{LUMO} - E_{HOMO})$. The hardness has been associated with the stability of chemical system. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, $\mu = 1/2(E_{HOMO} + E_{LUMO})$. The global electrophilicity index, $\omega = \mu^2/2\eta$ is also calculated and listed in Table 4.

Molecular electrostatic potential (MEP)

The 3D plots of molecular electrostatic potential (MEP) of N'-[(E)-(4-Bromophenyl)(phenyl)

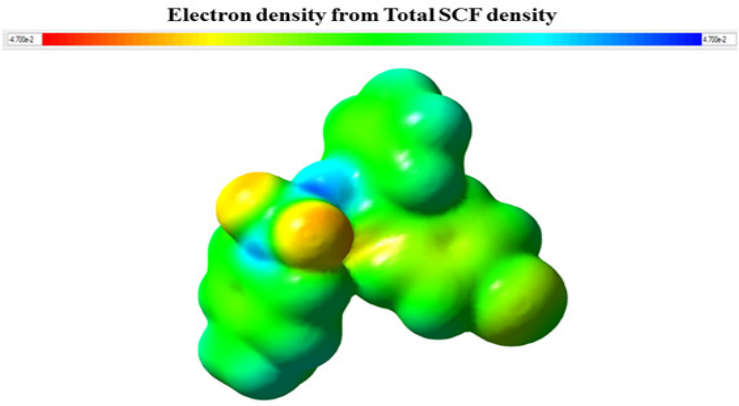

Fig. 10: The total electron density surface mapped with electrostatic potentialN'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methylbenzenesulfonohydrazide molecules

methylidene]-4-methyl benzene sulfonohydrazide molecule is illustrated in Fig. 9. The MEP is a plot of electrostatic potential mapped onto the constant electron density surface. The MEP surface super-imposed on top of the total energy density. The MEP is a useful property to study reactivity given that an approaching electrophile will be attracted to negative region (where the electron distribution effect is dominant). In the majority of the MEPs, while the maximum negative region which preferred site of for electrophilic attack indication as red colour, the maximum positive region which preferred site for nucleophilic attack symptoms as blue colour. The importance of MEP lies in the fact that it simultaneous displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of colour grading (Fig. 9) and is very useful in research of molecular structure with its physiochemical property relationship[15, 16]. The resulting surface simultaneously displays molecular size and shape and electrostatic potential value.

The different values of the electrostatic potential at the surface are represented by different colours. The potential increases in the order red < orange < yellow < green< blue. The colour code of these maps is the range between the HOMO – 1.437 a.u. (Deepest red) to 1.437 a.u. (Deepest blue) and LUMO is – 1.521 a.u. (Deepest red) to 1.521 a.u in N'-[(E)-(4-Bromophenyl)(phenyl) methylidene]-4-methyl benzene sulfonohydrazide molecules. Whereas blue colour indicates the strongest attraction and red colour indicates the strongest repulsion. The regions of negative V(r) are usually associated with the lone pair of electro native atoms. The contour map of electrostatic potential of the N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecule has been constructed by the B3LYP STO-3gG basis set is shown in Fig. 10also confirms the different negative (-4.700 a.u.) and positive (-4.700 a.u.) potential sites of the molecules in accordance with the total electron density surface.

CONCLUSION

In present investigation, N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide crystals were grown by slow evaporation method . The X-ray single crystal structural refinement indicated monoclinic structure and good crystalline quality. The of HOMO-LUMO analyses, energy value of HOMO was computed -0.11757 a.u. and LUMO was 0.01354 a.u. and HOMO-LUMO energy was -0.10403 a.u. The molecular electrostatic potential result reflected, the surface simultaneously displays molecular size and shape and electrostatic potential value. The total electron density surface mapped with electrostatic potential have different negative (-4.700 a.u.) and positive (-4.700 a.u.) potential sites. The Mulliken atomic charges calculated at the B3LYP STO-3gG. It was worthy to mention that C6, C7, and C17 atoms of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide molecules exhibit positive charge, while C1, C2, C3, C4, C5, C8, C9, C10, C11, C12, C13, C14, C15, C16, C18, C19, and C20 atoms exhibited negative charges, Oxygen O1

and O2 have been a maximum negative charges -0.46224 and -0.47788 for those values B3LYP STO-3gG basis set. The theoretical molecular structures of N'-[(E)-(4-Bromophenyl)(phenyl)methylidene]-4-methyl benzene sulfonohydrazide were determined by the B3LYP STO-3gG. It is suggested this crystal will be used for nonlinear electro optic field.

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