การศึกษาทางทฤษฎีของการตรวจจับแอนไอออนด้วยการสร้างพันธะไฮโดรเจนและฮาโลเจนกับรีเซ็ปเตอร์อนุพันธ์เอไมด์

Theoretical Investigation of Anion Recognition via Hydrogen and Halogen Bonding with Amide Derivative Receptors

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บทคัดย่อ

งานวิจัยนี้ศึกษาสมบัติทางโครงสร้าง สมบัติทางพลังงาน สมบัติทางเทอร์โมไดนามิกส์ และสมบัติทางอิเล็กทรอนิกส์ของการเกิดสารประกอบเชิงซ้อนระหว่างรีเซ็ปเตอร์อนุพันธ์เอไมด์ 7 ชนิด (**R1-R7**) กับเฮไลด์ไอออน ซึ่งได้แก่ ฟลูออไรด์ คลอไรด์ และโบรไมด์ไอออน โดยใช้ทฤษฎีฟังก์ชันนัลความหนาแน่นที่ระดับของทฤษฎี B3LYP/6-31G(d,p) จากการศึกษาพบว่ารีเซ็ปเตอร์และเฮไลด์ไอออนสร้างสารประกอบเชิงซ้อนผ่านพันธะไฮโดรเจนร่วมกับพันธะฮาโลเจน ซึ่งเป็นกระบวนการคายความร้อนที่เกิดเองได้ ความเสถียรของสารประกอบเชิงซ้อนระหว่างรีเซ็ปเตอร์ **R1-R7** กับเฮไลด์ไอออน มีลำดับดังนี้ F^- > Cl^- > Br^- โดยพบว่าฟลูออไรด์ไอออนมีการยึดจับที่แข็งแรงกับทุกรีเซ็ปเตอร์เนื่องจากความเป็นเบสที่สูง สารประกอบเชิงซ้อนที่มีความเสถียรมากที่สุดคือ **R5**/F^- มีค่าพลังงานการยึดจับเท่ากับ -151.39 กิโลแคลอรีต่อโมล นอกจากนี้การเปลี่ยนแปลงพลังงานอิสระกิบส์ของสารประกอบเชิงซ้อนดังกล่าวยังมีค่าสูงสุดเท่ากับ -142.30 กิโลแคลอรีต่อโมล โดยสารประกอบเชิงซ้อนนี้เกิดขึ้นจากพันธะไฮโดรเจน 3 พันธะ และพันธะฮาโลเจน 2 พันธะ

คำสำคัญ: รีเซ็ปเตอร์อนุพันธ์เอไมด์ การตรวจจับแอนไอออน พันธะฮาโลเจน พันธะไฮโดรเจน

Abstract

This research investigates structural, energetic, thermodynamic and electronic properties of complexation between 7 amide derivative receptors (**R1-R7**) and halide ions including fluoride, chloride, and bromide ions using the density functional theory at B3LYP/6-31(d,p) level of theory. The results show that receptors and halide ions form complexes through hydrogen bond augmented with halogen bond. The complexes' formation is a spontaneous exothermic reaction. The stability of the complexes between **R1-R7** receptors and halide ions follows the order as F^- > Cl^- > Br^-. Fluoride ion has the strongest binding with all of the receptors due to its high basicity. The highest stability complex is **R5**/F^- with binding energy of -151.39 kcal/mol. Moreover, the Gibbs free energy change of this complex has the highest value of -142.30 kcal/mol. This complex is formed via 3 hydrogen bonds and 2 halogen bonds.

Keywords: Amide derivative receptor, Anion recognition, Halogen bond, Hydrogen bond

1. Introduction

Anion recognition is a study of host-guest interactions, in which the receptor molecule is defined as the host and the anion is called the guest. This area has gained a growing research attention because anion plays an essential role in a wide variety of chemical and biological applications, for example, catalysis and DNA enzyme process [1]-[4]. Generally, host-guest interactions are non-covalent interactions, which include electrostatic interaction, hydrogen bonding [5]-[7] and Lewis acid and base.

