Quantum Chemical Studies of Carbazochrome Molecule

[1]Fatma Genç*, [2]Hanan Bsehen and [2]Fatma Kandemirli
[1]Department of Analytical Chemistry, Faculty of Pharmacy, Istanbul YeniYuzyil University, Istanbul, Turkey.
[2]Department of Biomedical Engineering, Faculty of Engineering and Architecture, Kastamonu University, Kastamonu, Turkey.
fatma.genc@yeniyuzyil.edu.tr; ftmgenc@yahoo.com*

Summary: Control of spontaneous and postoperative bleeding is of particular concern to surgeons, anesthetists, hematologists, and the patient. Mainly carbazochrome(2-(1,2,3,6-tetrahydro-3-hydroxy-1-methyl-6-oxo-5H-indol-5-ylidene)-hydrazinecarboxamide,CBZ), adrenochrome derivative, currently used as hemostatic drugs. With Density Functional Theory (DFT), at B3LYP level with 6–311G(d,p), 6–311+G(d,p), 6–311++G(d,p), 6–311++G(2d,2p), 6-311++G(3df,3pd) basis sets. Molecular structure of carbazochrome ($C_{10}H_{12}N_4O_3$) in the basic state in gas phase and solvent (ethanol, N, N-dimethyl form amide, N, N-dimethyl sulfoxide, water) phases, energy Parameters such as the lowest empty molecular orbital (E_{LUMO}), the highest energy filled molecular orbital (E_{HOMO}), the energy difference between E_{LUMO} and E_{HOMO}, hardness, softness, electrophilicity index, chemical potential, electrofugality and nucleofugality were calculated and its effect on carbazochrome molecule has been investigated. In this study, the stabilization energy and hybridization of carbazochrome optimized by using DFT with B3LYP/6-311G(d, p) level in gas phase solvent phase, using natural bond orbital theory as integrated with NBO 3.1 were studied. Quantum mechanical calculations by using time-dependent DFT at B3LYP level 6–311G(d,p), 6–311+G(d,p), 6–311++G(d,p), 6–311++G(2d,2p), 6-311++G(3df,3pd) basis sets were performed to obtain some valuable information about the UV spectrum of the carbazochrome molecule in gas and solvent medium (ethanol, N, N-dimethylformamide, N, N-dimethylsulfoxide, water) and compared with experimental values. Based on Gaussian's output data, on the basis of vibration analysis and statistical thermodynamics, standard thermodynamicfunctions of the carbazochrome molecule at different temperatures (200°C-1000°C): thermodynamic properties such as heat capacity entropy, enthalpy, Gibbs free energy were calculated and the effect of base sets and solvent on these properties was investigated.

Introduction

Derived from a semicarbazide, carbazochrome is a member of indoles and is a hemostatic agent that promotes coagulation by preventing blood loss from open wounds. Carbazochrome is the oxidation product of adrenaline that increases the microcirculation tone. Carbazochrome has been investigated in a mixture with [DB13124] for use in the treatment of non-surgical acute uncomplicated hemorrhoids, and this combination therapy demonstrated local or systemic level efficacy and safe tolerability. IUPAC name of carbazochrome is (3,6-dihydroxy-1-methyl-2,3-dihydroindol-5-yl)iminourea [1].

It was said that the hemostatic effect of carbazochrome and its derivatives is applied only to capillaries. As the Ventouse technique shows, capillary resistance increases in both guinea pigs and humans [2]. They found that the bleeding time in humans decreased from a 'normal' value of 200 seconds to 110-130 seconds one hour after carbazochrome (Adrenoxyl®) injection.

Roskam and Derouaux (1944) showed that carbazochrome given intravenously, intramuscularly, or subcutaneously significantly shortened the bleeding time in volunteers for a period of up to two hours after treatment [3].

Perkins (1957) studied 24 patients who underwent surgical dental procedures. The first quadrant of the mouth was operated and then Adrenosem® was given [4]. Blood loss was determined by aspiration from the mouth into a glass jar. Blood loss following Adrenosem® was reported to be 11.1 ml (mean) less than the first procedure (p <0.01).

Squadrito et al., (2000) tried to determine the efficacy and safety of 150 mg troxerutin and 1.5 mg carbazochrome combination in patients with acute simple hemorrhoids compared to carbazochrome alone [5]. It has been reported that patients with acute uncomplicated hemorrhoids were treated intramuscularly with the combination drug, resulting in a significantly greater improvement in subjective symptoms and objective signs of disease than those in

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*To whom all correspondence should be addressed.

the control group. It has been reported that the consumption of local anesthetics was also positively affected by the combination product.

Carbazochrome is an antihemorrhagic that is thought to act as a capillary stabilizer [6, 7]. Carbazochrome was visualized with LTQ-Orbitrap and an ion trap was verified using the LCMSMS approach.

Oh-oka et al, (2014) examined the effect of carbazochrome sodium sulfonate, an agent that reduces capillary permeability, on refractory chronic prostatitis and concluded that carbazochrome effectively ameliorated storage and post-voiding symptoms as well as pain in patients with refractory chronic prostatitis [8].

Using a computational model of the spike protein (S-protein) of SARS-CoV-2, which interacts with the human ACE2 receptor, SUMMIT, the world's most powerful supercomputer, implement a group docking virtual high throughput screening campaign and they used it to identify small molecules that are predicted to bind to the isolated viral S-protein or the S-protein-human ACE2 interface. 8669 ligands were performed and the highest exposure score for each ligand was recorded for ligand sequencing (see SI for complete sequencing). From sequencing, 47 ligands were found to make up S-protein: ACE2 interface-ligand binding complexes with scores equal to or better than the score threshold (Vina score better and -7 kcal/mol) and 41 of these were reported (as indicated) in the ZINC15 database40 has 21 regulatory approvals that can be purchased, one of which is carbazochrome [9].

They investigated the effect of carbazochrome sodium sulfonate on colonic diverticular bleeding and concluded that CSS may not reduce in-hospital mortality, length of stay, total costs, or the need for blood transfusions in patients with colonic diverticular bleeding [10].

They proposed HPLC method to analyze troxerutin and carbazochrome in tablets. The proposed method has been validated for specificity, linearity, accuracy, precision, LOQ and LOD and then successfully applied for the analysis of these substances in tablets [11].

Experimental

In this study, all calculations were carried out with the Gaussian 09W package program. At DFT and B3LYP level 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,3p). Geometric, electronic, spectroscopic and thermodynamics of the molecule were calculated in the gas phase and in different solvents such as ethanol, DMF, DMSO and water using 311++G(3df,3pd) base sets [12]. First of all, the stable three-dimensional structure of the molecule was drawn in the "Gaussview 5.0" program [13] and the molecule was optimized with the method and basis set we chose in the Gaussian 09W program.

Excited state calculations, B3LYP functional and 6-311G(d,p), 6-311+Gd,p), 6-311++G(d,p), 6-311++G(2d,2p) performed in a time-dependent DFT frame work toc alculate the UV-Vis spectra of the carbazochrome molecule using base sets of 6-311++G(3df,3pd). UV / Visible spectra were simulated using the PCM model in gas phase and in different solvents such as ethanol, DMF, DMSO and water. Second order transmit/receive perturbation energies were calculate dusing Gaussian NBO Version3.1 programs [14].

Results and Discussion

The geometry of the studied carbazochrome molecule was determined by optimizing without any symmetry delimitations. Optimization form, HOMO, LUMO and electron density form of carbazochrome molecule calculated with B3LYP level and 6-311G basis set in gas phase is given in Fig 1. MEP appears to be a useful property for studying reactivity, considering that an approaching electrophile will be attracted to negative regions (where the electron dispersion effect is dominant) or that the nucleophile will be attracted to positive regions (regions with less electron density will be attracted. The different electrostatic potential values of the surface are symbolized by different colors, the maximum negative zone is shown as the red and yellow zone. The result calculated in the present study shows that the negative potentials are primarily in the phenyl group.

The surfaces for the HOMO and LUMO were drawn to understand the bonding scheme of the present compound. The highest value of HOMO and LUMO of the carbazochrome molecule is seen in the benzene ring belonging to the indolinegroup, the nitrogen atom bound to the benzene group and the nitrogen atom of the 5-member group belonging to the indoline group.
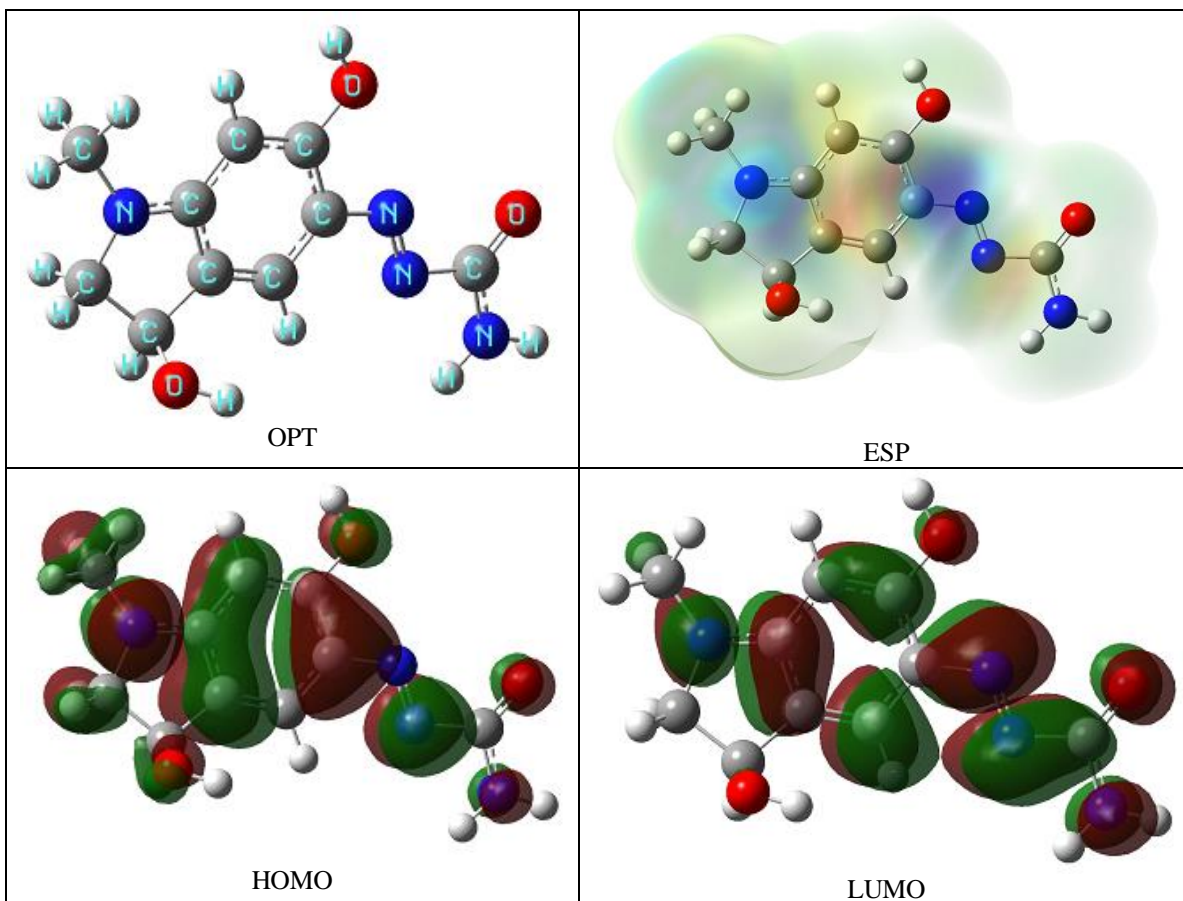
Fig. 1: Optimized form, HOMO, LUMO and molecular electrostatic potential surface of carbazochrome molecule.

Carbazochrome molecule with the B3LYP level with 6-311G(d, p), 6-311+G(d, p), 6-311++G(d, p), 6-311++G(2d, 2p) and 6-311++G(3df, 3pd) 6-311G(d, p) basis sets in the gas phase and solvent phases [ethanol (ε = 21.01), DMF (ε = 36.71), DMSO (ε = 46.68), water (ε = 78.39)] at the B3LYP level was optimized and molecular properties were calculated. The bond lengths obtained from the optimized structure in gas phase and solvent phases are given in Tables 1-4. As can be seen from Table 1-4, there is no significant change in the bond lengths in the calculations made in the gas phase and solvent phases (ethanol, DMF, DMSO and water) according to the base sets used.

O_1-C_8, C_8-C_9, C_9-N_4, N_4-C_{11}, N_5-N_6, C_{17}-O_3 bond lengths of the carbazochrome molecule in gas phaseare found as 1.434, 1.539, 1.469, 1.365, 1.258, 1.207 Å, respectively at 6-311G(d, p) basis set, 1.438, 1.539, 1.470, 1.365, 1.257, 1.209 Å, respectively at 6-311+G(d, p) basis set, 1.438, 1.539, 1.470, 1.365, 1.257, 1.209 Å, respectively at 6-311++G(d, p) basis set, 1.437, 1.537, 1.469, 1.364, 1.255, 1.208 Å, respectively at 6-311++G(2d, 2p) basis set, 1.434, 1.537, 1.467, 1.362,

1.254, 1.206 Å. respectively at 6-311++G(3df, 3pd).O_1-C_8, C_9-N_4, N_5-N_6, C_{17}-O_3 bond lengths of carbazochrome molecule at 6-311+G(d, p) basis set are 0.28%, 0.07%, 0.08%, 0.16% bigger than those bond lengths of carbazochrome molecule at 6-311G(d, p) basis set. No change was observed in C_8-C_9 and N_4-C_{11} bond lengths compared to the basis set.

O_1-C_8, C_9-N_4, N_5-N_6, C_{17}-O_3 bond lengths of carbazochrome molecule at 6-311++G(d, p) basis set are 0.28%, 0.07%, 0.08%, 0.16% bigger than those bond lengths of carbazochrome molecule at 6-311G(d, p) basis set, the length of N_5-N_6 bond at 6-311++G(d, p) basis set is 0.08% shorter than the length at 6-311++G(d, p). No change was observed in C_8-C_9 and N_4-C_{11} bond lengths compared to the basis set.

O_1-C_8, C_9-N_4, N_5-N_6, C_{17}-O_3 bond lengths of carbazochrome molecule at 6-311++G(2d,2p) basis set are 0.21%, 0.12%, 0.07%, 0.24%, 0.08% bigger than those bond lengths of carbazochrome molecule at 6-311G(d, p) basis set. No change was observed in C_9-N_4 bond length compared to the basis set.

C_8-C_9, C_9-N_4, N_4-C_{11}, N_5-N_6, C_{17}-O_3 bond lengths of carbazochrome molecule at 6-311++G(3df,3pd) basis set are respectively 0.13%, 0.14%, 0.22%, 0,32%, 0.08% bigger than those bond lengths of carbazochrome molecule at 6-311G(d, p) basis set. No change was observed in O_1-C_8 bond length compared to the basis set. As can be seen from the% calculations, there is no significant change in the bond lengths according to the base sets used.

In the calculations performed B3LYP / 6-311G(d, p) level in the gas phase, O_1-C_8, C_{16}-O_2, C_{17}-O_3 bond lengths were calculated as 1.434, 1.350, 1.207 Å, respectively. These bond lengths were calculated as 1.436, 1.351, 1.220 Å in ethanol solvent, 1.437, 1.351, 1.221 Å in DMF solvent, 1.437, 1.351, 1.221 Å in DMSO solvent, and 1.437, 1.351, 1.221 Å in water. When ethanol was used as solvent instead of gas phase, there was an increase of 1.11% in C_{17}-O_3 bond. There was a decrease of N_4-C_{11}, C_{15}-N_{15} and N_6-C_{17}, 0.89%, 1.12%,

1.10%. However, there was no significant change according to the type of solvent used.

