THEORETICAL STUDIES ON 3-AMINORHODANINEDERIVATIVES IN THE GAS PHASE: CHARGE DELOCALIZATION AND NLO PROPERTIES

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Abstract: The effect of type and substituent position of 5-X-3-aminorhodanine derivatives (X= Cl,F and Br) were analyzed at HF and B3LYP method using 6-311++G(d,p) basic set in gas phase. The second order perturbation energies of the most interacting NBO's and the population of electrons in core, valence and Rydberg sub-shells have been predicted. In this study, the natural atomic orbital occupancies showed the presence of charge delocalization within the molecules. The natural hybrid atomic orbital studies enhance us to know about the type of orbitals and its percentage of *s*-type and *p*-type character. Important NLO properties such as electric dipole moment, anisotropy polarizability and first hyperpolarizability of 5-X-3-amino rhodanine (5X3AR) have been computed at different levels of quantum chemical calculation. In addition to that, the complete molecular orbital simulations, Mullikan population and HOMO–LUMO energy gap of the molecules were also derived and interpreted.

Keywords: 3 aminorhodanine; Tautomerism; NBO; HOMO-LUMO; NLO; Mullikan charges; Uv-visible spectra

1. INTRODUCTION

Rhodanine are heterocyclic contain two sulfer and one nitrogen atom that exist in constitutional isomeric form (2-sulfanylidene-1,3-thiazolidine-4-one-3 amine).These heterocyclic compounds are a great importance in many areas of chemistry and biochemistry. Rhodanine, and its derivatives have wide biological activities including antibacterial [1], antiviral [2], antidiabetical [3], anti-inflammatory action[4], and anticancer agent[5] and industrial applications are vulcanizing agents of synthetic rubbers, extreme-pressure lubricants, intermediates in the synthesis of dyes, as well as pharmacological [6]. The interesting aspect of these compounds is their donating power to metal ions, which makes them strong ligands in coordination compounds [7, 8]. They compounds are also used in analytical chemistry as highly sensitive reagents for heavy metals [9, 10].

Tautomerism interconversions have been investigated bychemists for the last few years. The tautomerism of rhodanine was studied experimentally by several authors [11,12]. Most theoretical investigations have been carried out at a semi-empirical level and are devoted to the structure and electronic spectra of rhodanine[7, 12–14].

In recent years, the charge delocalization and chemical reactivity of polyatomic molecules have been focused widely. This information is helpful to the drug designers to design new type of drugs. The natural bond orbital (NBO) is an effective tool for the predicted of residual resonance delocalization effects of a molecule and it also illustrates the molecular wave function in terms of Lewis structure's change, bond order, bond type, hybridization, resonance, donor-acceptor interactions, etc [15].Therefore, the NBO analysis of certain pharmaceutical compounds has been performed by various spectroscopists [16-18].

Only a few articles were found in the literature that deals with the relative stabilities and structures of the potential five tautomeric forms of rhodanine. For example Boyd et al. measured the cluster analysis and charge distribution [19].El-Gogary and his co-worker studied temperature and substituent effect of 5-

azorhodanine [20].Al-Sehemi and his co-worker studied tautomers and rotamers of rhodanine derivatives using MP2 and DFT method with 6-311++G(d,p) [21].According to the literature the previous studies was limited to the parent 2-sulfanylidene-1, 3-thiazolidine-4-one-3 amine or rhodanine derivatives in the gas and solvent phase. The emphasis of the present investigate, for the first time, the substituent effect of isotopic form and studied in charge transformation of 3amino rhodanine using HF and DFT methods.

2. COMPUTATIONAL METHODS

The electronic structures of these molecules were optimized by solving SCF(self- consistent field) equation and molecular structure were fully optimized without symmetry constrainsat the two levels viz., the HF and DFT using 6-311++G(d,p) basis sets[22-25].The entire calculations are performed using the GAUSSIAN 09 [26] program package.

3. RESULTS AND DISCUSSION

3.1 Geometric Structure

The structure parameters of the amino conformers of substituted 5X3AR (X=Cl, F and Br)calculated using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods are given in Table 1.The structures and numbering of these compounds are given in Figs. 1 – 2.The alternative single and double bonds of the ring indicate itsaromatic character.Comparing the bondlength ofC7–X9,the values are increasing trend by the substituting of lighter to the heaver atom(F<Cl<Br).Comparing the geometric parameters of the substituted3-aminorhodanine, the little changes were observed due to substituent and its position. The maximum difference in bondlength was found in orientation of electron withdrawing group. The presence of nitro group bended to C2 and C5 atoms resulted in slightly elongation of bondlength with N4 as well as a shorting of the C–S bond in amino level.

The keto–enoltautomerism is accompanied by significant changes of the corresponding C–O bond length [21]. In the present case, the C5=O6 bond is slightly elongated by B3LYP/6-311++G(d,p) method. Thethioketo–thioenoltautomerism is also accompanied by significant changes of the corresponding C–S bond length [21]. In the present case, the C7–S1 bond is elongated by 0.183–0.186 Å in H. There is also a decrease of the N4–C5–O6 bond angle ranging from 2.5 to 5.2˚. Detailed distances and angles of 5X3AR optimized tautomer at two computational methods are given in Table 1. It is worth noticing that in all the tautomer's structure in substitution effect, all of the intra-ring distances and angles, show pronounced changes. Comparison of calculated bond lengths and bond angles indicate that there is good agreement between the computed HF/6-311++G(d,p) and B3LYP/6-311++G(d,p).The geometry of rhodanine conformers, as heterocycles containing third row elements of the periodic table, are very sensitive to the asthma treatment, especially on basis set extension and electron correlation effects.

Rhodanine biologically active compounds should beable to interact with a receptor in several ways. Theamide moiety of the rhodanine can form one or two hydrogenbonds to the backbone or side chains of a protein receptor. In the case of a single hydrogen bond, rhodanine can act as a hydrogen donor (N···H) or hydrogen acceptor (=O). In the case of two hydrogen bonds, the configuration of the cyclic amide makes it well suitedfor interacting with is peptide bonds in the protein. In addition, the dithioester moiety of the rhodanine ring could be involvedin hydrophobic binding to lipophilic surfaces of a proteinreceptor [21].

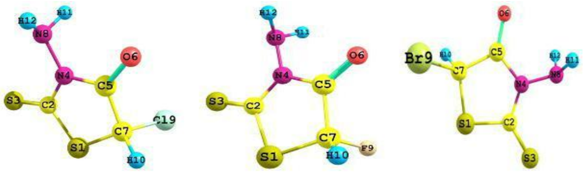


Figure 1. Optimized Molecular Geometry of amino 5X3AR (X=Cl,F,Br) at HF/6-311++G(d,p) Level.

Figure 2. Optimized Molecular Geometry of amino 5X3AR (X=Cl,F,Br) at B3LYP /6-311++G(d,p) Level.

Table 1: Calculated bond length (A^0) and bond angles (^{0}) for 5X3AR (X=Cl, F and Br).

