**International Journal of Current Research and Review**
**DOI:** http://dx.doi.org/10.31782/IJCRR.2018.6469

Review Article

IJCRR
Section: General Science
Sci. Journal Impact Factor: 5.385 (2017)
ICV: 71.54 (2015)

# An Insight into the Stability Of 3′-(Trifluoromethyl) and 4′-(Trifluoromethyl) Acetophenones Through Molecular Geometry and Charge Transfer Analyses – A Comparative Study

**V. Ragavendran**[*1], **S. Helen Kumari**[2]

[1,2]Department of Physics, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Kanchipuram - 631561, Tamilnadu, India.

## ABSTRACT

The optimized geometry, molecular stability, mulliken atomic charges and natural bond orbital analysis of the title compounds were obtained at DFT level for theory with complete relaxation in the potential energy surface using 6-311G** basis set. The global minimum energy obtained for the titled compounds was observed to be -722.1339 a.u. and -722.1333 a.u. respectively. The influence of substitution on the geometry of the molecule have been thoroughly investigated. The bonding capability of a molecule depends on the electronic charge on the chelating atoms. The reason for the stability of the molecules under investigation arising from intermolecular charge transfer that occurs within the molecule from bond pairs and lone pairs was also investigated from natural bond orbital analysis. The atomic charge values were obtained by mulliken population analysis for the titled compounds.

**Key Words:** DFT, Mulliken charges, NBO, 3TFMA, 4TFMA

## INTRODUCTION

Acetophenone is the simplest aromatic ketone. It is a colorless, viscous liquid and it is useful in preparation of resins and fragrances. Acetophenone occurs naturally in chicory, beef, apple, cauliflower, cheese, banana and apricot [1-10]. The trifluoromethyl group substituted compounds are often strong acids due to their significant electronegativity. This group shows enhanced medical applications owing to their presence in certain drugs, pharmaceuticals and abiotically synthesized natural based compounds[6-10]. A study had been attempted on Synthesis and structural study of the ligand *o*-OH acetophenoneazine and its Cu(II), Ni(II), Co(II) and Zn(II) complexes by B. AEl-Sayed et. Al[4]. An attempt has been made in investigating the Synthesis, structural elucidation and DFT studies of ortho-hydroxyacetophenones by Saikat K.Seth et.al [5]. Two ortho-hydroxyacetophenones, namely 2,6-dihydroxy-4-methyl acetophenone [$C_9H_{10}O_3$] and 2,4-dihydroxy-3-acetyl-6-methyl acetophenone [$C_{11}H_{12}O_4$] had been synthesized and characterized by spectroscopic and X-ray structural studies. An investigation has been made on adsorption of activated ketones on platinum and their reactivity to hydrogenation using a DFT study by Angelo Vargas[6].A detailed study of the basicities of a series of p-substituted acetophenones and their O-protonated counterparts had been performed by Senapati et.al [7].In the present study, a complete vibrational analysis of 3’-(trifluoromethyl) acetophenone (3TFMA) and 4’-(trifluoromethyl)acetophenone (4TFMA) has been done using experimental (FTIR & FT Raman) techniques and DFT computational procedure. A comparative study on the geometrical parameters and mulliken charges was done. The charge transfer mechanism by comparing the result of the both titled compounds from the natural bond analysis.

**Corresponding Author:**
**V. Ragavendran,** Department of Physics, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Kanchipuram - 631561, Tamilnadu, India; Phone: +91 9994015808; E-mail: ragav910@gmail.com.

