



ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(17):119-128
(<http://derpharmachemica.com/archive.html>)

Molecular Structure, Vibrational Spectra and theoretical HOMO-LUMO analysis of (E)-3, 5-dimethyl-1-phenyl-4-(p-tolyldiazenyl)-1H-pyrazole by DFT Method

Sunil L. Dhonnar^{a*}, Bapusaheb S. Jagdale^a, Arun B. Sawant^b, Thansing B. Pawar^a
and Santosh S. Chobe^a

^aOrganic research laboratory, P.G. Department of Chemistry, Loknete Vyankatrao Hiray Arts, Science and Commerce College, Panchavati, Nashik (M.S) India

^bDepartment of chemistry, M.S.G. Arts, Science and Commerce College, Malegaon camp, Malegaon (M.S) India

ABSTRACT

The Compound (E)-3, 5-dimethyl-1-phenyl-4-(p-tolyldiazenyl)-1H-Pyrazole was synthesized and characterized by FT-IR and ¹H NMR. The optimized molecular geometry, bond length, atomic charges, bond angle, harmonic Vibrational frequencies of title compound have been investigated by density functional theory (DFT) using standard B3LYP method with 6-311++G (d, p) basic set. The parameters depending on HOMO, LUMO such as Electronic Chemical potential, Chemical softness, Global electrophilicity, index Global hardness are also been studied. Finally molecular electrostatic potential was studied to determine the reactive sites within molecule. The result indicates a high correlation between the theoretical and experimental values.

Keywords: DFT, FT-IR, ¹H NMR, HOMO-LUMO, MEP

INTRODUCTION

Pyrazoles are the important class of nitrogen heterocycles having considerable attraction towards pharmaceutical and agrochemical industries because of their pharmacological and biological activities such as anti-inflammatory [1,2] antimicrobial [3,4] anticonvulsant [5] anti-tumor [6-7] anti-tubercular [8] antiviral [9] analgesic, antiulcer [10] antidepressant [11] herbicidal [12] antioxidant [13] etc. Some pyrazole also shows good insecticidal activity against American cockroach [14]. Pyrazole having azo exhibited a wide variety of biological and pharmaceutical activities and therefore they play important role in medicinal chemistry [15]. Pyrazoles having azo group has been found to exhibit a wide range of biological activities like antibacterial [16] antifungal [17, 18] CDK inhibitor [19] analgesic [20] etc. Azopyrazole are widely used as dye [21]. Now days Azopyrazole are applies towards as light responsive Molecular switches [22-23]. FT-IR, FT-Raman and NMR study of 4-(Substituted Phenyl azo)-3,5-diacetamido-1H-Pyrazoles by DFT method was reported by S Kinali *et al.* [24] Rodrigo Faundez-Gutierrez *et al* reported the synthesis and DFT study of some new azo pyrazole derivatives [25]. Arun B.Sawant *et al* reported the Synthesis and DFT study of 6, 8-dichloro-2-(4-chlorophenyl)-4H-chromene-4-one [26]. The main objective of this paper is to synthesis the title compound and study their molecular structure, geometrical properties, vibrational spectra by using DFT/B3LYP/6-311++G(d,p) method. In present paper we also investigate the reactive sites of the title compound by Molecular Electrostatic Map. In addition to those FMOs, Global chemical reactivity descriptors and thermodynamic properties also been studied by same method and level.

MATERIALS AND METHODS

2.1 Synthesis:

All chemicals required for synthesis were obtained from commercial source (AR grade with purity >99%) and used without further purification. Melting Points is determined in open capillaries and are uncorrected. Purity of the compound was checked by TLC using silica gel-G coated Al-plates and spot visualize under UV radiation. IR Spectrum was recorded on Shimadzu spectrophotometer on KBr pellets. ^1H NMR spectra were recorded in CDCl_3 on a Bruker Avance II 400 MHz spectrometer using TMS as an internal Standard. The title compound was synthesized by using publish method [27] and structure confirm by IR and ^1H NMR. Yield: 65 % M.P. 142-144 $^\circ\text{C}$, IR (KBr, cm^{-1}) 3061, 3022 (Ar -H), 2993 (CH_3) 1597, 1552 ($\text{C}=\text{C}$), 1508 ($\text{C}=\text{N}$), 1427 ($\text{N}=\text{N}$), 1070 ($\text{N}-\text{N}$). ^1H NMR: (CDCl_3 , 400MHz): 2.59 (s, 3H, CH_3 -Ar), 2.65 (s, 6H, 3, 5- CH_3), 7.24-7.65 (m, 9H, Ar-H)

2.2 Computational details

The DFT calculations were perform on an Intel (R) core (TM) i7 personal computer using Gaussian-03 program package [28] without any constraint on the geometry. Geometry of the title compound were optimized by DFT/B3LYP method 6-311++G (d, p) basic set. The vibrational frequencies were calculated at the same level of theory for the optimized structure and the obtained frequencies were scaled by 0.96 [29]. Vibrational band assignments were made using the Gauss View 4.1.2 molecular visualization program [30]. To investigate the reactive sites of the title compound, the molecular electrostatic potentials were calculated using the same method [31]. All the calculations were done for the optimized structure in gas phase.

