



Int. J. New. Chem., 2021, Vol. 8, Issue 3, pp 345-355.

International Journal of New Chemistry

Published online 2021 in <http://www.ijnc.ir/>
Open Access

Print ISSN: 2645-7237

Online ISSN: 2383-188x



Original Research Article

Computational Review of Conformers 2- Chloroacetaldehyd

Reza Fazaeli^{1*}, Abdullah Ghasemi²

^{1*}Department of Chemistry, Faculty of Science, South Tehran Branch, Islamic Azad University, Tehran, Iran.

²Department of Chemistry, Faculty of Science, Arak Branch, Islamic Azad University, Arak, Iran.

Received: 2020-06-11

Accepted: 2020-12-05

Published: 2021-07-01

ABSTRACT

Abstract In studies performed on 2- chloroacetaldehyde by abinitio beginning with the LC-WPBE, B3LYP and m06-2x functionals and 6-311++G (d, p) basis set. Also, by checking the total energy, HOMO-LUMO gaps and dipole moment, it was found that the keto form is more stable than the enol form. Theoretical calculations With LC-WPBE/6-311G(d,p) shows the more stability of I- conformer in compared to other conformers . NBO analysis was practical for illustrating the negative hyperconjugative effect on the conformers. In the basis of NBO analysis, the $LP(2)O \rightarrow \sigma^*(C-H)$ and $LP(2)O \rightarrow \sigma^*(C-C)$ Interactions were responsible of the negative hyperconjugation in the examined compounds. The deletion of all thw donor – acceptor electronic interaction from the fock matrices and off –diagonal elements, values of these interaction were reported.

Keywords: 2- chloroacetaldehyd, NBO (natural bond orbital analysis), Negative hyperconjugative effect, Second order the stabilization energies (E_2)

Introduction

According to the calculations made by Leo Radom and Noel V. Riggs in 1979 by the means of a modified version of the Gaussian 70 and the STO-3G and 4-31G [1,2] in which they achieved the point that the total energy for the acetaldehyde molecule in the eclipsed conformation is -150.947 and -152.685 respectively and for the staggered conformation is -150.944 and -152.683 respectively Hartry. This revealed that the eclipsed conformation of the acetaldehyde is more stable than its staggered conformation. In this study, Professor Radom considered the stability of the eclipsed conformation in accordance with the interaction of the methyl group with the double bond of the carbonyl group. He argued that the methyl group primarily could be considered as a predominant π -group. If methyl binds to a double bond, it acts as a supercharger.

In 1994, Professor Goodman et al. via MP2 / 6-311G ** conducted research studies on acetaldehyde [3]. They reported a C-C bond length of 1.499 for the eclipsed conformation and 1.500 for the staggered conformation and for the carbonyl group for both conformers reported 1.209. Albeit, in this paper, the length of the bond for hydrogen attached to the carbonyl group considered 1.107 for the eclipsed conformation and 1.1058 for the staggered conformation as well.

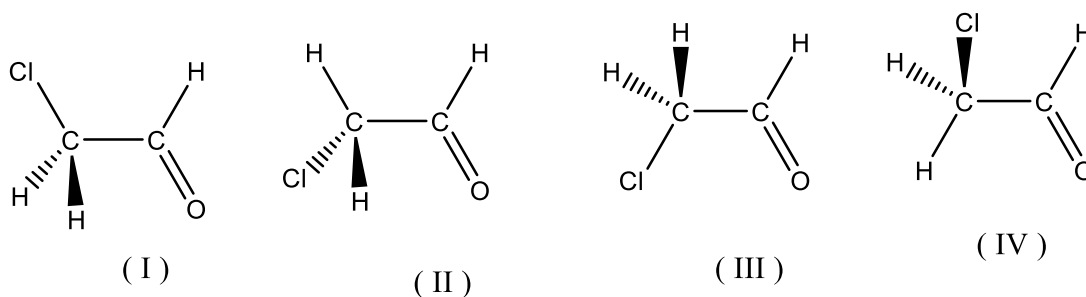


Figure 1. Possible conformers of 2- chloroacetaldehyd.