Parameter	HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
Bonds(A^0)	3AR	Cl	F	Br	3AR	Cl	F	B
S1–C2	1.8535	1.7615	1.7653	1.7611	1.7690	1.7728	1.7773	1.7734
S1–C7	1.8671	1.8027	1.7998	1.8000	1.8327	1.8332	1.8239	1.8158
C2–S3	1.6548	1.6163	1.6148	1.6167	1.6445	1.6407	1.6392	1.6408
C2–N4	1.3683	1.3708	1.3723	1.3702	1.3739	1.3734	1.3747	1.3723
N4–C5	1.3878	1.3813	1.3794	1.3826	1.3901	1.3880	1.3858	1.3896
N4–N8	1.3858	1.3840	1.3838	1.3839	1.4033	1.4039	1.4039	1.4039
C5=O6	1.2100	1.1776	1.1781	1.1780	1.2091	1.2044	1.2049	1.2049
C5–C7	1.4968	1.5213	1.5250	1.5180	1.5146	1.5294	1.5334	1.5243
C7–X9	1.0744	1.7836	1.3514	1.9488	1.0902	1.8108	1.3847	1.9862
C7–H10	1.0744	1.0760	1.0781	1.0754	1.0909	1.0868	1.0895	1.0856
N8–H11	0.9948	0.9998	0.9999	0.9997	1.0196	1.0197	1.0197	1.0195
N8–H12	0.9949	1.0000	0.9999	1.0000	1.0180	1.0178	1.0178	1.0178
Angles (^{0})	3AR	Cl	F	Br	3AR	Cl	F	B
C2–S1–C7	92.191	93.601	93.698	93.529	92.772	92.779	92.768	92.719
S1–C2–S3	122.53	122.21	122.31	122.20	124.72	124.29	124.33	124.32
S1–C2–N4	109.28	109.77	109.80	109.71	110.04	110.12	110.21	109.98
S3–C2–N4	128.18	128.00	127.86	128.07	125.23	125.57	125.43	125.68
C2–N4–C5	119.44	118.47	118.33	118.43	119.32	119.24	119.04	119.22
C2–N4–N8	120.55	120.83	120.90	120.82	121.78	121.78	121.96	121.70
C5–N4–N8	120.00	120.57	120.74	120.55	118.78	118.49	118.70	118.47
N4–C5–O6	122.31	123.83	124.17	123.69	123.01	123.77	124.13	123.55
N4–C5–C7	113.01	111.17	111.94	110.98	110.67	110.39	110.75	110.15
O6–C5–C7	124.66	124.98	124.28	125.32	126.30	125.80	125.03	126.27
S1–C7–C5	106.06	106.14	106.14	106.27	107.11	106.96	106.81	107.27
S1–C7–X9	110.12	113.52	111.94	113.82	110.89	113.30	111.64	113.52
S1–C7–H10	110.13	111.44	111.65	111.78	110.85	110.99	111.17	111.63
C5–C7–X9	110.15	109.32	108.24	109.18	109.56	109.49	108.44	109.11
C5–C7–H10	110.14	109.53	110.47	109.81	109.26	109.94	110.98	110.48
X9–C7–H10	110.15	106.84	108.32	105.95	109.10	106.13	107.76	104.81
N4–N8–H11	112.38	108.97	109.00	108.94	106.95	106.67	106.68	106.75
N4–N8–H12	112.38	109.11	109.11	109.11	107.02	107.49	107.51	107.38
H11–N8–H12	114.24	109.06	109.07	109.06	111.41	111.05	110.98	111.15

3.2 Natural atomic orbitals

The occupancies and energies of bonding molecular orbitals of 5X3AR in amino substituent effect of Cl, F and Br molecules are predicted at B3LYP/6311++G(d,p) level of theory and presentin Table 2.The variations in occupancies and energies directly give the evidence for the delocalization of charge upon substitution and this leads to the variationof bond lengths between the moleculesas shown in Figs 1 and 2.

Table 2: Comparison of occupancies and energies of bonding molecular orbitals of 5X3AR (X=Cl, F and Br) calculated at the level the B3LYP/6-311++G level.

Atomic orbitals	Occupancies (e)				Energies (a.u)			
	3AR	Cl	F	Br	3AR	Cl	F	Br
BD (S_1–C_2)	1.9728	1.9709	1.9712	1.9708	–0.6836	–0.6774	–0.6785	–0.6768
BD (S_1–C_7)	1.9813	1.9802	1.9774	1.9810	–0.6512	–0.6591	–0.6475	–0.6616
BD (C_2–S_3)	1.9879	1.9878	1.9881	1.9880	–0.8238	–0.8156	–0.8175	–0.8160
BD$_2$ (C_2–S_3)	1.9769	1.9739	1.9730	1.9742	–0.3895	–0.3797	–0.3806	–0.3780
BD (C_2–N_4)	1.9856	1.9848	1.9850	1.9841	–0.9106	–0.8999	–0.9009	–0.8989
BD (N_4–C_5)	1.9823	1.9820	1.9821	1.9815	–0.9022	–0.8909	–0,8899	–0.8902
BD (N_4–N_8)	1.9865	1.9866	1.9868	1.9866	–0.9544	–0.9447	–0.9452	–0.9439
BD (C_5–O_6)	1.9948	1.9948	1.9948	1.9948	–1.1403	–1.1214	–1.1271	–1.1195
BD$_2$(C_5–O_6)	1.9892	1.9869	1.9858	1.9871	–0.4449	–0.4389	–0.4326	–0.4393
BD (C_5–C_7)	1.9707	1.9665	1.9638	1.9670	–0.5598	–0.5693	–0.5644	–0.5688
BD (C_5–X_9)	1.9883	1.9885	1.9953	1.9847	–0.5825	–0.7287	–1.0021	–0.6671
BD (C_7–H_{10})	1.9867	1.9862	1.9853	1.9858	–0.5833	–0.6052	–0.6113	–0.6025
BD (N_8–H_{11})	1.9841	1.9833	1.9833	1.9836	–0.6902	–0.6804	–0.6805	–0.6799
BD (N_8–H_{12})	1.9878	1.9871	1.9871	1.9872	–0.6954	–0.6856	–0.6858	–0.6851

3.3 Natural population analysis

The natural population analysis [27] performed on the electronic structures of 5X3AR (X=Cl, F and Br)clearly describes the distribution of electrons in various sub-shells of their atomic orbitals.The accumulation of charges on the individual atoms and the accumulation of electrons on the core, valence and Rydberg sub-shells are also presented in Table 3 and 4. In the case of 5X3AR (X=Cl, F and Br), the most electronegative charge of –0.5896 e and –0.5898 e is accumulated on N with F and N with Br atom. According to an electrostatic point, the views of molecule electro negative atoms have a tendency to donate an electron. Whereas, the most electro positive atoms such as; C have a tendency to accept an electron. Further, the natural population analysis showed that electrons in the distribution on the sub-shells values are presented in table 5. In particular, Br in 5X3AR is produced 110 electrons distribution on the sub-shell are predicted.

Table 3 Accumulation of natural charge, population of electron in core, valence, Rydberg orbitals of **5X3AR** (X=3AR and Cl) calculated at the B3LYP/6-311++G level.

