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## NBO, HOMO-LUMO AND ELECTRONIC STRUCTURAL ANALYSIS OF 2-AMINO 5-NITROBENZOPHENONE

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### Abstract

In this paper, the spectral analysis of 2-amino 5-nitrobenzophenone is carried out using the UV -Vis spectra of the compound with the help of quantum mechanical computations using ab-initio and density functional theories. The Ultra-Violet Visible (UV-Vis) (200-800 nm) spectrum was recorded in ethanol solution phase. The Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital (HOMO-LUMO) mappings are reported which reveals the different charge transfer possibilities within the molecule. Natural Bond Orbital (NBO) analysis is carried out to picture the charge transfer between the localized bonds and lone pairs. The Molecular Electrostatic Potential (MEP) and local reactivity of the molecule has been studied using the Fukui function.

**Keywords:** 2-amino 5-nitrobenzophenone, NBO, HOMO-LUMO, Fukui function.

### INTRODUCTION

Benzophenone is an important compound in organic photochemistry and perfumery as well as in organic synthesis. It is used as a constituent of synthetic perfumes and as a starting material for the manufacture of dyes, pesticides and drug. 2-Amino-5-Nitrobenzophenone is used as an intermediate for the synthesis of Nitrazepam which belong to a class benzodiazepines (anxiolytic drugs and hypnotic drugs).

2-amino 5-nitrobenzophenone has been the object of many spectral, structural and theoretical investigations because of interesting physical and

chemical properties<sup>[1,2]</sup>. The greatest utility of ANBP is probably its application as an agent for efficient triplet state energy transfer<sup>[3,4]</sup>. To our knowledge ab initio calculations on the structure of ANBP have been performed, and the density functional theory (DFT) approaches, have evolved to a powerful and very reliable tool, being routinely used for the determination of various molecular properties. B3LYP functional have been previously shown to provide an excellent compromise between accuracy and computation efficiency of vibrational spectra for large and medium size molecules<sup>[5-8]</sup>.

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## EXPERIMENTAL DETAILS

The compound 2-amino 5-nitrobenzophenone (2A5NBPN) was purchased in the powder form from Sigma–Aldrich Chemicals, Chennai. The UV-Vis spectra were recorded in liquid phase dissolved in ethanol in the range of 200 nm to 800 nm, with the scanning interval of 0.5 nm, using the UV-1700 series instrument.

## COMPUTATIONAL DETAILS

The entire quantum chemical calculations are performed using the Gaussian 09 software on a Pentium IV/3.02GHz personal computer [9]. In DFT methods, B3LYP is the combination of Becks three-parameter hybrid function, and the Lee-Yang-Parr correlation function. The Fukui function of the title molecule are computed using B3LYP method with the 6-311++G (d, p) basis set. In addition, the electronic properties, such as Natural Bond Orbital (NBO) and HOMO-LUMO were calculated using B3LYP/6-311++G (d,p) and (Time dependent-Self Consistent Field) TD-SCF - B3LYP functional with 6-311+G (d, p) method under the same basis set.

## RESULTS AND DISCUSSION

### Global Softness and Local Region-Selectivity

Besides the traditional reactivity descriptors, such as HOMO & LUMO, there are certain other chemical reactivity descriptors such as global hardness ( $\eta$ ), global softness (S) local softness ( $\Delta S$ ), Fukui function ( $f$ ) global electrophilicity ( $\omega$ ) and local electrophilicity ( $\Delta\omega$ ) [10-13] which are defined by Koopmans's theorem [14,15] as follows. The above descriptors are calculated using the formulae cited in the previous works [16]. All these parameters are computed using B3LYP method 6-311+ G (d, p) and 6-311++G (d,p) basis set and the values are presented in Table.1&2.

**Table 1: HOMO, LUMO, Kubo gap, global electro negativity, global hardness and softness, global electrophilicity index of 2-amino-5-nitrobenzoquinone**

Parameters	Benzene ring	2-amino-5-nitrobenzoquinone			
		Transition state by TD-SCF			Optimized state
		Gas	CCl4	Ethanol	B3LYP 6-311++G(d,p)
$E_{\text{HOMO}}$ (eV)	7.0101	6.76584	6.69726	6.62543	6.7655
$E_{\text{LUMO}}$ (eV)	0.4215	2.57828	2.67733	2.82372	2.5780
$\Delta E_{\text{HOMO-LUMO gap}}$ (eV)	6.5886	4.18576	4.01993	3.80171	4.1875
Electro negativity ( $\chi$ )	3.7163	4.67206	4.68729	4.72458	4.6717
Chemical hardness ( $\eta$ )	3.2943	2.09378	2.00996	1.90086	2.0937
Global softness ( $\sigma$ )	0.3035	0.47761	0.49752	0.52608	0.4776
Electro -philicity index ( $\omega$ )	2.0961	5.21262	5.46544	5.87146	5.2119
Dipole moment ( $\mu$ )	0.0001	9.3910	10.6993	12.4650	9.3887

