International Journal of Trend in Scientific Research and Development (IJTSRD)
Volume 10 Issue 5, Sep-Oct 2026 Available Online: www.ijtsrd.com e-ISSN: 2456 – 6470

DFT investigation of Hydrogen bonding in Methyl Chloride-Formic Acid Complexes

Arjun Singh[1], Jyoti Tyagi[2], Sanjeev Kumar Mishra[3]*

[1]SBM Sr. Sec. School, Directorate of Education, GNCT of Delhi, Delhi, India
[2,3]Department of Chemistry, Zakir Husain Delhi College, University of Delhi, Delhi, India
*Corresponding Author: Sanjeev Kumar Mishra

ABSTRACT

The complex formed between methyl chloride and formic acid provides a suitable model system for exploring the nature and characteristics of weak as well as unconventional hydrogen-bonding interactions. In the present study, four minima corresponding to distinct van der Waals complexes of formic acid (HCOOH) and methyl chloride (CH3Cl) are considered. DFT study using B3LYP/6-311+G** level of theory has been used to find the minima of the four van der Waals complex. Binding and activation energies were evaluated at the same level of theory. RHF and RMP2 level calculations were also performed to present a comparative account. The four optimized minima are connected through low-lying energy barriers of approximately 0.9–2.6 kcal mol-1, suggesting that facile interconversion between these structures is possible. The study highlights the significance of cyclic arrangements in which multiple weak hydrogen bonds contribute to the overall structural stability, with the combined stabilization being enhanced through cooperative interactions among these hydrogen bonds. The findings provide deeper insight into the nature and significance of unconventional hydrogen-bonding interactions.

KEYWORDS: *B3LYP, van der Waals complex, binding energy, activation energy.*

How to cite this paper: Arjun Singh | Jyoti Tyagi | Sanjeev Kumar Mishra "DFT investigation of Hydrogen bonding in Methyl Chloride-Formic Acid Complexes" Published in International Journal of Trend in Scientific Research and Development (ijtsrd), ISSN: 2456-6470, Volume-10 | Issue-5, October 2026, pp.461-466, URL: www.ijtsrd.com/papers/ijtsrd142246.pdf

IJTSRD142246

INTRODUCTION

Conventionally hydrogen bonds are generally formed when hydrogen is directly attached with electronegative atoms such as oxygen, nitrogen, fluorine etc., but interaction of CH_3Cl and HCOOH provides an interesting model to investigate the non-conventional weak hydrogen bond. These kinds of interactions also prevail in many chemical and biochemical processes.

Hydrogen bonding has emerged as a subject of extensive contemporary research due to its ubiquitous nature and fundamental importance in a wide range of chemical and biochemical process [1-3]. In recent years, unconventional hydrogen bonding involving C–H groups has attracted increasing attention in structural chemistry and biological research [4-5]. The major role of C-H---O hydrogen bonds in conformational analysis [6], molecular recognition processes [7], the stabilization of inclusion complexes [8,9], crystal packing [10] and the important role of such interaction in determining the stability and structure, and possibly the biological activity, of biological macromolecules has been well established [11].

Depending on the nature of the interacting species, the strength of hydrogen bonds can range from approximately 1 to 40 kcal/mol, reflecting a broad continuum of interaction strengths. Weak hydrogen bonds often exhibit interaction characteristics that closely resemble those of van der Waals forces, making them difficult to distinguish unambiguously [12-13].