RESULTS AND DISCUSSION

3.1 Molecular geometry

The optimized structural parameters of (E)-3, 5-dimethyl-1-phenyl-4-(p-tolyldiazenyl)-1H-pyrazole calculated by DFT/B3LYP level with the 6-311-G ++ (d, p) basis set. The calculated parameters of title compound are given in Table 1 and the optimized structures with numbering of the atoms are shown in Figure 1. The title molecule contains three rings (Ring A, B and C) out of these, rings A and C are phenyl rings and Ring B is pyrazole ring. The Phenyl ring A is connected to the pyrazole Ring B via Trans azo ($\text{N}=\text{N}$) bridge. The self consistent field (SCF) energy of title molecule at same level and basic sets is found to be - 915.95537829 a.u. from Table 1 it is note that bond distance of N_6-N_{35} ($\text{N}=\text{N}$) bond in title compound is 1.2659 \AA and it is longer as compared to diazene ($\text{HN}=\text{NH}$) (1.252 \AA) [32] as well 2-Chloro-4-dimethylamino azobenzene (1.259) [33] molecules. This increase in bond length of N_6-N_{35} bond is due to conjugation with pyrazole ring. The Bond distance of N_4-N_5 bond (pyrazole ring) is observe at 1.3748 \AA . bond lengths of C_7-C_9 , $\text{C}_{12}-\text{C}_{14}$, C_8-C_{10} , $\text{C}_{10}-\text{C}_{14}$, C_7-C_8 , and C_9-C_{12} bonds shows double bond character (aromatic) were as Bond lengths of $\text{C}_{14}-\text{C}_{37}$, C_3-C_{20} , and C_1-C_{16} shows single bond character. Similarly bond lengths of $\text{C}_{24}-\text{C}_{26}$, $\text{C}_{24}-\text{C}_{25}$, $\text{C}_{26}-\text{C}_{29}$, $\text{C}_{29}-\text{C}_{31}$, $\text{C}_{27}-\text{C}_{31}$ and $\text{C}_{25}-\text{C}_{27}$ shows aromatic double bond character

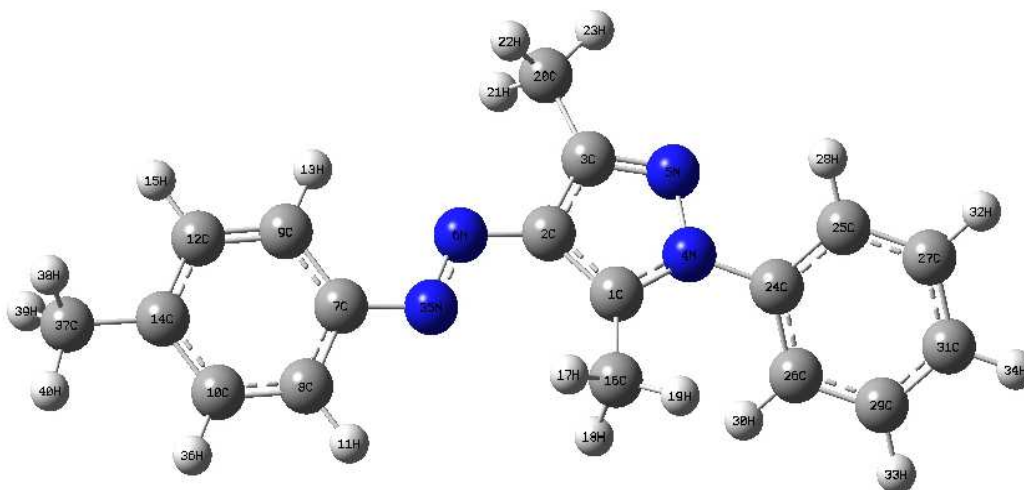


Figure 1: Optimized structure of (E)-3, 5-dimethyl-1-phenyl-4-(p-tolyldiazenyl)-1H-pyrazole

Table 1: Selected geometrical parameters of title molecule at B3LYP/6-311++G (d, p) level.

Geometrical Parameters			
Bond	Bond length (Å)	Bond	Bond length (Å)
C1-C2	1.4024	C14-C37	1.505
C1-N4	1.3649	C16-H17	1.0887
C1-C16	1.4908	C16-H18	1.0957
C2-C3	1.4321	C16-H19	1.0945
C2-N6	1.3833	C20-H21	1.0953
C3-N5	1.317	C20-H22	1.0911
C3-C20	1.4928	C20-H23	1.0908
N4-N5	1.3748	C24-C25	1.4003
N4-C24	1.4182	C24-C26	1.3987
N6-N35	1.2659	C25-C27	1.3891
C7-C8	1.4016	C25-H28	1.0808
C7-C9	1.4028	C26-C29	1.3945
C7-N35	1.4129	C26-H30	1.0793
C8-C10	1.3895	C27-C31	1.3959
C8-H11	1.0847	C27-H32	1.0843
C9-C12	1.3865	C29-C31	1.3924
C9-H13	1.0822	C29-H33	1.0843
C10-C14	1.3996	C31-H34	1.0832
C10-H36	1.0856	C37-H38	1.0966
C12-C14	1.404	C37-H39	1.0930
C12-H15	1.0858	C37-H40	1.0929
Bond angle (°)			
C2-C1-N4	105.1849	H17-C16-H18	106.1206
C2-C1-C16	129.0942	H17-C16-H19	109.8631
N4-C1-C16	125.1626	H18-C16-H19	108.0653
C1-C2-C3	105.7323	C3-C20-H21	111.0479
C1-C2-N6	133.0771	C3-C20-H22	111.0409
C3-C2-N6	121.1482	C3-C20-H23	110.1768
C2-C3-N5	110.597	H21-C20-H22	107.0821
C2-C3-C20	128.1499	H21-C20-H23	107.8081
N5-C3-C20	121.2406	H22-C20-C23	109.5809
C1-N4-N5	112.5508	N4-C24-C25	118.5286
C1-N4-C24	130.0074	N4-C24-C26	121.8179
N5-N4-C24	117.4394	C25-C24-C26	119.6342
C3-N5-N4	105.932	C24-C25-C27	119.8397
C2-N6-N35	117.9014	C24-C25-H28	118.8968
C8-C7-C9	119.037	C27-C25-H28	121.262
C8-C7-N35	115.9674	C24-C26-C29	119.8674
C9-C7-N35	124.9946	C24-C26-H30	121.1102
C7-C8-C10	120.5511	C29-C26-H30	118.9796
C7-C8-H11	118.3993	C25-C27-C31	120.8427
C10-C8-H11	121.0843	C25-C27-H32	118.9713
C7-C9-C12	119.8167	C31-C27-H32	120.1859
C7-C9-H13	119.2374	C26-C29-C31	120.6816
C12-C9-H13	120.9454	C26-C29-H33	118.9548
C8-C10-C14	120.9483	C31-C29-H33	120.3563
C8-C10-H36	119.4621	C27-C31-C29	119.1178
C14-C10-H36	119.5893	C27-C31-H34	120.4211
C9-C12-C14	119.6975	C29-C31-H34	120.4586
C9-C12-H15	119.0876	N6-N35-C7	114.6682
C14-C12-H15	119.2149	C14-C37-H38	111.119
C10-C14-C12	117.9479	C14-C37-H39	111.7267
C10-C14-C37	121.2215	C14-C37-H40	111.6991
C12-C14-C37	120.8148	H38-C37-H39	106.9965
C1-C16-H17	108.5873	H38-C37-H40	107.0589
C1-C16-H18	112.5198	H39-C37-H40	107.9934
C1-C16-H19	111.5324		