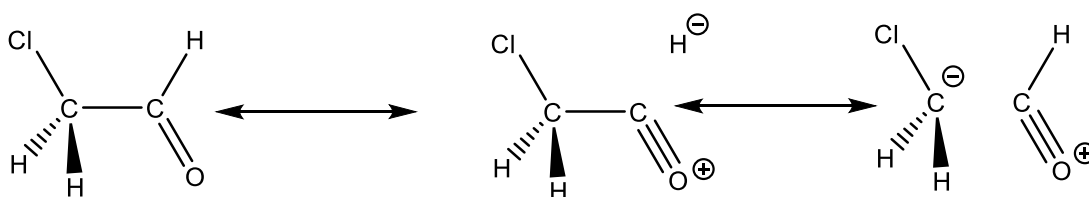


Figure 2. The predicted resonance structures of 2- Chloroacetaldehyde with NBO analysis.

Computational Methods

The Gaussian 09 program bundle was utilized in our calculations [4]. Geometries of the considered particles were optimized utilizing the Standard 6-311++G(d,p) premise set [5-6], LC-wPBE useful [7], the crossover useful of M06-2X, as created by Truhlar and Zhao[8] and cross breed utilitarian of the B3LYP [9] were utilized. LC-wPBE may be a long-range rectified (or extend isolated) cross breed where the sum of exact exchange raises with expanding inter-electronic separate to form them more exact for moves to higher-lying orbitals [10]. A vibrational investigation was conducted at each stationary point watched, affirming its characteristics as the slightest vitality. In addition, the populace has been analyzed utilizing the NBO handle [11] at LC-WPBE /6-311++G(d,p) level of hypothesis with the NBO 6.0 program [12] through the computer program of Gaussian 09. Visualization of the NBOs was plotted with Multiwfn 3.5 computer program bundle [13].

Results and Discussion

Vitality content Conformers and truncations of the 2- choroacetaldehyd

particle are delineated in Figure 1. The outright vitality and relative vitality values of conformers of the keto and enol shapes of the 2- choroacetaldehyd are calculated at three levels of the hypothesis: LC-wPBE/6-311++G(d,p), M062X/6-311++G(d,p) and B3LYP/6-311++G(d,p) (Table 1). As can be seen, the keto frame has more steadiness than the enol frame. On the other hand, the I-conformer encompasses a bigger steady conformer at LC-wPBE/6-311++G(d,p) level. Two other levels appear that I-conformer and IV-conformer are iso-energetic. The more solidness of I-conformer compared to other conformers is ascribed to negative hyper conjugation impacts. Figure 2 speaks to the canonical reverberation structure of the mentioned negative hyper conjugation intuitive.

Total dipole moment

The full dipole minute values of the different conformers of 2- choroacetaldehyd atom are recorded in Table 1. Add up to dipole minute esteem utilizing the x, y, z components are characterized as: $\mu_{tot} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$ Total dipole minute values of polar I-conformer uncover the littlest add up to dipole moment values. The gotten comes about are reliable with littler add up to dipole minute values for more steady conformers [14]

Atomic orbital analysis

The wilderness orbital vitality and HOMO-LUMO crevice values of the different conformers of 2- choroacetaldehyd particle is calculated. The calculated values in Table 2 appear that the foremost solidness of HOMO and the lowest stability of LUMO within the I-conformer. Plots of wilderness orbital of these conformers are displayed in Figure 3. It is additionally possible to discover out that the biggest HOMO-LUMO crevice and hardness esteem within the I-conformer. The hardness esteem is calculated by the taking after condition: $\eta = (E_{LUMO} - E_{HOMO})/2$ this increment is congruous with the greatest hardness principle (MHP) and the least vitality guideline (MEP). Based on MHP, whereas a conformer changes from the foremost steady to the less steady species in most cases, the vitality increments, and the hardness diminishes [15-16]. The electrophilicity record, ω , for each atom measured utilizing the expression [17]: $\omega = \mu^2/2\eta$ where μ the chemical potential is: $\mu = (E_{HOMO} + E_{LUMO})/2$ and η is the hardness. The calculated electrophilicity (ω) values are recorded in Table 2. It can be watched the littler ω values in I-conformer in comparison to other conformers. This drift is congruous with the least electrophilicity rule (MEP) [18, 19] that is, whereas a conformer change from the foremost steady to other less steady species in most cases, the vitality rises, and the electrophilicity increments.