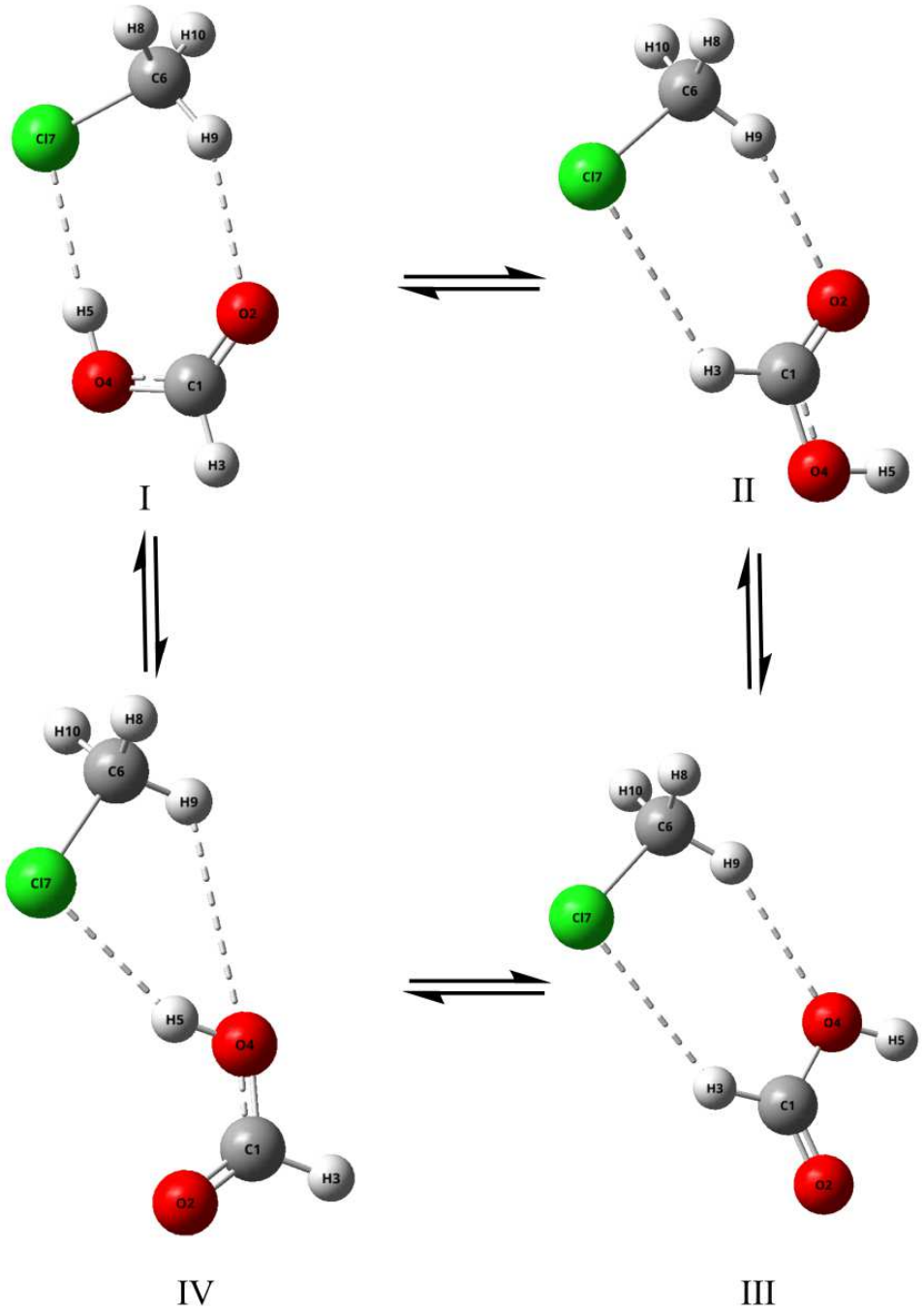

Fig. 1: Optimized Geometry of van der Waals complex of formic acid and methyl chloride

With the exception of a few recent and significant investigations, most studies of hydrogen bonding have traditionally regarded hydrocarbons as too weak proton donors to participate effectively in hydrogen-bond formation. Weak hydrogen bonds are predominantly electrostatic in nature; however, their interaction acquire progressively greater covalent character as the bond strength increases [14].

