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Spectroscopic and Quantum Chemical Calculations of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4 methoxyphenyl)benzo[h][1,4,7]triazecin-8(1h)-one from leaves of *Cassia auriculata* (Avaram)

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Abstract - *We disclose a detailed DFT study and phytochemical study of Cassia auriculata product, 4-(2,5dichlorobenzyl) -2,3,4,5,6,7-hexahydro-7-(4methoxyphenyl) benzo [h] [1,4,7] triazecin-8 (1H)-one have been carried out. The present work is an investigation to describe a correlation between experimental and theoretical at DFT-B3LYP/6-311++G(d,p). Theoretically predicted FT-IR spectra of title molecule have been made on the basis of the calculated potential energy disruptions (PED). The energy gap of the present compound was calculated related to HOMO-LUMO energies which confirm the occupancy of charge transformation. The analysis of MEP map plays an important role as shows the negative, the positive potential sites and determining stability of the molecule was computed using B3LYP 6-311++G(d,p) basis set.*

Key Words*: DFT, *Cassia auriculata, FT-IR, HOMO-LUMO

1. INTRODUCTION

The prestigious position in an Ayurveda, siddha and unani system of medicine. The surrounded by more than 2,50,000 species, of plants, only 5-10% are chemically investigated [1] and discovery of new compounds from plants to find out novel and nontoxic compound [2]. The medicinal plants in Indian system of medicine for their, antibiotic, purgative and cathartic properties[3]. The plants generate phenolic compounds with an assorted polarity, physicochemical properties for its survival but have good pharmacological activity in humans, other application for agriculture and veterinary [4]. Recent years medicinal plants have renewed interest in line plant-derived therapeutic agents.

The medicinal plants of *Cassia auriculata* family (Caesalpiniaceae, common name: Tanner's cassia) common know as Tamil name Avaram in various part of the plant are used in traditional medicine. The *Cassia auriculata* medication plant is a mixture kalpa drug (roots, leaves, flower, bark and unripe fruits) is called avarai panchaga choornam for the control of sugar the levels. *Cassia auriculata* properties derived from the antioxidant and free-radical scavenging properties [5]. Some phytochemical constituents are reported such as, alkaloids, flavonoids, tannins, anthracence, properties toward, cancer, asthma, skin disease, diabetes, liver disorder, dyslipidemia, renal and conjunctivitis [6]. In the middle of the constituents, the pale yellow and scantily soluble substances such as flavonel, group of flavonoids are extensively present in 80% higher plants [7]. The preliminary work that phytochemical investigation into the chemical constituents of *Cassia auriculata* leaves on new 4-(2,5 dichlorobenzyl) -2,3,4,5,6,7- hexahydro-7-(4-methoxyphenyl) benzo[h] [1,4,7] triazecin-8(1H)-one compound was isolated and experimental characterized by reported this work [8]. Were also evaluated of the title compound have been estimated for the first theoretically. Now the present work is goes to describe a comparative study for reported experimental and density functional theory (DFT) have also been performed to theoretically simulate the geometrical spectroscopic properties.

2. Molecular Modeling Calculations

The quantum chemical calculations (QCC) were performed at the density functional theory (DFT), calculation especially who those using hybrid functional, have evolved to a powerful and very much reliable tool, the determination of various properties of molecules. The theoretical calculations were performed using the Gaussian 09W program [9].

The optimized geometry of the title compound is made up of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one were carried out using the Becke's three-Parametric hybrid exchange functional [B3] [10], combined with the Lee-yang Parr correlation functional [LYP] [11] level of theory supplemented with the standard6-311++ G(d,p) respectly; augmented by 'd' polarization function for hydrogen atoms to denote the better representation of polar bonds in the molecules [12,13] and VEDA 4 program [14] was used for vibrational frequency as well as analysis of structure PED. For the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have been simulated, energy band gap, molecular electrostatic potentional (MEP) and natural bond orbital were also performed [15]. Were performed using NBO programmed as carried out is Gauss view.