Atom[a]	Charge(e)	Natural population(e)			Total(e)	Atom[b]	Charge(e)	Natural population(e)			Total(e)
		core	valence	Rydberg				core	valence	Rydberg	
S	0.2621	9.9991	5.7173	0.0215	15.7379	S	0.3186	9.9989	5.6377	0.0448	15.6813
C	−0.1571	1.9994	4.1251	0.0326	6.1571	C	−0.1522	1.9993	4.1103	0.0426	6.15223
S	0.0564	9.9988	5.9231	0.0216	15.9435	S	0.0655	9.9987	5.8995	0.0363	15.9345
N	−0.3352	1.9989	5.3083	0.2783	7.3352	N	−0.3414	1.9989	5.3082	0.0343	7.34141
C	0.6261	1.9994	3.3348	0.0397	5.3739	C	0.6759	1.9993	3.2726	0.0522	5.32415
O	−0.5687	1.9997	6.5567	0.0123	8.5687	O	−0.5803	1.9997	6.5627	0.0178	8.58028
C	−0.5443	1.9994	4.5341	0.0108	6.5443	C	−0.4348	1.9992	4.4055	0.0299	6.43477
N	−0.5843	1.9995	5.5631	0.0217	7.5843	N	−0.5890	1.9995	5.5623	0.0273	7.58904
H	0.2434	0.0000	0.7548	0.0017	0.7566	Cl	0.0309	9.9996	6.9484	0.0211	16.9691
H	0.2476	0.0000	0.7508	0.0017	0.7524	H	0.2500	0.0000	0.7472	0.0028	0.75000
H	0.3666	0.0000	0.6319	0.0015	0.6334	H	0.3679	0.0000	0.6287	0.0033	0.63201
H	0.3874	0.0000	0.6107	0.0019	0.6126	H	0.3888	0.0000	0.6076	0.0036	0.61115

[a] For numbering of atom of 3AR refer Fig.1

[b] For numbering of atom of 5Cl3AR refer Fig.2

Table 4: Accumulation of natural charge, population of electron in core, valence, Rydberg orbitals of 5X3AR (X=F and Br) calculated at the B3LYP/6-311++G level.

Atoms[c]	Charge(e)	Natural population(e)			Total(e)	Atoms[d]	Charge(e)	Natural population(e)			Total(e)
		core	valence	Rydberg				core	valence	Rydberg	
S	0.2794	9.9989	5.6787	0.0428	15.7206	S	0.3257	9.9988	5.6296	0.0458	15.6742
C	–0.1502	1.9993	4.1085	0.0424	6.1502	C	–0.1526	1.9993	4.1105	0.0428	6.1526
S	0.0693	9.9987	5.8958	0.0361	15.9306	S	0.0640	9.9987	5.9007	0.0366	15.9359
N	–0.3407	1.9989	5.3084	0.0339	7.3407	N	–0.3384	1.9989	5.3080	0.0316	7.3384
C	0.6405	1.9993	3.3084	0.0517	5.3595	C	0.6798	1.9993	3.2688	0.0521	5.3202
O	–0.5789	1.9997	6.5614	0.0178	8.5789	O	–0.5823	1.9997	6.5642	0.0183	8.5823
C	0.0485	1.9992	3.9165	0.0357	5.9515	C	–0.5241	1.9993	4.4975	0.0272	6.5241
N	–0.5896	1.9995	5.5629	0.0272	7.5896	N	–0.5898	1.9995	5.5623	0.0279	7.5897
F	–0.3532	1.9999	7.3410	0.0122	9.3532	Br	0.1077	27.999	6.8731	0.0198	34.8923
H	0.2182	0.0000	0.7793	0.0025	0.7818	H	0.2537	0.0000	0.7437	0.0029	0.7463
H	0.3679	0.0000	0.6287	0.0033	0.6321	H	0.3677	0.0000	0,6289	0.0034	0.6323
H	0.3888	0.0000	0.6077	0.0036	0.6112	H	0.3886	0.0000	0.6076	0.0037	0.6114

[a] For numbering of atom of 5F3AR refer Fig.3

[b] For numbering of atom of 5Br3AR refer Fig.

Table 5: Calculated at Core, Valence and Rydberg for 5X3AR (X=Cl, F and Br).

Properties	3AR	Cl	F	Br
Core	31.99438(99.9824% of 32)	41.99326(99.9840% of 42)	33.99361(99.9812% of 34)	59.99292(99.9882% of 60)
Valence	43.81077(99.5699% of 44)	49.69071(99.3814% of 50)	49.69699(99.3940% of 50)	49.69464(99.3893% of 50)
Rydberg	0.19484(0.2564% of 76)	0.31603(0.3435% of 92)	0.30940(0.3683% of 84)	0.31244(0.2840% of 110)

3.4 Donor–acceptor interaction energy analysis

In order to explain the hyper conjugative interactions, inter-intermolecular hydrogen bonding, intermolecular Charge transfer (ICT), electron density transfer (EDT) and cooperative effect due todelocalization of electron density from the filled lone pairs of ‘‘Lewis base’’ into the unfilled antibond of ‘‘Lewis acid’’ in hydrogen bonding systems, one can find naturalbond orbital (NBO) analysis as an effective tool [28].

Table 6 and 7 lists the occupancy and energies of most interacting NBO’s along with their percentage of hybrid atomic orbital [29] contribution. The percentage of hybrid atomic orbitals of sulfur lone pair atoms LP (1)S_3 and LP(2)S_3 of 5X3AR(X=Cl, F and Br) showed that they are partially contributed to both *s*-type and *p*-typesub-shells. In contrast, all the anti-bonding orbitals of this same molecule are mainly contributed to *p*-type sub-shell.

Table 6: Natural atomic orbital occupancies of most interacting NBO's of 5X3AR(X=3AR and Cl) along with their percentage of hybrid atomic orbital's.