Hydrogen-bonded complexes involving a C-H group as the proton donor have been widely employed to investigate and characterize hydrogen-bonding interactions across a broad range of strengths, including strong, moderate, and weak interactions [15]. Among these, the C-H···O hydrogen bond is generally regarded as one of the weaker types of hydrogen bonding and has been the subject of numerous theoretical and experimental investigations reported in the literature [16-20].

Reynolds [21] investigated two theoretical approaches to characterize the van der Waals complex formed between formic acid and methyl chloride with particular emphasis on the associated hydrogen-bonding interactions and their strengths. In the present study, density functional theory (DFT) employing the B3LYP functional has been used to investigate the relative stability of four minima identified for the formic acid-methyl chloride van der Waals complexes and to characterize the corresponding hydrogen-bonding interactions.

METHOD OF CALCULATION

All quantum-chemical calculations were carried out using the Gaussian 98 computational package. The molecular geometries were optimized at the B3LYP/6-311+G** level of theory. To have a comparative study, additional calculations were carried out at the levels of RHF and RMP2 keeping the same basis set. All stationary points were characterized by analyzing the number of imaginary vibrational frequencies and the eigenvalues of the corresponding Hessian matrix. The bonding characteristics were examined by calculating Bader's topological analysis of $\rho(r_c)$ and the corresponding Laplacian of the electron density ($\nabla^2\rho c$) using the AIM command [22, 23].

Table-1: Selected Optimized geometry parameters of complexes I and II[a]

Parameter	System					
	I			II		
Lengths (in Å)	A	B	C	A	B	C
O2-C1	1.181	1.210	1.204	1.180	1.208	1.202
H3-C1	1.086	1.097	1.098	1.084	1.094	1.096
O4-C1	1.341	1.339	1.336	1.319	1.346	1.343
H5-O4	0.950	0.975	0.979	0.947	0.969	0.971
C6-H9	1.077	1.786	1.087	1.096	1.782	1.814
Cl7-C6	1.800	2.324	1.810	3.921	5.558	3.814
H8-C6	1.078	1.088	1.086	1.078	1.088	1.087
C9-C1	3.429	1.087	3.270	1.077	1.087	1.087
H10-C6	1.078	1.088	1.086	1.078	1.088	1.087
Angles (in Degrees)						
H3-C1-O2	124.0	110.0	124.3	124.5	110.2	125.0
O4-C1-O2	125.3	125.6	125.7	124.6	124.8	124.7
H5-O4-C1	110.2	107.2	109.2	109.5	106.4	108.0
C6-C9-C1	134.7	101.4	134.1	82.5	83.7	81.0
Cl7-C6-H9	107.8	178.8	107.4	80.9	43.4	83.5
H8-C6-H9	111.5	108.2	111.7	107.8	108.6	107.8
H9-C1-O2	33.4	108.4	35.4	107.8	108.4	107.6
H10-C6-H9	111.5	108.2	111.7	107.8	108.6	107.8

a. See Fig. 1
A. RHF/6-311+G** optimized geometry
B. RMP2/6-311+G** optimized geometry
C. RB3LYP/6-311+G** optimized geometry

Table-2: Selected Optimized geometry parameters of complexes III and IV[a]

Parameter	System					
	III			IV		
Lengths (in Å)	A	B	C	A	B	C
O2-C1	1.177	1.198	1.198	1.177	1.206	1.200
H3-C1	1.084	1.096	1.096	1.086	1.097	1.098
O4-C1	1.325	1.352	1.352	1.319	1.346	1.342
H5-O4	0.947	0.971	0.971	0.949	0.973	0.977
C6-H9	1.793	1.810	1.811	1.078	1.783	1.087
Cl7-C6	4.053	4.904	3.922	1.794	2.381	1.812
H8-C6	1.078	1.087	1.087	1.078	1.088	1.086
C9-C1	1.078	1.087	1.087	4.589	1.089	4.409
H10-C6	1.078	1.087	1.087	1.078	1.088	1.086
Angles (in Degrees)						
H3-C1-O2	125.1	125.6	126.0	124.3	109.6	124.8
O4-C1-O2	124.4	124.5	124.5	125.2	125.4	125.5
H5-O4-C1	109.1	107.7	107.7	110.1	107.2	109.1
C6-C9-C1	87.6	84.2	85.4	120.3	91.2	117.8
Cl7-C6-H9	156.6	155.4	154.6	108.2	146.5	108.1