Table-1: Bond lengths of the carbazochromemolecule in the gas phase (Å).

Bond Type	6-311G (d,p)	6-311+G (d,p)	6-311++G (d,p)	6-311++G (2d,2p)	6-311++G (3df,3pd)
O_1-C_8	1.434	1.438	1.438	1.437	1.434
C_8-C_9	1.539	1.539	1.539	1.537	1.537
C_8-C_{10}	1.511	1.511	1.511	1.509	1.508
C_9-N_4	1.469	1.470	1.470	1.469	1.467
N_4-C_{11}	1.365	1.365	1.365	1.364	1.362
C_{10}-C_{11}	1.420	1.421	1.421	1.418	1.417
C_{10}-C_{12}	1.368	1.368	1.421	1.365	1.364
C_{11}-C_{13}	1.395	1.395	1.395	1.392	1.391
C_{12}-C_{15}	1.416	1.417	1.417	1.415	1.414
C_{13}-C_{16}	1.400	1.400	1.400	1.397	1.396
C_{15}-C_{16}	1.419	1.420	1.420	1.417	1.417
C_{16}-O_2	1.350	1.351	1.351	1.351	1.348
N_4-C_{14}	1.444	1.445	1.445	1.444	1.442
C_{15}-N_5	1.389	1.388	1.388	1.387	1.385
N_5-N_6	1.258	1.257	1.257	1.255	1.254
N_6-C_{17}	1.459	1.458	1.458	1.457	1.455
C_{17}-O_3	1.207	1.209	1.209	1.208	1.206
C_{17}-N_7	1.364	1.365	1.365	1.363	1.361

Table-2: Bond lengths of the carbazochrome molecule in ethanol and DMF phase(Å).

Bond Type	6-311G (d,p)		6-311+G (d,p)		6-311++G (d,p)		6-311++G (2d,2p)		6-311++G (3df,3pd)	
Bond Type	Ethanol	DMF	Ethanol	DMF	Ethanol	DMF	Ethanol	DMF	Ethanol	DMF
O_1-C_8	1.436	1.437	1.441	1.441	1.441	1.442	1.440	1.440	1.437	1.437
C_8-C_9	1.538	1.538	1.537	1.537	1.537	1.537	1.536	1.536	1.437	1.535
C_8-C_{10}	1.514	1.514	1.513	1.513	1.513	1.513	1.512	1.512	1.511	1.511
C_9-N_4	1.471	1.471	1.472	1.473	1.472	1.472	1.470	1.470	1.469	1.469
N_4-C_{11}	1.353	1.352	1.351	1.351	1.351	1.351	1.349	1.349	1.348	1.469
C_{10}-C_{11}	1.427	1.427	1.429	1.429	1.429	1.429	1.426	1.426	1.425	1.425
C_{10}-C_{12}	1.363	1.363	1.362	1.362	1.362	1.362	1.359	1.359	1.358	1.358
C_{11}-C_{13}	1.399	1.400	1.401	1.401	1.401	1.401	1.398	1.398	1.397	1.397
C_{12}-C_{15}	1.424	1.424	1.426	1.427	1.426	1.427	1.424	1.424	1.423	1.424
C_{13}-C_{16}	1.394	1.394	1.392	1.392	1.392	1.392	1.389	1.389	1.389	1.388
C_{15}-C_{16}	1.428	1.428	1.430	1.430	1.430	1.430	1.427	1.427	1.427	1.427
C_{16}-O_2	1.351	1.351	1.352	1.352	1.352	1.353	1.352	1.352	1.349	1.349
N_4-C_{14}	1.449	1.449	1.450	1.450	1.450	1.450	1.448	1.448	1.446	1.446
C_{15}-N_5	1.374	1.373	1.370	1.369	1.370	1.369	1.368	1.368	1.366	1.365
N_5-N_6	1.269	1.270	1.270	1.271	1.270	1.271	1.270	1.270	1.267	1.268
N_6-C_{17}	1.443	1.442	1.438	1.437	1.438	1.437	1.437	1.436	1.435	1.434
C_{17}-O_3	1.220	1.221	1.225	1.226	1.225	1.226	1.225	1.225	1.222	1.223
C_{17}-N_7	1.355	1.355	1.355	1.355	1.355	1.355	1.353	1.353	1.352	1.352

Table-3: Bond lengths of the Carbazochromemolecule in DMSO and water phase(Å).

Bond Type	6-311G (d,p)		6-311+G (d,p)		6-311++G (d,p)		6-311++G (2d,2p)		6-311++G (3df,3pd)	
Bond Type	DMSO	water	DMSO	water	DMSO	water	DMSO	water	DMSO	water
O_1-C_8	1.437	1.437	1.441	1.441	1.442	1.442	1.440	1.440	1.437	1.437
C_8-C_9	1.538	1.538	1.537	1.537	1.537	1.537	1.536	1.536	1.535	1.535
C_8-C_{10}	1.514	1.514	1.513	1.513	1.513	1.513	1.512	1.512	1.511	1.511
C_9-N_4	1.472	1.472	1.473	1.473	1.473	1.473	1.471	1.471	1.469	1.469
N_4-C_{11}	1.352	1.352	1.350	1.350	1.351	1.351	1.348	1.348	1.347	1.347
C_{10}-C_{11}	1.428	1.428	1.429	1.429	1.429	1.429	1.426	1.426	1.425	1.426
C_{10}-C_{12}	1.362	1.362	1.362	1.362	1.362	1.362	1.359	1.359	1.358	1.358
C_{11}-C_{13}	1.400	1.400	1.401	1.401	1.401	1.401	1.398	1.398	1.397	1.397
C_{12}-C_{15}	1.424	1.424	1.427	1.427	1.427	1.427	1.425	1.425	1.424	1.424
C_{13}-C_{16}	1.393	1.393	1.391	1.391	1.391	1.391	1.389	1.389	1.388	1.388
C_{15}-C_{16}	1.428	1.428	1.430	1.430	1.430	1.430	1.427	1.427	1.427	1.427
C_{16}-O_2	1.351	1.351	1.353	1.353	1.353	1.353	1.352	1.352	1.349	1.349
N_4-C_{14}	1.449	1.449	1.450	1.450	1.450	1.450	1.448	1.448	1.446	1.446
C_{15}-N_5	1.373	1.373	1.369	1.369	1.369	1.369	1.367	1.367	1.365	1.365
N_5-N_6	1.270	1.270	1.271	1.271	1.271	1.271	1.271	1.271	1.268	1.268
N_6-C_{17}	1.442	1.442	1.437	1.437	1.437	1.437	1.436	1.436	1.434	1.434
C_{17}-O_3	1.221	1.221	1.226	1.226	1.226	1.226	1.226	1.226	1.223	1.223
C_{17}-N_7	1.355	1.355	1.355	1.355	1.355	1.355	1.353	1.353	1.352	1.352

Mulliken Atomic Charges

Mulliken atomic charges, having ansignificant role in the application of quantum chemical calculations in the molecular system, is associated with many properties such as, dipole moment in the molecular system, polarizability, and electronic structure. In atomic charge distributions, donor and acceptor parts of the molecule can be predicted during charge transfer. Mulliken atomic charges, at the DFT / B3LYP level and using 6-311G(d, p), 6-311+G(d, p), 6-311++G(d, p), 6-311++G(2d, 2p), 6-311++G(3df, 3pd) basis sets in gas phase and solvent phases with different dielectric constants [ethanol (ε= 21.01), DMF (ε= 36.71), DMSO (ε= 46.68) , water (ε= 78.39)] were calculated and given in Tables 4-6.

As can be seen from Table-4, in the Mulliken atomic charges calculated in the gas phase, negative charges were summed up on O_1, O_2, O_3, N_4, N_5, N_6, N_7 atoms, C_{10}, C_{13}, C_{14} atoms belonging to phenyl group and C atom belonging to methyl group.

Solvatation free energy

Solvation free energy in 4 solvents: Ethanol (21.01 kJmol^{-1}), DMF (36.71kJmol^{-1}), DMSO (46.68kJmol^{-1}), water (78.39kJmol^{-1}), B3LYP with

B3LYP functional and 6-311G(d, p) 6-311+G(d, p), 6-311++G(d, p), 6-311++G(2d, 2p), 6-311++G(3df, 3pd) using base sets calculated and given in Fig 2.

Table-4: Mulliken atomic charges of carbazochrome in water phase (ē).

Bond Type	6-311G (d,p)	6-311+G (d,p)	6-311++G (d,p)	6-311++G (2d,2p)	6-311++G (3df,3pd)
O_1	-0.392	-0.251	-0.184	-0.367	-0.875
O_2	-0.308	-0.158	-0.138	-0.349	-0.896
O_3	-0.345	-0.338	-0.319	-0.453	-0.731
N_4	-0.476	0.055	0.123	0.018	-0.745
N_5	-0.130	-0.363	-0.390	-0.443	-0.755
N_6	-0.282	0.177	0.185	-0.094	-0.341
N_7	-0.453	-0.403	-0.377	-0.270	-0.872
C_8	0.052	-0.246	-0.432	-0.268	0.554
C_9	-0.022	-0.175	-0.291	-0.075	0.212
C_{10}	-0.209	0.271	0.644	0.513	0.402
C_{11}	0.334	-0.288	-0.879	-0.018	-0.046
C_{12}	0.017	-0.192	-0.038	-0.427	0.385
C_{13}	-0.124	-0.062	0.301	-0.048	0.291
C_{14}	-0.155	-0.278	-0.337	-0.238	0.219
C_{15}	-0.017	-0.120	-0.491	-0.266	-0.152
C_{16}	0.202	-0.100	-0.102	0.342	0.282
C_{17}	0.456	0.238	0.180	0.572	1.315
H_{18}	0.122	0.168	0.202	0.109	0.021
H_{19}	0.117	0.158	0.177	0.101	-0.011
H_{20}	0.136	0.175	0.206	0.142	0.014
H_{21}	0.096	0.141	0.230	0.208	0.110
H_{22}	0.087	0.098	0.147	0.074	-0.003
H_{23}	0.123	0.144	0.143	0.100	0.013
H_{24}	0.124	0.151	0.157	0.112	-0.009
H_{25}	0.113	0.160	0.178	0.120	0.009
H_{26}	0.238	0.236	0.245	0.252	0.432
H_{27}	0.245	0.263	0.286	0.272	0.542
H_{28}	0.225	0.262	0.255	0.159	0.298
H_{29}	0.228	0.278	0.319	0.223	0.338

Table-5: Mulliken atomic charges of carbazochrome in ethanol and DMF phase.

Atom Type	6-311G (d,p)		6-311+G (d,p)		6-311++G (d,p)		6-311++G (2d,2p)		6-311++G (3df,3pd)	
	ethanol	DMF	ethanol	DMF	ethanol	DMF	ethanol	DMF	ethanol	DMF
O_1	-0.426	-0.427	-0.317	-0.318	-0.256	-0.257	-0.429	-0.430	-0.943	-0.944
O_2	-0.353	-0.353	-0.228	-0.229	-0.210	-0.211	-0.420	-0.421	-0.949	-0.950
O_3	-0.430	-0.431	-0.471	-0.474	-0.453	-0.456	-0.591	-0.594	-0.829	-0.831
N_4	-0.479	-0.479	0.033	0.033	0.107	0.107	0.048	0.050	-0.722	-0.721
N_5	-0.178	-0.179	-0.302	-0.300	-0.335	-0.334	-0.351	-0.350	-0.720	-0.720
N_6	-0.297	-0.297	-0.005	-0.010	0.008	0.004	-0.305	-0.309	-0.504	-0.508
N_7	-0.446	-0.445	-0.419	-0.419	-0.392	-0.392	-0.284	-0.284	-0.878	-0.878
C_8	0.035	0.035	-0.306	-0.307	-0.470	-0.471	-0.343	-0.345	0.471	0.469
C_9	-0.018	-0.018	-0.194	-0.195	-0.320	-0.320	-0.072	-0.071	0.215	0.215
C_{10}	-0.186	-0.186	0.421	0.424	0.810	0.813	0.649	0.653	0.467	0.468
C_{11}	0.332	0.332	-0.239	-0.236	-0.839	-0.837	-0.033	-0.035	0.010	0.011
C_{12}	0.012	0.012	-0.010	-0.005	0.148	0.152	-0.223	-0.215	0.471	0.473
C_{13}	-0.125	-0.125	-0.089	-0.089	0.239	0.238	-0.121	-0.123	0.254	0.253
C_{14}	-0.155	-0.155	-0.279	-0.279	-0.334	-0.334	-0.234	-0.234	0.236	0.236
C_{15}	-0.021	-0.021	-0.176	-0.176	-0.526	-0.526	-0.270	-0.269	-0.099	-0.096
C_{16}	0.197	0.196	-0.265	-0.270	-0.288	-0.292	0.203	0.199	0.249	0.248
C_{17}	0.442	0.442	0.287	0.287	0.232	0.233	0.629	0.630	1.342	1.342
H_{18}	0.143	0.144	0.196	0.196	0.233	0.234	0.136	0.136	0.036	0.036
H_{19}	0.143	0.144	0.188	0.189	0.214	0.215	0.126	0.126	0.001	0.001
H_{20}	0.140	0.140	0.187	0.187	0.214	0.214	0.147	0.147	0.013	0.013
H_{21}	0.105	0.105	0.156	0.157	0.238	0.239	0.205	0.205	0.110	0.110
H_{22}	0.126	0.126	0.142	0.143	0.208	0.209	0.124	0.125	0.015	0.015
H_{23}	0.136	0.136	0.161	0.161	0.160	0.160	0.113	0.114	0.018	0.018
H_{24}	0.136	0.136	0.167	0.167	0.174	0.174	0.121	0.122	-0.004	-0.004
H_{25}	0.131	0.132	0.181	0.181	0.195	0.196	0.133	0.133	0.013	0.013
H_{26}	0.259	0.259	0.271	0.271	0.279	0.279	0.284	0.284	0.479	0.480
H_{27}	0.281	0.282	0.308	0.308	0.331	0.331	0.319	0.319	0.579	0.579
H_{28}	0.247	0.248	0.295	0.296	0.289	0.290	0.191	0.191	0.320	0.320
H_{29}	0.247	0.248	0.307	0.308	0.344	0.344	0.247	0.248	0.350	0.350

Table-6: Mulliken atomic charges of carbazochrome in DMSO and water phase.