Parameters^a	Occupancies(e)	Hybrid	AO^b(%)	Parameters^c	Occupancies(e)	Hybrid	AO^b(%)
LP(1) S_3	1.9800	sp0.29	S(77.73)P(22.27)	LP(1) S_3	1.9845	sp0.31	S(76.49)P(23.47)
LP(2) S_3	1.8080	sp99.99	S(0.46)P(99.54)	LP(2) S_3	1.8068	sp99.99	S(0.42)P(99.51)
				LP(1) Cl_9	1.9935	sp0.17	S(85.50)P(14.49)
				LP(2) Cl_9	1.9613	sp99.99	S(0.11)P(99.87)
				LP(3) Cl_9	1.9433	sp99.99	S(0.01)P(99.96)
BD*(1) S1–C2	0.1202	sp5.48	S(15.42)P(84.58)	BD*(1) S1–C2	0.1118	sp5.17	S(16.10)P(83.25)
		sp2.60	S(27.79)P(72.21)			sp2.60	S(27.72)P(72.15)
BD*(1) S1–C7	0.0266	sp5.54	S(15.29)P(84.71)	BD*(1) S1–C7	0.0524	sp5.50	S(15.29)P(84.11)
		sp3.84	S(20.64)P(79.36)			sp3.55	S(27.72)P(77.86)
BD*(1) C2–S3	0.0259	sp1.45	S(40.76)P(59.24)	BD*(1) C2–S3	0.0216	sp1.43	S(41.03)P(58.83)
		sp4.06	S(19.75)P(80.25)			sp3.63	S(21.45)P(77.92)
BD*(2) C2–S3	0.3758	sp0.78	S(0.78)P(99.22)	BD*(2) C2–S3	0.3625	sp99.99	S(0.56)P(99.27)
		sp2.87	S(2.87)P(97.13)			sp39.75	S(2.44)P(97.16)
BD*(1) C2–N4	0.0959	sp2.26	S(30.67)P(69.33)	BD*(1) C2–N4	0.0962	sp2.27	S(30.58)P(69.32)
		sp1.83	S(35.37)P(64.63)			sp1.84	S(35.17)P(64.80)
BD*(1) N4–C5	0.0881	sp2.05	S(32.83)P(67.17)	BD*(1) N4–C5	0.0856	sp2.04	S(32.89)P(67.06)
		sp1.92	S(34.22)P(65.78)			sp1.86	S(35.17)P(65.80)
BD*(1) N4–N8	0.0266	sp2.16	S(31.66)P(68.34)	BD*(1) N4–N8	0.0267	sp2.15	S(31.72)P(68.22)
		sp2.79	S(26.37)P(73.63)			sp2.82	S(26.61)P(73.71)
BD*(1) C5–O6	0.0200	sp2.21	S(31.20)P(68.80)	BD*(1) C5–O6	0.0191	sp2.16	S(31.59)P(68.22)
		sp1.51	S(39.91)P(60.09)			sp1.38	S(41.91)P(57.98)
BD*(2) C5–O6	0.2576	sp99.99	S(0.94)P(99.06)	BD*(2) C5–O6	0.2536	sp99.99	S(0.84)P(98.71)
		sp98.62	S(1.00)P(99.00)			sp98.62	S(0.90)P(98.97)
BD*(1) C5–C7	0.0945	sp1.95	S(33.92)P(66.08)	BD*(1) C5–C7	0.1379	sp2.05	S(32.77)P(67.19)
		sp5.24	S(16.03)P(83.97)			sp4.70	S(17.54)P(82.37)
BD*(1) C7–H9	0.0168	sp2.17	S(31.54)P(68.46)	BD*(1) C7–Cl9	0.0549	sp2.89	S(25.86)P(73.94)
			S(100.00)			sp5.85	S(14.53)P(84.97)

[a] For numbering of atom of 3AR refer Fig.1

[b] Percentage of *s*-type and *p*-type subshell of an atomic orbitals are given in their respective brackets [c] For numbering of atom of 5Cl3AR refer Fig.1

Table 7: Natural atomic orbital occupancies of most interacting NBO's of 5X3AR(X=F and Br) along with their percentage of hybrid atomic orbital's.

Parameters^d	Occupancies(e)	Hybrid	AO^b(%)	Parameters^e	Occupancies(e)	Hybrid	AO^b(%)
LP(1) S$_3$	1.9804	sp0.31	S(76.49)P(23.48)	LP(1) S$_3$	1.9805	sp0.31	S(76.48)P(23.48)
LP(2) S$_3$	1.8093	sp99.99	S(0.44)P(99.49)	LP(2) S$_3$	1.8054	sp99.99	S(0.43)P(99.50)
LP(1) F$_9$	1.9908	sp0.35	S(74.01)P(25.99)	LP(1) Br$_9$	1.9947	sp0.12	S(89.16)P(10.84)
LP(2) F$_9$	1.9588	sp99.99	S(0.07)P(99.91)	LP(2) Br$_9$	1.9673	sp99.99	S(0.04)P(99.94)
LP(3) F$_9$	1.9441	sp1.00	S(0.01)P(99.97)	LP(3) Br$_9$	1.9499	sp1.00	S(0.01)P(99.97)
BD*(1) S1–C2	0.1129	sp5.12	S(16.24)P(83.12)	BD*(1) S1–C2	0.1123	sp5.17	S(16.09)P(83.25)
		sp2.61	S(27.68)P(72.19)			sp2.60	S(27.71)P(72.16)
BD*(1) S1–C7	0.0545	sp5.75	S(14.72)P(84.71)	BD*(1) S1–C7	0.0483	sp5.40	S(15.53)P(83.25)
		sp3.47	S(22.34)P(77.46)			sp3.48	S(22.26)P(77.56)
BD*(1) C2–S3	0.0216	sp1.43	S(41.04)P(58,81)	BD*(1) C2–S3	0.0210	sp1.43	S(41.03)P(58,82)
		sp3.62	S(21.50)P(77.87)			sp3.62	S(21.52)P(77.85)
BD*(2) C2–S3	0.3560	sp99.99	S(0.55)P(99.27)	BD*(2) C2–S3	0.3655	sp99.99	S(0.52)P(99.31)
		sp40.84	S(2.38)P(97.22)			sp40.66	S(2.39)P(97.22)
BD*(1) C2–N4	0.0959	sp2.26	S(30.60)P(69.29)	BD*(1) C2–N4	0.0961	sp2.26	S(30.63)P(69.26)
		sp1.84	S(35.19)P(64.77)			sp1.85	S(35.13)P(64.84)
BD*(1) N4–C5	0.0872	sp2.05	S(32.82)P(67.13)	BD*(1) N4–C5	0.0856	sp2.03	S(32.94)P(67.01)
		sp1.92	S(34.98)P(64.90)			sp1.87	S(34.82)P(65.05)
BD*(1) N4–N8	0.0269	sp2.15	S(31.76)P(68.18)	BD*(1) N4–N8	0.0266	sp2.15	S(31.69)P(68.25)
		sp2.81	S(26.18)P(73.69)			sp2.82	S(26.15)P(73.71)
BD*(1) C5–O6	0.0167	sp2.10	S(32.18)P(67.64)	BD*(1) C5–O6	0.0198	sp2.17	S(31.45)P(68.36)
		sp1.38	S(42.05)P(57.84)			sp1.38	S(41.89)P(57.99)
BD*(2) C5–O6	0.2529	sp99.99	S(0.50)P(99.05)	BD*(2) C5–O6	0.2543	sp99.99	S(0.90)P(98.65)
		sp99.99	S(0.51)P(99.36)			sp99.83	S(0.99)P(98.88)
BD*(1) C5–C7	0.1329	sp2.07	S(32.51)P(67.45)	BD*(1) C5–C7	0.1332	sp2.04	S(32.90)P(67.06)
		sp4.62	S(17.78)P(82.12)			sp4.69	S(17.55)P(82.36)
BD*(1) C7–F9	0.0643	sp2.98	S(25.02)P(74.57)	BD*(1)	0.0605	sp2.93	S(25.42)P(74.45)
				Br9			
		sp2.85	S(25.97)P(73.96)			sp8.05	S(11.01)P(88.58)

[a]For numbering of atom of 5F3AR refer Fig.1

[b]Percentage of *s*-type and *p*-type subshell of an atomic orbitals are given in their respective brackets [c]For numbering of atom of 5Cl3AR refer Fig.1

For each donor (i) and acceptor (j) the stabilization energy $E(2)$ associated with the delocalization $i \rightarrow j$ is estimated as:

$$E(2) = \Delta E_{ij} = q_i \frac{F(ij)^2}{\varepsilon_j - \varepsilon_i} \quad \text{……….} \quad (1)$$

Where q_i is the donor orbital occupancy, ε_i , ε_j are diagonal elements and $F(ij)$ is the off diagonal NBO Folk matrix elements. The NBO analysis is provides an efficient method for study intra and inters molecular bonding and also provides a convenient basis for investigating charge transfer (or) conjugative interaction in molecular systems [30].

