

Theoretical study of Bromine substituent effects in ortho-, meta- and para- positions of acetophenone on electronic - structural properties and IR spectrum via density functional theory

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Abstract:

Density functional theory (DFT) was used to systematically examine the effects of bromine (Br) substituted on electronic and structural properties of acetophenone. The B3LYP/CEP-121G protocol has been used for structure optimization and all other properties. The optimized structures, total energies, thermodynamic data, electronic states, energy gaps, ionization potentials, electron affinities, chemical potential, global hardness, softness, global electrophilicity, dipole moment, dipole polarizability and isodesmic reaction were calculated. A complete vibrational assignment aided by the theoretical harmonic frequency analysis has been proposed for all compounds and compared with available experimental data (3-bromoacetophenone isomer only). The observed and the calculated frequencies are found to be in a good agreement. The results showed a decrease in gap energies for bromoacetophenone isomers leads to high reactivity.

Key words: DFT, Ionization potential, electron affinity, energy gap, and IR spectrum

1. Introduction

Aromatic compounds are a large class of conjugated π -electron systems of great importance in many research areas, such as materials science, astrochemistry and molecular electronics [1].

Aromatic ketones such as acetophenone, propiophenone and their derivatives have great analytical and pharmaceutical applications. 3-bromoacetophenone is used as an intermediate product for the preparation of fenoprofen which is an anti-inflammatory, analgesic and antipyretic drug [2,3]. Bromoacetophenone compounds are used to synthesis analytical reagents for Pd(II) [4] and a gravimetric reagent for V(V) [5]. 4-Bromoacetophenone derivatives which upon excitation can generate monophenyl radicals capable of hydrogen atom abstraction were investigate as photoinducible DNA cleaving agents [6] , the isomer is also used in multiple tandem reactions with catalysis[7]. 2-Bromoacetophenone with cytosine are used for the determination of global DNA methylation which provide biologically important information [8] . Chemically it is called as 1-(3-bromophenyl)-ethanone. Alzheimer's disease (progressive form of presenile dementia) is treated with the drug which was invented from 3-bromoacetophenone [9]. It is used as a reaction initiator with organopolysiloxane, which is the base polymer to prepare silicone rubber [10]. It is also used as a coupling partner in microwave accelerated cross- coupling of a range of aryl boronic acids with aryl chlorides [11]. Substituted bromoacetophenone are used to synthesis dicationic diarylpyridines which are used as nucleic acid binding agents [12].

The title compound is used as an antibacterial agent [13]. It is also used as a photo radical polymerization initiator to provide a cross linkable silyl group terminated vinyl poly [14]. Density functional theory (DFT), accepted by the ab initio quantum chemistry community is a cost-effective general procedure for studying physical properties of the molecules. DFT calculations of vibrational spectra of many organic systems [15,16], have shown promising conformity with experimental results. Therefore, in this present investigation DFT technique is employed to study the complete vibrational

spectra of the title compounds and to identify the various normal modes with greater wave number accuracy.

Literature survey reveals that to the best of our knowledge no DFT/ B3LYP/CEP-121G frequency calculations of acetophenone and its bromoacetophenone isomers have been reported so far. It may be due to difficulty in interpreting the spectra of these molecules because of their complexity and low symmetry. Hence the present investigation was undertaken to study the vibrational spectra of these molecules completely and to identify the various normal modes with greater wave number accuracy. Assuming C₁ point group symmetry the band assignments have made. Density Functional Theory (DFT) calculations has been performed to support our wave number assignments. The theoretically predicted IR intensities are well in agreement with that of experimental spectral data.

2. Computational details

The entire calculations conducted in the present work were performed at B3LYP levels included in the Gaussian 03W package [17] program together with the CEP-121G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization[18]. All the geometries were then optimized using CEP-121G by density functional theory (DFT) [19] employing the Becke's three-parameter hybrid functional [20] combined with Lee-Yang-Parr correlation [21] functional (B3LYP) method. The hybrid functional B3LYP had been shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [22],[23].