Atom Type	6-311g (d,p)		6-311+g (d,p)		6-311++g (d,p)		6-311++g (2d,2p)		6-311++g (3df,3pd)	
	DMSO	water	DMSO	water	DMSO	water	DMSO	water	DMSO	water
O_1	-0.427	-0.427	-0.319	-0.319	-0.258	-0.258	-0.430	-0.431	-0.944	-0.945
O_2	-0.354	-0.354	-0.230	-0.231	-0.212	-0.212	-0.422	-0.423	-0.951	-0.951
O_3	-0.432	-0.433	-0.475	-0.476	-0.458	-0.459	-0.596	-0.597	-0.832	-0.833
N_4	-0.479	-0.478	0.033	0.033	0.107	0.107	0.050	0.051	-0.721	-0.721
N_5	-0.179	-0.180	-0.300	-0.299	-0.333	-0.333	-0.349	-0.348	-0.720	-0.720
N_6	-0.298	-0.298	-0.012	-0.014	0.002	0.000	-0.312	-0.314	-0.509	-0.512
N_7	-0.445	-0.445	-0.419	-0.420	-0.392	-0.392	-0.284	-0.284	-0.878	-0.878
C_8	0.035	0.035	-0.307	-0.307	-0.471	-0.471	-0.347	-0.347	0.469	0.469
C_9	-0.018	-0.018	-0.195	-0.195	-0.321	-0.321	-0.071	-0.071	0.215	0.215
C_{10}	-0.185	-0.186	0.424	0.425	0.813	0.814	0.654	0.655	0.468	0.469
C_{11}	0.332	0.332	-0.236	-0.236	-0.836	-0.837	-0.037	-0.037	0.011	0.012
C_{12}	0.012	0.012	-0.003	-0.001	0.154	0.156	-0.212	-0.210	0.474	0.475
C_{13}	-0.125	-0.125	-0.089	-0.089	0.237	0.237	-0.124	-0.124	0.253	0.253
C_{14}	-0.155	-0.155	-0.279	-0.279	-0.334	-0.334	-0.234	-0.234	0.236	0.237
C_{15}	-0.021	-0.021	-0.177	-0.177	-0.527	-0.527	-0.268	-0.268	-0.097	-0.096
C_{16}	0.196	0.196	-0.272	-0.274	-0.294	-0.296	0.197	0.196	0.247	0.248
C_{17}	0.441	0.441	0.288	0.288	0.234	0.234	0.631	0.631	1.342	1.342
H_{18}	0.144	0.144	0.197	0.197	0.234	0.234	0.137	0.137	0.036	0.037
H_{19}	0.144	0.145	0.189	0.190	0.215	0.215	0.127	0.127	0.001	0.001
H_{20}	0.140	0.140	0.187	0.187	0.214	0.214	0.147	0.147	0.013	0.013
H_{21}	0.105	0.105	0.157	0.157	0.239	0.239	0.205	0.205	0.110	0.110
H_{22}	0.127	0.127	0.143	0.144	0.210	0.210	0.125	0.126	0.015	0.015
H_{23}	0.136	0.136	0.162	0.162	0.160	0.160	0.114	0.114	0.018	0.018
H_{24}	0.136	0.136	0.167	0.167	0.174	0.174	0.122	0.122	-0.004	-0.004
H_{25}	0.132	0.132	0.181	0.182	0.196	0.196	0.133	0.133	0.013	0.014
H_{26}	0.259	0.259	0.272	0.272	0.280	0.280	0.284	0.285	0.480	0.481
H_{27}	0.282	0.283	0.309	0.309	0.332	0.332	0.320	0.320	0.580	0.580
H_{28}	0.248	0.248	0.296	0.296	0.290	0.290	0.191	0.192	0.320	0.320
H_{29}	0.248	0.248	0.308	0.308	0.344	0.345	0.248	0.248	0.350	0.350

The free energy of solvation (ΔG) is calculated according to the following equation.

$$\Delta G = G(sol) - G(gas)$$

where,

G(gas) = Sum of electronic and thermal free energy in gas phase
G(sol) = Sum of electronic and thermal free energy in solvent

The solvation energy of the carbazochrome molecule in ethanol DMF, DMSO, and water solutions are found as -75.63, -77.02, -77.51, -78.47 kJmol^{-1}, respectively, at 6-311G(d, p) basis set, -83.39, -85.10, -85.69, -86.81 kJmol^{-1} at 6-311+G(d, p) basis set, -83.39, -85.01, -85.62, -86.73 kJmol^{-1} at 6-311++G(d, p) basis set, -80.02, -81.59, -82.17, -83.24 at 6-311++G(2d, 2p) basis set, and -78.34, -79.91, -80.59, -81.52 kJmol^{-1} at B3LYP level using the 6-311++G(3df,3pd) basis set. The solvation energies constantly increase as the transition from high dielectric constant to low dielectric constant, i.e. with decreasing polarity of the solvent, free energy increases[15].

Electron density of p_z orbitals of C_{10}, C_{11}, C_{12}, C_{13}, C_{15}, C_{16} atoms belonging to phenyl ring of carbazochrome molecule in calculations with 6-311G(d, p) base set at B3LYP level is 1.1031 ē, 0.9246 ē, 0.9399 ē, 1.1708 ē, 1.1239 ē, and 0.9076 ē in gas phase. 11.0853 ē, 0.9106 ē, 0.9415 ē, 1.1587 ē, 1.1318 ē, and 0.9060 ē in ethanol phase. C_{10}, C_{13}, C_{15} atoms have negative charge density in p_z orbitals, while C_{11}, C_{12}, C_{16} atoms have positive charge density in p_z orbitals. The charge density in the benzene ring in gas ethanol, DMF, DMSO, and water phase is -0.1699 ē, -0.1339 ē, -0.1329 ē, -0.1322 ē, -0.1318 ē, respectively. This shows that there is electron density in both gas and solvent phases in the benzene ring. The electron density in the p_z orbitals of the benzene ring of the carbazochrome molecule obtained from the calculations performed in the gas phase is higher than the electron density obtained from the calculations performed in ethanol. The opposite is true for the p_z orbitals of C_{12} and C_{15} atoms. The same trend is seen in calculations made with the 6-311+G(d, p) base set.

The energy of 4 molecular orbitals close to HOMO and the energy of 4 molecular orbitals close to LUMO, E_{HOMO} and E_{LUMO} values of the carbazocromemolecule were computed at B3LYP/6-31G(d) level with 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets in gas and solvents (ethanol, DMF, DMSO and water) phases
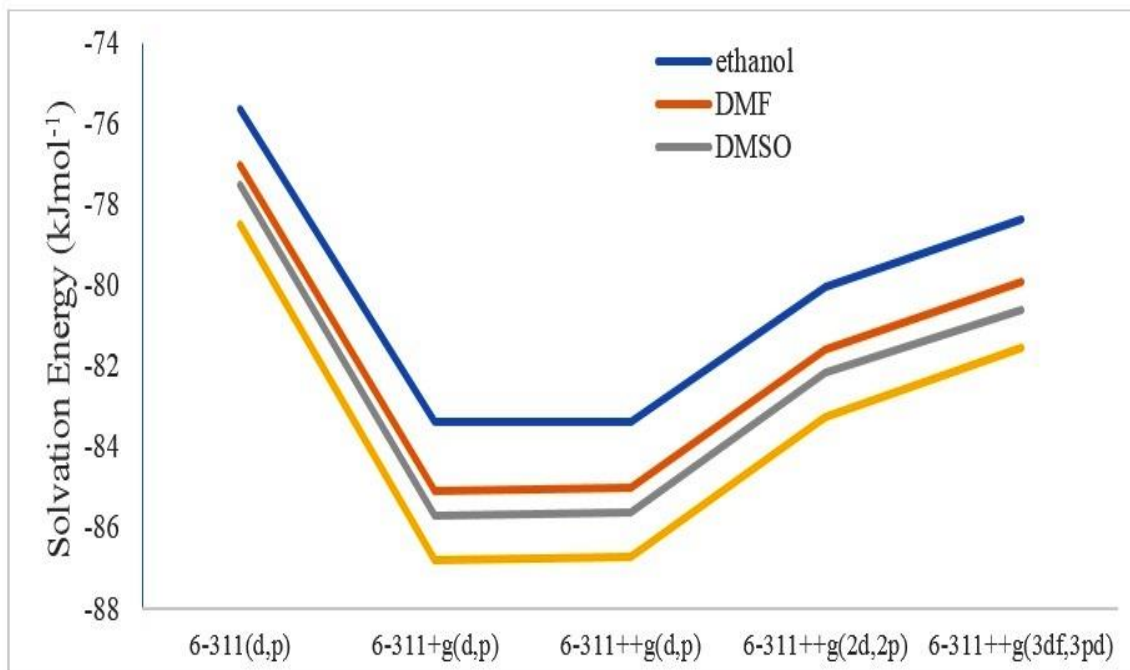
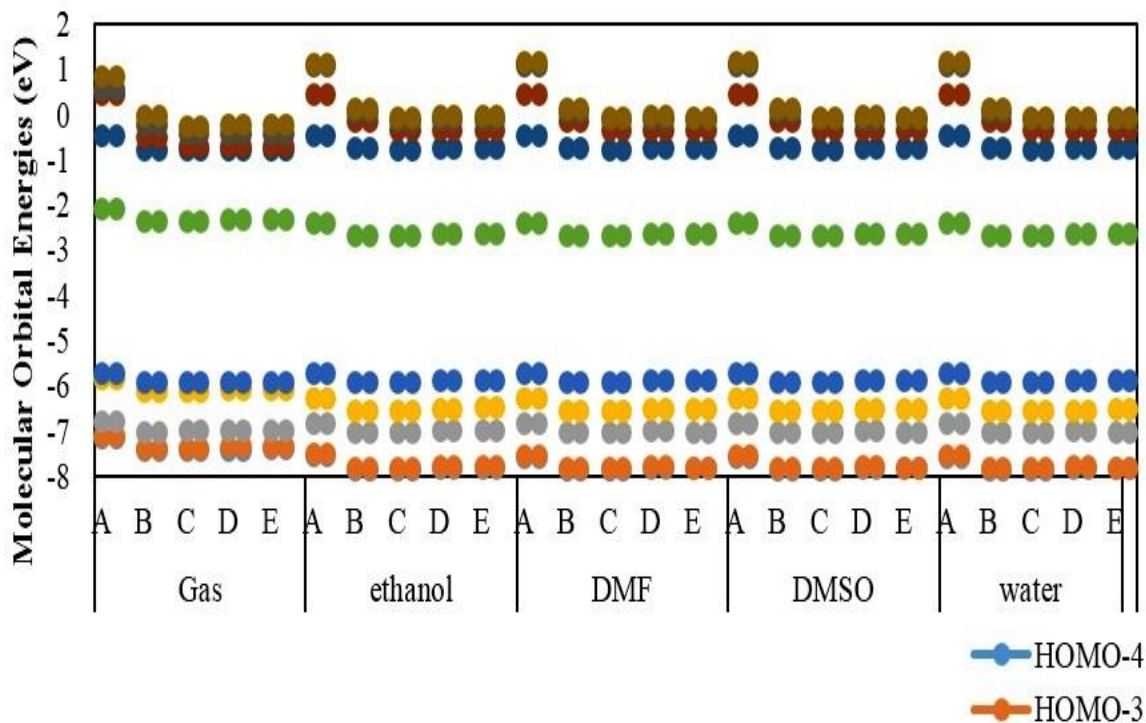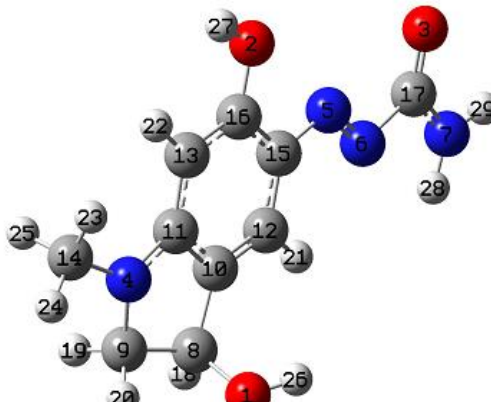Fig. 2:   Solvation free energy of the carbazochrome molecule.

Fig. 3:   The energy of 4 molecular orbitals close to HOMO and the energy of 4 molecular orbitals close to LUMO, E_{HOMO} and E_{LUMO} values of the carbazochrome molecule

Table-7: The p_z electrons in the benzene ring of the carbazacrome molecule and the total charge in the benzene ring

	Gas	Ethanol	DMF	DMSO	Water
p_z		6-311G(d,p)			
C_{10}	1.1031	1.0853	1.0848	1.0846	1.0843
C_{11}	0.9246	0.9106	0.9103	0.9100	0.9099
C_{12}	0.9399	0.9415	0.9416	0.9416	0.9417
C_{13}	1.1708	1.1587	1.1584	1.1583	1.1580
C_{15}	1.1239	1.1318	1.1318	1.1317	1.1318
C_{16}	0.9076	0.9060	0.9060	0.9060	0.9061
Benzene ring					
ē	-0.1699	-0.1339	-0.1329	-0.1322	-0.1318
		6-311+G(d,p)			
C_{10}	1.0994	1.0797	1.0791	1.0788	1.0785
C_{11}	0.9231	0.9063	0.9058	0.9055	0.9053
C_{12}	0.9379	0.9379	0.9379	0.9379	0.938
C_{13}	1.1658	1.1514	1.151	1.1509	1.1506
C_{15}	1.1233	1.1278	1.1276	1.1275	1.1275
C_{16}	0.9057	0.9036	0.9036	0.9036	0.9036
Benzene ring					
ē	-0.1552	-0.1066	-0.1051	-0.1041	-0.1035

E_{HOMO} values of the carbazochrome molecule calculated at B3LYP level by using 6-311G(d, p), 6-311+G(d, p), 6-311++G(d, p), 6-311++G(2d, 2p), and 6-311++G(3df,3pd) basis sets in gas phase were found to be -5.688, -5.893, -5.893, -5.877, -5.877 eV. The HOMO energy was found to be the largest in the calculations made with the 6-311G(d, p) base set among the studied base sets. For 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p) basis sets are added to 6-311G basis set, one set of d-functions to all nonhydrogenatoms and one set of p-functions to all hydrogen atoms. The polarization functions used in 6-311G(d, p), 6-311+G(d, p), 6-311++G(d, p) base sets are the same but diffuse functions are different. To reflect the addition of diffuse basis functions on all nonhydrogen atoms, a +-sign is added to the standard basis set notation. If diffuse s-type functions are also added to the basis set of hydrogen atoms, a second +-sign is appended.

In the gas phase, the HOMO energy of the carbazochrome molecule obtained from the calculations at 6-311+G(d,p) basis set is 3.59% more than the HOMO energy of the carbazochrome molecule obtained from the calculations at 6-311G(d,p) basis set, while LUMO energy is 13.44% less. HOMO and LUMO energy values obtained in calculations with 6-311+G(d, p) base set and 6-31++G(d,p) basis set are almost close to each other. In the gas phase, the HOMO energy of the carbazochrome molecule obtained from the calculations at 6-311++G(d,p) basis set is 0.27% more than the HOMO energy of the carbazochrome molecule obtained from the calculations at 6-311G(d,p) basis set, while LUMO energy is 0.96% less. HOMO and LUMO energy values obtained in calculations with 6-311+G(3df,3pd) basis set and 6-31++G(d,p) basis set are almost close to each other, while LUMO energy is 0.96% more. HOMO energy values obtained in calculations using HOMO energy values obtained in calculations using 6-311++G (2d, 2p) base set and calculations carried with 6-311++G(3df, 3pd) basis set are almost close to each other. In calculations with 6-311++G(3df, 3pd) basis set, LUMO energy values increased by 0.52% compared to 6-311++G(2d, 2p) basis set.

In the gas phase, the HOMO-LUMO energy gap of the carbazochrome molecule obtained from the calculations at 6-311+G(d,p) basis set is 1.98% less than the HOMO-LUMO energy gap of the carbazochrome molecule obtained from the calculations at 6-311G(d,p) basis set. HOMO-LUMO energy gap values obtained in calculations with 6-311+G(d,p) base set and 6-31++G(d,p) basis set are almost close to each other. In the calculations carried out with 6-311++G(d,p) base set in the gas phase, the HOMO-LUMO energy difference of the carbazochrome molecule was found to decrease 1.99% according to the calculations made with 6-311G(d, p) basis set in the gas phase. The HOMO-LUMO energy difference obtained from the calculations using the 6-311++G(2d,2p) base set is 0.34 more than the HOMO-LUMO energy difference obtained in the calculations with the 6-311++G(3df,3pd) basis set.