Table 8 presents the second order perturbation energies (often called as the stabilization energies (or) interaction energies) of most interacting NBOs of 5X3AR(X= Cl, F and Br) using B3LYP/6-311++G(d,p).The second order perturbation energies corresponding to hyper conjugative interactions of 5X3AR such as: LP(1)N4→BD*(2)C2–S3, LP(1)N4→BD*(2)C5–O6,LP(2)O6→BD*(1)C5 C7, LP(2)O6→BD*(1)N4–C5, LP(2)S1→BD*(2)C2–S3 are considerably very large. The aforesaid hyper conjugative interaction are the most responsible for the stability of 5X3AR in (X = Cl, F and Br).The BD(1) and BD(2) distinguish multiple bond between the same atoms and similar LP(1) ,LP(2) and LP(3) labels distinguish multiple lone pair orbitals at each center. In the case of 5X3AR,the most significant hyperconjugativeinteractions of (51.24, 49.69, 49.72 and 50.00) are obtained LP(1)N4→BD*(2)C2–S3respectively,and a few of non-bonding interaction of this molecule LP(1)N4→BD*(1)C5–C6 and LP(1)N4→BD*(2)(0.57 and 49.05) kcal/mol are obtained. Also such non-bonding interaction increases the stability of a molecule as well.

Table 8: Second-order perturbation energy E(2) kcal/mol, E(j)–E(i) a.u and F(i,j) a.u between donor and acceptor orbitals of Fock Matrix in NBO basis.

Donor(i)→Acceptor (j)	**3AR**			**5Cl3AR**			**5F3AR**			**5NH$_2$3AR**		
	E(2)	E(j)–E(i)	F(i,j)	E(2)	E(j)–E(i)	F(i,j)	E(2)	E(j)–E(i)	F(i,j)	E(2)	E(j)–E(i)	F(i,j)
LP(1)S1→BD*(1)C2–S3	1.16	0.93	0.029	1.11	0.99	0.030	1.14	0.99	0.030	1.09	0.99	0.029
LP(1)S1→BD*(1)C2–N4	2.31	1.00	0.044	2.35	1.03	0.045	2.34	1.03	0.045	2.36	1.03	0.045
LP(2)S1→BD*(2)C2–S3	25.85	0.19	0.066	24.85	0.21	0.067	24.70	0.21	0.066	25.01	0.21	0.067
LP(2)S1→BD*(1)C7–X9	4.78	0.60	0.050	8.13	0.34	0.049	10.81	0.42	0.063	8.38	0.29	0.046
LP(2)S1→BD*(1)C7–H10	4.49	0.60	0.048	4.18	0.61	0.047	3.38	0.59	0.042	4.34	0.61	0.048
LP(1)S3→BD*(1)S1–C2	4.56	0.83	0.056	4.54	0.86	0.057	4.58	0.86	0.057	4.52	0.86	0.057
LP(1)S3→BD*(1)C2–N4	3.74	1.09	0.058	3.93	1.10	0.058	3.63	1.11	0.058	3.62	1.10	0.058
LP(2)S3→BD*(1)S1–C2	20.71	0.31	0.073	18.67	0.37	0.073	18.86	0.34	0.073	18.67	0.34	0.073
LP(2)S3→BD*(1)S1–C7	0.89	0.33	0.016	0.81	0.34	0.015	0.79	0.34	0.015	0.82	0.34	0.016
LP(2)S3→BD*(1)C2–N4	17.61	0.57	0.092	17.06	0.59	0.092	17.02	0.59	0.092	16.99	0.59	0.092
LP(1)N4→BD*(2)C2–S3	51.24	0.26	0.103	49.69	0.26	0.103	49.72	0.26	0.103	50.00	0.26	0.103
LP(1)N4→BD*(1)C5–O6	0.57	0.85	0.022							0.52	0.89	0.021
LP(1)N4→BD*(2)C5–O6	49.05	0.29	0.112	46.73	0.31	0.112	47.83	0.30	0.112	46.51	0.31	0.112
LP(1)N4→BD*(1)N8–H11	4.73	0.68	0.057	4.62	0.69	0.056	4.64	0.69	0.057	4.63	0.69	0.056
LP(1)O6→BD*(1)N4–C5	0.96	1.08	0.029	0.95	1.11	0.029	0.88	1.11	0.028	0.96	1.11	0.030
LP(1)O6→BD*(1)C5–C7	0.94	0.79	0.025	1.04	0.80	0.026	0.89	0.80	0.025	1.11	0.80	0.027
LP(2)O6→BD*(1)S1–C7	0.78	0.40	0.016	0.78	0.41	0.016	0.68	0.41	0.015	0.81	0.41	0.017
LP(2)O6→BD*(1)N4–C5	26.52	0.66	0.121	24.96	0.69	0.119	25.16	0.69	0.120	24.97	0.69	0.119

LP(2)O6→BD*(1)C5–C7	28.93	0.38	0.095	31.42	0.38	0.098	30.40	0.38	0.097	31.24	0.38	0.098
LP(2)O6→BD*(1)N8–H12	0.63	0.66	0.019	0.60	0.67	0.019	0.61	0.67	0.019	0.61	0.67	0.019
LP(1)N8→BD*(2)C2–S3	0.58	0.30	0.013	0.50	0.33	0.012	0.50	0.33	0.012			
LP(1)N8→BD*(1)N4–C5	4.18	0.74	0.050	4.28	0.78	0.052	4.27	0.78	0.052	4.27	0.78	0.052
LP(1)N8→BD*(2)C5–O6	0.53	0.34	0.013									
LP(1)X9→BD*(1)C7–H10				1.16	1.32	0.035	0.65	1.42	0.027	1.25	1.37	0.037
LP(2)X9→BD*(1)S1–C7				4.43	0.45	0.040	6.06	0.55	0.052	3.39	0.43	0.034
LP(2)X9→BD*(1)C5–C7							0.88	0.52	0.020			
LP(2) X9→BD*(1)C7–H10				4.97	0.68	0.052	6.92	0.77	0.065	3.92	0.66	0.045
LP(3) X9→BD*(1)S1–C7				1.48	0.45	0.023	3.02	0.55	0.037	0.98	0.43	0.018
LP(3) X9→BD*(1)C5–C7				7.31	0.42	0.050	9.90	0.52	0.065	5.72	0.39	0.043
LP(3) X9→BD*(1)C7–H10				0.70	0.68	0.020	0.56	0.77	0.019	0.63	0.66	0.018

3.5 Dipole moment and electronic polarizability

Calculation of electric properties was performed on HF and B3LYP levels of geometry. In order to evaluate the reliability of different levels of theory to determine μ,$\alpha_0$and β_{tot} valuesare listed in Table 9.