3.2 Mullikan atomic charges

Mullikan atomic charge calculation has an important role in the application of quantum chemical calculation to Molecular system because of atomic charge effect dipole moment, electronic structure and some other properties of molecular system. Mullikan atomic charges calculated at the B3LYP level with 6-311++G(d,p) basic sets and reported in Table 2 It is clear from the Table 2 that the C₂₆ atom carries the largest positive charge (0.550477) among the other carbon atoms therefore expected to be the site for nucleophilic attack in title compound. However, C₂₄ atoms carry the highest negative charge (- 0.732533). The Table 2 also shows that C₁, C₈, C₉, C₂₅, C₂₆, C₂₉ atoms of title compound exhibit positive charges, while other carbons exhibit negative charge. However all hydrogen and Nitrogen carries positive charge.

Table 2: Mullikan atomic charges for title compound at B3LYP/6-311++G (d, p) level

Atom	Charge	Atom	Charge
1C	0.431945	21H	0.177455
2C	-0.431740	22H	0.163561
3C	-0.159501	23H	0.158920
4N	0.316112	24C	-0.732533
5N	0.023229	25C	-0.077020
6N	0.141240	26C	0.550477
7C	-0.507533	27C	-0.191026
8C	-0.006597	28H	0.205806
9C	0.015208	29C	-0.083367
10C	-0.283111	30H	0.153142
11H	0.148055	31C	-0.383998
12C	-0.501611	32H	0.184271
13H	0.173223	33H	0.185520
14C	0.546317	34H	0.153980
15H	0.177563	35N	0.013400
16C	-0.561642	36H	0.166730
17H	0.202650	37C	-0.547057
18H	0.182766	38H	0.168956
19H	0.165154	39H	0.144698
20C	-0.627147	40H	0.143507

3.3 Vibrational assignments

FT-IR spectrum has been recorded at region of 4000-500 cm^{-1} (solid phase) and observe spectrum are shown by Figure 2. The theoretical Vibrational frequency have been calculated by using B3LYP/6-311++G (d, p) basic set. None of the predicted Vibrational frequencies have an imaginary frequency, implying that the optimized geometry is located at local minimum point on the potential energy surface. There are 40 atoms in title molecule corresponding 114 fundamental modes of vibrations. The molecule possesses C_1 symmetry. The scaling factor of 0.96 is used to getting theoretical Vibrational frequency. Some of the theoretical and experimental vibrations with intensity and their assignments are represented in Table 3. The FT-IR spectra contain some characteristic bands of the Stretching vibrations of the C-H, CH_3 , C=C, N=N, C=N, C-N, N-N and C-C group

3.3.1 Phenyl ring vibrations

The aromatic C-H stretching vibrations were normally seen in the region at 3100-3000 cm^{-1} [34, 35]. Theoretical band observe at 3062 cm^{-1} is due to the symmetric C-H stretching of ring C and it correlate with the experimentally observed C-H stretching at 3061 cm^{-1} . Similarly theoretical band observe at 3026 cm^{-1} because of the asymmetric C-H stretching vibrations of ring A shows close agreement to experimentally observed band at 3022 cm^{-1} . The theoretical calculated bands due to the C-H stretching vibrations of ring A and ring C is observed in the range of 3081-3026 cm^{-1} . Aromatic C-H in plane bending vibrations were calculated at 1378, 1084 cm^{-1} for ring A and 1452, 1299, 1148, 1081 cm^{-1} for ring C. Experimentally C-H in plane bending vibration mode was observe at 1373, 1101 cm^{-1} for ring A and 1452, 1302, 1151, 1070 cm^{-1} for ring C. The C-H out-of plane bending vibrations are determined by the number of adjacent atoms on the ring. Normally these vibrations usually occur in the region 1000-675 cm^{-1} [35]. For the experimental FT-IR of title compound the C-H out-of plane bending vibration observed at 759 and 831 cm^{-1} shows good agreement with the theoretically calculated values 764 and 813 cm^{-1} for ring C and ring A respectively. All experimental C-H vibrations show good agreement with the theoretical results. Aromatic Ring C-C stretching vibration generally occurs in the region 1625-1430 cm^{-1} [36]. The C=C stretching modes experimentally observed at 1597 and 1552 cm^{-1} and by DFT method it observed at 1580 and 1564 cm^{-1} for ring A and ring C. The bands observed at 601 and 721, 979 cm^{-1} are assigned to CCC deformation of phenyl ring however theoretically these bands are observe at 602 cm^{-1} for ring C and 724, 977 cm^{-1} for ring A and shows excellent agreement with experimental ones.