Natural bond analysis (NBO)

NBO examination is valuable to discover a exhaustive understanding of the impacts that coordinate the foremost steady conformations in an isolated phase. Also, NBO could be a noteworthy apparatus for outline of associate- and intramolecular holding intelligent, and as well as a reasonable root for investigating conjugative interaction or charge exchange in atomic frameworks. A few of the orbitals are electron benefactors or acceptors. The contrast of vitality between such holding and anti-bonding orbitals, $[E^{(2)}]$, impacts the helplessness of the atom to intelligent [20, 21]. There are more viable intelligence with the bigger $[E^{(2)}]$ values. This recommends a stronger giving propensity of an electron of one orbital and the next tolerating inclination of other orbitals, which causes a more grounded interaction between them. The second-order Fock network has been utilized for evaluating intuitive comparing to the donor-acceptor within

the NBO investigation [51]. For each benefactor (i) and acceptor (j), the stabilization vitality $E^{(2)}$ comparing to the delocalizing $i \rightarrow j$ is assessed as: $E^{(2)} = -q_i (F_{ij})^2 / (E_j - E_i)$ where q_i speaks to the i th benefactor orbital inhabitance and E_i and E_j compare to the giver and acceptor orbitals, separately. $E_j - E_i$ speaks to the contrast of vitality between the benefactor orbital and acceptor orbital; i.e., the more prominent giving propensity of the electron givers toward electron acceptors the bigger degree comparing to conjugating the full framework.

Second-order annoyance hypothesis investigation of Fock network in NBO basis NBO examination may be utilized for clarifying the higher soundness of the I-conformer comparing to other conformers. The stabilization energies of most vital donor-acceptor electron intelligence have exceptional impacts on the stabilities of the conformations of the considered particles (Table 3). These $LP(O_2) \rightarrow *(C-H)$ and $LP(O_2) \rightarrow *(C-C)$ intelligent are the negative hyper conjugation related to the inspected compounds (Figure 2). It can be found, $LP(O_2) \rightarrow *(C-H)$ interaction is more critical than $LP(O_2) \rightarrow *(C-C)$ interaction. These NBOs are visualized in Figure 4.

Within the current ponder, Common Bond Orbital (NBO) investigation was employed to segment the entire electronic vitality $E(tot)$ into Lewis $E(L)$ (orbital population=2.0) and Non-Lewis $E(NL)$ components (Table 4). The localized Lewis $E(L)$ component gave a great guess of all the steric and classical electrostatic impacts since comparing to over 99.5% of the total electron thickness, whereas all the conjugation sorts may well be depicted by the Non-Lewis $E(NL)$ component. Table 4 appears that the more noteworthy inclination of the I-conformer when as it was considering the conjugation impacts.

Calculations of the characteristic coulomb electrostatic energies $E(NCE)$, as well as the total electronic vitality and its Lewis components, were conducted [52]. Table 4 uncovers the best I-conformer based on NCE values. Calculation of the whole steric vitality $E(ST)$ was done through the NBO investigation. Table 4 advance displays the more articulated steric intuitive happening within the III-conformer. It can be seen, the least steric intelligence happens within the I-conformer.

Tables

Table 1. Energy (E, a.u), relative energy (ΔE , kcal/mol) and dipole moment (μ , Debye) of possible conformers of keto and enol forms of 2- Chloroacetaldehyde at the LC-wPBE/6-311++G(d,p), M062X/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory.