The global chemical reactivity descriptors of compounds such as electronegativity (χ), chemical potential (μ), hardness (η), softness (σ) and electrophilicity index (ω) were calculated from the HOMO and LUMO energy values as the following Parr et al. proposed the electrophilicity index (ω) as a measure of the energy drop due to the maximum electron flow between the donor and the receiver[16-18].

One of the important quantum chemical descriptors that define the toxicity and biological activities of molecules is the electrophilicity index[19, 20].

maxamount of electronic charge transfer (ΔN), which

$$\mu = -\chi \cong \left(\frac{E_{HOMO} + E_{LUMO}}{2}\right) \qquad (1)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \qquad (2)$$

$$\sigma = \frac{\eta}{2} \qquad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \qquad (4)$$

$$\Delta E_n = \pm \frac{(\mu + \eta)^2}{2\eta} \qquad (5)$$

$$\Delta E_e = \frac{(\mu - \eta)^2}{2\eta} \qquad (6)$$

$$\Delta N_{ideal} = -\frac{\mu}{\eta} \qquad (7)$$

The parameters computed related with the HOMO and LUMO energies are given in Table-8. To propose an electrophilicity index, Parr vd, (1999) assumed a sea of free electron gas at zero temperature and zero chemical potential [13].

Hard molecules resist changes in their electron number and distribution. MO theory is useful in the application of chemical hardness in one further way.

In calculations with 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis set, the hardness values of the carbazochrome molecule are 1.817, 1.781, 1.781, 1.784, 1.790 in gas phase, 1.674, 1.622, 1.622, 1.626, 1.635, in ethanol solvent, 1.671, 1.619, 1.618, 1.623, 1.631. in DMF solvent, 1.670, 1.617, 1.617, 1.621, 1.630 in DMSO solvent and 1.668, 1.615, 1.615, 1.620, 1.628 in water.

In calculations 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis set, the global hardness value of the carbazochrome molecule is 1.98%, 1.98%, 1.82%, 1.49% less in gas phase, 3.11%, 3.11%, 2.87%, 2.33% less in ethanol solvent, 3.11%, 3.11%, 2.87%, 2.33% less in DMF solvent, 3.11%, 3.17%,% 2.87, 2.39% less in DMSO solvent , 3.18%, 3.18%, 2.88%, 2.40% less in water solvent than calculations with 6-311G(d, p) basis set.

Table-8: HOMO, LUMO energy, HOMO-LUMO energy gap, hardness (η), softness(σ) electronegativity (χ), maximum amount of electronic charge transfer(ΔN_{max}).

BasisSet	E_{HOMO}(eV)	E_{LUMO}(eV)	ΔE(eV)	η(eV)	σ(eV^{-1})	χ(eV)	ΔN_{max}
6-311			**Gas**				
G(d,p)	-5.688	-2.054	3.634	1.817	0.275	3.871	2.131
+G(d,p)	-5.893	-2.331	3.562	1.781	0.281	4.112	2.309
++G(d,p)	-5.893	-2.331	3.561	1.781	0.281	4.112	2.309
++G(2d,2p)	-5.877	-2.309	3.568	1.784	0.280	4.093	2.294
++G(3df,3pd)	-5.877	-2.297	3.580	1.790	0.279	4.087	2.283
			Ethanol				
G(d,p)	-5.707	-2.359	3.348	1.674	0.299	4.033	2.409
+G(d,p)	-5.888	-2.643	3.244	1.622	0.308	4.266	2.629
++G(d,p)	-5.887	-2.643	3.244	1.622	0.308	4.265	2.629
++G(2d,2p)	-5.854	-2.601	3.253	1.626	0.307	4.227	2.599
++G(3df,3pd)	-5.861	-2.591	3.269	1.635	0.306	4.226	2.585
			DMF				
G(d,p)	-5.708	-2.366	3.342	1.671	0.299	4.037	2.416
+G(d,p)	-5.889	-2.651	3.238	1.619	0.309	4.270	2.638
++G(d,p)	-5.886	-2.651	3.235	1.618	0.309	4.268	2.639
++G(2d,2p)	-5.855	-2.609	3.246	1.623	0.308	4.232	2.608
++G(3df,3pd)	-5.862	-2.599	3.263	1.631	0.306	4.230	2.593
			DMSO				
G(d,p)	-5.709	-2.369	3.339	1.670	0.299	4.039	2.419
+G(d,p)	-5.889	-2.655	3.235	1.617	0.309	4.272	2.641
++G(d,p)	-5.888	-2.654	3.234	1.617	0.309	4.271	2.642
++G(2d,2p)	-5.855	-2.613	3.243	1.621	0.308	4.234	2.611
++G(3df,3pd)	-5.862	-2.602	3.260	1.630	0.307	4.232	2.596
			Water				
G(d,p)	-5.710	-2.373	3.336	1.668	0.300	4.041	2.423
+G(d,p)	-5.890	-2.659	3.231	1.615	0.310	4.275	2.646
++G(d,p)	-5.889	-2.659	3.230	1.615	0.310	4.274	2.646
++G(2d,2p)	-5.856	-2.617	3.239	1.620	0.309	4.236	2.616
++G(3df,3pd)	-5.863	-2.607	3.256	1.628	0.307	4.235	2.601

Table-9: Chemical potential (μ),and electrophilicity index (ω).

Basis Set	μ(eV)	ω(eV)	ΔEₙ(eV)	ΔEₑ(eV)	Molarvolume cm³/mol	SEZPE
6-311			**Gas**			
G(d,p)	-3.871	4.124	1.162	8.904	178.0	-832.917417
+G(d,p)	-4.112	4.746	1.525	9.748	149.9	-832.944767
++G(d,p)	-4.112	4.748	1.526	9.750	164.9	-832.945268
++G(2d,2p)	-4.093	4.695	1.494	9.680	147.5	-832.945468
++G(3df,3pd)	-4.087	4.666	1.474	9.647	184.9	-832.945794
			Ethanol			
G(d,p)	-4.033	4.858	1.662	9.728	166.3	-832.944767
+G(d,p)	-4.266	5.608	2.154	10.685	160.7	-832.972613
++G(d,p)	-4.265	5.606	2.152	10.682	170.1	-832.972907
++G(2d,2p)	-4.227	5.494	2.080	10.535	186.8	-832.997922
++G(3df,3pd)	-4.226	5.462	2.053	10.505	194.1	-833.032115
			DMF			
G(d,p)	-4.037	4.877	1.675	9.750	170.0	832.945268
+G(d,p)	-4.270	5.632	2.171	10.711	158.8	-832.973206
++G(d,p)	-4.268	5.631	2.172	10.708	153.2	-832.973488
++G(2d,2p)	-4.232	5.518	2.097	10.561	184.9	-832.998486
++G(3df,3pd)	-4.230	5.485	2.070	10.531	179.2	-833.032673
			DMSO			
G(d,p)	-4.039	4.885	1.681	9.759	183.1	-832.945268
+G(d,p)	-4.272	5.642	2.179	10.723	168.2	-832.973206
++G(d,p)	-4.271	5.641	2.178	10.721	155.1	-832.973488
++G(2d,2p)	-4.234	5.528	2.105	10.573	194.2	-832.998486
++G(3df,3pd)	-4.232	5.493	2.076	10.540	177.3	-833.032673
			Water			
G(d,p)	-4.041	4.896	1.688	9.771	175.7	-832.945794
+G(d,p)	-4.275	5.655	2.189	10.738	170.0	-832.973817
++G(d,p)	-4.274	5.654	2.188	10.735	166.3	-832.974102
++G(2d,2p)	-4.236	5.540	2.114	10.586	186.7	-832.999077
++G(3df,3pd)	-4.235	5.507	2.087	10.556	166.1	-833.033255

According to the calculations made in gas phase with 6-311G(d,p) basis set, the hardness value of the carbazochrome molecule is 1.817, 1.674, 1.671, 1.670, 1.668 in ethanol, DMF and DMSO and water solvents, respectively. The solvents are seen to further augment the decrease in the optical gap by stabilizing the frontier orbitals (HOMO and LUMO) [21].

When an electrophilic system (atom, molecule or ion) is immersed in the sea, there will be amount ΔN flow of electrons from the sea to the system until the chemical potential of the system is zero [22]. As can be seen from the definition, this index measures the propensity of chemical species to accept electrons. A good reactive nucleophile is characterized by a lower value of μ; and conversely a good electrophile is characterized by a high value of μ. In gas phase calculations with 6-311 base sets, the chemical potential value of the carbazochrome molecule is -3.871, -4.033, -4.033, -4.039, -4.041 in ethanol, DMF, DMSO and water solvents, respectively.

Ongoing from non-polar to polar solvent the chemical potential, were increased regardless of the, basis sets used. In calculations with 6-311G(d, p), the chemical potential in ethanol solvent was 0.11% more than in DMF solvent; It is 0.04% more in DMSO solvent than in DMF solvent, and 0.06% more in water solvent than DMSO solvent. In calculations with 6-311+G(d, p), the chemical potential in ethanol solvent

0.11% more than DMF solvent; It is 0.05% more in DMSO solvent than DMF solvent, and 0.06% more in water solvent than DMSO solvent. In the calculations of the studied base sets, it is seen that the solvent system used has no significant effect on the chemical potential value.

Parr et al. (1999) have defined a new descriptor to quantity the global electrophilic power of the compound as electrophilicity index (ω), which defines a quantitative classification of global electrophilic nature of a compound. Parr et al. have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor [16]. The quantity defined in equation electrophilicity describes the charge capacity of the molecule. The electrophilicity index has been used as structural depictor for the analysis of the chemical reactivity of molecules [23-25]. Electrophilicity index measures the tendency of a species to accept electrons. A good, more reactive nucleophile is characterized by a lower value, while a good electrophile is characterized by a high (ω) value. The effect of solvents on electrophilicity index of carbazochrome molecule shown in Table-9. In the calculations carried out with the 6-311G(d,p) basis set the electrophilicity indices of the carbazochrome molecule, in gas phase, ethanol, DMF, DMSO and water solution are 4.124, 4.858, 4.877, 4.885, 4.896, respectively. In the calculations made in ethanol,

DMF, DMSO and water phase instead of gas phase, the increase in electrophilicity indices was 17.70%, 18.25%, 18.44%, and 18.70%, respectively.

In calculations 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis set, the electrofugality values of the carbazochrome molecule is 115.07%, 15.11%, 13.83%, 13.12% more in the gas phase 15.44%, 15.40%, 13.10%, 12.43% in the ethanol solvent, 15.47 %, 15.46%, 13.13%, 12.46 % more in DMF solvent, 3% 15.50, % 15.47, % 13.16, % 12.44 more in DMF solvent 15.51 %, 15.49 %, 13.16 %, 12.49 % more in water solvent than calculations with 6-311G(d, p) basis set.

The charge transfer of electrons is given by ΔN_{max} or ΔN_{ideal} value: The maximum amount of electronic charge that an electrophile system can accept is given by equation 7. Hence, Equation(7) explains the system's tendency to take additional electronic charge from the environment; The amount of electrophilicity defines the charge capacity of the molecule [25].

In the calculations carried out with the 6-311G(d, p) base set of the carbazochrome molecule, the N_{max} indices in ethanol, DMF, DMSO and water in the gas phase are respectively 2.131, 2.409, 2.416, 2.419, 2.423. In the calculations made in ethanol, DMF, DMSO and water phase instead of gas phase, the increase in electrophilicity indices was 13.07%, 13.39%, 13.53%, and 13.71%, respectively.

The correlation coefficient (R^2) between ΔN_{max} values of the carbazochrome molecule obtained in calculations with the 6-311G(d, p) basis set and in calculations with 66-311+g(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis set is 1.

Ayers and co-workers [26, 27] have proposed nucleofugality (ΔE_n) and electrofugality (ΔE_e) indices to quantify nucleophilic and electrophilic capabilities of a leaving group.

In calculations with 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets, the nucleofugalitelity values of the carbazochrome molecule are respectively 1.162, 1.525, 1.526, 1.494, 1.474 in gas phase, 1.662,

2.154, 2.152, 2.080, 2.053 in ethanol solvent, 1.675, 2.171, 2.172, 2.097, 2.070, 1.681, 2.178 in DMSO solvent. 2.105, 2.076, in the water phase 1.688, 2.189, 2.188, 2.114, 2.087. In the gas phase and solvent phases, the nucleofugality values were found to be the lowest in the calculations carried out with the 6-311G(d, p) basis set.

In calculations with 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) according to the calculations with 6-311G(d, p) basis set, the nucleofugality values of the carbazochrome molecule increased by 31.29%, 31.37%, 28.64%, 26.89%, respectively, in gas phase, 29.57%, 29.51%, 25.16%, 23.55% in ethanol solvent, 29.58%, 29.63%, 25.18%, 23.57% in DMF solvent, 29.61%, 29.59%, 25.21%, 23.51%,in DMSO solvent, 29.62%, 29.59%, 25.19%, 23.58% increase in water solvent.

Dipole moment of the carbazochrome molecule calculated with B3LYP functional and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis set in the gas phase and solvent phases [ethanol (ε= 21.01), DMF (ε= 36.71), DMSO (ε= 46.68), water (ε= 78.39)] are given in Fig 4. Magnitude of the total static dipole moment (μ) using the x, y and z components can be calculated by the following equations

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \qquad (8)$$

Dipole moment (μ),of the carbazochromeme value calculated at B3LYP/6-311G(d,p), level of theory are 6.35 D in gas phase, 16.41 D in ethanol solvent, 16.74D in DMSO solvent, 16.92D in DMF solvent, 17.06 D in water. As can be seen, the dipole moment of the carbazochrome molecule increaseswhen passing from polar solvents to highly polar solvents. The dipole moment of the carbazochrome molecule in different solvents was higher than in the gas phase. The dipole moment gradually increased as it shifted from low dielectric constant to high dielectric constant, ie the dipole moment increases with increasing polarity of the solvent. Since the polarity of the solvent increases the delocalization of the charge in the molecule, it causes an increase in the dipole moment of the carbazochrome molecule in the solvent phase [28, 29].
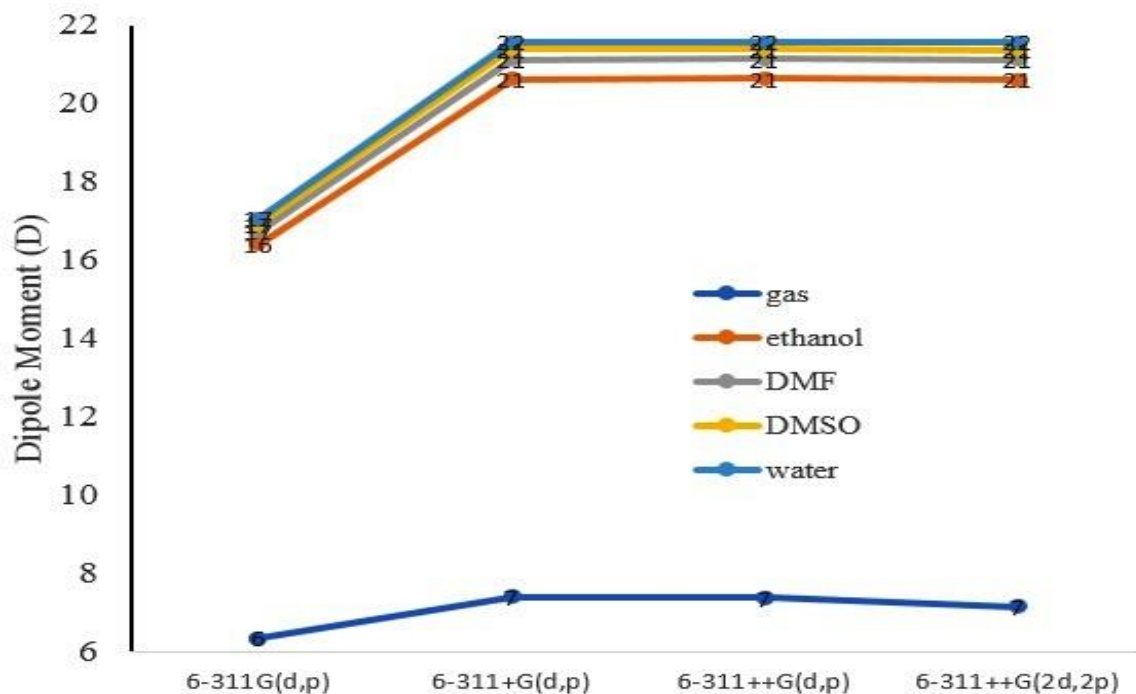
Fig. 4:   Dipol Moment for carbazochrome.

polarizability ($<\alpha>$) anisotropy polarisibility and the first hyperpolarizability of the carbazochrome molecule calculated with B3LYP functional and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis set in the gas phase and solvent phases [ethanol (ε= 21.01), DMF (ε= 36.71), DMSO (ε= 46.68), water (ε= 78.39)] are given in Fig 5-7. Magnitude of the polarizability ($<\alpha>$) anisotropy polarisibility and the first hyperpolarizability using the x, y and z components can be calculated by the following equations.