**Table 2: Fukui Function and global and local softness and Electrophilicity of 2-amino 5-nitrobenzophenone**

Atoms	$f^+ = (q+1)-q$	$f^- = q-(q-1)$	$\Delta f = (f^+) - (f^-)$	$\Delta S = \Delta f \sigma_{\text{gs}}$	$\Delta \omega = \Delta f \omega_{\text{gei}}$
1C	0.82694	-0.45423	1.281174	0.6118887	6.677350771
2C	-0.04034	-0.06959	0.029253	0.0139712	0.152463711
3C	-1.23584	1.452293	-2.688128	-1.2838499	-14.0102543
4C	0.860192	-0.96302	1.823212	0.8707661	9.502398623
5C	0.434094	-0.22823	0.662326	0.3163269	3.451976879
6C	-0.64483	0.336853	-0.981685	-0.4688528	-5.11644405
7H	-0.28492	0.290078	-0.574996	-0.2746181	-2.99682165
8H	-0.17458	0.159254	-0.333838	-0.159441	-1.73993027
9H	-0.24908	0.266271	-0.515355	-0.2461335	-2.68597872
10C	1.086153	-1.11818	2.204328	1.0527871	11.4887371
11C	0.35975	-0.32052	0.680265	0.3248946	3.545473154
12C	0.2094	-0.34737	0.55677	0.2659134	2.901829563
13C	0.465518	-0.41199	0.877506	0.4190969	4.573473521
14C	-0.59198	0.504801	-1.096781	-0.5238226	-5.71631289
15C	-1.10786	1.067678	-2.175533	-1.0390346	-11.3386604
16H	-0.17369	0.174207	-0.347893	-0.1661537	-1.81318353
17H	-0.19312	0.189858	-0.382974	-0.1829084	-1.99602219
18H	-0.16908	0.180564	-0.349642	-0.166989	-1.82229914
19H	-0.18739	0.183345	-0.370737	-0.177064	-1.93224417
20N	0.171397	-0.30649	0.477888	0.2282393	2.490704467
21O	0.018565	-0.0911	0.10966	0.0523736	0.571536954
22O	0.043762	-0.08142	0.125183	0.0597874	0.652441278
23N	0.722195	-0.36179	1.083989	0.5177131	5.649642269
24C	1.418623	-1.5346	2.953223	1.4104593	15.39190295

25O	0.245832	-0.30952	0.555353	0.2652366	2.894444301
26H	-0.30562	0.295428	-0.601051	-0.287062	-3.13261771
27H	-0.27969	0.268807	-0.548493	-0.2619603	-2.85869067
28H	-0.22442	0.228606	-0.453022	-0.2163633	-2.36110536

$\Delta S$  = local softness,  $\sigma_{gs}$  - global softness;  $-\Delta\omega$  local electrophilic index,  $\omega_{gei}$  - global electrophilic index.

The global hardness value (4.011 eV) in comparison with benzene (3.294 eV) shows that the hardness is increased for this molecule due to the attachment of amino group. This is also reflected in global softness value which gets decreased from 0.47761 eV for benzene to 0.249 eV for this molecule. The global electrophilicity value shows that it is increased from benzene (2.096 eV) to 5.21262 eV in this molecule. This electrophilicity of this molecule is also found to increase further in gas and ethanol phase.

In the case of local softness which indicate the reacting tendency of the individual atoms; the values shows that local softness is very high for C24 (1.4104) and C10 (1.0527) and minimum for C3 and C15, which shows C24 and C10 are more prone to reactions and C3 and C15 are highly inert. These two carbon atoms are where the ketone group is connected as bridge between the two phenyl rings. On the contrary, the electrophilicity index which shows the electron attracting ability of the individual atoms shows that C24 and C10 are highly electrophilic and C3 and C15 are highly electrophobic which again explains the local softness and hardness of these atoms respectively.