RESULTS AND DISCUSSION

3. Ground State Structure Analysis

The first discuss for a computational work is to determine optimized molecular structure along with atomic numbering in show in Fig.1. 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one, the most optimized structural (bond length, bond angle, dihedral angle) by B3LYP/6-311++G(d,p) basis set . The title compound belongs to C_1 point group symmetry. To the best of our knowledge, exact experimental data on the geometrical parameters of the title compound are not get it, however for comparison reason; simulated optimized geometric parameters at the levels of theory are correlated . The phenyl ring line in the C-C ring 1.3930 – 1.4083 A^0 [16]. In the present case, the bond lengths C_8-C_9, C_8-C_{14}, C_9-C_{10}, C_8-C_{11}, C_{11}-C_{12}, C_{12}-C_{43}, C_{16}-C_{21}, C_{11}-C_{18}, C_{19}-C_{20}, C_{26}-C_{27} and C_{25}-C_{26}, are in 1.5085, 1.3988, 1.4038, 1.4098, 1.4021, 1.403, 1.3953, 1.3986, 1.3948 and corresponding the reported values 1.5248, 1.3521, 1.4109A^0 [17]. C-N bond length of different Pyrazole complex is 1.33-1.44A^0 [18]. The bond angles of calculated at C-N-N bond N_1-C_{10}-O_{15}, C_{10}-C_9-C_{11}, C_2-N_1-C_{10}, C_{24}-C_{25}-C_{26}, 22.1561, 121.4738, 123.6106 and 123.3345A^0 respectively, the dihedral angles among N_1-C_{16}-C_{21}-H_{49} and C_{47}-C_{18}-C_{19}-C_{22} are 179.62 to -172.59. This show that the molecular structure is well optimized with selected B3LYP 6-311++G(d,p) basis set. These values are reported in the Table 1.

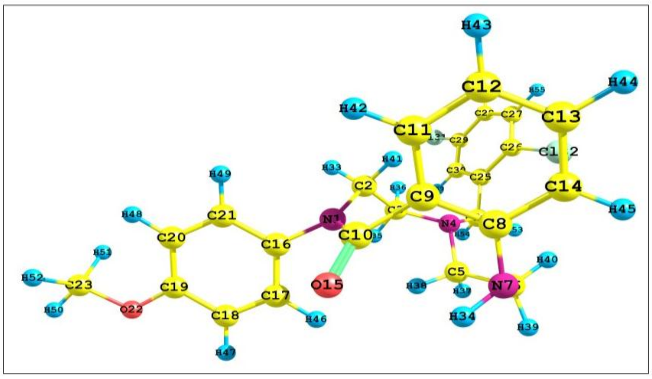

Fig.1. Optimized Structure:4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one.

Table 1 Optimized geometrical parameters of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one

Bond Lengths	B3LYP 6-311++G(d,p)	Bond Lengths	B3LYP 6-311++G(d,p)
N_1-C_2	1.4736	C_{12}-C_{43}	1.3971
N_1-C_{10}	1.3838	C_{13}-C_{14}	1.0856
N_1-C_{16}	1.44	C_{14}-H_{45}	1.0862
C_2-C_3	1.54	C_{24}-H_{54}	1.1066
N4-C5	1.474	C25-C26	1.4038
N4-C24	1.4721	C25-C30	1.402
C5-H38	1.0935	C26-C27	1.3948
C6-N7	1.4642	C21-H49	1.0857
C6-H38	1.0974	C2-N1-C10	123.6106
N7-C34	1.0153	N1-C10-O15	122.1561
C8-C9	1.4098	C24-C25-C26	123.3345
C8-C14	1.4021	N1-C16-C21-H49	179.62
C9-C10	1.5085	C47-C18-C19-C22	-179.59

4. Vibrational modes description

On account of such a huge molecule, the detailed description of a vibrational assignments of fundamental modes of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl) benzo[h][1,4,7]triazecin-8(1H)-one along with PED calculation. The title molecular structure has $C_{25}H_{25}Cl_2N_3O_2$ atoms with 165 normal vibration modes. This molecule has C_1 symmetry. A completed vibrational assignment of the fundamentals was proposed based on the calculated PED values in Table.2 and using the VEDA program. The observed FT-IR spectra of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl) benzo [h] [1,4,7] triazecin-8(1H)-one are shown in Fig.2 respectively.