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (9)$$

$$\Delta\alpha = \left[\frac{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2+6(\alpha_{xz}^2+\alpha_{xy}^2+\alpha_{yz}^2)}{2}\right]^{1/2}$$
$$(10)$$

Since the values of the polarizability α of Gaussian 09 output are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) (α: 1 a.u. = 0.1482x10^{-24}esu;).

For polarizability, 6-311++G(3df,3pd)basis set gives higher values (29.10^{-24}esu in gas phase)

compared to those calculated using 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), basis sets (26.18x10^{-24}, 28.69x10^{-24}, 28.76x10^{-24}, 29.19x10^{-24}esu, respectively in gas phase). Polarizability values calculated with B3LYP/6-311+G(d,p) level in gas phase, ethanol solution, DMF solution, DMSO solution and water are   26.18x10^{-24}, 37.46x10^{-24}, 37.73x10^{-24}, 37.84x10^{-24}, 37.99x10^{-24}esu. As seen from the gas phase to the solvent phase, polarizability values increases. The hardness and softness concepts of atoms and molecules are closely related to their polarizability and size. Softness and polarizability are related, so a soft type is more easily polarized. Therefore, a soft species has high polarizability [30]. When going from gas phase to solvent phase There was an increase in softness value (0.275 in gas phase, 0.299 in ethanol solution) and polarizability value (26.18x10^{-24}esu in gas phase, 37.46x10^{-24}esu.

The results calculated at the B3LYP level and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), basis sets are depicted in Fig. 5. As seen from the gas phase to the solvent phase, anisotropic polarizability values increases at all studied basis sets.
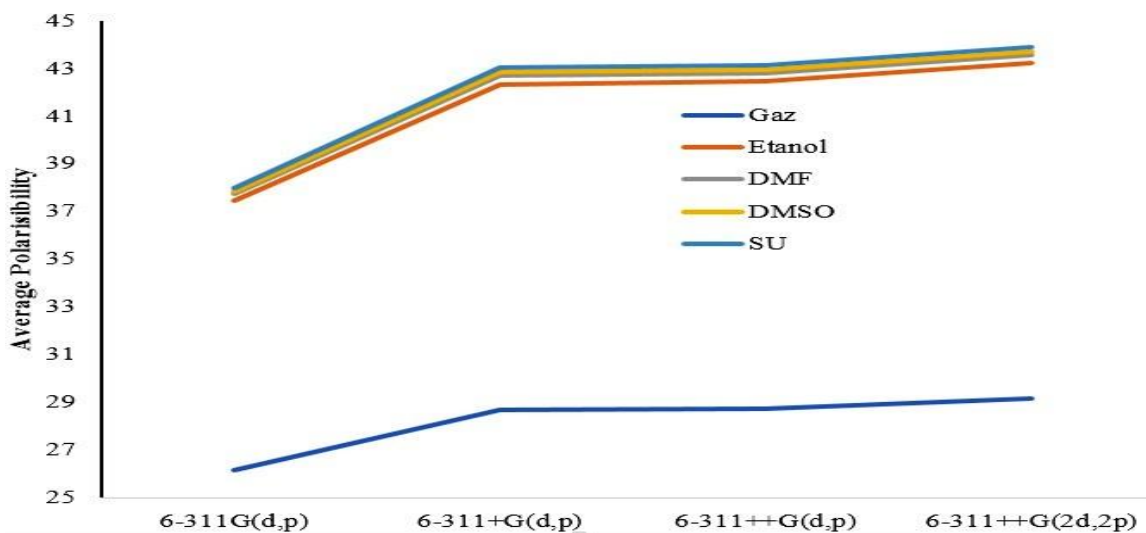
Fig. 5:   Average Polarizability for Carbazochrome.
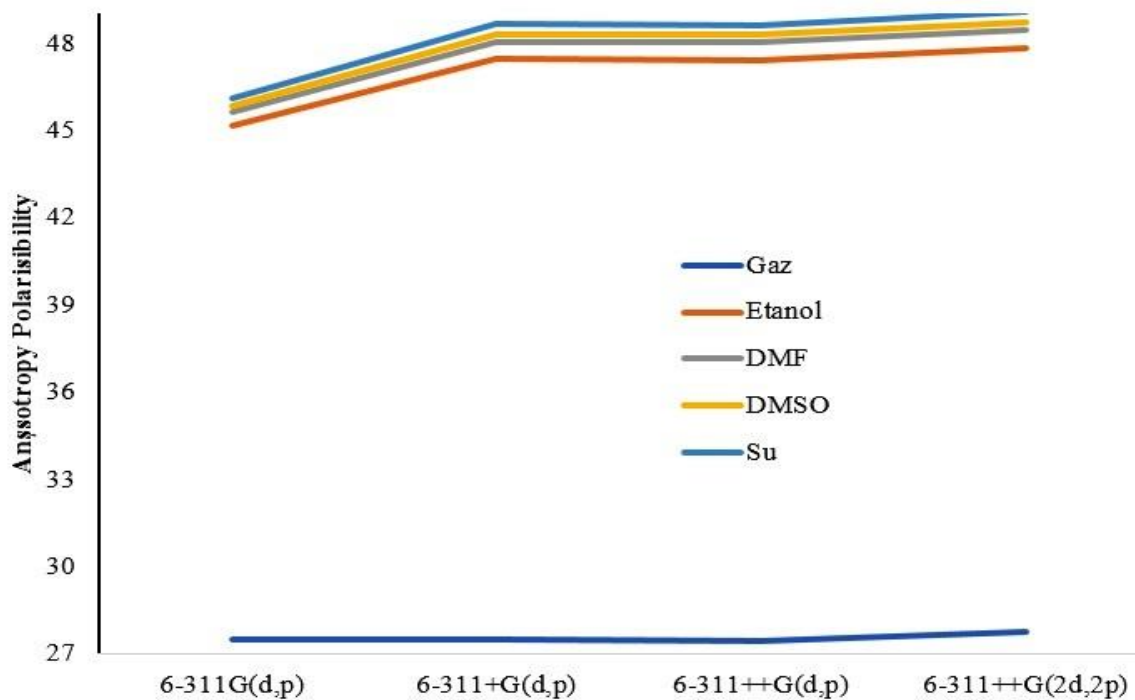
Fig. 6   Anisotropy Polarizability for carbazochrome.

The magnitude of the total first hyperpolarizability from GAUSSIAN 09W output is given by the following Equation.

$$\beta = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \qquad (11)$$

$$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2} \qquad (12)$$

Maximum total hyperpolarizability β_{tot} for carbazochrome molecule are obtained, as 30.00, 29.38, 29.38, 29.17x10^{-30}esu, respectively using 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p) basis set in gas phase, as 85.77, 109.12, 108.44, 106.67x10^{-30}esu in etanol phase, 87.60, 111.63, 110.93, 109.07x10^{-30}esu in DMF phase, 88.26, 112.53, 111.81, 109.91x10^{-30}esu in DMSO, 91.34, 114.41, 113.70, 111.76x10^{-30}esu in water phase (Fig 7)

In calculations with 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), according to the calculations with 6-311G(d, p) basis set, the hyperpolarizability values of the carbazochrome molecule decreased by 2.05%, 2.05%, 2.76%, respectively, in gas phase, increased 27.23%, 26.43%, 24.37%, in ethanol solvent, 27.44%, 26.63%, 24.51%, in DMF solvent, 27.49%, 26.69%, 24.53%, in DMSO solvent and 25.27%, 24.48%, 22.36%, increase in water solvent.

In the calculations performed with ethanol, DMF, DMSO and water phase instead of gas phase by using the .6-311G(d, p) base set, the increase in the hyperpolarity indices of the carbazochrome molecule was 185.91%, 192.02%, 194.22%, 204.48%, respectively.

UV-visible spectrum values (nm) of the carbazochrome molecule calculated using TDB3LYP level and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets, and excitation energies (eV) and oscillation forces (f) at these levels. All transitions of the molecules on the TDB3LYP band gap and all values of oscillation forces above 0.08 are given. In Table-10 for gas phase and solvent phase (ethanol, DMF, DMSO, water).

Carbazochrome molecules have conjugated π bonds and free electron pairs which are donated as n. This compound show $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The absorption maxima of these was found to be 355 nm for carbazochromemolecule [11].
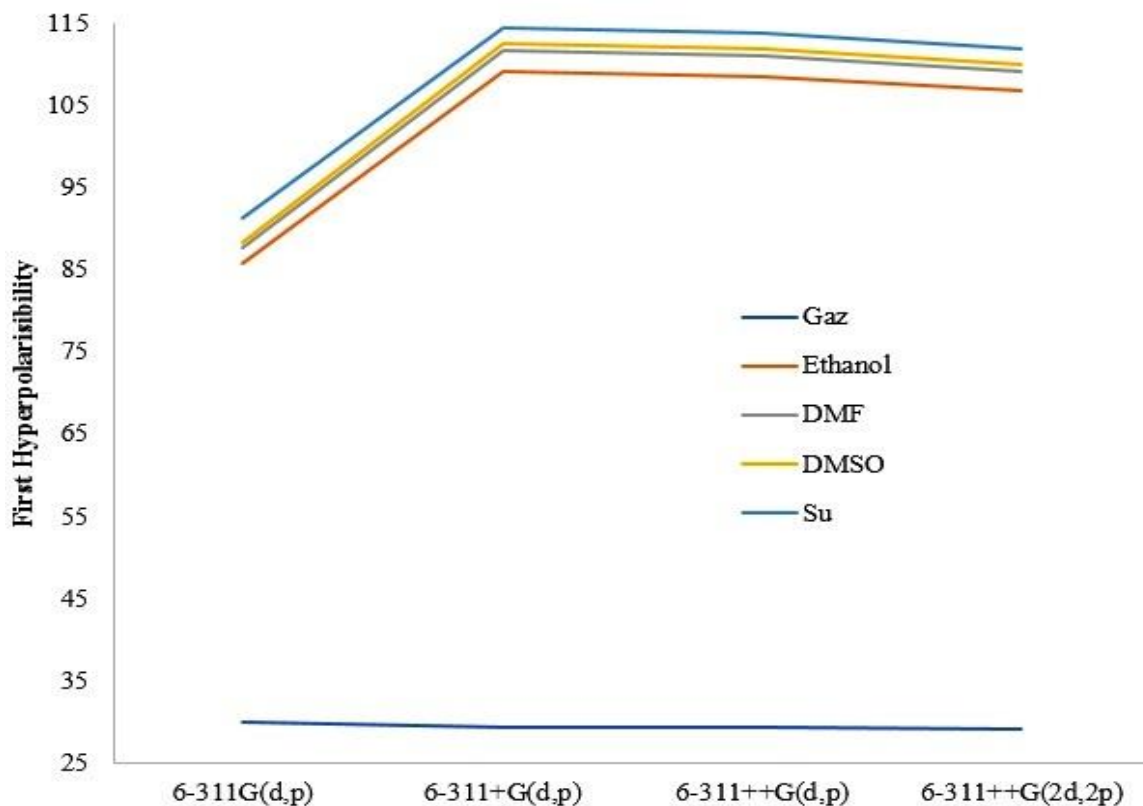

Fig. 7:   First Hyperpolarizability for carbazole.

Table-10: UV-visible spectrum values (nm) for the carbazochrome molecule in the gas phase, calculated using the TDB3LYP level and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets.

Basissets	Absorbance Wavelength nm	Excitation Energies eV	Oscillator strength	Excited State	Transition	Major contributions
6-311G(d,p)	349.71	3.54	0.63	2	HOMO→LUMO	97.62
	267.07	4.64	0.10	7	HOMO-2 → LUMO	10.20
					HOMO-2 →LUMO+2	2.14
					HOMO →LUMO+1	83.82
6-311+G(d,p)	359.68	3.45	0.64	2	HOMO→LUMO	97.59
	274.96	4.51	0.10	7	HOMO-2 → LUMO	10.37
					HOMO →LUMO+1	84.31
6-311++G(d,p)	359.85	3.44	0.64	2	HOMO→LUMO	97.55
	275.79	4.50	0.10	7	HOMO-2 →LUMO	9.96
					HOMO →LUMO+1	84.12
6-311++G(2d,2p)	359.76	3.45	0.64	2	HOMO→LUMO	97.47
	275.79	4.50	0.09	7	HOMO-2 →LUMO	9.52
					HOMO-1→LUMO+1	3.08
					HOMO →LUMO+1	81.83
6-311 ++G(3df,3pd)	358.77	3.46	0.64	2	HOMO→LUMO	97.49
	275.48	4.50	0.09	7	HOMO-2 →LUMO	9.89
					HOMO→LUMO+1	84.56

Table-11: UV-visible spectrum values (nm) for the carbazochrome molecule in the ethanol solution calculated using the TDB3LYP level and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets.