Based on the finite-field approach, the non-linear optical Parameters such as dipole moment (μ), Polarizability (α_0), amisotropy polarizability (Δ_∞) and first order hyper polarizability (β_{tot}) of 5X3AR(X= Cl, F and Br) molecules are calculated using HF/6-311++G(d,p), B3LYP/6-311++G (d,p).

In the presence of an external electric field.First hyper polarizability is a third rank tenser that can be described by a 3x3x3 matrix.The 27 components of the 3D matrix can be reduced to 10 components because of the Kleinman symmetry[31] of β are defined as the amplitude of coefficients in the Taylor series expansion of energy in an external electric field.

When an external external field is weak and homogeneous, Taylor series expansion becomes.

$$E = E^{0} - \frac{\mu_i F_i}{1!} - \frac{\alpha_{ij} F_i F_j}{2!} - \frac{\beta_{ijk} F_i F_j F_k}{3!} - \frac{\gamma_{ijkl} F_i F_j F_k F_l}{4!}$$

………. (2)

Where E is the energy of the unperturbed molecules, F_i is the field at origin and μ_i, α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, first polarizabilities and the second hyper polarizability respectively.

The total static dipole moment μ, mean polarizability α_o, anisotropy of the polarizability $\Delta\acute{a}$ and firs hyper polarizability β_{tot} using x, y and z components, are defined as, Dipole moment,

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \quad \text{……….(3)}$$

Mean polarizability

$$\alpha_o = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

……………(4)

Anisotropic polarizability

$$\Delta\acute{a} = 2^{-1/2}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha_{xz}^2\right]^{1/2}$$

……(5)

First-order polarizability

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

………………..(6)

Where,

$$\beta_x = \beta_{xxx} + \beta_{yyy} + \beta_{zzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Urea is one of the prototypical molecules used in study of the NLO properties of molecular systems. Therefore it was used frequently as a threshold value for comparative purpose. The Calculated highest value of first hyper polarizability is 5X3AR with amino Br is148.85x10^{-31} esu Calculated by the B3LYP/6311++G(d,p).The values of μ,α_0 and β_{tot} o urea are 3.874 D, 5.0424 $A^{\circ 3}$ and 0.7648×10^{-30} cm^5/esu obtained at the same level[32]. Theoretically, the first-order hyperpolarizability of the title compound with of Urea and thus the title compound possesses considerable NLO properties. bromine is of ~15 times than that of urea. According to these results, all the substitution of 5X3AR(X= Cl, F and Br) is much higher than that

Table 9

Electric dipole moment µ (Debye), mean polarizability á$_o$ (x10^{-22}esu), anisotropy Polarizability á (x10^{-25}esu) and first hyperpolarizability â$_{tot}$ (x10^{-31}esu) for5X3AR (X=Cl,F and Br) in amino level.

Parameters	HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
	3AR	Cl	F	Br	3AR	Cl	F	Br
µ$_x$	–3.3561	1.4650	–1.4948	1.4260	–1.6035	0.1875	0.1206	0.4132
µ$_y$	–0.8863	1.0083	0.7502	1.1553	–1.1017	–0.0373	0.0470	–0.0421
µ$_z$	–0.0007	1.2941	–1.4978	1.2569	1.0725	–0.0867	–0.1807	–0.1811
µ	3.4711	2.1995	2.2451	2.2244	2.2215	0.2099	0.2223	0.4531
á$_{xx}$	–77.198	–85.059	–79.076	–89.633	–71.174	–79.261	–73.444	–84.220
á$_{yy}$	–57.795	–73.991	–63.273	–81.746	–56.681	–77.292	–66.176	–84.852
á$_{zz}$	–59.464	–70.304	–63.572	–75.585	–61.816	–71.575	–65.855	–75.916
á$_{xy}$	4.3906	–7.5100	4.9518	–8.7873	7.0731	–7.0029	6.8519	–6.3451
á$_{xz}$	–0.0004	0.2586	2.6806	–1.5904	–0.0023	4.0062	4.6685	3.6231
á$_{yz}$	–0.0023	–2.4276	2.3342	–2.8638	–3.6389	–5.9537	6.2083	–5.9592
á$_o$	–64.819	–76.451	–68.640	–82.321	–63.224	–76.043	–68.492	–81.663
á	–37.248	–26.691	–32.659	–23.762	–25.455	–19.592	–21.967	–21.352
â$_{xxx}$	3.4566	31.685	–24.917	108.48	–2.6575	14.180	–13.504	88.563
â$_{yyy}$	21.152	23.595	21.903	11.147	13.794	5.0317	6.3953	–5.7835
â$_{zzz}$	–0.0025	–0.9239	4.4567	–9.4698	0.9783	0.2192	4.3120	–8.2446
â$_{xyy}$	–21.723	–10.074	–3.6212	7.6106	–8.9189	–6.1905	1.9070	17.744
â$_{xxy}$	–20.528	–3.9087	–14.445	–7.5069	–13.063	1.9348	–4.5345	5.9854
â$_{xxz}$	–0.0015	5.3535	–7.2161	1.5274	–0.7225	–3.0064	–5.2585	–14.798
â$_{xzz}$	–10.384	9.2924	–9.5101	29.398	–8.0662	9.8530	–10.009	28.567
â$_{yzz}$	8.2276	8.9197	8.7603	6.1176	–0.6686	4.3964	2.0410	3.5731
â$_{yyz}$	–0.0027	–4.5761	1.1632	–11.541	9.7899	–13.469	12.757	–17.793
â$_{xyz}$	–0.0001	–5.9563	–7.5882	–3.8692	–0.4589	3.6888	–1.6017	7.6324
â$_{tot}$	29.987	42.112	41.392	148.85	17.496	26.677	24.931	140.97

3.6 Frontier molecular orbitals

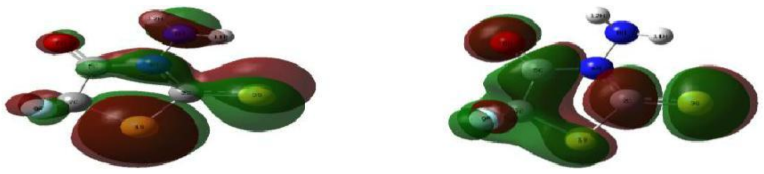
The most important frontier molecular orbitals (FMOs) such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plays a crucial part in the chemical stability of the molecule. The HOMO represents the ability to donate an electron. Which can be thought as the outermost orbital containing electrons, tends to give these electrons and acts as an electron donor; LUMO can be thought as the innermost orbital containing free places and accepts electrons [33]. Energy gap between HOMO and LUMO characterizes the molecular chemical stability and it is a critical parameter in determiningmolecular electrical transport properties because it is a measure of electron conductivity.