Currently, hosts-guests bonding is supported by various forms of interactions such as halogen bond, XB (C-X···anion) which is a type of non-covalent interactions. Halogen bond, which is formed when there is an interaction between halogen atom in one molecule and a negative site in another, has presently been widely applied in crystal engineering, supramolecular chemistry, and biological design [8]-[11].

Hosts that make suitable receptors of anion include amide, sulphonamide, urea, thiourea, and pyrrole. Therefore, molecules of hosts with amide functional groups were chosen for this study. Moreover, halogen atoms (VIIA) were added to the host structures for the examination of host-anion interactions. The anions of interest in the present study belong to halide ions such as fluoride ion (F^-), chloride ion (Cl^-), and bromide ion (Br^-). Therefore, this research aims to investigate structural, energetic, thermodynamic and electronic properties of complexation between 7 amide derivative receptors (receptors **R1-R7**) and halide ions such as fluoride, chloride, and bromide ions using the density functional theory at B3LYP/6-31(d,p) level of theory.

2. Computational details

In the present study, a group of 7 types of receptors of amide derivatives were designed. The designed chemical structures of **R1-R7** receptors are shown in Figure 1. The structures of receptors and receptor-anion complexes, and receptor-anion bonding behaviors were examined using Gaussian 09 [12] together with DFT at the B3LYP [13]-[15] level of theory and basis set of 6-31G (d,p). Structural, energy, thermodynamic, and electronic properties of complexation between 7 amide derivative receptors (receptors **R1-R7**) and halide ions were also studied. The vibrational frequency was calculated at 298.15 K and 1 atmosphere, which also provided standard enthalpy (ΔH) and Gibbs free energy changes (ΔG) of the reactions. The energy gaps (E_{gap}) referred to the energy difference between the highest occupied molecular orbital energies (E_{HOMO}) and the lowest unoccupied molecular orbital energies (E_{LUMO}). The partial charge transfers (PCTs) during anion recognition were defined as a change in charges of anion during the anion recognition process by means of the natural bond orbital (NBO) analysis.

3. Results and discussion

3.1. Structural properties

The optimizations of molecular structures of **R1-R7** receptors and their complexes with F^-, Cl^-, and Br^- ions were performed using the Density Functional Theory at B3LYP/6-31G(d,p) level of theory. Stable structures of all receptors are shown in Figure 2 and the complexes between receptors and anions are shown in Figure 3. The results show that all the receptors form stable complexes with anions through only hydrogen bond for **R1** receptor, and through hydrogen bond augmented with halogen bond for **R2-R7** receptors. The average distances of hydrogen bond and halogen bond of the complexes are shown in Table 1. The study of receptor-halide ion binding behavior reveals that the receptors bond to halide ions via 2 hydrogen bonding patterns. The first pattern is formed by -NH of amide group of receptor with halide ion NH-X (X = F^-, Cl^- or Br^-). The second bond pattern is formed by CH of the benzene with halide ion CH-X, reported to be essential for the detection of anion [16]-[18]. It supplements the receptor-anion complexes to be more stable. In addition, in the receptor of which hydrogen is replaced with a halogen atom (C-F, C-Cl), a halogen bond is formed between C-F···X and C-Cl···X.