(a)keto form							
	LC-wPBE/6-311++G(d,p)			M062X/6-311++G(d,p)		B3LYP/6-311++G(d,p)	
	E	ΔE	μ	E	ΔE	E	ΔE
I	-613.2544	0.00	1.06	-613.3989	0.00	-613.4986	0.00
II	-613.2488	3.51	3.29	-613.3937	3.26	-613.4934	3.26
III	-613.2525	1.13	3.72	-613.3972	1.07	-613.4969	1.07
IV	-613.2531	0.82	2.20	-613.3981	0.50	-613.4981	0.31
(b)enol form							
	LC-wPBE/6-311++G(d,p)			M062X/6-311++G(d,p)		B3LYP/6-311++G(d,p)	
	E	ΔE^+		E	ΔE	E	ΔE
I	-613.2377	10.48		-613.3852	8.61	-613.4832	9.63
II	-613.2440	3.01		-613.3920	1.07	-613.4895	2.44
III	-613.2440	5.33		-613.3920	3.26	-613.4895	7.64
IV	-613.2377	9.63		-613.3852	8.07	-613.4832	9.33

Table 2. Frontier orbital energy (E , eV), HOMO-LUMO gap (ΔE , kcal/mol), hardness (η , eV), electrophilicity (ω , eV) of possible conformers of 2-Chloroacetaldehyde at the LC-wPBE/6-311++G(d,p) level of theory

	E(HOMO)	E(LUMO)	ΔE	η	ω
I	-10.86	0.97	11.83	5.92	2.07
II	-10.73	0.59	11.32	5.66	2.26
III	-10.81	0.83	11.64	5.82	2.14
IV	-10.77	0.83	11.60	5.80	2.13

Table 3. Second order perturbation theory analysis of Fock matrix in NBO basis of LP (2) O $\rightarrow \sigma^*(C-H)$ and LP (2) O $\rightarrow \sigma^*(C-C)$ negative hyperconjugation interactions of possible conformers of 2-Chloroacetaldehyde at the LC-wPBE/6-311++G(d,p) level of theory.

Molecule	LP(2)O $\rightarrow \sigma^*(C-H)$			LP(2)O $\rightarrow \sigma^*(C-C)$		
	E(2)*	E(NL)-E(L)**	F(L,NL)**	E(2)*	E(NL)-E(L)**	F(L,NL)**
I	28.65	0.85	0.142	26.43	0.85	0.136
II	29.61	0.84	0.143	26.98	0.85	0.137
III	31.15	0.83	0.146	28.07	0.83	0.146
IV	29.18	0.85	0.142	26.00	0.85	0.135

Table 4. Results of the NBO analysis and energy decomposition of total electronic energy E(total) into Lewis E(L), non-Lewis E(NL), total steric E(steric) and electrostatic E(NCE) energies (in kcal/mol) of possible conformers of 2-fluoroacetaldehyde at the LC-wPBE/6-311++G(d,p) level of theory.

Molecule	E(steric)	ΔE (steric)	E(NCE)	ΔE (NCE)	E(NL)	ΔE (NL)
I	55.15	0	-0.11940	0.00	0.04903	0.00
II	61.42	6.27	-0.09834	13.22	0.04223	-4.27
III	63.22	8.07	-0.09515	15.22	0.04445	-2.87
IV	60.66	5.51	-0.10922	6.39	0.04506	-2.49

*ina.u.