The DFT partitions the electronic energy as $E = E_T + E_V + E_J + E_{XC}$, where E_T , E_V , and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The optimized structural

parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of acetophenone and its derivatives with Bromine substituent are used for harmonic vibrational frequency calculations resulting in IR frequencies with intensities. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in comparison to the other DFT methods; therefore, scaling factors have to be used to obtain considerably better agreement with experimental data. Thus according to the work of Rauhut and Pulay [24]. Finally, calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. By combining the results of the Gauss. view program [25] with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the Gauss. view program. To achieve a close agreement between observed and calculated frequencies, the least square fit refinement algorithm was used. HOMO-LUMO energy gaps has been computed and other related molecular properties are calculated. In this investigation, the more relevant ionization potential (IP), electron affinities (EA), hardness (η), electric dipole polarizability (α), softness (S), electrophilic index (ω) and chemical potential (K) (it is the negative of electronegativity (χ)), were calculated. The HOMO and LUMO energy was used to estimate the IP and EA in the frame work of Koopmans' theorem:

$IP = -EHOMO$ and $EA = -ELUMO$, The hardness corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO energy gap the harder the molecule. The global hardness, $\eta = 1/2(ELUMO - EHOMO)$. The hardness has been associated with the stability of chemical

system [26]. Here, α is a second-rank tensor property called the dipole polarizability and mean polarizability $\langle \alpha \rangle$ is evaluated using the relation [27], $\langle \alpha \rangle = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, $K=1/2(E_{\text{HOMO}}+E_{\text{LUMO}})$, The global electrophilicity index, $\omega = K^2/2\eta$ is also calculated and softness $S= 1/2\eta$ [28]. Density functional theory has also been used to calculate the dipole moment μ , the total dipole moment is defined by [29],[30]:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} .$$

3. Results and discussion

3.1. Molecular geometry:

Geometry optimization is one of the most important steps in the theoretical calculations. The molecular structure, XRD studies have been studied for the compound m-chloroacetophenone and m-nitroacetophenone. Since the compound chosen for the present study has close structural relation with the above-mentioned compounds, the molecular parameters have been taken from m-chloroacetophenone and m-nitroacetophenone [31,32]. The optimized structure parameters of molecules calculated by DFT-B3LYP levels with the CEP-121G basis set are listed in the table1 in accordance with the atom numbering scheme given in figure1. Table 1 compares the calculated bond lengths and angles for acetophenone molecule with those of its bromoacetophenone isomers, on the other side the table include comparison with experimentally available from X-ray diffraction data fore (3- bromoacetophenone isomer only) while for other studied isomers it has not been found a reference data, the calculated bond lengths and angles for 3-bromoacetophenone with those experimentally available from X-ray diffraction data [31, 32]. From the theoretical values, we can find that most of the optimized bond angles and bond

length are slightly larger than the experimental values, due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state[26], on the other side there is small difference between the optimized bond angles and bond length for acetophenone from its for bromoacetophenone isomers excepting that the nearest angles and bonds to Br substitute which are slightly larger than its in acetophenone may be due to the withdrawing effect for Br substitute .

3.2 Energies

Table 2 shows the values of the total energy and electronic states for the analyzed structures and the energy gap(of the studied molecules). The total energies for all studied molecules as a linear function of bromine substituted to the acetophenone molecule. It is clear that from table 2, the total energy for all isomers is increase and depending on the atomic number of halogen atom, and it is observed that substitution of bromine (electron-accepting) causes decreasing the HOMO and LUMO energy, it is known that the electron accepting substituents decreasing the LUMO and HOMO energies [33], and energy gap decreased. The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity[34] The LUMO-HOMO energy gaps of bromoacetophenone is small than that of the original molecule, with decreasing energy gap, electrons can be easily excited from the ground state. This effect of the side group was the largest in 3-bromoacetophenone which have energy gap of (0.179 a.u). The table 2 shows also the symmetry of studied molecules, the all molecules have C_1 symmetry.

3.3 Some important variables

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied

molecules, such as ionization potentials (**IP**), electron affinities (**EA**), chemical potential (**K**), absolute hardness (**η**), absolute softness (**S**), electrophilic index (**ω**). The properties are computed by the way that is based on the differences between the HOMO and the LUMO energies of the neutral molecule and is known as orbital-vertical (Koopmans' theorem).

The calculated properties for each variable clearly reveal that the ionization potential for the bromoacetophenone isomers is higher than that for the original molecule, but the 2-Bromo1-phenylethanone molecule has the largest value of ionization potential, this indicates that this molecule needs high energy to become cation comparing with the others.