## Natural Bond Orbital (NBO) Analysis

The NBO output parameters such as occupancy, donors and acceptors, stabilization energy, polarization energy etc, calculated using B3LYP/6-311+ G (d, p) method, are presented in Table 3. The table 3 shows the various possible donors and acceptors in molecule with their occupancy value in each position, similarly the various possible transitions among these donors and acceptors. The stabilization energy for these transitions give a measure of the probabilities of these transitions; which indicate the highly probable in this molecule are C1-C2 to C3- C4 ( $\pi-\pi^*$ , 14.20 Kcal/mol), C1-C2 to C5-C6 ( $\pi-\pi^*$ , 23.82 Kcal/mol), C3-C4 to C1-C2 ( $\pi-\pi^*$ , 27.78 Kcal/mol), C3-C4 to C5-C6 ( $\pi-\pi^*$ , 13.14 Kcal/mol), C1-C2 to N20-O21 ( $\pi-\pi^*$ , 28.14 Kcal/mol), O21 to N20-O22 ( $n-\pi^*$ , 19.09 Kcal/mol) and O22 to N20-O21 ( $n-\pi^*$ , 158.63 Kcal/mol).

Of which the most probable transition is  $n-\pi^*$  transition from O22 to N20-O21 ( $n-\pi^*$ , 158.63 Kcal/mol) the possible single and double bond atmosphere in nitro groups provides a chance to store much electronegative region and having very high stabilization energy. And the next probable transitions are C1-C2 to N20-O21 ( $\pi-\pi^*$ , 28.14 Kcal/mol), which also takes place between benzene and nitro group. There six  $\pi-\pi^*$  transitions in the two phenyl ring, rings among them C3-C4 to C1-C2 ( $\pi-\pi^*$ , 27.78 Kcal/mol) is the most probable transition inside the phenyl rings.

**Table. 3 Second order Perturbation theory of Fock matrix in NBO basis of 2-amino 5-nitrobenzophenone**

Donor	Type of Bond	Occupancy	Acceptor	Type of Bond	Occupancy	Energy E(2) kcal/mol	Energy difference E(j)-E(i) a.u.	Polarized energy F(i,j) a.u.
C1-C2	$\Pi$	1.65094	C3-C4	$\pi^*$	0.43787	14.20	0.28	0.058
			C5-C6	$\pi^*$	0.28012	23.82	0.29	0.076
			N20-O21	$\pi^*$	0.63876	28.14	0.15	0.062
C3-C4	$\Pi$	1.58576	C1-C2	$\pi^*$	0.37284	27.78	0.28	0.080
			C5-C6	$\pi^*$	0.28012	13.14	0.28	0.057
			C24-O25	$\pi^*$	0.14289	9.20	0.28	0.048
C5-C6	$\Pi$	1.71973	C1-C2	$\pi^*$	0.37284	14.44	0.29	0.059
			C3-C4	$\pi^*$	0.43787	22.55	0.28	0.074
			C11-C12	$\pi^*$	0.31746	18.19	0.29	0.065
C10-C15	$\Pi$	1.65005	C13-C14	$\pi^*$	0.28777	19.60	0.29	0.069
			C24-O25	$\pi^*$	0.01277	15.13	0.28	0.061
			C10-C15	$\pi^*$	0.37719	22.36	0.28	0.071
C13-C14	$\Pi$	1.64502	C13-C14	$\pi^*$	0.01485	17.95	0.29	0.065
			C10-C15	$\pi^*$	0.37719	19.64	0.28	0.066
			C11-C12	$\pi^*$	0.31746	21.64	0.28	0.070
N20-O21	$\Pi$		N20-O21	$\pi^*$	0.63876	7.86	0.32	0.054
C3-C4	$\Pi$	1.58576	C5-C6	$\pi^*$	0.28012	264.80	0.01	0.080
N20-O21	$\Pi$	1.98674	C1-C2	$\pi^*$	0.37284	17.32	0.14	0.062
O21	N	1.90000	C1-N20	$\pi^*$	0.09997	11.86	0.58	0.074
O21	N	1.90000	N20-O22	$\pi^*$	0.05545	19.09	0.72	0.106

O22	N	1.90152	C1-N20	$\pi^*$	0.09997	11.62	0.58	0.073
O22	N	1.90152	N20-O21	$\pi^*$	0.05445	18.79	0.72	0.105
O22	N	1.46448	N20-O21	$\pi^*$	0.63876	158.63	0.14	0.138
N23	N	1.77757	C3-C4	$\pi^*$	0.43787	39.40	0.30	0.103
N23	N	1.97923	C24	$\sigma^*$	0.01565	14.66	1.61	0.137
O25	N	1.88608	C3-C24	$\pi^*$	0.06569	19.57	0.68	0.104
O25	N	1.88608	C15-C24	$\pi^*$	0.06706	18.90	0.69	0.103

### Ultra Violet-Visible (UV-Vis) Spectra Analysis

The electronic characteristics of the present compound 2-amino 5-nitrobenzophenone are studied using TD-SCF B3LYP functional with 6-311+G (d, p) basis set. And percentage of the energy distribution among the orbital is calculated using Gauss sum 2.1.2 free software. The experimental and theoretical spectrum of the compound is presented in Fig.1.