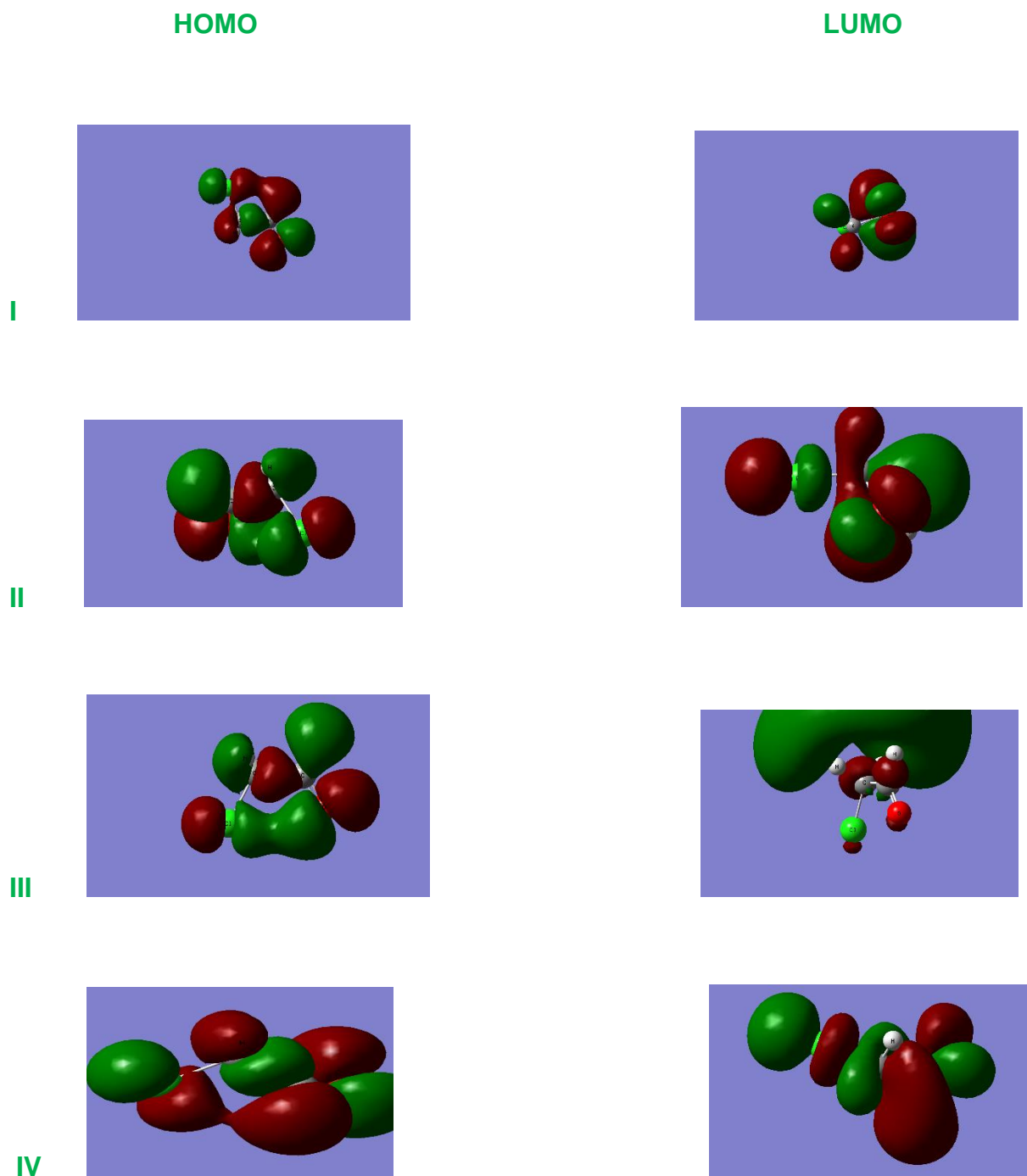


Figure. 3. Plots of frontier orbital of the possible conformers of 2- chloroacetaldehyd.

Conclusion

Within the current think about, we examined the steadiness comparing to the different conformers of 2- chloroacetaldehyd. The most computation of current work can be laid out as follows:

1. I- compliance has more prominent soundness than other conformations in all examined particles at the LC-WPBE/6-311++G(d,p) level of hypothesis. The more noteworthy soundness of this compliance was ascribed to a negative hyper conjugative effect.
2. The negative hyper conjugative anomeric impact of these particles was explored by the LP(O2) *(C-H) interaction.
3. The biggest HOMO-LUMO crevice esteem, the littlest electrophilicity (ω) esteem for the I- conformer are is consistent with the standards of least vitality (MEP), and greatest hardness (MHP), the least electrophilicity guideline (MEP).