Table 10: Selected HOMO and LUMO energies and energy gap of 5X3AR (X=Cl,Fand Br)

Molecular orbitals	HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
	3AR	Cl	F	Br	3AR	Cl	F	Br
HOMO	–9.5211	–9.6762	-9.7116	-9.6572	–6.8653	–7.1700	–7.2136	–7.1453
LUMO	0.8871	1.0013	0.9768	0.9850	–2.3565	–2.9142	–2.9142	–3.0367
Energy gap (eV)	10.4081	10.6775	10.6884	10.642	4.5088	4.2558	4.2994	4.1086

The patterns of the HOMO and LUMO for the title compound calculated at HF and B3LYP method with 6-311++G(d,p) basis set. Fig. 3, 4Shows the distributions and energy levels of HOMO and LUMO orbitals for the stable monomer of 5X3AR (X= Cl, F and Br,) molecule in gaseous phase. [34]. As a result, a very small energy gap is observed between HOMO and LUMO molecular orbitals of 5X3AR and the value of energy gap in Bromine is 4.1086eVat B3LYP/6-311++G(d,p) method are given in Table 10. Hence the probability of proton transition is highly possible in between HOMO and LUMO orbitals for the substituted 5X3AR (X = Cl, F and Br). The energy gap of HOMO–LUMO explains the eventual charge transfer interactionwithin the molecule, which influences the biological activity of the molecule. Further the increasing value of the energy gap and molecule sbecomes more stable. In this subsututional effect, the bromine are high stable molecule (4.1086 eV) inB3LYP/6-311++G(d,p) to compare in HF/6-311++G(d,p) are predicted.

X=F(HF)HOMO = –9.7116 eV, LUMO=0.9768 eV, Energy gap(ÄE)= 10.6884 eV



X=F(B3LYP) HOMO=–7.2136 eV , LUMO=–2.9142 eV, Energy gap(ÄE)= 4.2994 eV

Figure 3: The atomic orbital compositions of the frontier molecular orbital for 3-aminorhodanine (X= F) molecule in gas phase.

X=Cl(HF)HOMO=–9.6762 eV LUMO=1.0013 eV Energy gap(ÄE)= 10.6775 eV

X=Cl(B3LYP) HOMO=–7.1700eV, LUMO=–2.9142 eV, Energy gap(ÄE)= 4.2558 eV

Figure 4: The atomic orbital compositions of the frontier molecular orbital for 3-aminorhodanine(X= Cl) molecule in gas phase.

3.7 Atomic charge

The Mulliken atomic charges are calculated by determining the electron population of each atom as defined by the basis function. The Mulliken atomic charges of 5X3AR(X= Cl, F and Br) molecule calculatedby DFT/B3LYP and HF method using 6-311++G(d,p) basis set in gas phase are shown in Table 11 The charge changes with basis set presumably occurdue to polarization. For example, the charge of F(9) atom in5X3AR isfor –0.0665 e− forHF/6-311++G(d,p), –0.0444e− forB3LYP/6-311++G(d,p) and Br(9) atom is0.0132e−B3LYP/6-311++G(d,p),–0388e−for HF/6-311++G(d,p), The charge distribution of Florien and bromine atom isincreasing trend in HF and B3LYP methods. The charge of S3 is negativein both HF and DFT diffuse functions. The same trend reflectsin fluorine atom, considering the all methods and basis sets usedin the atomic charge calculation, the carbon atom C2 exhibit a substitution negative charge, which is a donor atom. Hydrogen atom exhibits a positive charge, which is an acceptor atom. For example, the bromine atom exhibit donor in HF/6-311++G(d,p) and acceptor in B3LYP/6-311++G(d,p).

Table 11: Mullikan charges of 5X3AR (X=Cl,F and Br)

aAtom	HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
	3AR	Cl	F	Br	3AR	Cl	F	Br
S1	0.2213	–0.0635	0.1621	0.0018	0.1129	–0.0177	0.2237	0.0887
C2	–0.5577	–0.2835	–0.1883	–0.1697	–0.0847	–0.1292	–0.0993	–0.0796
S3	–0.2665	–0.3739	–0.3594	–0.3701	–0.4263	–0.4148	–0.4077	–0.4100
N4	0.2341	0.3221	0.3958	0.3565	0.4436	0.3514	0.4627	0.4002
C5	0.5987	–0.0133	0.4823	0.1003	0.1305	–0.2271	0.2270	–0.0638
O6	–0.4464	–0.3236	–0.3621	–0.3329	–0.3236	–0.2697	–0.3027	–0.2768
C7	–0.8677	0.2058	–0.4492	0.0146	–0.4923	0.0764	–0.4554	–0.1447
N8	–0.3452	–0.4184	–0.4345	–0.4174	–0.3283	–0.2947	–0.3508	–0.3108
X9	0.3508	0.0740	–0.0665	–0.0388	0.2428	0.1201	–0.0444	0.0132
H10	0.3507	0.3180	0.2634	0.2981	0.2358	0.3105	0.2546	0.2926
H11	0.3638	0.2829	0.2819	0.2845	0.2147	0.2170	0.2164	0.2156
H12	0.3638	0.2733	0.2744	0.2731	0.2727	0.2776	0.2760	0.2755

3.8. Theoretical UV-Visible spectra and solvent effect

In order to identify the electron transition between the two energy levels, the lowest singlet→singlet spin allowed excited states are to be taken into account. In present study, the maximum absorption wavelengths ë$_{max}$(nm),excitation energies E(eV) and oscillator strengths*f*(a.u) of the molecules in the gaseous phase are computed using TD-DFT/B3LYP/6311++G(d,p)method. The 5X3AR(X=F) molecule has three maximum absorption peaks of very low oscillator strengths (say~0.0005a.u)[Fig.6].The observed peaks in the spectrum may cause one electron excitation from HOMO-LUMO,HOMO–1→ LUMO, and HOMO–2→ LUMO while in the case of5X3AR (X= Br) 402.34,331.43 and 313.44 nm, respectively.

The solvent effect on the absorption wavelengths and excitation energies are also examined by applying polarizable continuum model (PCM) TD-DFT method with B3LYP/6311++G (d,p) basic set. The calculated absorption wavelength, oscillator strengths, excitation energies of molecule in gas as well as in water, acetone and ethanol solvent medium are presented in Table 12 and theoretically simulated UV-Visible spectrum of 5X3AR (X= Cl, F and Br) in different solvent as shown in Fig 4, 5,6 and 7 respectively for comparing their energetic behavior. In the electronic spectrum of 5X3AR (X=H), the strong intensity peaks at the maximum absorption wavelength of 300.93(water), 300.99(acetone) and 301.13(ethanol) are caused by n→ð* transitions and the similar intensity bands calculated above of 320 nm in all the phases of this molecule are strongly forbidden and therefore, the value of its oscillator strength of nearly~0.1 au. In this case the bromine shows very strongly forbidden and strong intensity peaks also.