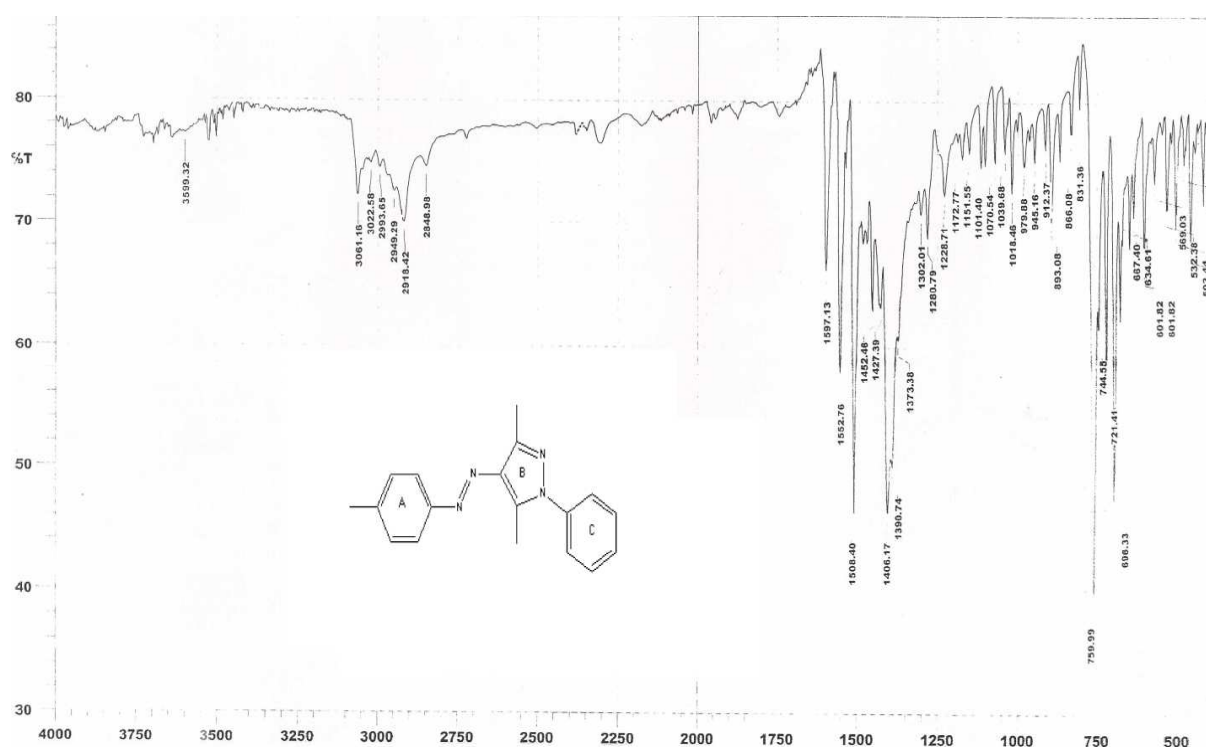


Figure 2: Experimental FT-IR spectra of title compound in the range 4000–400 cm^{-1}

3.3.2. Methyl group vibrations

The peaks due to asymmetric and symmetric methyl stretching modes commonly observed at 2965 and 2880 cm^{-1} [36]. Asymmetric and symmetric stretching of CH_3 groups calculated in the range of 3007-2901 cm^{-1} . In experimental FT-IR asymmetric stretching vibrations for methyl groups has been observed at 2993, 2949 cm^{-1} and symmetric stretching at 2918, 2848 cm^{-1} as shown in Table 3. This theoretically calculated peaks are observed at 2998, 2946 cm^{-1} and 2916, 2901 cm^{-1} is due to asymmetric and symmetric modes of stretching vibrations of methyl group respectively. It shows that experimentally observed modes are in close agreement with calculated ones. Asymmetric and symmetric deformation of methyl group normally appears in the region of 1465-1440 cm^{-1} and 1390-1370 respectively [37]. Asymmetric and symmetric deformation of CH_3 groups calculated in the range of 1452-1357 cm^{-1} and observed at 1452, 1406, 1390 cm^{-1} . The rocking vibrations of methyl groups usually appear in the region of 1070-1010 cm^{-1} [38]. Theoretically these modes are calculated at 1019 cm^{-1} and in experimental FT-IR it was observed at 1018 cm^{-1} .

3.3.3. Pyrazole ring vibrations

We assign the pyrazole ring C-C, N-N, C-N stretching vibrations and ring deformation by using Gauss View 04 program. The strong C=N and C=C mixed stretching vibrational mode of pyrazole was experimentally observed at 1508 cm^{-1} and by theoretical calculation it was calculated at 1514 cm^{-1} . The N-N stretching modes were observed at 1070 cm^{-1} and calculated at 1081 cm^{-1} . The C₁-N₄ stretching vibration mode was observed at 1228 cm^{-1} and calculated at 1195 cm^{-1} . Pyrazole ring deformation was experimentally observed at 634 cm^{-1} and by theoretical calculation it was observed at 640 cm^{-1} . All experimental pyrazole vibrations were in good agreement with the theoretical results.