The strength of an acceptor is measured by its electron affinity (EA) which the energy released when adding one electron to LUMO. An acceptor must have a high EA, adding the Br atom to acetophenone molecule leads to increasing the ability of the electron affinity for the molecule; EA for molecule 2-Bromo1-phenylethanone is the largest, as we see in table 4. The Koopmans' theorem is a crude but useful and fast approach [33,35]. The behavior of electronegativity, softness and electrophilic index for the studied molecules shows the magnitude larger than these for the original molecule, adding the Br atom gives the molecules more softness. The larger the HOMO-LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system[34]. In the present study, acetophenone molecule is the largest HOMO-LUMO gap and hardness of the molecules as shown in table 2 and table 4, which clearly indicates that the molecule is the most stable .

3.4 Molecular polarizability and the Dipole moment

One of the objectives of the present investigation is to study the effect of the basis sets B3LYP/ CEP-121G levels on molecular polarizability of acetophenone and its bromo acetophenone

isomers using the Gaussian03W program. In this study, the computation of the molecular polarizability $\langle \alpha \rangle$ was reported, 4-Bromoacetophenone molecule has the largest polarizability. The calculated dipole moment values show that the acetophenone molecule is highly polar and more than its bromoacetophenone isomers. The calculated dipole moment and polarizabilities by DFT method are summarized in Table 3.

3.5 Thermodynamic properties

On the basis of vibrational analysis at B3LYP/ CEP-121G level, several thermodynamic parameters are calculated and are presented in Table 5. Table 5 showed that acetophenone compound less entropy ΔS° and larger in the ΔU° , ΔH° , ΔA° and ΔG° properties than those of its bromoacetophenone isomers, this because Br substituent effect.

3.6 Electronic densities

The electron densities for acetophenone molecule and their bromoacetophenone isomers were listed in (Table 6). Electron densities are different in the molecules because the Br substituent effect.

3.7 Isodesmic reaction

The stabilizing effect of a substituent is often assessed by using isodesmic reactions (conserved bond type). A positive energy difference (Δ) (Table 7) indicates stabilization of the reactant by substituent [36], so the negative Δ refers to more reactivity for reactants (bromoacetophenone) than those for products (acetophenone). The largest Δ was reported for 2-Bromo1-phenylethanone isomer so it is high reactive.

3.8 Vibrational assignments

3.8.1 C-H Vibrations

The aromatic structure shows the presence of C-H stretching vibrations in the region 3250 cm^{-1} - 2950 cm^{-1} which is characteristic region for the ready identification of C-H stretching vibrations and particularly the regions 3250 cm^{-1} - 3100 cm^{-1} for asymmetric stretching and 3100 cm^{-1} - 2950 cm^{-1} for symmetric stretching modes of vibration [37]. For most cases, the aromatic compound C-H vibration absorption bands are usually weak; in many cases it is too weak for detection. In this region, the bands are not affected, appreciably by the nature of substituents. In the present work, for the bromoacetophenone isomers, the FTIR bands observed at 3238 cm^{-1} , 3228 cm^{-1} , 3220 cm^{-1} and 3197 cm^{-1} have been assigned to C-H stretching vibration. The B3LYP level at CEP-121G gives slightly different frequency values at 3211 cm^{-1} , 3201 cm^{-1} , 3164 cm^{-1} and 3137 cm^{-1} as indicated in Table 8. In general the aromatic C-H stretching vibrations calculated theoretically are in good agreement with the experimentally reported values [38-39] for di substituted benzene in the region 3200 - 2900 cm^{-1} . The titled compounds have both out-of-plane and in-plane aromatic C-H bending vibrations. The out of plane bending mode of C-H vibration is found well in agreement with the experimentally predicted in the region 1000 - 600 cm^{-1} [40]. At B3LYP/ CEP-121G, 982 and 834 cm^{-1} , is calculated. The observed FTIR value of 996 cm^{-1} is in excellent agreement with 982 cm^{-1} of B3LYP/ CEP-121G results. The out of plane C-H deformation vibrations of 3-bromoacetophenone is experimentally predicted in the region 636 and 996 cm^{-1} coincides satisfactorily with the calculated values in the same region. The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region 1300 - 1000 cm^{-1} [41]. The C-H in plane bending vibrations assigned even though

found to be contaminated by C-CH₃ stretch are found in literature [42,43], while the experimentally observed values for 3-bromoacetophenone is at 1268 cm⁻¹. The C-H in-plane bending vibration of 3-bromoacetophenone coincides satisfactorily with the experimentally observed values in this region.