H8-C6-H9	108.0	107.9	107.9	110.9	108.6	111.0
H9-C1-O2	108.0	108.0	107.9	122.9	108.8	121.3
H10-C6-H9	108.0	107.9	107.9	110.9	108.6	111.0

a. See Fig. 1
A. RHF/6-311+G** optimized geometry
B. RMP2/6-311+G** optimized geometry
C. RB3LYP/6-311+G** optimized geometry

Table-3: Bonding properties of some selected bonds using RB3LYP/6-311+G**

System[a]	Bond	Bond Length (in Å)	$\rho(r_c)$ (e/au^3)	$\nabla^2\rho(r_c)$ (e/au^5)
I	O---H	2.393	0.0106	0.0338
	Cl---H	2.352	0.0169	0.0503
II	O---H	2.453	0.0095	0.0294
	Cl---H	3.056	0.0049	0.0152
III	O---H	2.605	0.0066	0.0214
	Cl---H	3.006	0.0054	0.0156
IV	O---H	2.821	0.0056	0.0194
	Cl---H	2.439	0.0104	0.0455

a. See Fig. 1,

Table-4: Energetics of Formic Acid-Methyl Chloride systems[a]

System[a]	Binding Energy(kcal/mol)	
	RB3LYP/6-311+G**	RMP2/6-311+G**
I	3.9	5.0
II	1.7	2.8
III	0.9	2.4
IV	2.0	3.7
	Activation Energy(kcal/mol) (RB3LYP/6-311+G**)	
I → II	2.6	
II → III	1.0	
III → IV	0.9	
IV → I	0.1	

a. See Fig. 1

RESULTS AND DISCUSSION

In the present study, four minima (I-IV) corresponding to distinct van der Waals complexes of formic acid (HCOOH) and methyl chloride (CH_3Cl) are considered (Fig. 1). The optimized geometries of I & II minima are listed in Table 1 and that of III & IV minima are listed in Table 2. RB3LYP/6-311+G** along with RHF/6-31l+G** and RMP2 / 6-311+G** basis set are listed for comparison. Calculated bonding properties of some selected interactions for I-IV minima are given in Table 3. These selected geometric parameters selected were the one which has direct relevance to hydrogen-bonding interactions. Moreover, these geometric parameters exhibit the most significant variations between the RB3LYP and ab-initio results.

The calculated results show a good agreement with high level ab initio methods [21]. The most notable deviations between the RB3LYP and ab-initio calculations are observed in the predicted O···H hydrogen-bond distances [Table 1 & 2]. Calculation shows that O···H bond distances are systematically smaller than the bond distances calculated using ab initio methods. Similarly, the calculated Cl···H bond distances are also shorter using the RB3LYP method than the ab initio results. It may be of interest to note that an increase in $\rho(r_c)$ values leads to a decrease in the length of the bond. It can be observed that, for minima I-IV, the variations in O···H hydrogen -bond distances are consistent with the corresponding changes in the electron density values (I > II > III > IV order of $\rho(r_c)$ values are reported). Similarly, changes in Cl···H bond length in I–IV minima correlate well with the corresponding changes in $\rho(r_c)$ values.