Basissets	Absorbance Wavelength nm	Excitation Energies eV	Oscillator strength f	Excited State	Transition	Major contributions
6-311G(d,p)	381.00	3.25	0.87	2	HOMO→LUMO	99.92
	273.14	4.54	0.10	5	HOMO-2→LUMO	3.02
					HOMO-2→LUMO+2	2.02
					HOMO→LUMO+1	91.99
6-311+G(d,p)	395.91	3.13	0.89	2	HOMO→LUMO	99.73
	280.32	4.42	0.09	5	HOMO-2→LUMO	2.32
					HOMO→LUMO+1	94.50
6-311++G(d,p)	396.04	3.13	0.89	2	HOMO→LUMO	99.72
	280.69	4.42	0.10	5	HOMO-2→LUMO	2.31
					HOMO→LUMO+1	94.56
6-311++G(2d,2p)	395.55	3.13	0.64	2	HOMO→LUMO	99.66
	281.15	4.41	0.09	5	HOMO-2→LUMO	2.38
					HOMO→LUMO+1	99.51
6-311++G(3df,3pd)	394.15	3.14	0.90	2	HOMO→LUMO	99.62
	280.22	4.42	0.09	5	HOMO-2→LUMO	2.40
					HOMO→LUMO+1	94.50

The bands assigned at 349.71, 359.68, 359.85, 359.76, 358.77 nm, respectively with the calculation TDB3LYP/6-311G(d,p), TDB3LYP/6-311+G(d,p), TDB3LYP/6-311++G(d,p), TDB3LYP/6-311++G(2d,2p), TDB3LYP/6-311++G(3df,3pd) in gas phase are due to transitions mainly from HOMO to LUMO and the contributions of these migrations are 97.62%, 97.59%, 97.55%, 97.47%, 97.49%, respectively. The bands assigned at 267.07, 267.07, 274.96, 275.79, 275.79,275.48 nm, respectively with the calculation TDB3LYP/6-311G(d,p), TDB3LYP/6-311+G(d,p), TDB3LYP/6-311++G(d,p), TDB3LYP/6-311++G(2d,2p), TDB3LYP/6-311++G(3df,3pd) in gas phase are due to transitions mainly from HOMO-2→LUMO and HOMO→LUMO+1. The contribution of HOMO-2→LUMO transition is 10.20%, 10.37%, 9.96%, 9.52%, 9.89%, respectively. The contribution of HOMO→LUMO+1 transition consists of 83.82, 84.31, 84.12, 81.83, 84.56, respectively.

The bands assigned at 349.71 nm in gas phase with the calculation TDB3LYP/6-311G(d,p), due to transitions mainly from HOMO to LUMO shifted to 381.00 nm, 383.57, 383.32, 380.78 nm respectively in ethanol, DMF, DMSO, water and the band assigned at 267.07 nm in gas phase with the calculation TDB3LYP/6-311G(d,p), due to transitions mainly from HOMO-2→LUMO and HOMO→LUMO+1shifted to 273.14, 273.39, 273.35, 273.09 nm respectively in ethanol, DMF, DMSO, water.

Table-12: UV-visible spectrum values (nm) for the carbazochrome molecule in the DMF solution calculated using the TDB3LYP level and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets.

Basissets	Absorbance Wavelength nm	Excitation Energies eV	Oscillator strengt f	Excited State	Transition	Majorcontributions
6-311G (d,p)	383.57	3.23	0.79	2	HOMO→LUMO	99.94
	273.39	4.54	0.11	6	HOMO-3→LUMO	2.53
					HOMO-2→LUMO	2.85
					HOMO→LUMO+1	90.86
6-311+G (d,p)	398.88	3.11	0.91	2	HOMO→LUMO	99.73
	280.55	4.42	0.09	5	HOMO-2→LUMO	2.19
					HOMO→LUMO+1	94.76
6-311++G (d,p)	398.99	3.11	0.91	2	HOMO→LUMO	99.72
	280.90	4.41	0.09	5	HOMO-2→LUMO	2.31
					HOMO→LUMO+1	94.56
6-311++G (2d,2p)	398.48	3.11	0.92	2	HOMO→LUMO	99.62
	281.37	4.41	0.09	5	HOMO-2→LUMO	2.26
					HOMO→LUMO+1	94.73
6-311 ++G (3df,3pd)	397.05	3.12	0.92	2	HOMO→LUMO	99.63
	280.42	4.42	0.09	5	HOMO-2→LUMO	2.40
					HOMO→LUMO+1	94.50

Table-13: UV-visible spectrum values (nm) for the carbazochrome molecule in DMSO solution calculated using the TDB3LYP level and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets

Basissets	Absorbance Wavelength nm	Excitation Energies eV	Oscillator strengt f	Excited State	Transition	Majorcontributions
6-311G(d,p)	383.32	3.23	0.88	2	HOMO→LUMO	99.56
	273.35	4.54	0.09	5	HOMO-3→LUMO	2.27
					HOMO-2→LUMO	2.83
					HOMO→LUMO+1	91.11
6-311+G(d,p)	398.61	3.11	0.91	2	HOMO→LUMO	99.75
	280.50	4.42	0.09	5	HOMO-2→LUMO	2.18
					HOMO→LUMO+1	94.80
6-311++G(d,p)	398.72	3.11	0.91	2	99.73	100
	280.86	4.4	0.09	5	HOMO-2→LUMO	2.15
					HOMO→LUMO+1	94.81
6-311++G(2d,2p)	398.21	3.11	0.92	2	HOMO→LUMO	99.69
	281.32	4.41	0.09	5	HOMO-2→LUMO	2.21
					HOMO→LUMO+1	94.76
6-311 ++G(3df,3pd)	396.77	3.12	0.92	2	HOMO→LUMO	99.64
	280.39	4.42	0.09	5	HOMO-2→LUMO	2.24
					HOMO→LUMO+1	94.74

Table-14: UV-visible spectrum values (nm) for the carbazochrome molecule in water calculated using the TDB3LYP level and 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets.

Basissets	Absorbance Wavelength nm	Excitation Energies eV	Oscillator strengt f	Excited State	Transition	Major contributions
6-311G(d,p)	380.78	3.26	0.66	2	HOMO→LUMO	99.72
	273.09	4.54	0.11	6	HOMO-3→LUMO	48.86
					HOMO→LUMO+1	46.50
6-311+G(d,p)	395.75	3.13	0.89	2	HOMO→LUMO	99.78
	280.25	4.42	0.09	5	HOMO-2→LUMO	2.17
					HOMO→LUMO+1	94.64
6-311++G(d,p)	395.86	3.13	0.89	2	HOMO→LUMO	99.77
	280.60	4.42	0.09	5	HOMO-2→LUMO	2.16
					HOMO→LUMO+1	94.69
6-311++G(2d,2p)	395.36	3.14	0.90	2	HOMO→LUMO	99.72
	281.07	4.41	0.09	5	HOMO-2→LUMO	2.22
					HOMO→LUMO+1	94.64
6-311 ++G(3df,3pd)	393.98	3.15	0.90	2	HOMO→LUMO	99.67
	280.12	4.43	0.09	5	HOMO-2→LUMO	2.24
					HOMO→LUMO+1	94.63

Thermodynamic Properties

On the basis of vibrational analyses and statistical thermodynamics, the standard thermodynamic functions of the carbazochrome molecule: heat capacity ($C_{p,m}^o$),entropy ($S_{p,m}^o$),enthalpy ($H_{p,m}^o$) and Gibbs free energy (G) are obtained with B3LYP/6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) in gas phase and with B3LYP/6-311G(d,p) in water phase and listed in Tables 15-17. The scale factor for frequencies is taken as 0.96, which is utilized for a precise prediction for the determination of thermodynamic functions, in gas phase and water.

As can be seen from Table 15-17, all values of ($C_{p,m}^o$), ($S_{p,m}^o$), ($H_{p,m}^o$) and (G),depend on temperature and increase with increasing temperature (from 200.0 to 1000.0 K), which is attributed to the increase of molecular vibration as the temperature increases, because a constant pressure (dp = 1atm) $C^o_{p,m}$, $S^o_{p,m}$ and $H^o_{p,m}$ values change with temperature [31].

These equations can be used for further study on the carbazochrome molecule. For example, when investigating the interaction or reaction between the carbazochrome molecule and another compound, thermodynamic properties can be obtained from these equations and then used to calculate the change of Gibbs free energy, enthalpy energy change, entropy change. It will help us judge whether the reaction will be spontaneous or not.

The graph between the mentioned thermodynamic properties and the temperatures T calculated at the B3LYP/6-311+G(d,p) levelin water is shown in Fig 9 and the correlation coefficients between temperature and thermodynamic parameters obtained with 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets are shown in Table 18. Correlation equations calculated at the B3LYP/6-311+G(d,p) level in gas phase are as follows:

$C = -9E\text{-}05T^2 + 0,2142T + 5,9068$ ($R^2 = 0,9997$)

$S = -6E\text{-}05T^2 + 0,247T + 63,458$ ($R^2 = 1.000$)

$H = 5E\text{-}05T^2 + 0,0386T - 4,8421$ ($R^2 = 0,9998$)

$G = -9E\text{-}05T^2 - 0,0836T + 4,2268$ ($R^2 = 1,0000$)

Table-15: Thermodynamic properties at different temperatures at B3LYP/6-311G(d,p) level in gas phase and water phase

T	C	S	H	G	C	S	H	G
		Gasphase(6-311G(d,p))				Waterphase(6-311G(d,p))		
200	44.874	110.01	5.609	-16.3924	44.614	108.690	5.524	-16.214
250	53.269	121.368	8.163	-22.1793	53.150	120.008	8.068	-21.934
300	61.552	132.177	11.133	-28.5203	61.545	130.805	11.035	-28.207
350	69.564	142.578	14.512	-35.3903	69.648	141.212	14.416	-35.008
400	77.119	152.631	18.281	-42.7723	77.270	151.282	18.191	-42.322
450	84.088	162.357	22.413	-50.6482	84.287	161.028	22.332	-50.131
500	90.426	171.76	26.878	-59.0023	90.654	170.453	26.807	-58.419
550	96.143	180.84	31.643	-67.8188	96.386	179.556	31.585	-67.171
600	101.285	189.603	36.681	-77.0814	101.531	188.341	36.635	-76.370
650	105.911	198.055	41.962	-86.774	106.153	196.812	41.928	-86.000
700	110.083	206.207	47.463	-96.8819	110.317	204.981	47.441	-96.046
750	113.859	214.07	53.163	-107.39	114.080	212.860	53.152	-106.493
800	117.289	221.658	59.042	-118.284	117.497	220.461	59.042	-117.327
850	120.416	228.984	65.085	-129.551	120.610	227.800	65.095	-128.535
900	123.277	236.062	71.278	-141.178	123.456	234.888	71.298	-140.102
950	125.902	242.906	77.608	-153.154	126.068	241.742	77.636	-152.020
1000	128.317	249.529	84.063	-165.466	128.470	248.373	84.100	-164.274

Table-16: Thermodynamic properties at different temperatures at B3LYP/6-311+G(d,p), B3LYP/6-311++G(d,p) levels in gas phase.

T	C	S	H	G	C	S	H	G
		(6-311+G(d,p))				(6-311++G(d,p))		
200	45.185	110.826	5.647	-16.518	45.146	111.184	5.609	-16.392
250	53.570	122.258	8.215	-22.349	53.487	122.599	5.609	-16.392
300	61.841	133.117	11.201	-28.734	61.740	133.445	5.609	-16.392
350	69.843	143.562	14.594	-35.653	69.736	143.873	5.609	-16.392
400	77.387	153.652	18.377	-43.084	77.279	153.949	5.609	-16.392
450	84.344	163.409	22.521	-51.013	84.239	163.693	5.609	-16.392
500	90.668	172.838	26.999	-59.420	90.568	173.111	5.609	-16.392
550	96.370	181.941	31.777	-68.291	96.275	182.205	5.609	-16.392
600	101.496	190.722	36.825	-77.609	101.406	190.979	5.609	-16.392
650	106.107	199.191	42.117	-87.358	106.021	199.440	5.609	-16.392
700	110.265	207.356	47.627	-97.523	110.183	207.599	5.609	-16.392
750	114.027	215.231	53.335	-108.089	113.948	215.469	5.609	-16.392
800	117.444	222.829	59.223	-119.041	117.367	223.062	5.609	-16.392
850	120.559	230.164	65.274	-130.366	120.485	230.393	5.609	-16.392
900	123.409	237.251	71.473	-142.053	123.336	237.475	5.609	-16.392
950	126.025	244.133	77.807	-154.118	125.953	244.322	5.609	-16.392
1000	128.429	250.730	84.271	-166.460	128.361	250.947	5.609	-16.392

Table-17: Thermodynamic properties at different temperatures at B3LYP/6-311++G(2d,2p), B3LYP/6-311++G(3df,3pd) level in gas phase

T	C	S	H	G	C	S	H	G
	(6-311++G(2d,2p))				6-311++G(3df,3pd)			
200	45.196	110.827	5.651	-16.515	46.340	112.432	5.791	-16.695
250	53.577	122.258	8.219	-22.345	55.075	124.155	8.426	-22.612
300	61.847	133.122	11.205	-28.731	63.667	135.322	11.495	-29.101
350	69.849	143.567	14.598	-35.650	71.910	146.069	14.986	-36.138
400	77.392	153.656	18.381	-43.082	79.605	156.445	18.876	-43.702
450	84.349	163.414	22.526	-51.010	86.636	166.467	23.134	-51.776
500	90.672	172.844	27.004	-59.418	92.978	176.139	27.727	-60.343
550	96.374	181.948	31.782	-68.289	98.661	185.462	32.620	-69.384
600	101.500	190.724	36.830	-77.604				
650	106.111	199.193	42.122	-87.354	108.306	203.088	43.185	-88.823
700	110.269	207.366	47.633	-97.523	112.407	211.414	48.803	-99.187
750	114.030	215.240	53.341	-108.089	116.111	219.435	54.617	-109.959
800	117.447	222.837	59.229	-119.041				
850	120.562	230.173	65.280	-130.368	122.527	234.623	66.758	-132.671
900	123.412	237.262	71.480	-142.056	125.319	241.819	73.055	-144.583
950	126.026	244.111	77.816	-154.089				
1000	128.432	250.709	84.276	-166.433	130.228	255.494	86.037	-169.457

Table-18: Regression analysis.

		R²			R²
6-311G(d,p)-gas	C=-9E-05T²+0,2142T+5,9068	0,9997	6-311G(d,p) water	C=-9E-05T²+0,2168T+5,271	0,9997
	S=-6E-05T²+0,247T+63,458	1.000		H=-6E-05T²+0,2471T+62,055	1.000
	H=5E-05T²+0,0386T-4,8421	0,9998		S=5E-05T²+0,0386T-4.9546	0,9998
	G=-9E-05T²-0,0836T+4,2268	1.0000		G=-1E-04T²-0,0676T	0,9998
6-311+G(d,p)-gas	C=9E-05T²+0,214T+6,2746	0,9997	6-311+G(d,p)-gas	C=-9E-05T²+0,2138T+6,2359	0,9995
	H=-6E-05T²+0,2482T+64,088	1.000		H=-6E-05T²+0,2478T+64,51	1.000
	S=5E-05T²+0,039T-4,875	0,9998		S=5E-05T²+0,0388T-4,807	0,9997
	G=5E-05T²-0,0844T+4,2775	1.000		G=-9E-05T²-0,0848T+4,3243	1.000
6-311++G(2d,2p)	C=-9E-05T²+0,214T+6,2875		6-311++G(3df,3pd)	C=-1E-04T²+0,2208T+6,4659	0,9995
	H=-6E-05T²+0,2483T+64,066			H=-7E-05T²+0,2565T+64,14	1.000
	S=5E-05T²+0,039T-4,8725			S=5E-05T²+0,0404T-5,0398	0,9997
	G=-9E-05T²-0,0845T+4,3005			G=-9E-05T²-0,0853T+4,3618	1.000

In Fig 8 and 9, the enthalpy for both phases of carbazochrome molecule increases with the temperature at a constant rate outside the phase equilibrium, while the Gibbs energy decreases, as expected from the enthalpy expression H=G+TS.