3.8.2 C-Br Vibrations

The compounds under consideration bromoacetophenone isomers have a bromine substitution. The heavier mass of bromine obviously makes the C-Br stretching mode to appear in longer wavelength region. Bellamy has assigned the region 700-600 cm⁻¹ for the C-Br stretching [44,45]. Based on this, the band observed at 660 cm⁻¹ in FTIR is assigned to C-Br stretching. The theoretically calculated value for 3-bromoacetophenone 662 cm⁻¹ is well agreed with the experimental value, in the other isomers was 635, 652, 704 cm⁻¹ for 4-bromoacetophenone, 2-bromoacetophenone and 2-Bromo1-phenyl ethanone respectively, in the last one the value is more than the other because the substitution is on the aliphatic C atom, so the C-Br stretching is higher than its in the other due to shorter C-Br bond and absence the ring delocalization[45] .

3.8.3 Methyl group Vibrations

The compounds under consideration excepting 2-Bromo1-phenyl ethanone possess a CH₃ group in the side substitution chain. There are nine fundamentals one can expect to a CH₃ group, namely the symmetrical stretching in CH₃ (CH₃ sym. stretch) and asymmetrical stretching (in plane hydrogen stretching mode); the symmetrical (CH₃ sym. deform) and asymmetrical (CH₃ asym. deform) deformation modes; in-plane rocking, out-of-plane rocking, twisting and bending modes [46]. Each methyl group has three stretching vibrations, one being symmetric and other two asymmetric. The frequencies of asymmetric vibrations are higher than the symmetric one [47].

The theoretically computed values 3016 cm^{-1} for CH₃ symmetric stretching and 3091 cm^{-1} , 3137 cm^{-1} for CH₃ asymmetric stretching shows an excellent agreement with the range allotted by Williams and Fleming [48]. CH₃ asymmetric and symmetric in-plane bending are observed at 1470 and 1315 cm^{-1} in FTIR, respectively [49]. The torsion vibrations are not observed in the FTIR because these appear at very low frequency. The observations at 41 cm^{-1} in 3-bromoacetophenone is in agreement with theoretical results of similar compounds ($69, 34\text{ cm}^{-1}$ for 4-bromoacetophenone and 2-bromoacetophenone respectively), table 8.

3.8.4 C=O Vibrations

The C=O stretching vibration in acetophenone and its bromoacetophenone isomers have a main contribution in the mode, with B3LYP/ CEP-121G) predicted frequencies at 1624 cm^{-1} (Table 8) for 3-bromoacetophenone, this is in agreement with the very strong experimental frequencies at 1635 cm^{-1} in FTIR spectrum, while in the other compounds, the C=O stretching was $1632, 1619, 1626$ and 1612 cm^{-1} for 4-bromoacetophenone, 2-bromoacetophenone, 2-Bromo1-phenylethanone and acetophenone respectively. The out of plane C=O bending vibration mode of 3-bromoacetophenone with the experimental frequency of 140 cm^{-1} found to be in excellent agreement. The above conclusions are in agreement with the literature value [50], and the same mode (out of plane C=O bending) was $148, 112, 125$ and 160 cm^{-1} for 4-bromoacetophenone, 2-bromoacetophenone, 2-Bromo1-phenylethanone compounds and acetophenone respectively.

4. Conclusion

The results of the study lead to the following conclusions. (i) The proper frequency assignments for the compounds is

performed for the first time from the FTIR. The experimental FTIR spectra for 3-bromoacetophenone was compared with the theoretical DFT calculations of the vibrational spectra of the molecule. (ii) The equilibrium geometries of compounds were determined and analyzed both at DFT level utilizing CEP-121G basis set, Geometry optimization for 3-bromoacetophenone has been found in a good agreement with experimental data. (iii) The HOMO-LUMO energy gap and other related molecular properties were discussed and reported. The presence of the Br substituent decreases the energy gap of the molecules study, this is one of the important properties obtained in this work, and a small energy gap means small excitation energies of manifold of the excited states. (iv) molecular polarizability was calculated and the results were discussed, the results showed that the Br substitution leads to increase the average polarizability and cause to more reactive than original molecule. (v) The electronic properties (IP, EA, K, η , S, ω) were calculated by using DFT.