The Laplacian of the electron density, $\nabla^2\rho(r_c)$, provides information on the local concentration or depletion of electronic charge [Table 3]. Negative values of $\nabla^2\rho(r_c)$ is generally associated with regions of electron-density concentration and indicate a

predominantly covalent character. Positive value on the other hand correspond to regions of electron-density depletion and suggests a non-covalent interaction. Calculated values of $\nabla^2\rho(r_c)$ indicate non-covalent character of O···H and Cl···H interactions in I to IV minima. All interactions are predicted to be non-covalent. Weak hydrogen bonds are predominantly electrostatic in nature, although their interactions may acquire increasing covalent character, as reflected by the corresponding $\nabla^2\rho(r_c)$ values. Most of the $\nabla^2\rho(r_c)$ values of O···H and Cl···H interactions are in close agreement with typical range reported for hydrogen bonds (0.024 to 0.139 au) [24,25].

B3LYP/6-311+G** level calculations were carried to estimate the binding energies and activation energies for I–IV minima of HCOOH and CH_3Cl complexes and are listed in Table 4. For comparison, the binding energies were also calculated at the MP2 level using the same basis set. Calculated binding energies of four minima are in a range of 0.9 to 3.9 kcal mol^{-1}, which support the existence of weak hydrogen bonding between formic acid and methyl chloride. The order of binding energies of I to IV minima is recognized as I > IV > II > III, which corresponds to their stability. Our calculated binding energies are in good agreement with the binding energies as reported by others [21].

The four minima seem to be separated only by a relatively small energy barrier (0.9 to 2.6 kcal mol^{-1}) leading to facile interconversion. The I minima of HCOOH and CH_3Cl complexes is predicted to be the most stable followed by the IV minima with a difference in their binding energies by 1.9 kcal mol^{-1}.

CONCLUSION

The significant hydrogen-bonding interactions predicted by the present theoretical study between methyl chloride and formic acid provide further evidence for the prevalence of C–H···O hydrogen bonds. Interestingly, the presence of a single chlorine atom appears to provide sufficient electronic activation to enable the carbon-bound hydrogen to act as hydrogen-bond donor. This observation suggests that molecules containing two chlorine atoms or other electron withdrawing groups may likewise exhibit enhanced hydrogen-bond capability. Overall, the present study demonstrates that carbon-bound hydrogen atoms can participate in hydrogen more readily than is conventionally recognized.

REFERENCES

[1] R.D. Green, "Hydrogen Bonding by C–H Groups", Wiley-Interscience: New York (1974).

[2] A. D. Buckingham, A.C. Legon and S.M. Roberts, "Principles of Molecular Recognition", Blackie Academic & Professional: London (1993).

[3] P. R. Varadwaj , A Varadwaj and B. Jin, "Halogen bonding interaction of chloromethane with several nitrogen donating molecules: addressing the nature of the chlorine surface σ-hole" Phys. Chem. Chem. Phys. (2014) 16 (36): 19573–19589

[4] G.R. Desiraju and T. Steiner, "The Weak Hydrogen Bond in Structural Chemistry and Biology", Oxford University Press: Oxford, U.K. (1999).

[5] Z.S. Derewenda, L. Lee and U. Derewenda, "The occurrence of C–H···O hydrogen bonds in proteins" , J. Mol. Biol., 252, 248 (1995).

[6] T. Steiner, "Influence of C–H···O interactions on the conformation of methyl groups quantified from neutron diffraction data.", J. Phys. Chem. A, 104, 433 (2000).

[7] L.J.W. Shimon, M. Vaida, L. Addadi, M. Lahav and L. Leiserowitz, "A "relay" mechanism for the effect of solvent on crystal growth and dissolution", J. Am. Chem. Soc., 112, 6215 (1990).

[8] D. Braga, F. Grepioni, J.J. Byrne, and A. Wolf, "Hosting paramagnetic $[Cr(C_6H_6)_2]^+$ in an organic anion framework via C–H···O hydrogen bonds,", J. Chem. Soc. Chem. Commun., 125 (1995).