3.3.4. N=N, C-N, C-C vibrations

The N=N stretching vibration is expected in the region 1440–1380 cm^{-1} [39]. In the present study, N=N stretching vibration was observed at 1427 cm^{-1} while the calculated value is 1428 cm^{-1} . Calculated N=N stretching frequency is only 1 cm^{-1} lower than observed in experimental frequency. C-N stretching vibrations of azo compounds are expected to occur in the region 1200–1130 cm^{-1} [40-41]. In the present study, C-N stretching vibration between ring carbon and azo nitrogen was observed at 1172 cm^{-1} and it correlates with calculated stretching vibration 1169 cm^{-1} . CH_3 -C stretching vibrations were observed at 696, 1039 cm^{-1} and calculated at 703, 1027 cm^{-1} for C₃₇ and C₁₆.

Table 3: Selected experimental and theoretical Vibrational assignment of title molecule calculated at B3LYP/6-311++G (d, p) level

Mode no.	Calculated frequencies In cm^{-1}	IR intensity	Experimental Frequencies (cm^{-1})	Assignment
114	3081	0.8	-	ν_{sym} CH (Ring c)
113	3077	3	-	ν_{sym} CH (Ring a)
112	3072	4	-	ν_{sym} CH (Ring c)
111	3062	26	3061	ν_{sym} CH (Ring c)
106	3026	24	3022	ν_{asym} CH (Ring a)
105	3007	8	-	ν_{asym} 16 CH_3
104	2998	12	2993	ν_{asym} 20 CH_3
103	2978	19	-	ν_{asym} 37 CH_3
102	2970	9	-	ν_{asym} 16 CH_3
101	2966	11	-	ν_{asym} 20 CH_3
100	2946	16	2949	ν_{asym} 37 CH_3
99	2916	19	2918	ν_{sym} 20 CH_3
97	2901	44	2848	ν_{sym} 37 CH_3
96	1580	24	1597	ν C=C (Ring a)
94	1564	4	1552	ν C=C (Ring c)
92	1514	149	1508	ν C=C + ν C=N
89	1452	11	1452	β CH (Ring c) + 20 CH_3 asym. def.
87	1437	58	-	16 CH_3 asym. def.
86	1430	8	-	37 CH_3 asym. def.
85	1428	42	1427	ν N=N
84	1426	7	-	37 CH_3 asym. def.
81	1404	36	1406	16 CH_3 asym. def.
80	1400	283	1390	20 CH_3 asym. def.
79	1378	19	1373	ν CC (Ring a) + β CH (Ring a)
78	1367	43	-	16 CH_3 sym. def.
77	1361	106	-	20 CH_3 sym. def.
76	1357	1	-	37 CH_3 sym. def.
74	1299	2	1302	β CH (Ring c)
72	1280	2	1280	ν CC (Ring a) + ν CC (Ring c)
69	1195	10	1228	ν C ₁ -N ₄ (Pz)
68	1179	3	-	ν 37 CH_3 -C
67	1169	1	1172	ν C ₇ -N ₃₅
66	1148	1	1151	β CH (Ring c)
63	1084	7	1101	β CH (Ring a)
62	1081	36	1070	ν N ₄ -N ₅ + β HC (Ring c)
60	1027	45	1039	ν 16 CH_3 -C
59	1019	2.	1018	ρ 20 CH_3
53	977	0.12	979	β CCC (Ring a)
48	946	0.10	945	Γ HCCC (Ring c)
46	895	3	893	Γ HCCC (Ring c)
43	813	19	831	γ CH (Ring a)
40	764	8	759	γ CH (Ring c)
37	703	4	696	ν 37 CH_3 -C
38	724	20	721	β CCC (Ring a)
36	680	35	696	γ C-H (Ring c)
33	640	7	634	Pz ring def.
31	602	0.03	601	β CCC (Ring c)

ν - stretching; asym-asymmetric; sym-symmetric; def-deformation; β -In-plane bending; γ -out of plane bending, ρ -rocking, Γ -torsion

3.4 Global Chemical reactivity

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are named as frontier molecular orbital's (FMO). HOMO-LUMO orbital's are the main orbital's involved in the chemical stability of molecule. The HOMO represents donor, the ability to donate electrons, while LUMO as an electron acceptor. In present study HOMO-LUMO energies and the energy gap for title molecules have been calculated using B3LYP level with 6-311++G (d, p) basis set. Frontier orbital's (HOMO and LUMO) were drawn to understand bonding scheme of title compound and it is shown in Figure 3.