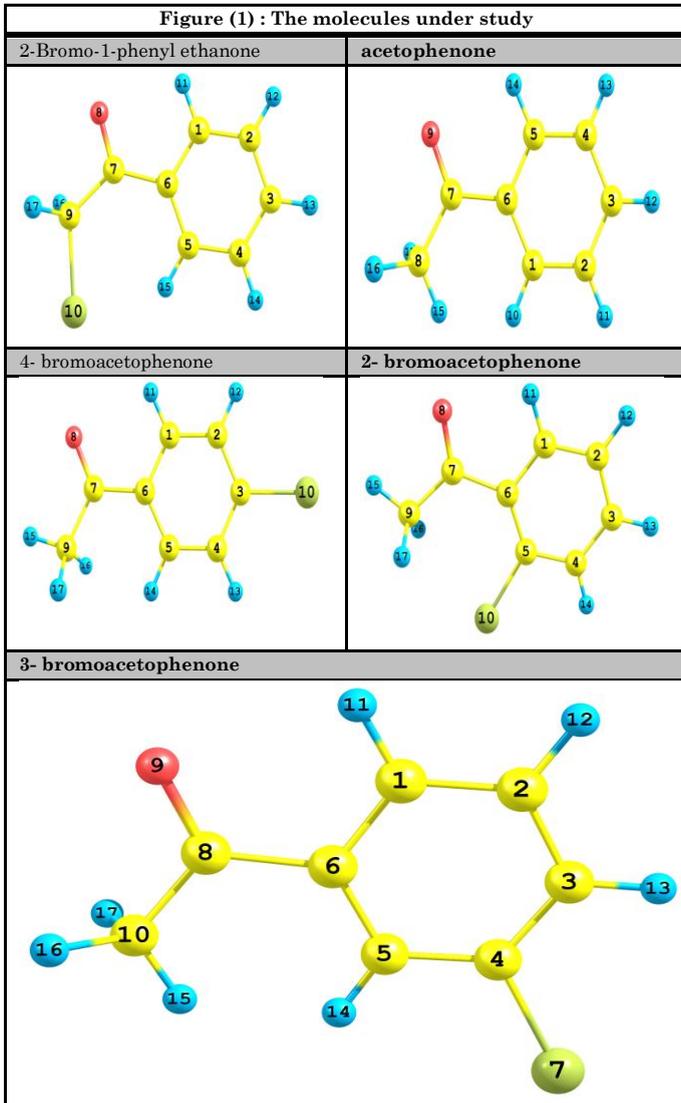


Table 1: Optimized geometrical parameters of acetophenone and bromoacetophenone isomers, bond length (Å), Interaxial angles (°)

Molecules	bond length	Our data	Expt.[31,32]	bond angles	Our data	Expt.[31,32]
acetophenone	C8-H17	1.097	-	H12-C3-C4	120.085	-
	C6-C7	1.510	-	C5-C4-C3	120.021	-
	C10-C8	1.532	-	H14-C5-C4	121.310	-
	C4-H13	1.087	-	C6-C1-C2	120.388	-
	C7-O9	1.265	-	C6-C7-O9	119.795	-
	C5-C4	1.408	-	H10-C1-C2	118.855	-
	C2-C3	1.413	-	C8-C7-C6	121.716	-
2-Bromo acetophenone	C1-C6	1.420	-	H11-C2-C1	120.076	-
	C9-H17	1.095	-	H13-C3-C4	119.567	-
	C6-C7	1.529	-	C5-C4-C3	120.107	-
	C7-C9	1.525	-	Br10-C5-C6	125.043	-
	C5-Br10	1.983	-	C6-C1-C2	122.532	-
	C7-O8	1.264	-	C6-C7-O8	117.856	-
	C5-C4	1.415	-	H11-C1-C2	121.039	-
3-Bromo acetophenone	C2-C3	1.413	-	C9-C7-C6	123.855	-
	C1-C6	1.430	-	H12-C2-C1	119.893	-
	C10-H15	1.097	1.113	H13-C3-C4	120.578	120.000
	C6-C8	1.514	1.351	C5-C4-C3	122.021	120.000
	C10-C8	1.531	1.512	H14-C5-C6	121.538	120.000
	C4-Br7	1.972	1.881	C6-C1-C2	120.492	120.000
	C8-O9	1.264	1.208	C6-C8-O9	119.634	120.000
4-Bromo acetophenone	C5-C4	1.409	1.395	H11-C1-C2	121.365	120.000
	C2-C3	1.417	1.395	C10-C8-C6	121.819	120.000
	C1-C6	1.422	1.395	H12-C2-C1	120.076	120.000
	C9-H17	1.098	-	Br10-C3-C4	119.059	-
	C6-C7	1.510	-	C5-C4-C3	118.731	-
	C7-C9	1.529	-	H14-C5-C6	120.643	-
	C3-Br10	1.966	-	C6-C1-C2	120.863	-
2-Bromo1-phenylethanone	C7-O8	1.263	-	C6-C7-O8	120.142	-
	C1-C2	1.409	-	H11-C1-C2	120.727	-
	C4-C3	1.410	-	C9-C7-C6	119.767	-
	C1-C6	1.419	-	H12-C2-C1	120.753	-
	C9-H17	1.091	-	H13-C3-C4	120.128	-
	C6-C7	1.500	-	C5-C4-C3	120.462	-
	C7-C9	1.552	-	H15-C5-C4	119.214	-
2-Bromo1-phenylethanone	C9-Br10	2.037	-	C6-C1-C2	120.717	-
	C7-O8	1.268	-	C6-C7-O8	119.840	-
	C5-C4	1.413	-	H11-C1-C2	120.960	-
	C2-C3	1.417	-	C9-C7-C6	129.967	-
	C1-C6	1.428	-	H12-C2-C1	119.815	-