**ISSN:** 2231-2196 (Print) **ISSN:** 0975-5241 (Online)
**Received:** 10.09.2018 **Revised:** 15.10.2018 **Accepted:** 02.11.2018

## Computational details:

The combination of spectroscopic methods with DFT calculations are powerful tools for understanding the fundamental vibrational properties, molecular stability and the electronic structure of the compounds. Quantum chemical calculations were performed on the title molecules by applying DFT method using the Gaussian 09 Program suite [11] at the Becke-3-Lee-Yang-Par [B3LYP] level [12-13], using 6-31G** basis sets. The global minimum energy of the stable conformers of 3 TFMA and 4 TFMA has been determined by energy optimization at the DFT level of theory. The global minimum energy obtained for the titled compounds was observed to be -722.1339 a.u. and -722.1333 a.u. respectively. All the geometrical parameters were allowed to relax during the optimization procedure. The Natural bonding orbital(NBO) calculation was performed using NBO 5.1 program [14] as implemented in the Gaussian 09 package at DFT/B3LYP level. The hyperconjucation and the interaction energy within the molecule were deduced from the second order perturbation approach [15-17]. The Mulliken charge analysis for the titled compounds was also carried out at the same DFT level of theory.

## RESULTS AND DISCUSSION

### Molecular Geometry:

Molecular geometries were fully optimized using redundant internal coordinates. To establish the most stable conformation as the initial point and for further calculations the molecule was submitted to a conformational analysis and the optimized energies of the titled molecules at the B3LYP level with6-311G** basis set has been tabulated in Table 1 and their optimized structures were shown in Figures 1 and 2 respectively. Generally the C-C bond length of methyl acetophenone was found to be 1.393Å. For the titled compounds, this bond length was found to be elongated from their default values. In particular for 3TFMA C1-C(1.504Å), C5-C11(1.505Å) and C11-C12 (1.501 Å). For 4TFMA C1-C4 (1.505Å), C5-C11(1.082Å) and C11-C12 (1.516 Å) were found to be elongated from their default values of 1.393 Å. The reason for this elongation is may be due to their presence in the vicinity of electronegative F7, F8, F9 and O13 atoms. These results were further confirmed by mulliken charge analysis and NBO analysis.