References

- [1] L. Radom, J. Baker, P.M. Gill, R.H. Nobes, & N.V. Riggs, *J. Mol. Struct.*, 126, 271(1985).
- [2] N.R. Carlsen, L. Radom, N.V. Riggs, W.R. Rodwell, *J. Am. Chem. Soc.* 101, 2233(1979).
- [3] L. Goodman, R. Zwarich, *J. Am. Chem. Soc.* 93, 2068 (1971).
- [4] B. E. Smart, *Organofluorine Chem.*, 57. (1994).
- [5] R. Sahnoun, Y. Fujimura, K. Kabuto, Y. Takeuchi, R. Noyori, *Bull. Chem. Soc. Jpn.*, 79, 555 (2006).
- [6] E.D. Raczyńska, W. Kosińska, B. Ośmiałowski, R. Gawinecki, *Chem. Rev.*, 105, 3561 (2005).
- [7] C.C. Su, C.K. Lin, C.C. Wu, M. H. Lien, *J. Phys. Chem. A.*, 103, 3289 (1999).
- [8] J. Andres, L.R. Domingo, M.T. Picher, V.S. Safont, *Int. J. Quantum Chem.*, 66, 9 (1998).
- [9] K. Suenobu, M. Nagaoka, T. Yamabe, *J. Mol. Struc-Theochem.*, 461, 581 (1999).
- [10] R.A. King, W.D. Allen, H.F. Schaefer III, *J. Chem. Phys.*, 112, 5585 (2000).
- [11] W.O. George, B.F. Jones, R. Lewis, J.M. Price, *J. Mol. Struct.*, 550, 281(2000).
- [12] K. Lammertsma, & P.V. Bharatam, *J. Org. Chem*, 65, 4662 (2000).
- [13] A.J. Aquino, D. Tunega, G. Haberhauer, M.H. Gerzabek, & H. Lischka, *J. Phys. Chem. A*, 106, 1862 (2002).
- [14] N. Heinrich, W. Koch, G. Frenking, H. & Schwarz, *J. Am. Chem. Soc.*, 108, 593(1986).
- [15] K. Yamada, K. Isobe, T. Okuda, & Y. Furukawa, *Z. Naturforsch A.*, 49, 258 (1994).
- [16] G. da Silva, C.H. Kim, & J.W. Bozzelli, *J. Phys. Chem. A*, 110, 7925 (2006).
- [17] N. Klinhom, N. Saengsuwan, S. Sriyab, P. Prompinit, S. Hannongbua, S. & Suramitr, *Spectrochim. Acta. A. Mol. Bio. Spect.*, 206, 359 (2019).
- [18] V.L. Freitas, P.J. Ferreira, M.D.R. & da Silva, *J. Chem. Thermodyn.*, 118, 115 (2018).