Fig. 8:   The correlation graphs between various temperature versus Heat capacity, Entropy, Enthalpy and Gibbs free energy of the carbazochrome molecule for B3LYP/6-31G(d) levels in gas.
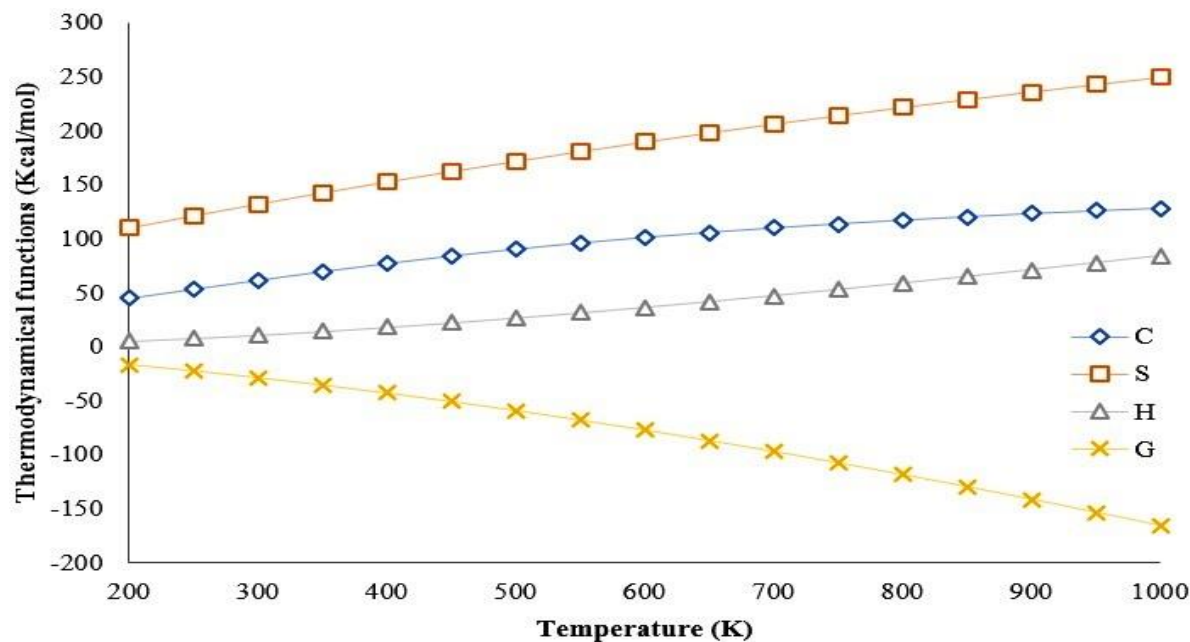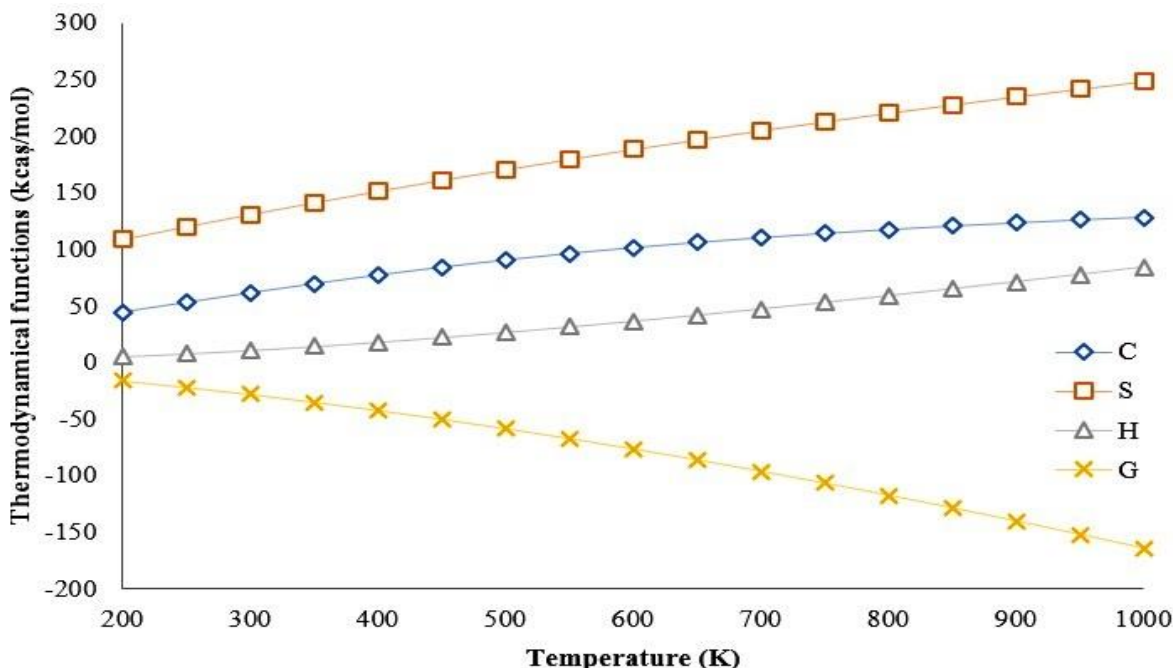
Fig. 9:   The correlation graphs between various temperature versus Heat capacity, Entropy, Enthalpy and Gibbs free energy of the carbazochrome molecule for B3LYP/6-31G(d) levels in water.

The regression values of the heat capacity, entropy, thermal entalphy and gibbs free energy at the B3LYP level with 6-311G(d,p) in gas phase and water are found as 0.9997, 1.0000, 0.9998, 1.0000. These equations given in Table-18 are used to estimate the values of the any thermodynamic parameters for any temperature. The regressions factors (R^2) of these observed relations of the thermodynamic functions versus temperature are all not less than 0.9997.

NBO Analysis

In order to understand the various quadratic interactions between the full orbit of a subsystem and the empty orbit of another subsystem, NBO calculations were carried out using the NBO 3.1 program [14] implemented at the DFT / B3LYP level in the Gaussian 09 package. The value of E (2) in NBO analysis shows the intense interaction between electron donors and electron acceptors. With the NBO method, it can improve the analysis of intramolecular and molecular interactions, as it provides information about the interactions of both filled and virtual orbital spaces. NBO Fock matrix element. For each donor (i) and recipient (j), the stabilization energy related delocalization is determined by the equation given below.

$$E_{(2)} = \Delta E_{ij} = q_i \frac{F_{ij}^2}{(E_j - E_i)} \qquad (13)$$

q_i: donor orbital occupancy, E_i, E_j: diagonal elements, F_{ij}: the off diagonal. The large E (2) value in NBO analysis shows the intense interaction between electron donors and electron acceptors and the extent of conjugation of the entire system. Possible intensive interference in the gas phase and solvent phases (ethanol, DMF, DMSO and water) for the carbazochrome molecule is given in Table-19.

The second order delocalization energies of $\sigma(O_2-H_{27}) \rightarrow \sigma*(C_{15}-C_{16})$ for the carbazocrome molecule are 4.86 kcalmol^{-1} at gas phase, 4.88 kcalmol^{-1} at ethanol, DMF and water, 4.87 kcalmol^{-1} at DMSO. The second order delocalization energies of $\pi(N_5-N_6) \rightarrow LP(1)C_{15}$ for the carbazochrome molecule at ethanol, DMF, DMSO and water are 17.28, 17.31, 17.34, 17.33 kcalmol^{-1}. However there is no interaction energy between $\pi(N_5-N_6)$ and $LP(1)C_{15}$ in gas phase. The interaction energies $\pi(C_{10}-C_{12}) \rightarrow \pi*(C_{11}-C_{13})$, $\pi(C_{10}-C_{12}) \rightarrow \pi*(C_{15}-C_{16})$, $\pi(C_{11}-C_{13}) \rightarrow \pi*(C_{10}-C_{12})$, $\pi(C_{15}-C_{16}) \rightarrow \pi*(C_{11}-C_{13})$ 22.64, 11.93, 11.71, 29.06, 4.88 kcalmol^{-1} at gas phase but, there is no interaction for them in solvent phase studied.

The calculated hybridization of the carbazochrome molecule by NBO analysis in gas and ethanol mediun with B3LYP functional and 6-311G(d, p) calculation is given in Table-20 and Table-21. According to the NBO interactions, $C_{10}-C_{12}$ bond in

gas phase is formed $\sigma(C_{10}-C_{12})$ which has the equation $0.7114C_{10}(sp^{1.62})+ 0.7028\ C_{12}(sp^{1.65})$ and $\pi(\ C_{10}-C_{12})$ which has the equation $0.7458\ C_{10}(p)+ 0.6662\ C_{12}(p)$. $\sigma(C_{10}-C_{12})$ NBO is formed from an $sp^{1.62}$ hybrid on carbon interacting with an $sp^{1.65}$ hybrid on C_{10}. $sp^{1.62}$ hybrid on C_{10} has 61.83 % p-character and 38.14% s-character. $sp^{1.65}$ hybrid on C_{12} has 62.23% p-character and 37.73% s-character. The polarization coefficients in the equation $\sigma(C_{10}-C_{12})$ were found as 0.7114 and 0.7028. $\pi(C_{10}-C_{12})$. NBO is formed from an p orbital on C_{10} interacting with an p orbital on C_{12}. Polarisation coefficient of C_{10} and C_{12} are 0.7458 and 0.6662.

According to the NBO interactions, $C_{10}-C_{12}$ bond in ethanol phase is formed $\sigma(C_{10}-C_{12})$ which has the equation $0.7106C_{10}(sp^{1.61})+ 0.7036C_{12}(sp^{1.63})$ and $\pi(C_{10}-C_{12})$ which has the equation $0.7405C_{10}(sp^{99.99})+ 0.6721C_{12}(p)$. $\sigma(C_{10}-C_{12})$ NBO is formed from an $sp^{1.61}$ hybrid on carbon interacting with an $sp^{1.63}$ hybrid on C_{10}. $sp^{1.61}$ hybrid on C_{10} has 61.62% p-character and 38.34% s-character. $sp^{1.63}$ hybrid on C_{12} has 62.01% p-character and 37.95% s-character. The polarization coefficients of C_{10} and C_{12} are 0.7106 and 0.7036.

$\pi(C_{10}-C_{12})$ NBO is formed from an p orbital on carbon 12 interacting with an p orbital on C_{12}. Polarisation coefficient of C_{10} and C_{12} are 0.7405and 0.6721.

$(C_{10}-C_{12})\rightarrow LP^*(1)C_{11}$ interactions energies in ethanol, DMF, DMSO and water solvents, respectively, and $C_{10}-C_{12}\rightarrow LP(1)C_{15}$ interaction energies are 45.53, 45.45, 45.40, 45.37, $C_{10}-C_{12}$ kcalmol^{-1}, respectively, but no interaction was observed in the solvent phase studied. In gas phase, stabilization energies of 27.82, 23.14, 12.87 kcalmol^{-1} are caused by $\pi(C_{15}-C_{16})\rightarrow\pi^*(\ N_5-N_6)$, $\pi(C_{15}-C_{16})\rightarrow\pi^*(\ C_{10}-C_{12})$, $\pi(C_{15}-C_{16})\rightarrow\pi^*(\ C_{11}-C_{13})$ interactions, but there are no interaction in solvent phases studied.

There is a stabilization energy of 121.81, 122.35, 122.62, 122.74 kcalmol^{-1} in ethanol, DMF, DMSO and water solvents from $LP(1)N_4\rightarrow LP^*(1)C_{11}$ interaction. However, $LP(1)N_4\rightarrow LP^*(1)C_{11}$ interaction was not observed in the gas phase. As can be seen, there are different interactions in the gas phase and solvent medium.

Table-19: Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at B3LYP level with 6-311G(d,p) basis set.

				Gas	Etanol	DMF	DMSO	Water
O_2-H_{27}	σ	C_{15}-C_{16}	σ*	4.86	4.88	4.88	4.87	4.88
N_4-C_9	σ	C_{11}-C_{13}	σ*	5.01	5.18		5.19	5.19
N_5-N_6	π	LP(1)C_{15}			17.28	17.31	17.34	17.33
N_5-N_6	π	O_3-C_{17}	π*	14.44	16.80	16.88	16.93	16.94
N_5-N_6	π	C_{15}-C_{16}	π*	9.25				
N_6-C_{17}	σ	N_5-C_{15}	σ*	6.30		5.79	5.77	5.77
C_8-C_9	σ	C_{10}-C_{12}	σ*	4.80	4.77	4.77	4.76	4.77
C_{10}-C_{11}	σ	N_4-C_{14}	σ*	5.50	5.80	5.80	5.81	5.81
C_{10}-C_{12}	π	LP*(1)C_{11}			45.53	45.45	45.40	45.37
C_{10}-C_{12}	π	LP(1)C_{15}			30.57	30.56	30.54	30.56
C_{10}-C_{12}	σ	C_{10}-C_{11}	σ*	4.88		4.63	4.63	4.63
C_{10}-C_{12}	π	O_1-C_8	π*	6.72		6.43	6.42	6.42
C_{10}-C_{12}	π	C_{11}-C_{13}	π*	22.64				
C_{10}-C_{12}	π	C_{15}-C_{16}	π*	11.93				
C_{11}-C_{13}	π	C_{10}-C_{12}	π*	11.71				
C_{11}-C_{13}	π	C_{15}-C_{16}	π*	29.06				
C_{12}-C_{15}	σ	C_8-C_{10}	σ*	5.47	3.76	5.51	5.51	5.51
C_{12}-H_{21}	σ	C_{10}-C_{11}	σ*	5.40	5.54	5.54	5.55	
C_{13}-C_{16}	σ	N_4-C_{11}	σ*	5.33	5.14	5.13	5.12	5.12
C_{13}-C_{16}		LP*(1)C_{11}			62.92	62.84	62.77	62.75
C_{13}-C_{16}		LP(1)C_{15}			29.24	29.22	29.19	29.22
C_{15}-C_{16}	π	N_5-N_6	π*	27.82				2.50
C_{15}-C_{16}	π	C_{10}-C_{12}	π*	23.14				
C_{15}-C_{16}	π	C_{11}-C_{13}	π*	12.87				
LP(2)O_1		C_8-C_{10}	σ*		6.05	6.08	6.10	6.10
LP(2)O_1		C_8-H_{18}	σ*	7.97	5.53	5.48	5.45	5.45
LP(1)O_2		C_{13}-C_{16}	σ*	6.15	6.14	6.14	6.14	6.14
LP(2)O_2		C_{13}-C_{16}	π*	33.74	34.73	34.72	34.70	34.69
LP(2)O_3		N_6-C_{17}	σ*	29.60	26.65	26.57	26.52	26.51
LP(2)O_3		N_7-C_{17}	σ*	24.30	22.20	22.16	22.12	22.11
LP(1)N_4		LP*(1)C_{11}			121.81	122.35	122.62	122.74
LP(1)N_4		C_9-H_{19}	σ*	6.36	5.88	5.86	5.85	5.85
LP(1)N_4		C_{11}-C_{13}	π*	51.23				
LP(1)N_4		C_{14}-H_{25}	σ*	7.98			7.09	7.08
LP(1)N_5		C_{12}-C_{15}	σ*	8.70	8.99	9.00	9.01	9.01
LP(1)N_6		O_3-C_{17}	σ*	6.69	7.24	7.26	7.26	7.27
LP(1)N_7		O_3-C_{17}	π*	57.50	64.46	64.57	64.66	64.72
LP(1)C_{15}		N_5-N_6	π*		110.34	111.25	111.78	112.03
LP(1)C_{15}		C_{10}-C_{12}			58.45	58.26	58.14	58.08
LP(1)C_{15}		C_{13}-C_{16}			81.40	81.13	80.97	80.86

Table-20: NBO calculated hybridisation for carbazocrome by using the B3LYP at 6-311G(d,p) basis set in gas phase.