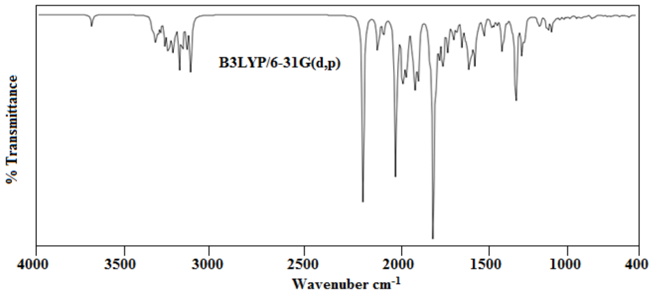

Fig.2. FT-IR spectra, of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4 methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one.

4.1 C-H Vibrational

Regularly, in aromatic benzene compounds, C-H stretching vibrations are normally appear in the region 2800–3200 cm^{-1} [19]. The C-H stretching vibration, the band appeared at 2924 cm^{-1} in FT-IR band, and same theoretical investigation have compounded at strongly 2931, 3016, 3042, 3069, 3077, 3088, 3099, 3104, 3208 good agreement with recorded FT-IR respectively. In the aromatic benzene C-H in plane bending vibrational and out-of plane binding vibrational commonly occur within region of 1300 – 1000 cm^{-1} respectively [20]. The experimental bands at 1294, 1223, 1162, 1124 and 1035 cm^{-1}. The corresponding theoretically bands are 4-(2,5-dicshlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl) benzo [h] [1,4,7] triazecin-8(1H)-one with PED contribution of respectly, solving good agreement with experimental value.

4.2 C=O Vibrational

Very sensitive of C=O stretching vibrations is the positions several of factor such as the electronic effects by substituent's ring strains and physical state [21]. The carbon–Oxygen double bond and alone pair of electron on oxygen. For the title compound, carbonyl stretching group vibrations are expected to appear as very strong located at region 1850-1550 cm^{-1} [22]. The calculated value 1729 cm^{-1} is quite in good agreement with the strong band FT-IR line at 1729 cm^{-1}

S.No	B3LYP/6-3++G(d,p) cm^{-1}	FT-IR cm^{-1}	Vibrational assignments + PED (%)
1	3440	3434	ʋNH(100)
2	3235	-	ʋCH(91)
3	2931	2924	ʋCH(93)
4	1729	1735	ʋOC(85)
5	1629	1622	ʋCC(34)
6	1498	1497	δHCH(48)
7	1464	1452	ʋCC(19)
8	1393	1377	δHCN(16)+τHCNC(25)+ ʋCC(10)
9	1273	1294	ʋNC(10)+δHCN(12)
10	1244	1223	δHCN(17)
11	1176	-	ʋNC(10)
12	1166	1162	δCC(37)
13	1123	1124	ʋCC(31)+δHCC(32)
14	1028	1035	δHCC(11)+δCCC(13)
15	1020	-	ʋNC(14)
16	989	991	δHCC(12)
17	903	917	τHCCC(40)
18	883	-	τHCCC(16)+τHCCN(26)
19	829	842	τHCCC(87)
20	741	-	τONCC(35)
21	730	730	δCCC(11)
22	574	602	δCIC(21)

Table 2 Vibration assignment of optimized structure:4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4 methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)- One

4.3 C-Cl Vibrational

The vibrations belonging to bonds created between the ring and the halogen atoms, are quite informative since mixing of vibrations are possible due to the lowering of molecular symmetry and the pressure of heavy atoms. The normally observed C-Cl stretching frequency in the region 800-500 cm^{-1} [23-25], which is depending on the configurations and complete conformation of the compound. The regarding the above information in FT-IR absorption bands at 602 cm^{-1} and the theoretical calculation by B3LYP6-311++ G(d, p), methods gives the C-Cl stretching mode at 574 cm^{-1} and 283, 200 and 306 cm^{-1} there is a very slightly deviation in both the in-plane and out-of-plane vibrations have been observed calculated only.