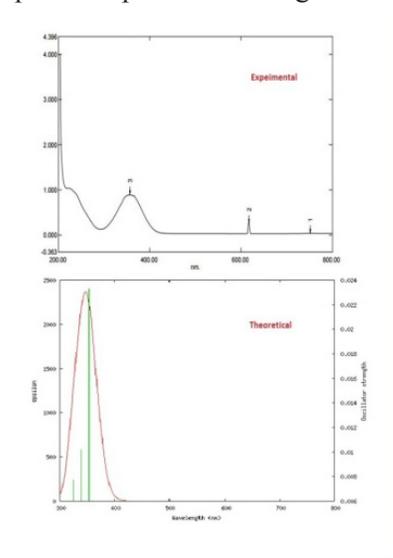


Fig.1 Experimental & theoretical UV-Vis spectra of 2-amino 5-nitrobenzophenone

The other theoretical parameters with the possible transitions are presented in Table 4. Table 4 shows these three transitions in both gas and ethanol phase, with corresponding energy difference between homo and lumo and the oscillator strengths.

From the above three NBO transitions which are known to have high stabilization energy are the probable cause for three transition of three peaks observed in UV-vis region. From table 4 there are three possible transitions with maximum wavelengths 358, 351 and 327 nm with oscillator strengths 0.1780, 0.2670 and 0.0040 respectively. Here the second transition 351 nm 70% for energy transition is found to be from HOMO to LUMO, while other transition are with low energy and oscillator strengths.

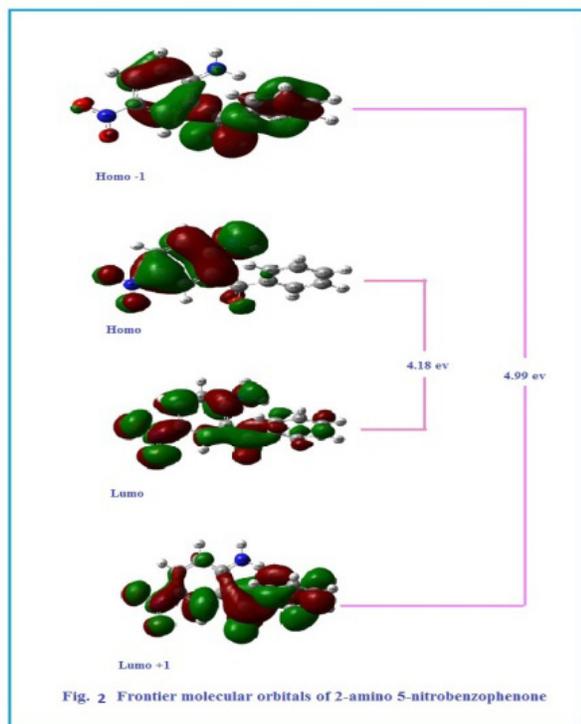
**Table 4: Theoretical electronic absorption spectra of (absorption wavelength  $\lambda$  (nm), excitation energies E (eV) and oscillator strengths (f) using the TD-DFT/B3LYP/6-311++G (d,p) method**

$\lambda$ (nm)	E (eV)	(f)	Major Contribution	Assign-ment	Region
<b>Gas</b>					
353.44	3.5079	0.0233	H>L (15%)	$\pi \rightarrow \pi^*$	Quartz UV
338.77	3.6598	0.0102	H>LUMO (19%)	$n \rightarrow \pi^*$	Quartz UV
325.48	3.8093	0.0077	H>LUMO (44%)	$\pi \rightarrow \pi^*$	Quartz UV
<b>CCl4</b>					
353.92	3.5032	0.0424	HOMO>L (89%)	$n \rightarrow \pi^*$	Quartz UV
339.00	3.6574	0.3326	H>L (14%)	$\pi \rightarrow \pi^*$	Quartz UV
333.36	3.7192	0.0689	H>L (54%)	$n \rightarrow \pi^*$	Quartz UV
<b>Ethanol</b>					
358.70	3.4565	0.1780	HOMO>LUMO (27%)	$\pi \rightarrow \pi^*$	Quartz UV
351.47	3.5276	0.2670	HOMO->LUMO (70%)	$n \rightarrow \pi^*$	Quartz UV
327.33	3.7878	0.0040	H->L (15%)	$\pi \rightarrow \pi^*$	Quartz UV