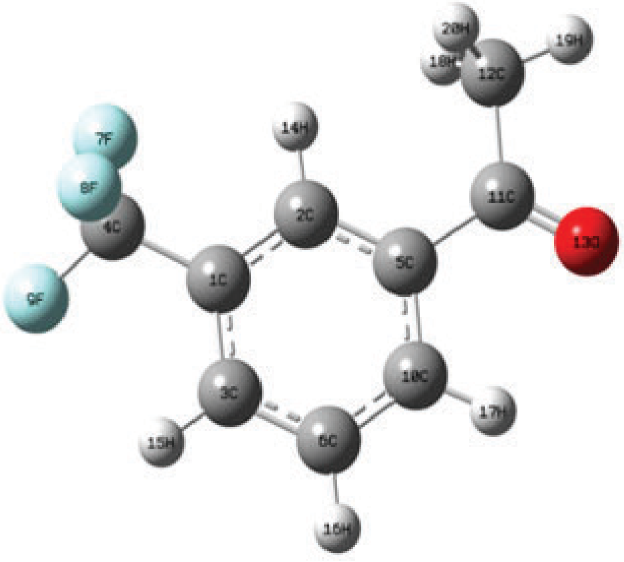

**Figure 1:** Optimized structure of 3TFMA.

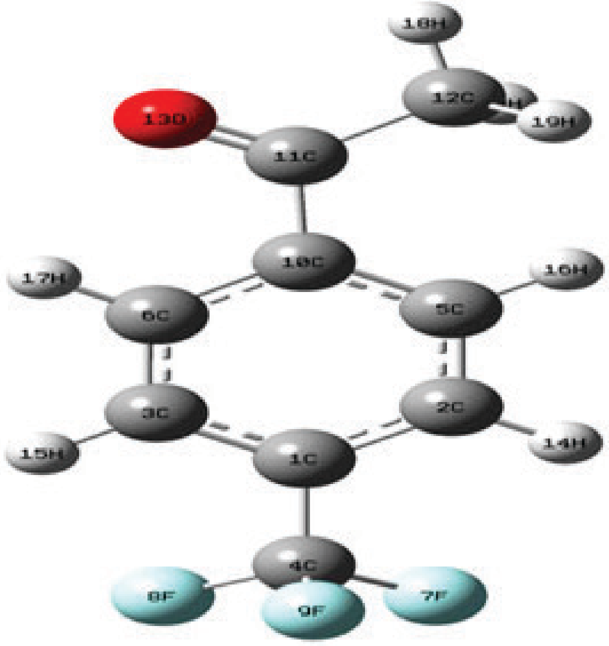

**Figure 2:** Optimized structure of 4TFMA.

**Table 1: Comparison of optimized parameters of the title compounds**

| Parameters | Bond length (Å) | | Parameters | Bond angle (º) | |
|---|---|---|---|---|---|
| | 3TFMA | 4TFMA | | 3TFMA | 4TFMA |
| C1-C2 | 1.393 | 1.392 | C2-C1-C3 | 120.3 | 120.3 |
| C1-C3 | 1.394 | 1.397 | C2-C1-C4 | 119.7 | 120.3 |
| C1-C4 | 1.504 | 1.505 | C1-C2-C5 | 120.1 | 119.7 |
| C2-C5 | 1.397 | 1.391 | C1-C3-C6 | 119.6 | 119.7 |
| C3-C6 | 1.393 | 1.386 | C1-C4-F7 | 112.0 | 112.2 |
| C4-F7 | 1.351 | 1.349 | C1-C4-F8 | 111.6 | 111.8 |
| C4-F8 | 1.353 | 1.350 | C1-C4-F9 | 112.0 | 111.4 |
| C4-F9 | 1.350 | 1.352 | C2-C5-C10 | 119.1 | 120.5 |
| C6-C10 | 1.388 | 1.401 | C2-C5-C11<br>(C5-C10-C11) | 122.6 | 122.8 |
| C5-C11<br>(C5-H16) | 1.505 | 1.082 | C5-C11-C12<br>(C10-C11-C12) | 118.8 | 118.8 |
| C11-C12 | 1.501 | 1.516 | C5-C11-O13<br>(C10-C11-O13) | 120.1 | 120.2 |
| C11-O13 | 1.213 | 1.213 | C1-C2-H14 | 119.0 | 119.8 |
| C2-H14 | 1.081 | 1.082 | C1-C3-H15 | 119.7 | 119.9 |
| C3-H15 | 1.082 | 1.083 | C3-C6-H16<br>(C2-C5-H16) | 119.7 | 118.9 |
| C6-H16<br>(C6-H17) | 1.083 | 1.082 | C5-C10-H17 (C3-C6-H17) | 118.0 | 121.1 |
| C10-H17 (C10-C11) | 1.082 | 1.505 | C11-C12-H18 | 110.9 | 108.5 |
| C12-H18 | 1.093 | 1.088 | C11-C12-H19 | 108.5 | 110.9 |
| C12-H19 | 1.088 | 1.093 | C11-C12-H20 | 111.0 | 110.9 |
| C12-H20 | 1.093 | 1.093 | | | |

## Natural Bond Orbital Analysis:

For hybridization study and effect of co-valency in polyatomic wave functions natural bond analysis is a simple technique. NBO analysis has been performed on the titled compound using NBO 4.1 program as implemented in Gaussian 09 package at the DFT-B3LYP/6-311G** level, in order to investigate the inter and intra molecular charge transfer takes place within the molecule. The donor-acceptor interactions in the NBO analysis were calculated by second order perturbation theory analysis as shown in **Table 2** and **Table 3** for the titled compounds respectively. In the anti-bonding orbitals (π*, σ*), the electron density (ED) changes and their energies (E2) have been calculated by NBO analysis at DFT-B3LYP/6-311G** level stabilization of energy emerging from the molecular interactions [17-22].