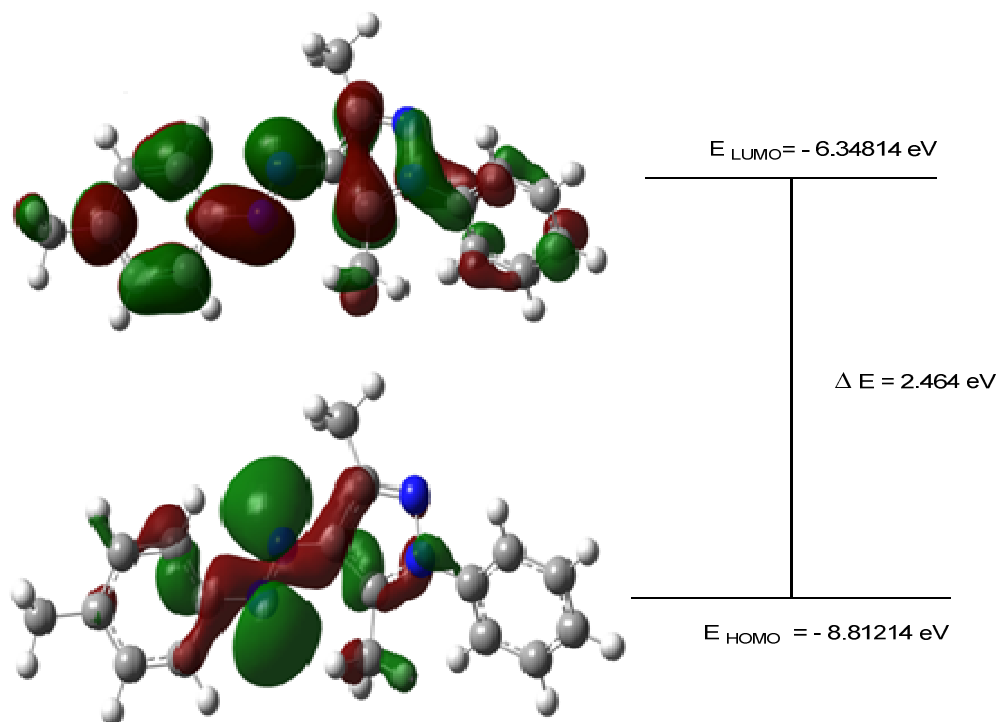


Figure 3: Pattern of the principle highest occupied and lowest unoccupied molecular orbital of title molecule

The computed energy values of HOMO and LUMO in gas phase are - 8.81214 eV and -6.34814 eV respectively. The (LUMO-HOMO) energy gap is 2.4640 eV. The chemical reactivity descriptors calculated by using DFT /B3LYP/6-311++G (d, p) level are Total energy (E), Ionization potential (I), Electron Affinity (E), Chemical hardness (η), Electronic chemical potential (μ), Chemical softness (S), Global Electrophilicity index (ω) and these values are listed in Table 4. Chemical hardness is a useful concept to understand the behavior of chemical systems and is associated with the stability and reactivity of a chemical system. Chemical hardness [42] is defined by equation,

$$\eta = \frac{1}{2} (I - E) \dots\dots\dots (1)$$

Where I and E are ionization potential and electron affinity of the compound respectively ($I = -\epsilon_{\text{HOMO}}$) and ($E = -\epsilon_{\text{LUMO}}$). Hard molecules having a large energy gap are more stable than soft molecules having a small energy gap. Softness (S) is a property of molecule that measures the extent of chemical reactivity. It is the reciprocal of hardness and it is calculated by equation,

$$S = 1/\eta \dots\dots\dots (2)$$

Soft molecules have a small HOMO–LUMO energy gap means they have small excitation energies. Therefore, hard molecules, with a large gap and their electron density changed more hardly than a soft molecule [45]. Electronic chemical potential is defined as the negative of electro negativity of a molecule [44] and determined with equation,

$$\mu = \frac{1}{2} (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}) \dots\dots\dots (3)$$

It also describes the escaping tendency of electrons from an equilibrium system [45]. The greater the electronic chemical potential, the less stable or more reactive is the compound. The Global electrophilicity index (ω) measures the capacity of a species, to accept electrons [42, 43]. The index is given by In terms of the electronic chemical potential and chemical hardness [45].

$$\omega = \mu^2 / 2\eta \dots\dots\dots (4)$$

Theoretically computed energies (a.u.), zero point vibration energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol^{-1}) and dipole moment (D) are tabulated in Table 5.

Table 4: Global chemical reactivity indices for Title compound

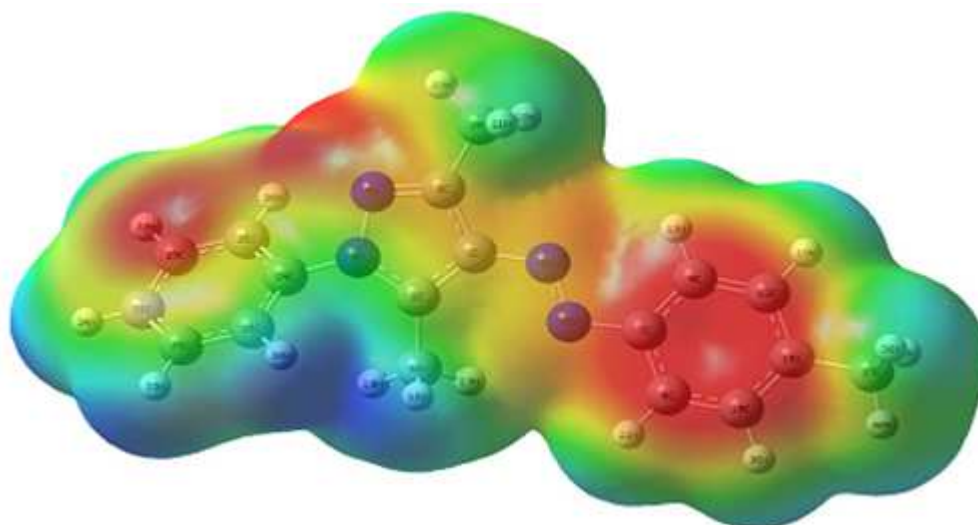
Molecular properties	B3LYP/6311++G(d,p)
E_{LUMO} (eV)	- 6.34814
E_{HOMO} (eV)	- 8.81214
$\Delta E = E_{LUMO} - E_{HOMO}$ (eV)	2.464
Electron affinity (E)	6.34814
Ionization energy (I)	8.81214
Global hardness (η)	1.232
Chemical Softness (S)	0.8116
Electronic chemical potential (μ)	-7.58014
Global electrophilicity index (ω)	23.319