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Table 2: Total energy, Electronic states and Energy gap for molecules calculated by DFT with B3LYP system and CEP-121G basis set.

Molecule	Symmetry	Energy (a.u)	Electronic States(a.u)		Energy Gaps (a.u)
			HOMO	LUMO	
acetophenone	C ₁	-65.8964	-0.2597	-0.0728	0.1869
2-Bromoacetophenone	C ₁	-78.6563	-0.2665	-0.0808	0.1857
3-Bromoacetophenone	C ₁	-78.6637	-0.2638	-0.0843	0.1757
4-Bromoacetophenone	C ₁	-78.6662	-0.2649	-0.0816	0.1832
2-Bromo1-phenylethanone	C ₁	-78.6553	-0.2735	-0.0885	0.1850

Table 3: calculated dipole moment μ (debye), components of α_i ($i = xx,yy,zz$) an average of the dipole polarizability $\langle \alpha \rangle$ in atomic units for molecules.

Molecule	μ	α_{xx}	α_{yy}	α_{zz}	$\langle \alpha \rangle$
acetophenone	3.4867	126.317	98.521	45.104	89.98
2-Bromoacetophenone	2.8226	139.675	129.797	47.821	105.76
3-Bromoacetophenone	1.4260	155.397	116.150	47.160	106.23
4-Bromoacetophenone	2.7222	173.288	103.635	47.200	108.04
2-Bromo1-phenylethanone	2.3747	142.377	128.394	46.472	105.74

Table 4: Comparison of related molecular properties of acetophenone with its bromoacetophenone isomers calculated by DFT with B3LYP system and CEP-121G basis set.

Molecule	IP	EA	K	S	η	X
acetophenone	0.2597	0.0728	-0.1663	5.348	0.0934	0.1663
2-Bromoacetophenone	0.2665	0.0808	-0.1736	5.384	0.0928	0.1736
3-Bromoacetophenone	0.2638	0.0843	-0.1741	5.571	0.0897	0.1741
4-Bromoacetophenone	0.2649	0.0816	-0.1733	5.457	0.0916	0.1733
2-Bromo1-phenylethanone	0.2735	0.0885	-0.1810	5.404	0.0925	0.1810

Table 5: Comparison of Thermodynamic properties of acetophenone with its bromo -acetophenone isomers calculated by DFT with B3LYP system and CEP-121G basis set .

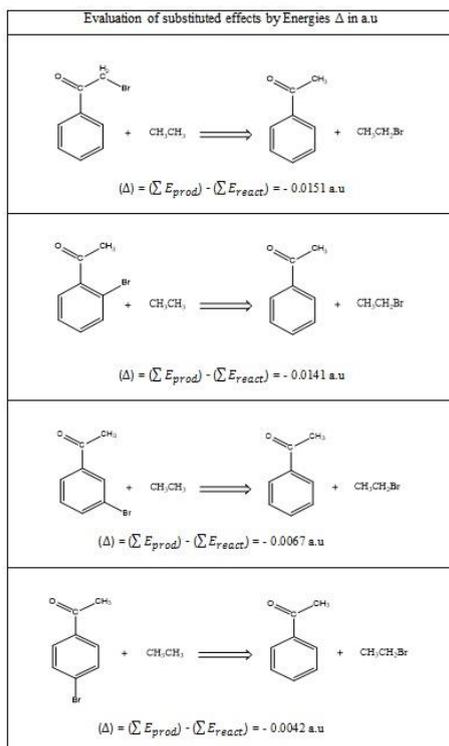
Molecule	ΔU^\ddagger (kcal/mole)	ΔH^\ddagger (kcal/mole)	ΔS^\ddagger (cal/mole K)	ΔA^\ddagger (kcal/mole)	ΔG^\ddagger (kcal/mole)
acetophenone	90.406	90.99842	85.330	64.96486	65.55728
2-bromo acetophenone	84.812	85.40442	91.568	57.51100	58.10342
3-bromo acetophenone	84.845	85.43742	95.579	56.34812	56.94054
4-bromo acetophenone	85.404	85.99642	97.503	56.33348	56.92590
2-Bromo1-phenylethanone	85.269	85.86142	95.905	56.67492	57.26734