4.4 N-H Vibrational

The secondary amines group is found in many naturally materials occurring substances. It has proved sometimes tedious in materials to identify it chemically [26]. The title molecules contains a secondary amine show a single week band in the region 3400-3220 cm^{-1} [27, 28]. These bands are shifted to longer wave length than primary amines due to hydrogen bonding. In the title compound at experimental band observed at 3434 cm^{-1} in FT-IR spectrum are assigned to N-H stretching vibrations. Respectively as can be seen in Table: 2, theoretical calculations by B3LYP 6-311++G(d, p) methods gives the N-H stretching vibrations at 3440 cm^{-1}. The PED value of N-H is observed to be 100%.

4.5 C-N Vibrational

The vibrational assignments C-N stretching vibration in the region 1266-1382 cm^{-1} for an aromatic amines [29]. The FT-IR spectrum observed to the title compound vibrations observed at 1377, 1294, 1223 cm^{-1} C-N stretching vibrations at 1393, 1273, 1244 cm^{-1} the theoretically calculated by B3LYP/6-311++G(d,p) method are in good agreement. In plane bending mode for –C-N are scattered on observed at 209,254,299,393,1244,1340 theoretically calculated respectively at B3LYP 6-311++G(d,p).

4.6 C-C Vibrational

Benzene, Naphthalene, Toluene and their derivatives are expected characteristic of the aromatic ring itself. The bands are expected a major contribution in the region 1620-1390 cm^{-1} [30-32]. Hence in the present study, the FT-IR characteristic bands in observed 1622, 1452 and 1377 cm^{-1} are assigned to C-C stretching vibrations. The theoretically calculated at 1629, 1464 and 1393 cm^{-1} by B3LYP/6-311++G(d,p) show a good agreement with experimental data. The absorption bands arising from C-C –in-plane bending vibration in the region 675-1000 cm^{-1} [33,34]. The calculated values are 1028, 989, 903, 829, and 730 cm^{-1} with maximum percentage, the experimental value calculated at 1035, 991, 917, 842, 730 cm^{-1} some of these have an overlap with CH in-plane bending mode of vibration as well. The PED corresponds to these vibrational are mixed vibrational as evident from Table.2. All the C-C vibrational frequencies are well as good as with those identified in the title of the compound.

5. Electronic Spectra

In order to understand in determining the electronic, transmittance (UV-Vis spectra) in title of the compound, TD - DFT calculation with the B3LYP/6-3++G(d,p) level of theory method. In the experimentally spectrum showed a few important and prominent absorption bands at 425, 254 and 220 nm and has correlation to the theoretical absorption band at 282.12 nm (gas phase). The gas phase, the tractions are simulated at 318.57, 308, and 282.12nm which appearance of bands with excited energy 3.8919, 4.0195, 4.3947 at DFT/ B3LYP 6-311++G(d,p) method. Table.3 showed in both gas phase and experimental absorption band values are very close to each other.