O_1-C_8	$0.8178O_1(sp^{2.37})$	66.87	29.65	70.28	$0.5756C_8(sp^{3.84})$	33.13	20.59	79.17
O_1-H_{26}	$0.8546O_1(sp^{3.91})$	73.04	20.33	79.58	$0.5756H_{26}(s)$	26.96	99.85	0.15
O_2-C_{16}	$0.8202O_2(sp^{1.78})$	67.28	35.91	64.01	$0.5720C_{16}(sp^{3.03})$	32.72	24.78	74.99
O_2-H_{27}	$0.8562O_2(sp^{4.04})$	73.31	19.81	80.10	$0.5166 H_{26}(s)$	26.69	99.84	0.16
O_3-C_{17}	$0.8060O_3(sp^{1.41})$	64.96	41.40	58.48	$0.5919C_{17}(sp^{1.78})$	35.04	35.91	63.97
O_3-C_{17}	$0.8381O_3(sp^{99.99})$	70.23	0.02	99.87	$0.5456C_{17}(sp^{99.99})$	29.77	0.02	99.51
N_4-C_9	$0.7924N_4(sp^{2.36})$	62.79	29.72	70.24	$0.6100C_9(sp^{3.24})$	37.21	23.57	76.29
N_4-C_{11}	$0.7820N_4(sp^{2.36})$	61.16	35.83	64.12	$0.6232C_{11}(sp^{2.47})$	38.84	28.77	71.14
N_4-C_{14}	$0.7896N_4(sp^{2.16})$	62.34	31.67	68.29	$0.6137C_{11}(sp^{2.80})$	37.66	26.30	73.59
N_5-N_6	$0.7111N_5(sp^{2.21})$	50.57	31.11	68.76	$0.7031N_4(sp^{2.17})$	49.43	31.53	68.34
N_5-N_6	$0.6717 N_5(p)$	45.12	0.00	99.74	$0.7408 N_6(p)$	54.88	0.00	99.79
N_5-C_{15}	$0.7649N_5(sp^{2.00})$	58.51	33.30	66.61	$0.6441 C_{15}(sp^{2.41})$	41.49	29.29	70.62
N_6-C_{17}	$0.7772 N_6(sp^{2.73})$	60.40	26.79	73.10	$0.6293C_{17}(sp^{2.18})$	39.60	31.42	68.46
N_7-C_{17}	$0.7889 N_7(sp^{1.53})$	62.24	39.44	60.50	$0.6145 C_{17}(sp^{2.07})$	37.76	32.56	67.34
N_7-H_{28}	$0.8355N_7(sp^{2.27})$	69.80	30.52	69.43	$0.5495 H_{28}(s)$	30.20	99.94	0.06
N_7-H_{29}	$0.8346N_7(sp^{2.34})$	69.65	29.93	70.03	$0.5509H_{29}(s)$	30.35	99.94	0.06
C_8-C_9	$0.7024C_8(sp^{2.82})$	49.34	26.16	73.78	$0.7118C_9(sp^{2.51})$	50.66	28.46	71.49
C_8-C_{10}	$0.7007C_8(sp^{2.43})$	49.09	29.13	70.83	$0.7135C_{10}(sp^{2.27})$	50.91	30.55	69.42
C_8-H_{18}	$0.7737C_8(sp^{3.15})$	59.86	24.10	75.83	$0.6335H_{18}(s)$	40.14	99.97	0.03
C_9-H_{19}	$0.7723C_9(sp^{3.24})$	59.65	23.59	76.34	$0.6352H_{19}(s)$	40.35	99.97	0.03
C_9-H_{20}	$0.7792C_9(sp^{3.09})$	60.71	24.42	75.52	$0.6268 H_{20}(s)$	39.29	99.96	0.04
C_{10}-C_{11}	$0.7005C_{10}(sp^{2.21})$	49.07	31.15	68.79	$0.7137 C_{10}(sp^{1.98})$	50.93	33.58	66.38
C_{10}-C_{12}	$0.7114C_{10}(sp^{1.62})$	50.61	38.14	61.83	$0.7028 C_{12}(sp^{1.65})$	49.39	37.73	62.23
C_{10}-C_{12}	$0.7458 C_{10}(p)$	55.62	0.05	99.92	$0.6662 C_{12}(p)$	44.38	0.01	99.92
C_{11}-C_{13}	$0.7128C_{11}(sp^{1.67})$	50.81	37.47	62.50	$0.7013C_{13}(sp^{1.76})$	49.19	36.22	63.73
C_{11}-C_{13}	$0.6303C_{11}(p)$	39.73	0.01	99.95	$0.7764C_{13}(p)$	60.27	0.00	99.96
C_{12}-C_{15}	$C_{12}(sp^{1.92})$	50.03	34.22	65.73	$0.7069C_{15}(sp^{1.72})$	49.97	36.72	63.25
C_{12}-H_{21}	$0.7859C_{12}(sp^{2.57})$	61.76	28.01	71.94	$0.6184H_{21}(s)$	38.24	99.95	0.05
C_{13}-C_{16}	$0.7101C_{13}(sp^{1.81})$	50.42	35.53	64.42	$0.7041C_{10}(sp^{1.65})$	49.58	37.74	62.22
C_{13}-H_{22}	$0.7762C_{13}(sp^{2.54})$	60.24	28.21	71.75	$0.6305H_{22}(s)$	39.76	99.96	0.04
C_{14}-H_{23}	$0.7731C_{14}(sp^{3.07})$	59.76	24.58	75.36	$0.6343H_{23}(s)$	40.24	99.96	0.04
C_{14}-H_{24}	$0.7748C_{14}(sp^{3.10})$	60.03	24.39	75.54	$0.6322H_{24}(s)$	39.97	99.96	0.04
C_{14}-H_{25}	$0.7719C_{14}(sp^{3.02})$	59.59	24.88	75.05	$0.6357H_{25}(s)$	40.41	99.96	0.04
C_{15}-C_{16}	$0.7063C_{15}(sp^{1.96})$	49.89	33.78	66.18	$0.7079C_{16}(sp^{1.69})$	50.11	37.19	62.77
C_{15}-C_{16}	$0.7707C_{15}(p)$	59.39	0.00	99.99	$0.6372C_{15}(p)$	40.61	0.00	99.96
LP1O_1	$O_1(sp^{1.03})$		49.27	50.70				
LP2O_1	$O_1(sp^{99.99})$		0.68	99.28				
LP1O_2	$O_2(sp^{1.25})$		44.33	55.63				
LP2O_2	$O_2(p)$		0.00	99.93				
LP1O_3	$O_3(sp^{0.70})$		58.69	41.2				
LP2O_3	$O_3(p)$		0.01	99.91				
LP1N_4	$N_4(sp^{36.02})$		2.70	97.28				
LP1N_5	$N_5(sp^{1.79})$		35.85	64.08				
LP1N_6	$N_6(sp^{1.39})$		41.84	58.11				
LP1N_7	$N_7(sp^{99.99})$		0.04	99.95				

Table-21: NBO calculated hybridisation for carbazochrome by using the B3LYP at 6-311G(d,p) basis set in ethanol phase.

O_1-C_8	$0.8191O_1(sp^{2.36})$	67.09	29.72	70.22	$0.5736C_8(sp^{3.88})$	32.91	20.43	79.34
O_1-H_{26}	$0.8578O_1(sp^{3.91})$	73.58	20.38	79.53	$0.5140H_{26}(s)$	26.42	99.85	0.15
O_2-C_{16}	$0.8199O_2(sp^{1.78})$	67.22	35.90	64.02	$0.5725C_{16}(sp^{3.02})$	32.78	24.82	74.97
O_2-H_{27}	$0.8642O_2(sp^{3.81})$	74.68	20.77	79.14	$0.5031H_{26}(s)$	25.32	99.84	0.16
O_3-C_{17}	$0.8065O_3(sp^{1.43})$	65.04	41.03	58.85	$0.5913C_{17}(sp^{1.84})$	34.96	35.21	64.66
O_3-C_{17}	$0.8502O_3(p)$	72.29	0.00	99.90	$0.5264C_{17}(p)$	27.71	0.00	99.51
N_4-C_9	$0.7928N_4(sp^{2.38})$	62.86	29.58	70.38	$0.6094C_9(sp^{3.26})$	37.14	23.42	76.45
N_4-C_{11}	$0.7820N_4(sp^{2.36})$	61.16	36.47	63.48	$0.6232C_{11}(sp^{2.42})$	38.84	29.17	70.74
N_4-C_{14}	$0.7951N_4(sp^{2.11})$	63.21	32.17	67.80	$0.6065C_{11}(sp^{2.90})$	36.79	25.60	74.28
N_5-N_6	$0.7122N_5(sp^{2.27})$	50.72	30.59	69.29	$0.7020N_4(sp^{2.22})$	49.28	30.99	68.89
N_5-N_6	$0.6618N_5(p)$	43.80	0.00	99.75	$0.7497N_6(p)$	56.20	0.00	99.80
N_5-C_{15}	$0.7679N_5(sp^{184})$	58.97	35.22	64.70	$0.6406 C_{15}(sp^{2.38})$	41.03	29.59	70.32
N_6-C_{17}	$0.7745N_6(sp^{2.59})$	59.98	27.79	72.10	$0.6326C_{17}(sp^{2.12})$	40.02	32.01	67.88
N_7-C_{17}	$0.7870N_7(sp^{1.52})$	61.94	39.67	60.27	$0.6169C_{17}(sp^{2.06})$	38.06	32.69	67.21
N_7-H_{28}	$0.8379N_7(sp^{2.29})$	70.20	30.37	69.59	$0.5459H_{28}(s)$	29.80	99.94	0.06
N_7-H_{29}	$0.8375N_7(sp^{2.34})$	70.14	29.90	70.06	$0.5464H_{29}(s)$	29.86	99.93	0.07
C_8-C_9	$0.7045C_8(sp^{2.80})$	49.64	26.33	73.62	$0.7097C_9(sp^{2.52})$	50.36	28.42	71.53
C_8-C_{10}	$0.7097C_8(sp^{2.45})$	49.03	29.01	70.94	$0.7139C_{10}(sp^{2.27})$	50.97	30.59	69.38
C_8-H_{18}	$0.7744C_8(sp^{3.12})$	59.97	24.23	75.71	$0.6327H_{18}(s)$	40.03	99.97	0.03
C_9-H_{19}	$0.7750C_9(sp^{3.21})$	60.06	23.73	76.20	$0.6320H_{19}(s)$	39.94	99.96	0.04
C_9-H_{20}	$0.7800C_9(sp^{3.08})$	60.84	24.47	75.46	$0.6258H_{20}(s)$	39.16	99.96	0.04
C_{10}-C_{11}	$0.7009C_{10}(sp^{2.23})$	49.12	30.91	69.04	$0.7133C_{10}(sp^{2.01})$	50.88	33.21	66.76
C_{10}-C_{12}	$0.7106C_{10}(sp^{1.61})$	50.50	38.34	61.62	$0.7036C_{12}(sp^{1.63})$	49.50	37.95	62.01
C_{10}-C_{12}	$0.7405C_{10}(sp^{99.99})$	54.83	0.04	99.93	$0.6721C_{12}(p)$	45.17	99.93	0.00
C_{11}-C_{13}	$0.7142C_{11}(sp^{1.67})$	51.01	37.43	62.53	$0.6999C_{13}(sp^{1.81})$	48.99	35.62	64.33
C_{11}-C_{13}								
C_{12}-C_{15}	$0.7067C_{12}(sp^{1.95})$	49.94	33.93	66.03	$0.7069C_{15}(sp^{1.73})$	50.06	36.62	63.34

C_{12}-H_{21}	$0.7854C_{12}(sp^{2.56})$	61.69	28.09	71.87	$0.6189H_{21}(s)$	38.31	99.96	0.04
C_{13}-C_{16}	$0.7087C_{13}(sp^{1.82})$	50.22	35.42	64.53	$0.7055C_{16}(sp^{1.61})$	49.78	38.25	61.72
C_{13}-C_{16}	$0.7716C_{13}(p)$	59.54	0.00	99.95	$0.6361C_{16}(p)$	40.46	0.00	99.92
C_{13}-H_{22}	$0.7845C_{13}(sp^{2.46})$	61.55	28.93	71.03	$0.6201H_{22}(s)$	38.45	99.95	0.00
C_{14}-H_{23}	$0.7778C_{14}(sp^{3.00})$	60.49	25.01	74.93	$0.6285H_{23}(s)$	39.51	99.96	0.04
C_{14}-H_{24}	$0.7771C_{14}(sp^{3.06})$	60.39	24.64	75.30	$0.6294H_{24}(s)$	39.61	99.96	0.04
C_{14}-H_{25}	$0.7740C_{14}(sp^{3.01})$	59.91	24.92	75.02	$0.6332H_{25}(s)$	40.09	99.96	0.04
C_{15}-C_{16}	$0.7079C_{15}(sp^{1.98})$	50.11	33.59	66.37	$0.7063C_{16}(sp^{1.73})$	49.89	36.65	63.31
C_{15}-C_{16}								
LP1O_1	$O_1(sp^{1.09})$		47.93	52.05				
LP2O_1	$O_1(sp^{50.10})$		1.96	98.01				
LP1O_2	$O_2(sp^{1.31})$		43.30	56.66				
LP2O_2	$O_2(p)$		0.00	99.94				
LP1O_3	$O_3(sp^{0.70})$		58.93	41.05				
LP2O_3	$O_3(sp^{99.99})$		0.01	99.92				
LP1N_4	$N_4(sp^{57.50})$		1.71	98.27				
LP1N_5	$N_5(sp^{1.91})$		34.38	65.56				
LP1N_6	$N_6(sp^{1.61})$		41.44	58.51				
LP1N_7	$N_7(p)$		0.00	99.99				
LP1C_{11}	$C_{11}(p)$		0.00	100.00				
LP1C_{15}	$C_{15}(p)$		0.00	100.00				

Conclusion

Theoretical calculations of the carbazochrome molecule at the B3LYP level with 6–311G(d,p), 6–311+G(d,p), 6–311++G(d,p), 6–311++G(2d,2p), 6-311++G(3df,3pd) basis sets were carried out in gas phase and solvent (ethanol, N, N-dimethyl form amide, N, N-dimethyl sulfoxide, water) phases using base sets, in basic condition.

Mulliken atomic charges and bond lengths were calculated. There is no important change in the bond lengths obtained from the optimized structure in the gas phase and solvent phases according to the base sets and the environment.

It has been observed that the negative charge distribution is different in the gas phase and the solution phases. In the gas phase, it is seen that negative charges collects on N_1, N_2 and N_3 and S_1 atoms. In the solvent medium, the highest negative charge is on N_1, O_1 and S_1 atoms. As the polarity of the solvent increased, the amount of charge on N_1, O_1 and S_1 atoms increased, but the amount of negative charge on N_2 and N_3 atoms decreased.

Theoretical electronic absorption spectra at TD-DFT level with 6–311G(d,p), 6–311+G(d,p), 6–311++G(d,p), 6–311++G(2d, 2p), 6-311++G(3df,3pd) basis sets in gas phase and solvent (ethanol, N, N-dimethyl form amide, N, N-dimethyl sulfoxide, water) phases.

The results of theoretical research showed that nonlinear optical properties increase significantly with increasing solvent polarity. The solvent has been found to be strongly affected by its hyperpolarizability compared to polarizability.

Correlations between statistical thermodynamics and temperature are also obtained. It has been observed that due to the increase in molecular vibration densities with increasing temperature, heat capacities, entropies and enthalpies also increase with increasing temperature.

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