The interaction between electron donors and electron acceptor will be more intensive when the E2 value is larger. The strength of the delocalization interaction can be estimated by the second-order energy lowering E(2)

$$E^2=\Delta E_{ij}=q_iF(_{i,j})^2/E_j-E_i$$

For 3TFMA, **Table 2** shows the possible interactions with donors, acceptors and their electron densities of strong intra molecular interaction of Π electron with greater energy contribution from Π(C1-C2) → Π*(C6-C10) (253.36 kcal/mol) , Π(C6-C10)→ Π*(C1-C3) (24.10 kcal/mol) , Π(C1-C3)→ Π(C1-C3) (22.54 kcal/mol).The lone pair interactions were prominent in 3TFMA as expected due to the charge transfer that taking place from lone pair atoms into the ring. The prominent interactions showing higher E(2) values were LP(O13)→ σ*(C11-C12) (19.70 kcal/mol), LP(O13)→ σ*(C5-C11) (19.64 kcal/mol), LP(F9) → σ*(C1-C4) (5.95 kcal/m), LP(F7) → σ*(C1-C4) (5.90 kcal/m), LP(F8) → σ*(C1-C4) (5.80 kcal/m).

For 4TFMA, the **Table 3** shows the possible interactions with donors, acceptors and their electron densities of strong intra molecular interaction of Π electron with greater energy contribution from: Π(C1-C2) → Π*(C3-C6) (247.98 kcal/mol), Π(C3-C6) → Π*(C1-C2) (22.30kcal/mol), Π(C5-C10) → Π*(C1-C2) (20.82 kcal/mol). The lone pair interactions were prominent in 4TFMA as expected due to the charge transfer that taking place from lone pair atoms into the ring. The prominent interactions showing higher E(2)values were LP(O13)→ σ*(C11-C12) (19.72kcal/mol), LP(O13)→ σ*(C10-C11) (19.60 kcal/mol), LP(F7)→ σ*(C1-C4) (6.04 kcal/mol), LP(F8)→ σ*(C1-C4) (5.94 kcal/mol) and LP(F9)→ σ*(C1-C4) (5.79 kcal/mol).

**Table 2: Natural bond orbital analysis of 3TFMA**

| Donor(i) | Acceptor(j) | E(2) Kcal/mol | $E_{(j)}$-$E_{(i)}$ (au) | F(i, j) au |
|---|---|---|---|---|
| Π(C1-C2) | Π*(C6-C10) | 253.36 | 0.01 | 0.082 |
| Π(C6-C10) | Π*(C1-C3) | 24.10 | 0.28 | 0.073 |
| Π(C1-C3) | Π*(C2-C5) | 22.54 | 0.29 | 0.073 |
| Π(C2-C5) | Π*(C6-C10) | 20.21 | 0.29 | 0.70 |
| Π(C2-C5) | Π*(C1-C3) | 19.60 | 0.28 | 0.066 |
| Π(C6-C10) | Π*(C2-C5) | 19.24 | 0.28 | 0.066 |
| Π(C2-C5) | Π*(C11-O13) | 16.94 | 0.29 | 0.66 |
| Π(C1-C3) | Π*(C6-C10) | 16.34 | 0.30 | 0.063 |
| Π(C11-O13) | Π*(C2-C5) | 5.13 | 0.40 | 0.044 |
| LP(O13) | σ*(C11-C12) | 19.70 | 0.65 | 0.102 |
| LP(O13) | σ*(C5-C11) | 19.64 | 0.68 | 0.105 |
| LP(F9) | σ*(C4-F7) | 11.25 | 0.66 | 0.011 |
| LP(F9) | σ*(C4-F9) | 11.20 | 0.66 | 0.077 |
| LP(F8) | σ*(C4-F7) | 10.36 | 0.65 | 0.074 |
| LP(F8) | σ*(C4-F9) | 10.26 | 0.65 | 0.074 |
| LP(F9) | σ*(C4-F8) | 9.42 | 0.66 | 0.071 |
| LP (F7) | σ*(C4-F8) | 9.30 | 0.66 | 0.071 |
| LP(F9) | σ*(C1-C4) | 5.95 | 0.79 | 0.061 |
| LP(F7) | σ*(C1-C4) | 5.90 | 0.79 | 0.061 |
| LP(F8) | σ*(C1-C4) | 5.80 | 0.79 | 0.060 |
| LP(F7) | σ*(C4-F8) | 5.26 | 0.66 | 0.053 |
| LP(F9) | σ*(C4-F8) | 5.24 | 0.66 | 0.053 |
| σ(C1-C3) | σ*(C1-C2) | 5.36 | 1.28 | 0.074 |
| σ(C1-C2) | σ*(C1-C3) | 5.30 | 1.27 | 0.073 |