### HOMO-LUMO Analysis

Analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground state to the excited state and is mainly described by one electron excitation from the highest occupied molecular orbital the lowest unoccupied orbital. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are computed with B3LYP functional with 6-311+ G (d, p) basis set and the pictorial diagram of the HOMO-LUMO are shown in Fig. 2. The HOMO-LUMO, energy gap reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron. HOMO represents the ability to donate an electron. And different reactivity descriptors of

molecule in both optimized and electronic transition levels are presented in Table. 1.



The energy gap of optimized benzene ring is 6.5886 eV, but by the addition of the substitution amino and nitro group it is widened by 4.1875 eV, where the energy flow is low. On the contrary in the transition state, the gap is doubly shortened by 4.1857 eV, which shows the possibility of high flow of energy from HOMO to LUMO.

Similarly other descriptors of the molecule do vary from the optimized to transition state and the values are presented in Table.1. The electro negativity, which is a measure of attraction of an atom for electrons in a covalent bond, has 3.71 eV in benzene and 4.6717 and 4.6720 eV in optimized and electronic states respectively. The chemical hardness of benzene is 3.29 eV and substituted molecule is 2.0937 & 2.09378 eV in optimized and transition state respectively, which shows that the present molecule is less stable compared to the benzene ring. The electrophilicity index is a measure of lowering of total energy due to the maximal electron flow between the donors and the acceptors. The electrophilicity indices of 2-amino 5-nitrobenzophenone is 5.2119 & 5.21262 eV in optimized and transition state respectively, whereas benzene ring is 2.09 eV. This shows that the electrophilicity index, which is the measure of the lowering of total energy, is increased during transition<sup>[17]</sup>.

The dipole moment in a molecule is another important electronic property. The dipole moment of the benzene ring is almost zero, whereas by addition of the amino and nitro group, dipole moment of the present molecule is increased by 9.3887 & 9.3910 Debye in optimized and transition state respectively, which shows the charge flow occur from negative to positive direction.

### Molecular Electrostatic Potential (MEP) Maps

The molecular electrostatic potential surfaces from Fig.3 illustrate the charge distributions of molecules three dimensionally. This map allows us to visualize variably charged regions of a molecule. The knowledge of the charge distributions can be used to determine how molecules interact with one another and it is also used to determine the nature of the chemical bond. Molecular electrostatic potential is calculated at the B3LYP/6-311++G(d,p) optimized geometry.<sup>[18,19]</sup> The figure shows the negative charges are more concentrated at the bottom of the nitro and ketone group, whereas the blue region is spread over at the top of the hydrogen atoms of the phenyl and amino and other regions are found to be neither red nor blue<sup>[20]</sup>, almost neutral. The color code of these maps is in the range between 6.652a.u. (deepest red) and 6.652 a.u. (deepest blue) in the compound. The positive (blue) regions of MEP are related to electrophilic reactivity and the negative (red) regions to nucleophilic reactivity.

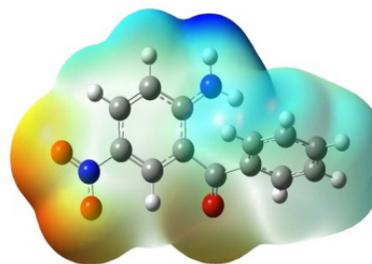


Fig. 3. MEP map of 2-amino 5-nitrobenzophenone

### CONCLUSION

In this study, Mullikan and Fukui calculations have identified the negatively and positively charged atoms in the molecule. The reactivity and electron attracting ability of individual atoms has been found, that the molecule is more active. In NBO analysis the most probable transitions are  $n \rightarrow \pi^*$  transition from O22 to N20-O21 ( $n \rightarrow \pi^*$ , 158.63 Kcal/mol) the next probable

transitions are C1-C2 to N20-O21 ( $\pi-\pi^*$ , 28.14 Kcal/mol), which takes place within the substitution group and C3-C4 to C1-C2 ( $\pi-\pi^*$ , 27.78 Kcal/mol), is the most probable transition inside the benzene ring. The HOMO-LUMO energy gap and other reactivity descriptors of the molecule are compared with optimized state of benzene ring. The energy gap, chemical harness and electro negativity are found decreased with the addition of the substitution group, whereas the electrophilicity index is increased. The value of the dipole moment, reveal that the present molecule is a good candidate for NLO (Non Linear optical) material.

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