- [19] C. Hanpaibool, T. Chakcharoensap, Y. Hijikata, S. Irle, P. Wolschann, N. Kungwan, & T. Rungrotmongkol, *J. Mol. Liq.*, 265, 16 (2018).
- [20] A.A. Adeniyi, J. & Conradie, *Electrochim. Acta.*, 297, 947 (2019).
- [21] G. J. Karabatsos, & D. J. Fenoglio, *J. Am. Chem. Soc.*, 91(5), 1124 (1969).
- [22] R. P. Orenha, R. Vessecchi, & S.E. Galembeck, *J. Struct. Chem.*, 29, 847 (2018).
- [23] M. Nasrolahi, R. Ghiasi, & F. Shafiei, *J. Struct. Chem.*, 60, 746 (2019).
- [24] M. Vafaei-Nezhad, R. Ghiasi, & F. Shafiei, *Chem. Methodol.*, 4, 161(2020).
- [25] A. Rathna, & J. Chandrasekhar, *J. Chem. Soc. Perkin Trans. 1.*, 2, 1661(1991).
- [26] T. Leyssens, & D. Peeters, *J. Org. Chem.*, 73, 2725 (2008).
- [27] J. Oomens, G. Berden, & T.H. Morton, *Chem. Phys. Chem.*, 16, 1992 (2015).
- [28] S. O. Nilsson Lill, G. Rauhut, & E. Anders, *Chem. Eur. J.*, 9, 3143 (2003).
- [29] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [30] R.B.J.S. Krishnan, J.S. Binkley, R. Seeger, & J.A. Pople, *J. Chem. Phys.*, 72, 650 (1980).
- [31] M.J. Frisch, J.A. Pople, J.S. Binkley, *J. Chem. Phys.*, 80, 3265 (1984).
- [32] L.A. Curtiss, M.P. McGrath, J.P. Blaudeau, N.E. Davis, R.C. Binning, & L. Radom, *J. Chem. Phys.*, 103, 6104 (1995).
- [33] O. A. Vydrov, & G. E. Scuseria, *J. Chem. Phys.*, 125, 234109 (2006).
- [34] Y. Zhao, & D.G. Truhlar, *J. Chem. Phys.*, 125(19), 194101 (2006).
- [35] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, & S. Dapprich, *J. Chem. Phys.*, 98, (1993).
- [36] D. Jacquemin, E.A. Perpète, G.E. Scuseria, I. Ciofini, & C. Adamo, *J. Chem. Theory Comput.* 4, 123 (2008).
- [37] A.E. Reed, L.A. Curtiss, & F. Weinhold, *Chem. Rev.*, 88, 899 (1988).
- [38] E. D. Glendening, C. R. Landis, and F. Weinhold, *J. Comput. Chem.*, 40, 2234 (2019).
- [39] T. Lu, & F. Chen, *J. Comput. Chem.*, 33, 580 (2012).
- [40] C.L. Perrin, K.B. Armstrong, & M.A. Fabian, *J. Am. Chem. Soc.*, 116, 715 (1994).
- [41] P. W. Ayers, & R.G. Parr, *J. Am. Chem. Soc.*, 122, 2010 (2000).
- [42] R. G. Parr, & P. K. Chattaraj, *J. Am. Chem. Soc.*, 122, 2010 (1991).
- [43] P. K. Chattaraj, P. A. T. R. I. C. I. O. Fuentealba, B. Gomez, & R. E. N. A. T. O. Contreras, *J. Am. Chem. Soc.*, 122, 348 (2000).
- [44] R.G. Pearson, *Chem. hard.*, (1997).
- [45] R. G. Pearson, *J. Chem. Educ.*, 76, 267 (1999).

- [46] R. G. Parr, L.V. Szentpály, Sh. Liu. *J. Am. Chem. Soc.*, 121, 1922 (1999).
- [47] E. Chamorro, P.K. Chattaraj, P. Fuentealba, *J. Phys. Chem. A.*, 107, 7068 (2003).
- [48] R. Parthasarathi, M. Elango, V. Subramanian, & P.K. Chattaraj, *Theor. Chem. Acc.*, 113, 257 (2005).
- [49] C. James, A.A. Raj, R. Reghunathan, V.S. Jayakumar, & I.H. Joe, *J. Raman Spectrosc.*, 37, 1381 (2006).
- [51] Y. Yang, W. Zhang, & X. Gao, *Int. J. Quantum Chem.*, 106, 1199 (2006).
- [52] F. Weinhold. C.R. Landis., John Wiley & Sons (2012).

How To Cite This Article

Reza Fazaeli, Abdullah Ghasemi, “**Computational Review of Conformers 2-choroacetaldehyd**” International Journal of New Chemistry., 2021; DOI: 10.22034/ijnc.2020.127669.1119