Table 5: Theoretically computed total thermal energies (kcal mol⁻¹), zero point vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (cal mol⁻¹) and dipole moment (D) for title compound

Parameters	B3LYP
Total Energy(thermal) E_{total} (kcal mol ⁻¹)	215.285
Heat Capacity at constant volume, C_v (cal mol ⁻¹)	76.087
Total entropy S (cal mol ⁻¹)	152.562
Zero point Vibrational Energy E_{v_0} (kcal mol ⁻¹)	202.66728
Rotational constant (GHz)	0.85856
	0.10504
	0.09522
Dipole moment (D)	1.9229

3.5 The Molecular Electrostatic Potential

The MEP is a plot of electrostatic potential mapped on constant electron density surface. MEP is very important in the study of molecular interactions, hydrogen bonding interactions prediction of relative sites for nucleophilic and electrophilic attack [46, 47]. The 3D plots of the molecular electrostatic potentials were calculated by using the optimized molecular structures at B3LYP/6-311++G (d, p) level and shown in figure 4. Gauss View 4.1.2 visualization program has been utilized to construct the MEP surface. The electrostatic potentials at the surface are represented by different colors; red, blue and green represent the regions of negative, positive and zero electrostatic potential respectively. Potential increases in the order red < orange < yellow < green < blue. The negative regions $V(r)$ were related to electrophilic reactivity (H acceptor) and the positive ones to nucleophilic reactivity (H donor), as easily can be seen in Figure 4. The Negative regions in the studied molecule were found localized above and below the planes of the both phenyl ring indicate that both phenyl ring are suitable for electrophilic attack. Negative potential around ring A is more than ring C. Negative potential also found over N_5 atom of pyrazole and N_{35}, N_6 atoms of azo group. N_5 atom of pyrazole ring has maximum negative potential than N_{35}, N_6 as seen in Figure 4 and it is more reactive towards electrophile. The positive regions are localized around the hydrogen atoms of both phenyl rings and hydrogen's of (16 CH_3) methyl group of pyrazole. Maximum positive potential are found over H_{30} and H_{19} more reactive towards nucleophile. The dominance of green color over C- N_4 , C-C bonds and 20 CH_3 and 37 CH_3 groups indicates low reactivity region. Both positive and negative region gives information about intermolecular interaction.

**Figure 4: Molecular electrostatic potential calculated at B3LYP/6-311++G (d, p) level**

CONCLUSION

(E)-3,5-dimethyl-1-phenyl-4-(p-tolyldiazenyl)-1H-pyrazole synthesized and characterized by FT-IR, ¹H NMR spectroscopy. Density functional theory B3LYP/6-311++G (d,p) calculations were carried out to study molecular structure, Vibrational spectra, HOMO-LUMO, thermodynamic properties, Global chemical reactivity of (E)-3,5-dimethyl-1-phenyl-4-(p-tolyldiazenyl)-1H-pyrazole. The calculated Vibrational frequencies show good agreement with experimental values. The MEP shows that the negative potential sites are on Nitrogens of azo group and one of the nitrogen of pyrazole. Negative potential also found over both phenyl rings. It also shows that positive potential localized on almost all hydrogen atoms. These sites give information about intermolecular interactions of title compound.

Acknowledgment

Authors are grateful and express the deepest sense of gratitude to sophisticated analytical instrument facility center at Punjab University, Chandigarh, KTHM and RYK College Nashik for spectral analysis. The author also expresses their sincere thanks to Dr. Apoorva Hiray (Co-ordinator M.G. Vidyamandir, Malegaon).