States	Experimental λ(nm)	TD-B3LYP/6-311++G(d,p) λ(nm)	Excited energy E(eV)
S1	425	318.57	3.8919
S2	254	308.46	4.0195
S3	220	282.12	4.3947

Table 3 UV-Vis spectra of 4-(2,5dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7 (4methoxyphenyl) benzo [h] [1,4,7] triazecin-8 (1H)-one calculated at TD-B3LYP/6-311++G(d,p)

6. Frontier molecular orbitals (HOMO–LUMO)

Two important molecular orbital (MO) were examined for the title compound. The highest occupied molecular orbital (HOMOs), lowest occupied molecular orbital (LUMOs) and Energy gap (E_g) are very useful important parameters for quantum chemistry. The HOMO and LUMO are named as frontier molecular orbital (FMOs). The HOMO defines ability to donate an electron, while LUMO defines ability to obtain an electron acceptor. The positive phase is red and the negative phase is green respectively, both HOMO – LUMO in an important properties of the electrical, optical and chemical properties of a molecule [35]. The bioactivity and chemical activity of the molecule represent on the value of HOMO – LUMO energy gap 11.2396 eV, are show in Table 4. Paulis introduced the concept of chemical reactivity described estimating using B3LYP/6-311++G(d,p) are softness (s), chemical potential (μ), Hardness (η), electronegativity (X) and global electrophilicity index (ω) are defined using Koopmen's theorem as [36], considering the chemical hardeness large homo-lumo energy gap means hard molecule 2.6274 eV and small HOMO - LUMO energy gap means soft molecules 0.1903 eV. One can also relate the stability of the molecule to hardness, which means that the molecule with least HOMO - LUMO gap means, it is more reactive [37] and shown in fig 3

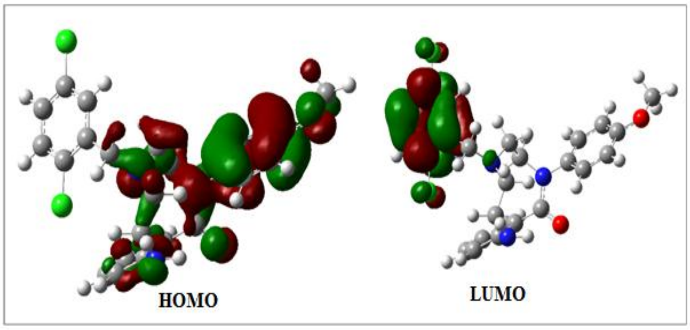

Fig.3 .HOMO-LUMO Energy Gap

Table 4 Molecular properties of 4-(2,5dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7 (4methoxyphenyl) benzo [h] [1,4,7] triazecin-8 (1H)-one

Molecular Properties	**Values**	**Molecular Properties**	**Values**
HOMO	8.2472	Chemical potential (μ)	-5.6198
LUMO	2.9924	Softness (s)	0.1903
HOMO-LUMO	11.2396	Electronegavity (X)	5.6198
Chemical hardness(μ)	2.6274	Electrophilic index (ω)	6.0101

7. Molecular electrostatic potential maps

To predicted with help investigation of the molecular structure activity relationship, physicochemical property relationship, included bimolecular and drugs [38-41] and also co-ordinate with a calculated partial charges dipole moment, and electronegativity of the molecule. The MEP is related (electrostatic potential mapped onto an electron iso-density surface) to the electronic density which is very useful descriptor in understanding site for electrophilic attack (elelctron rich region), and nucleophilic attack (electron poor region) MEP was calculated B3LYP/6-31++G(d,p) level of optimized geometry basis set as show in Fig.4.and The important of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl) benzo [h] [1,4,7] triazecin-8(1H)-one display molecular size shape and electrostatic potentional region at the MEP surface are represented by different increasing in the colour grading order, red<orange<yellow<green<blue. The Negative electrostatic potential corresponds to an attraction of the proton by the aggregate electron density in the molecules red (electron rich), while the positive electrostatic potential corresponds to repulsion of the proton by atomic nucli blue (electron definity).

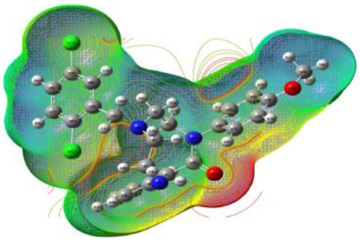

Fig.4. Molecular electrostatic potential map of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one calculated at B3LYP/6-311++G(d,p) level.