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Table 6. Electronic densities for all molecules calculated by DFT with B3LYP system and CEP-121G basis set

Atom	Aceto phenone	Atom	3-Br.aceto phenone	Atom	4-Br. aceto phenone	Atom	2-Br. aceto phenone	Atom	2-Br.1- phenyl ethanone
C ₁	4.185615	C ₁	4.258151	C ₁	4.235503	C ₁	4.258897	C ₁	4.261283
C ₂	4.16965	C ₂	4.112427	C ₂	4.10378	C ₂	4.140372	C ₂	4.142051
C ₃	4.14233	C ₃	4.119201	C ₃	4.359124	C ₃	4.110969	C ₃	4.143182
C ₄	4.143278	C ₄	4.393534	C ₄	4.123771	C ₄	4.11102	C ₄	4.188235
C ₅	4.254717	C ₅	4.131932	C ₅	4.132466	C ₅	4.457237	C ₅	4.125215
C ₆	3.651727	C ₆	3.638567	C ₆	3.68453	C ₆	3.582575	C ₆	3.576297
C ₇	4.128597	Br ₇	6.851167	C ₇	4.07901	C ₇	4.039487	C ₇	4.11998
C ₈	4.592329	C ₈	4.122377	O ₈	6.121537	O ₈	6.13181	O ₈	6.132769
O ₉	6.132994	O ₉	6.125523	C ₉	4.656785	C ₉	4.664267	C ₉	4.722883
H ₁₀	0.819933	C ₁₀	4.591251	Br ₁₀	6.850297	Br ₁₀	6.802792	Br ₁₀	6.917037
H ₁₁	0.843527	H ₁₁	0.776626	H ₁₁	0.782411	H ₁₁	0.779687	H ₁₁	0.777316
H ₁₂	0.842802	H ₁₂	0.833219	H ₁₂	0.801962	H ₁₂	0.828317	H ₁₂	0.835795
H ₁₃	0.83968	H ₁₃	0.807417	H ₁₃	0.805251	H ₁₃	0.835285	H ₁₃	0.838602
H ₁₄	0.783683	H ₁₄	0.782089	H ₁₄	0.806465	H ₁₄	0.813575	H ₁₄	0.835810
H ₁₅	0.845938	H ₁₅	0.84146	H ₁₅	0.807083	H ₁₅	0.814707	H ₁₅	0.846979
H ₁₆	0.811585	H ₁₆	0.807518	H ₁₆	0.824990	H ₁₆	0.814550	H ₁₆	0.768309
H ₁₇	0.811614	H ₁₇	0.807542	H ₁₇	0.825034	H ₁₇	0.814454	H ₁₇	0.768257

Table 7. Evaluation of substituted effects (energies Δ , in a.u)



Khulood Obaid Kzar- Theoretical study of Bromine substituent effects in ortho-, meta- and para- positions of acetophenone on electronic - structural properties and IR spectrum via density functional theory

Table 8: Vibrational wavenumbers obtained for 3-bromoacetophenone at B3LYP/ CEP-121G [harmonic frequency (cm⁻¹) IR intensities (km mol⁻¹) .