REFERENCES

- [1] M. Amir, H. Kumar, S. A. Khan, *Bioorg. Med. Chem. Lett.*, **2008**, 18,918.
- [2] S. Arunkumar, K. Ilango, R. S. Manikdhan, N. Ramalaxmi, *E. J. Chemistry*, **2009**, 6, 123.
- [3] V. Madhava Rao, P. Priyadarshini, B. Ujwala, C. Venkata Rao, *Der Pharm. Lett.*, **2012**, 4, 1123.
- [4] B. Chandrakantha, A.M. Isloor, S.K. Peethamber, P. Shetty, *Der Pharma Chemica*, **2012**, 4,1723.
- [5] A. Singh, A.C. Rana, *J. Chem. Pharm. Res.*, **2010**, 2, 505.
- [6] U. Sankappa Rai, A.M. Isloor, P. Shetty, K.S.R. Pai, H. K. Fun *Arab.J.Chem.* **2015**, 8,317.
- [7] Yong Xia, Zhi-Wu Dong, Bao-Xiang Zhao, Xiao Ge, Ning Meng, Dong-Soo Shin, Jun-Ying Miao, *Bioorg. Med. Chem.*, **2007**, 15, 6893
- [8] S.G. Kini, A.R.Bhat, B.Bryant, J.S.Williamson, F.E. Dayan, *Eur. J. Med. Chem.*, **2008**,41, 1.
- [9] A.E. Rashad, M. I. Higab, R.E. Abdel-Megeid, J.A. Micky, *Bioorg. Med. Chem.* **2008**,16,7102.
- [10] M. Amir, S. Kumar, *Ind. J Chem.*, **2005**, 44B, 2532.
- [11] M. Abdel-Aziz, G.E.D.A. Abu-Rahma, A.A. Hassan, *Eur. J. Med. Chem.*, **2009**, 44, 3480.
- [12] N. Kudo, S. Furuta, *Chem. Pharm. Bull.*, **1999**, 47,857.
- [13] J.S.M. Pasin, A.P.O. Ferreira, A.L.L. Saraiva, Ratzlaff, R. Andrighetto, P. Machado, S.Marchesam, R.A. Zanette, M.A.P. Martins, *J. Med. Biol. Res.*, **2010**,43,1193.
- [14] R.K. Varma, S.S. Nayal, *Ind. J. Chem. Techno.* **2003**, 10, 347.
- [15] U Garg, V. Sareen, V.Khatri, S. Chugh, *Ind. J. Hetero. Chem.*, **2002**, 12, 139.
- [16] M .Amir, S.A. Javed, M.Z. Hassan, *Ind. J. Chem.*, **2013**, 52(B), 1493.
- [17] V. Sareen, V.Khatri, P. Jain, *Hetroletters* **2011**, 1, 112.
- [18] U. Gupta, V. Sareen, V.Khatri, S. Chugh, *Ind. J. Het. Chem.*, **2005**, 14, 265.
- [19] R. Jorda, E. Schütznerová, P. Cankař, V. Brychtová, J. Navrátilová, V. Kryštof, *Bioor. Med. Chem.*, **2015**, 23, 1975.
- [20] E.E. Oruc, B. Koyigit-Kaymakcioglu, B. Oral, H.Z. Altunbas-Toklu, L. Kabasakal, S. Rollas, *Arch. Pharm. Chem. Life Sci.*, **2006**, 339, 267.
- [21] K.A. Çiğdem, K. Yeşim, G. Merve, K. Izzet, T. Tahir, K. Fikret, *J. Molec. Liquid*, **2016**, 215, 647.
- [22] S. Lucas, F. Eva-Corinna, P. Martin, L. D. Nikos, J.R. Bart, *J. Am. Chem. Soc.*, **2016**, 138, 4547.
- [23] C. E. Weston, R. D. Richardson, P. R Haycock, A.J.P. White, M. J. Fichter, *J. Am. Chem. Soc.*, **2014**, 136, 11878.
- [24] S. Kinali, S.Demirci, Z.Çalis, M. Kurt, A. Ataç, *J. Mol. Struct.*, **2011**, 993, 254.
- [25] R.Faundez-Gutierrez, D.Macleod-Carey, X. Zarate, C. Bustos, E. Molins, E. Schott *Polyhedron*, **2014**, 81, 414.
- [26] A.B. Sawant, R.S. Nirwan, *Ind. J. Pure App. Phys.*, **2012**, 50, 308.
- [27] N. R. Thakare, A.K. Dhawas., P.S. Ganoskar., P.D. Kale, *J. Chem. Pharm. Res.*, **2012**, 4, 3329.
- [28] M. J. Frisch, G.W. Trucks, H. B. Schlegel *et. al. Gaussian 03*, Revision C.02, Wallingford CT, Gaussian Inc., **2004**.
- [29] N. Sundaraganesan, G. Elango, S. Sebastian, P. Subramani, *Ind. J. Pure Appl. Phys.* **2009**, 47, 481.
- [30] R. Dennington II, T. Keith, J. Millam, *Gauss View, Version 4.1.2*, Semichem Inc., Shawnee Mission, KS, **2007**.
- [31] P. Politzer, J.S. Murray, *Theor.Chem.Acc.* **2002**,108,134.
- [32] M. Snehalatha, C. Ravikumar, I. H. Joe, N. Sekar, V.S. Jayakumar, *Spectrochim Acta A*, **2009**,72, 654.
- [33] H. Tanak, M. Toy, *J. Mol. Struct.* **2014**, 1068, 189.
- [34] M. Silverstein, B.G. Clayton, C. Morill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, **1981**.

- [35] G. Varsanyi, *assignment for Vibrational spectra of seven hundred benzene derivatives*, vol.1 and 2, academic kiado: budpest, **1973**.
- [36] N.B. Colthup, L.H. Daly., S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, **1990**.
- [37] B. Smith, *Infrared Spectral Interpretation, A Systematic Approach*, Washington, DC: CRC Press, **1999**.
- [38] M. Silverstein, G.C. Basseler, C. Morill, *Spectroscopic identification of organic compounds*, Wiley, New York, **1981**.
- [39] M. Snehathatha, C. Ravikumar, J.I. Hubert, *Solid State Sci.*, **2009**,11,1275.
- [40] P. Vandenberghe, L. Moens, H.G.M. Edwards, R. Dams, *J. Raman Spectrosc.*, **2002**, 31, 509.
- [41] P.J. Trotter, *Appl. Spectrosc.*, **1977**, 31, 30
- [42] R.G. Pearson, *J. Chem. Sci.*, **2005**,117, 369.
- [43] P.G. Parr, R.G. Pearson *J. Am. Chem. Soc.*, **1983**, 105, 7512.
- [44] M. Charles *J. Chem. Sci.*, **2011**,123, 727.
- [45] P.K. Chattaraj, B. Maiti *J. Am. Chem. Soc.*, **2003**, 125, 2705.
- [46] J.S. Murray, K. Sen. *Molecular Electrostatic, Potentials Concepts and Applications*, Elsevier, Amsterdam, **1996**.
- [48] E. Scrocco, J. Tomasi, *Adv. Quantum Chem.* **1978**, 11, 115.