**Table 3: Natural bond orbital analysis of TFMA**

| Donor(i) | Acceptor(j) | E(2) Kcal/mol | $E_{(j)}$-$E_{(i)}$ (au) | F(i, j) au |
|---|---|---|---|---|
| Π(C1-C2) | Π*(C3-C6) | 247.98 | 0.01 | 0.081 |
| Π(C3-C6) | Π*(C1-C2) | 22.30 | 0.28 | 0.071 |
| Π(C5-C10) | Π*(C1-C2) | 20.82 | 0.28 | 0.068 |
| Π(C3-C6) | Π*(C5-C10) | 20.28 | 0.28 | 0.068 |
| Π(C1-C2) | Π*(C5-C10) | 19.73 | 0.29 | 0.068 |
| Π(C5-C10) | Π*(C3-C6) | 19.02 | 0.29 | 0.068 |
| Π(C1-C2) | Π*(C3-C6) | 18.24 | 0.30 | 0.067 |
| Π(C5-C10) | Π*(C11-O13) | 16.48 | 0.29 | 0.065 |
| Π(C1-C2) | Π*(C4-F9) | 6.59 | 0.50 | 0.055 |
| Π(C11-O13) | Π*(C5-C10) | 5.20 | 0.40 | 0.044 |
| LP(O13) | σ*(C11-C12) | 19.72 | 0.65 | 0.102 |
| LP(O13) | σ*(C10-C11) | 19.60 | 0.68 | 0.104 |
| LP(F7) | σ*(C4-F8) | 10.94 | 0.66 | 0.076 |
| LP(F8) | σ*(C4-F7) | 10.93 | 0.66 | 0.076 |
| LP(F9) | σ*(C4-F7) | 10.36 | 0.65 | 0.074 |
| LP(F9) | σ*(C4-F8) | 10.28 | 0.65 | 0.074 |
| LP (F8) | σ*(C4-F9) | 9.74 | 0.66 | 0.072 |
| LP(F7) | σ*(C4-F9) | 9.73 | 0.66 | 0.072 |
| LP(F7) | σ*(C1-C4) | 6.04 | 0.79 | 0.062 |
| LP(F8) | σ*(C1-C4) | 5.94 | 0.79 | 0.061 |
| LP(F9) | σ*(C1-C4) | 5.79 | 0.79 | 0.060 |
| σ (C1-C2) | σ*(C1-C3) | 5.10 | 1.27 | 0.072 |
| σ(C1-C3) | σ*(C1-C2) | 5.06 | 1.27 | 0.072 |

## Mulliken Atomic Charge Analysis

In order to investigate the charges on atoms and their changes, the mulliken population analysis of the titled compounds has been carried out using DFT methodology at B3LYP/6-311G** level and the values obtained for 3TFMA and 4TFMA was shown in Table 4. The graphical representations of the atomic charges obtained were shown in the Fig. 3 and Fig. 4 respectively. The analysis shows that in 3TFMA the presence of large electronegative atoms C1 (-0.2947 e), F7 (-0.2116 e), C10 (-0.0052 e), $O_1$ (-0.2893 e), creates more positive charges on C4 (0.7232 e). The atom C12 shows largest electro negativity of (-0.3261 e) and the atom C4 shows largest electro positivity of (0.7232 e). This indicates the extensive charge delocalization within the molecule [18].