acetophenone		2-Br.1-phenyl ethanone		2-Br. aceto phenone		4-Br. aceto phenone		3-Br.acetophenone			Characterization of Normal modes
\square_{cal} cm ⁻¹	IR int.	\square_{exp} cm ⁻¹									
22	0.899	13	11.13	34	2.09	69	3.49	41	0.782	-	ν CH3 torsion
45	4.88	33	1.40	82	6.11	78	1.76	59	0.943	-	lattice vibration
160	0.077	125	1.83	112	0.426	148	3.58	140	7.97	-	γ C=O + γ CH
231	6.10	157	0.055	174	0.465	165	0.194	144	2.54	-	CH3 torsion
369	0.791	193	3.71	205	0.557	237	2.00	154	0.020	-	CH3 torsion+ δ CH
-	-	348	4.10	240	0.321	246	0.581	186	0.597	-	γ C-Br
-	-	415	0.058	270	8.39	273	2.69	276	3.19	-	δ C-Br
468	2.088	427	0.194	275	2.00	412	7.43	295	6.355	-	δ C-H
570	27.29	428	5.32	393	7.31	421	0.031	371	0.638	430	γ C-H
616	9.66	535	31.38	430	0.296	464	6.014	432	0.473	-	γ C-H
628	0.672	581	3.65	487	5.18	488	15.02	472	4.09	538	γ C-C-C
710	38.67	628	0.017	591	23.94	579	9.24	478	1.41	590	δ C-C-O
-	-	667	66.17	601	3.44	598	9.29	576	30.37	636	CH3 twisting+ ν C-Br
-	-	704	28.20	652	7.95	635	1.041	662	0.119	660	ν C-Br
889	0.475	745	40.17	723	5.78	714	8.07	661	14.32	683	ring breathing
972	3.531	792	78.61	743	12.98	744	26.71	701	16.47	785	δ C-C-C
979	20.32	886	1.72	804	74.10	856	53.09	768	26.97	838	γ C-H
1002	1.763	895	0.151	913	0.229	878	21.23	834	59.53	901	γ C-H
1020	0.978	985	1.572	977	19.67	971	45.73	919	13.70	960	γ C-H
1033	5.536	998	1.85	1010	3.76	988	0.082	975	1.18	987	γ C-H
1048	2.96	1024	16.22	1016	56.94	1015	54.95	982	16.66	996	γ C-H
1069	0.682	1029	0.549	1046	1.63	1034	0.963	998	6.85	1020	δ ring + γ C-H
1086	1.639	1048	2.13	1048	1.78	1062	28.41	1044	4.16	1064	CH3 twisting
1103	7.002	1049	0.715	1069	0.35	1066	0.144	1067	38.80	1091	γ C-H + δ C-C
1192	0.576	1105	3.44	1101	2.92	1093	11.96	1068	0.78	1101	δ C-H
1210	18.23	1195	0.790	1138	0.551	1129	5.43	1096	0.40	1124	ν C-C + δ C-H
1280	214.85	1200	1.250	1197	2.10	1209	15.17	1116	6.16	1186	δ C-H
1338	6.290	1217	34.31	1266	83.95	1289	195.47	1199	6.10	1268	ν C-C + δ C-H
1355	4.183	1259	106.6	1290	106.18	1329	3.27	1270	269.04	1315	ρ C-H
1421	37.03	1288	187.3	1323	13.23	1334	7.37	1319	18.10	1357	γ C-C
1462	16.94	1344	5.78	1425	25.46	1406	7.58	1340	2.19	1405	CH3 wagging
1495	9.92	1362	6.28	1441	42.51	1423	63.63	1427	39.15	1450	ν C-C
1497	11.32	1446	18.12	1480	37.33	1490	36.45	1483	0.53	1470	δ C-H
1518	6.805	1462	19.32	1483	27.63	1504	13.51	1494	10.54	1494	ν C-C
1586	106.13	1513	0.148	1496	15.65	1504	15.82	1509	17.24	1516	ν C-C
1618	62.59	1557	164.4	1574	8.13	1580	56.18	1573	143.7	1566	ν C-C
1629	16.28	1607	14.93	1602	108.8	1607	139.78	1607	29.16	1592	ν C-C
1612	6.988	1626	17.66	1619	71.43	1632	89.28	1624	50.93	1635	ν C=O
3090	11.90	3078	3.527	3017	3.07	2999	5.56	3016	5.28	3066	ν_s CH3
3133	21.39	3150	0.988	3100	10.61	3076	17.93	3091	10.08	3127	ν_{as} CH3
3147	0.504	3160	0.548	3133	20.69	3133	20.207	3137	20.60	3153	ν_{as} CH3
3160	13.76	3165	24.58	3158	5.62	3172	7.109	3164	10.99	3197	ring (ν C-H)+ ν C-H ₃
3174	36.89	3179	30.55	3177	17.32	3197	12.27	3201	14.79	3220	ring (ν C-H)+ ν C-H ₃
3194	9.68	3240	7.439	3201	17.61	3200	2.225	3211	2.19	3238	ring (ν C-H)

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