[9] K.N. Houk, S. Menzer, S.P. Newton, F.M. Raymo, J.F. Stoddart and D.J. Williams, "Theoretical and Experimental Studies of the Structure and Dynamics of [2]Catenanes", J. Am. Chem. Soc., 121, 1479 (1999).

[10] Z. Berkovitch-Yellin and L. Leiserowitz, "The role played by C–H···O and C–H···N interactions in determining molecular packing and conformation,", Acta Crystallogr., Sect. B, 40, 159 (1984).

[11] I. Berger, M. Egli and A. Rich, "Inter-strand C–H···O hydrogen bonds stabilizing four-stranded intercalated molecules: stereo-electronic effects of O_4' in cytosine-rich DNA,", Proc. Natl. Acad. Sci. U.S.A., 93, 12116 (1996).

[12] R. Parthasarathi, V. Subramanian, and N. Sathyamurthy, "Hydrogen Bonding Without Borders: An Atoms-in-Molecules Perspective," J. Phys. Chem. A, 110, 3349 (2006).

[13] A.Y. Li, "Theoretical Investigation of Hydrogen Bonds between CO and HNF_2, H_2NF, and HNO", J. Phys. Chem. A, 110, 10805 (2006).

[14] S.J.K. Jensen, T.H. Tang and I.G. Csizmadia, "Hydrogen-Bonding Ability of a Methyl Group", J. Phys. Chem. A, 107, 8975 (2003).

[15] G.R. Desiraju, "Hydrogen Bridges in Crystal Engineering: Interactions without Borders", Acc. Chem. Res., 35, 565 (2002).

[16] C.E. Cannizzaro and K.N. Houk, "Magnitudes and Chemical Consequences of R_3N^+–C–H···O=C Hydrogen Bonding", J. Am. Chem. Soc., 124, 7163 (2002).

[17] Y.X. Lu, J.W. Zou, Z.M. Jin, Y.-H. Wang, H.-X. Zhang, Y.-J. Jiang and Q.-S. Yu, "Proton Exchanges between Phenols and Ammonia or Amines: A Computational Study", J. Phys. Chem. A, 110, 9261 (2006).

[18] V. Venkatesan, A. Fujii, T. Ebata and N. Mikami, "Infrared and ab initio studies on 1,2,4,5-tetrafluorobenzene clusters with methanol and 2,2,2-trifluoroethanol: Presence and absence of an aromatic C–H···O hydrogen bond", J. Phys. Chem. A, 109, 915 (2005).

[19] E. Ruckenstein, I.L. Shulgin and J.L. Tilson, "The Structure of Dilute Clusters of Methane and Water by ab Initio Quantum Mechanical Calculations", J. Phys. Chem. A, 107, 2289 (2003).

[20] T. Tuttle, J. Gräfenstein, A. Wu, E. Kraka and D. Cremer, "Analysis of the NMR Spin–Spin Coupling Mechanism Across a H–Bond: Nature of the H–Bond in Proteins", J. Phys. Chem. B, 108, 1115 (2004).

[21] C.H. Reynolds, J. Am. Chem. Soc., "Methyl Chloride–Formic Acid van der Waals Complex: A Model for Carbon as a Hydrogen Bond Donor", 112, 7903 (1990).

[22] R.F.W. Bader, "Atoms in Molecules", Acc. Chem. Res., 18, 9 (1985).

[23] R.F.W. Bader, "Atoms in Molecules: A Quantum Theory", Clarendon Press, Oxford (1990).

[24] M. Biczysko and Z. Latajka, "The influence of water molecules on the proton position in H_3N–HX (X = F, Cl, Br) complexes", Chem. Phys. Lett., 313, 366 (1999).

[25] R. A. Cazar, A.J. Jamka and F.M. Tao, "Ab Initio Investigation of Proton Transfer in Ammonia–Hydrogen Chloride and the Effect of Water Molecules in the Gas Phase", J. Phys. Chem. A, 102, 5117(1998)