7. Mulliken Population Ananlysis (MPA)

The Mulliken atomic charges play an important role in the application of quantum mechanical calculation (QMC) to the molecular system, because atomic charges affect dipole moment, polarizablity electronic structure and much more properties of molecules, the mulliken population analysis(MPA) of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4-methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one are computed by the DFT/B3LYP 6-311++G(d,p) level of obtain to the assign charges to atom is show in Table 5. The charge distributions on the molecule calculated by milliken method for the equilibrium geometry mulliken population analysis chart is show in Fig 5.The analysis show that the presence of phenyl ring, all the carbon atoms have negative charges except C_8, C_9, C_{10}, C_{16}, and C_{19} which are attached with the nitrogen atom N_7 (0.587349) and oxygen atom O_{22} (-0.518238), It has maximum positive charge C_{10} (0.473954) and the atoms exhibit negative charges and has maximum negative charge C_{20} (-0.145717). To assign charges on H_{34} atoms has the maximum charge H_{34} 0.258507 among the hydrogen atom present in the title molecule at B3LYP/6-311++G(d,p). All the hydrogen atoms have a total positive charge.

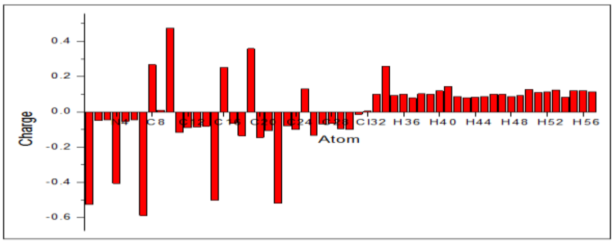

Fig.5. Mulliken Population Ananlysis of of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4 methoxyphenyl)benzo[h][1,4,7]triazecin-8(1H)-one calculated at B3LYP/6-311++G(d,p) level.

Table 5

Mulliken atomic charges of 4-(2,5dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7 (4methoxyphenyl) benzo [h] [1,4,7] triazecin-8 (1H)-one

Atom	Charge	Atom	Charge
N_1	-0.525608	O_{15}	-0.502083
N_7	-0.587349	C_{17}	-0.064453
C_8	0.267147	C_{18}	-0.134937
C_9	0.009153	C_{19}	0.358221
C_{10}	0.473954	C_{20}	-0.145717
C_{11}	-0.117187	C_{21}	-0.106653
C_{12}	-0.089655	O_{22}	-0.518238
C_{13}	-0.087626	H_{34}	0.258507
C_{14}	-0.081500	H_{35}	0.093328

8. CONCLUSIONS

The B3LYP/6-311++G(d,p) method was applied to investigation provides a comprehensive theoretical and experimental study 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4 methoxyphenyl)benzo[h][1,4,7]triazecin-8(1h)-one isolated from the levels of *cassia auriculata*. The spectroscopy characterized such as FT-IR and UV spectroscopy previously reported here the title compound. The structure and vibrational spectra of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4methoxyphenyl)benzo[h][1,4,7]triazecin-8(1h)-one isolated are carried out by B3LYP/6-311++G. Theses experimental characterization were followed by theoretical model was adopted at bond length, bond angle, and vibrational FT-IR and UV spectrum of compound simulated at B3LYP/6-311++G(d,p) level of showed nice correlation with experimental. The HOMO-LUMO gap of 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4 methoxyphenyl)benzo[h][1,4,7]triazecin-8(1h)-one isolated was determined to be about 11.2396 eV, which implies that the 4-(2,5-dichlorobenzyl)-2,3,4,5,6,7-hexahydro-7-(4 methoxyphenyl)benzo[h][1,4,7]triazecin-8(1h)-one isolated possesses relatively high chemical stability. The electronic properties such as moreover the density of states, MEP, Mulliken population, molecular electrostatic potential of the title compound were estimated for the first time.

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