In the same way for 4TFMA the presence of large electronegative atoms C12 (-0.3238 e), O13 (-0.2874 e), C1 (-0.2713 e), creates more positive charges on C4 (0.7248 e). The atom

C12 shows largest electro negativity of (-0.3238 e) and the atom C4 shows largest electro positivity of (0.7248). This indicates the extensive charge delocalization within the molecule [19]. These results further supports the observed elongation in the bond lengths as evident from the molecular geometry section.

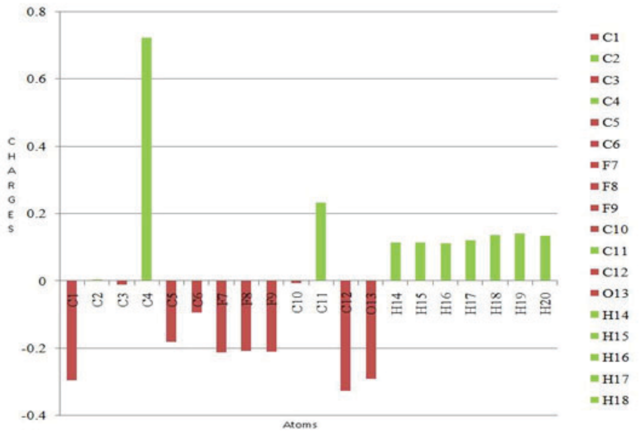

**Figure 3:** Mulliken Atomic Charges of 3TFMA.

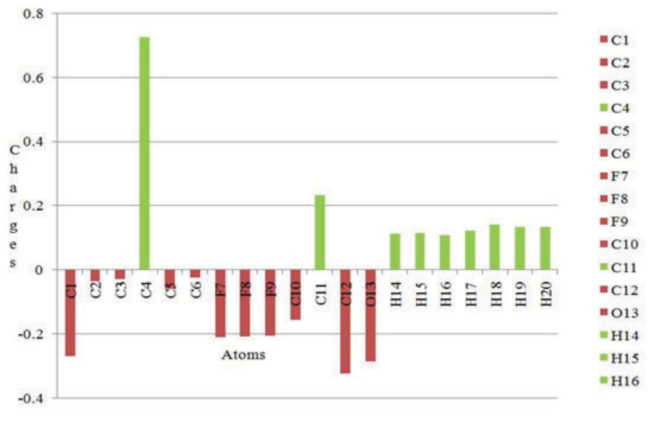

**Figure 4:** Mulliken Atomic Charges of 4TFMA.

**Table 4: Mullikenatomic charges**

| S. No. | Atoms | Charges (e) | |
|---|---|---|---|
| | | 3TFMA | 4TFMA |
| 1 | C1 | -0.2946 | -0.2713 |
| 2 | C2 | 0.0054 | -0.0362 |
| 3 | C3 | -0.0110 | -0.0297 |
| 4 | C4 | 0.7232 | 0.7248 |
| 5 | C5 | -0.1809 | -0.0604 |
| 6 | C6 | -0.0937 | -0.0255 |
| 7 | F7 | -0.2115 | -0.2109 |
| 8 | F8 | -0.2078 | -0.2085 |
| 9 | F9 | -0.2098 | -0.2070 |
| 10 | C10 | -0.0051 | -0.1566 |
| 11 | C11 | 0.2330 | 0.2309 |
| 12 | C12 | -0.3261 | -0.3238 |
| 13 | O13 | -0.2892 | -0.2874 |
| 14 | H14 | 0.1135 | 0.1126 |
| 15 | H15 | 0.1143 | 0.1149 |
| 16 | H16 | 0.1105 | 0.1060 |
| 17 | H7 | 0.1202 | 0.1209 |
| 18 | H18 | 0.1353 | 0.1401 |
| 19 | H19 | 0.1398 | 0.1336 |
| 20 | H20 | 0.1344 | 0.1335 |

## CONCLUSIONS

The optimized structures, their respective energies, optimized geometry, molecular stability and the intramolecular interactions of the two different title compounds were investigated with aid of Density Functional Theory. To obtain the most stable geometry, structure optimization was performed using the DFT method along with proper basis set chosen.