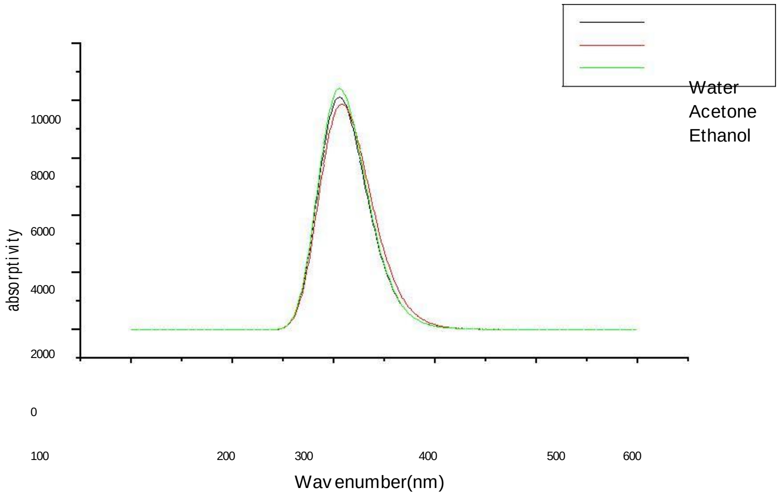


Figure 5: Calculated UV- visible spectra of 3AR in different solvent.

Table 12: Theoretical electronic absorption spectra (UV), (absorption wavelength ë_{max} (nm), excitation energies E (eV) and oscillator strengths (f) using B3LYP/6-311++G(d,p) method in amino level.

Solvent	Excitation States	absorption wavelength ë_{max} (nm)				Excitation energies E(eV)				Oscillator Strengths *f* (a.u)			
		3AR	Cl	F	Br	3AR	Cl	F	Br	3AR	Cl	F	Br
Water	Excitation state 1	393.87	400.37	400.14	401.32	3.1479	3.0967	3.0986	3.0894	0.0012	0.0017	0.0006	0.0035
	Excitation state 2	322.32	326.89	325.06	331.48	3.8466	3.7928	3.8139	3.7403	0.0615	0.0498	0.0770	0.0406
	Excitation state 3	300.93	309.29	306.68	313.25	4.1200	4.0087	4.0428	3.9580	0.1581	0.1124	0.0525	0.1116
Acetone	Excitation state 1	386.88	394.29	393.72	395.21	3.2047	3.1445	3.1490	3.1372	0.0013	0.0020	0.0008	0.0040
	Excitation state 2	324.51	331.11	331.40	334.47	3.8207	3.7445	3.7412	3.7069	0.0794	0.0707	0.0925	0.0525
	Excitation state 3	300.99	310.07	305.38	315.77	4.1192	3.9986	4.0600	3.9265	0.1415	0.0893	0.0375	0.1002
Ethanol	Excitation state 1	395.01	401.39	401.19	402.34	3.1388	3.0888	3.0904	3.0816	0.0011	0.0017	0.0005	0.0034
	Excitation state 2	322.20	326.78	324.97	331.43	3.8481	3.7941	3.8153	3.7409	0.0619	0.0502	0.0785	0.0409
	Excitation state 3	301.13	309.48	306.77	313.44	4.1173	4.0063	4.0416	3.9556	0.1648	0.1167	0.0545	0.1157

3.9. Other Molecular Properties

The standard thermodynamic functions: such as self-consistent field (SCF) energy, zero-point vibrational energies (ZPVE), thermal energies, molar capacities at constant volume, entropy, enthalpy and dipole, rotational constants, rotational temperature, specific heat capacity and Gibbs free energy have been presented in Table 13. Scale factors have been recommended [35] for an accurate prediction in determining the Zero-Point Vibration Energies (ZPVE) and the entropy were calculated. The variations in the ZPVE are to be significant. The ZPVE is much lowers by the bromine to the other substitution molecules. The biggest value of ZPVE is 47.944 Kcal/mol for H and the smallest value is 41.535 Kcal/mol for Br obtained at B3LYP/6-311++G(d,p). The total energies are found to Br >Cl> F > 3AR of the basis set dimension and the change in the total entropy of title molecule at room temperatureat different basis set are only marginal.

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Table 13: Theoretically computed dipole moment (Debye) SCF energy (a.u.), thermal energy (Kcal mol−1), entropy (cal mol−1 Kelvin−1), Enthalpy (Ä$_H$) (cal mol−1 temperatures (Kelvin) for 5X3AR (X=Cl,Fand NH$_2$)calculated at the B3LYP/6-311++G(d,p). Kelvin−1), Gibbs free energy (cal mol−1 Kelvin−1), zero-point vibrational energy (Kcal mol−1), rotational constants (GHz),ë$_{cal}$(nm) and rotational

Property		3AR	Cl	F	Br
Dipole moment		2.4115	1.2174	1.0701	1.3057
SCF energy		–1097.88	-1537.49	–1197.14	–3671.41
Thermal energy (E)		52.324	47.189	47.849	46.947
Entropy (S)		84.537	94.016	89.769	97.258
Enthalpy (Ä$_H$)		84.327	76.144	77.197	75.759
Gibbs free energy		49.161	31.475	34.544	29.549
Zero point vibration energy (ZPVE)		47.944	41.934	42.884	41.535
Rotational constants		2.0639	1.6723	1.7876	1.5489
		1.4591	0.7653	1.0432	0.5098
		0.8714	0.5614	0.6906	0.4130
ë$_{cal}$	ë$_1$	109.70	35.886	82.820	28.648
	ë$_2$	212.74	104.77	133.11	80.526
	ë$_3$	226.54	155.39	179.48	146.54
Rotational temperatures		2.0639	0.0802	0.0857	0.0766
		1.4591	0.0367	0.0500	0.0244
		0.8714	0.0269	0.0331	0.0918

The dipole moment of the molecule was also calculated withB3LYP/6-311++G(d,p) basis set. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor of the charge movement across the molecule depends on the centers of positive and negative charges. Dipole moments are determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. As a result of DFT calculations the highest dipole moments were observed for 3AR, whereas the smallest one was observed for fluorine of the 5X3AR.In Table 13 demonstrates several thermodynamic parameters of the title compound without the results of experimental.

3. CONCLUSION

In the present work, the complete molecular structure parameters viz; bond length and bond angle, thermodynamic properties of the optimized geometry of the compound have been determined from ab initio and

DFT calculations using 6-311++G(d,p) basic set.The delocalization patterns of charge and electron densities of atoms of 5X3AR (X= Cl, F and Br) moleculehave been explained by performing molecular orbital simulations at density functional B3LYP method with standard 6-311++G(d,p) basic set. The natural atomic orbital occupancies of the title molecule are clearly describing the different substituent in terms of difference in occupancy and energy. The natural population analysis on5X3AR(X=Cl,F and Br) thoroughly illustrates the accumulation of electrons in core, valence and Rydberg sub-shell of their atomic orbitals. The natural hybrid atomic orbitals performed in this study enabling us to know about sub-shell type, the contribution of specified atomic electrons to s-type and p-type sub-shells and their hybridization details. The second order perturbation results obtained in this study showed the most significant hyperconjugative interactions responsible for the stability of a molecule. The excited state electron transition along with their maximum absoption wavelengths, vertical excitation energies and oscillator strengths are predicted of B3LYP/6-311++G(d,p) method. From the electronic spectrum of 5X3AR(X= Cl,F and Br), the information about the allowed and forbidden transitions is found and the solvent effect is also examined. The frontier molecular orbitals have been visualized and the HOMO-LOMO energy gap has been calculated. The Mullikan charges calculated by HF and B3LYP/6-311++G(d,p) method have been compared with charges calculated by NBO. The inclusions of halogens in the title molecule change the non-linear optical properties significantly.

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