From the comparative study made on the geometrical parameters, some deviations in the bond lengths and bond angles were found in both the title compounds. The electron density changes in the bonding and antibonding orbitals and that of lone pairs due to the charge transfer of electrons between various bonds have been investigated by NBO analysis. The stabilization of the title compound seems to be highly dependent on the charge transfer equally from the bond pair to bond pair and also from the lone pairs to bond pairs.

### Conflicts of Interest

There are no conflicts of interest.

## REFERENCES

1. Yale, Harry L. Journal of Medicinal and Pharmaceutical Chemistry, 1959, 1 (2), 121–133.
2. Anant Prakash, Bibhesh K. Singh, Narendar Bhojak, Devjani Adhikari. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 76, 3–4.
3. V. Arjunan, L. Devi, R. Subbalakshmi, T. Rani, S. Mohan. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2014, 130,164-177.
4. B. AEl-Sayed, M. MAbo Aly, A.A.A Emara, S.M. EKhalil. Vibrational Spectroscopy, 2002, 30(1).
5. Saikat K. Seth, Dipak K. Hazra, Monika Mukherjee, Tanusree Kar. Journal of Molecular Structure, 2009, 936, 277-282
6. Angelo Vargas Thomas Bürgi, Alfons Baiker. Journal of catalyst, 2003.
7. Senapati, U De, D De, B R. NISCAIR online periodicals respiratory, 2008.

8. Joseph S. Bair, York Schramm, Alexey G. Sergeev, Eric Clot, Odile Eisenstein, and John F. Hartwig. Journal of American chemical society, 2014.
9. Aiping Fu, Wei Meng, Hongliang Li, Jing Nie and Jun-An Ma. Journal of organic and biomolecular chemistry, 2014, 12.
10. L. P. Avendaño Jiménez, G. A. Echeverría, O. E. Piro, S. E. Ulic, and J. L. Jios. Journal of American Chemical Society, 2014.
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; et al. Gaussian, Inc.: Wallingford, CT, 2009.
12. Lee, C.; Yang, W.; Parr, P.G. Phys. Rev. B, 37 (1988) 785.
13. Yan, G.; Xue, Y.; Xie, D. Int. J. Quant. Chem. 72 (1999) 53.
14. E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, J.A. Bohmann, C.M. Morales, NBO version 5.0, Theoretical Chemistry Institute (University of Wisconsin Madison, 2001).
15. F. Weinhold, Chemistry: A new twist on molecular shape, Nature 411 (1993) 539-541.
16. X.H. Li, R.Z. Zhang, X.Z. Zhang. Struc. Chem. 2 (1993) 1049-1054.
17. A.E. Reed, L.A. Curtis, F. Weinhold. Chemical Reviews, 1988, 88, 899-926.
18. S. Muthunatesan, V. Ragavendran, Spectrochim. Acta 134A (2015) 148-154.
19. G. Keresztury, S. Holly, J. Varga, G. Besenyei, A.V. Wang, J.R. Durig, Spectrochim. Acta 49A (1993) 2007.
20. R. Aldrich, P.R. Taylor (1981), The choice of basis sets for molecular electrons structure Calculations, J. Chem. Phys., Vol 78, pp 315 – 324.
21. T.H. Dunning(1989) Gaussian basis sets for use in correlated molecular calculations, J. Chem. Phy, 90, 1007 – 1023.
22. A.John. Pople(1970) Molecular orbital methods in organic chemistry. Acc. Chem. Res., 3 (7), 217 – 223.
23. Jan E. True; T. Darrah Thomas; Rolf W. Winter; Gary L. Gard (2003). Electronegativities from Core-Ionization Energies: Electronegativities of SF5 and CF3”.