Regarding receptor-halide ion complexes, 3 hydrogen bonds and 2 halogen bonds are present in all complexes, except the complexes of **R1** receptor, which form 5 hydrogen bonds, 2 of which are NH-X, and the other 3 are CH-X. As shown in Table 1, the hydrogen bond distances of complexes between **R1-R7** receptors and halide ions are in the range of 1.901-2.607, 1.609-2.389, 1.605-2.405, 1.602-2.374, 1.597-2.373, 1.596-2.369 and 1.600-2.369 Å, respectively, while the halogen bond distances of **R2-R7** complexes are in the range of 3.176-3.860, 2.768-3.329, 3.397-4.030, 3.295-3.663, 3.249-3.933 and 3.365-3.985 Å, respectively. The results suggest that the complexes between F^- and 7 receptors have the shortest hydrogen bond distances when compared to the complexes between 7 receptors and the other 2 anions (Cl^- and Br^- ions). The complex **R6**/F^- has the shortest hydrogen bond distance of 1.596 Å, indicating the strong interaction between F^- and receptors. Similarly, halogen bonding between F^- with the 7 receptors results in the shortest halogen bond distances. The bond strength has been reported to be inversely proportional to bond distance [19]. The presence of halogen bond in the complexes results in the decrease of hydrogen bond distances between the receptors and anions.

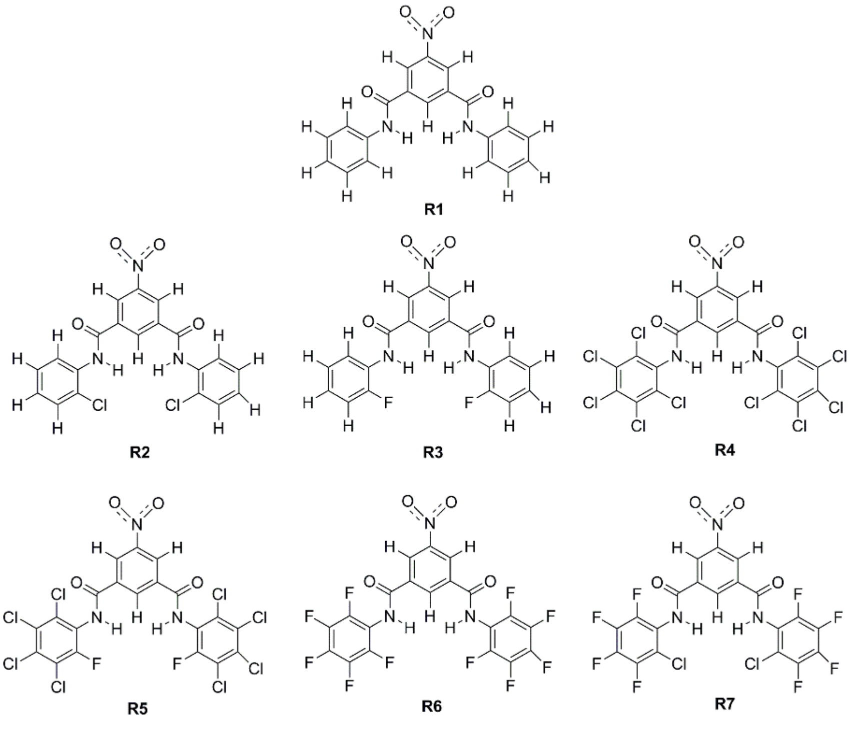

Figure 1 The formulae of **R1-R7** receptors

Table 1 The average hydrogen bond and halogen bond distances between receptors **R1**-**R7** and halide ions (in Å)

Complexes	HB	XB
R1/F^-	1.901	-
R1/Cl^-	2.475	-
R1/Br^-	2.607	-
R2/F^-	1.609	3.176
R2/Cl^-	2.254	3.860
R2/Br^-	2.389	3.842
R3/F^-	1.605	2.768
R3/Cl^-	2.258	3.329
R3/Br^-	2.405	3.308
R4/F^-	1.602	3.397
R4/Cl^-	2.233	4.030
R4/Br^-	2.374	3.953
R5/F^-	1.597	3.295
R5/Cl^-	2.246	3.663
R5/Br^-	2.373	3.619
R6/F^-	1.596	3.249
R6/Cl^-	2.240	3.604
R6/Br^-	2.372	3.571
R7/F^-	1.600	3.365
R7/Cl^-	2.235	3.985
R7/Br^-	2.369	3.933

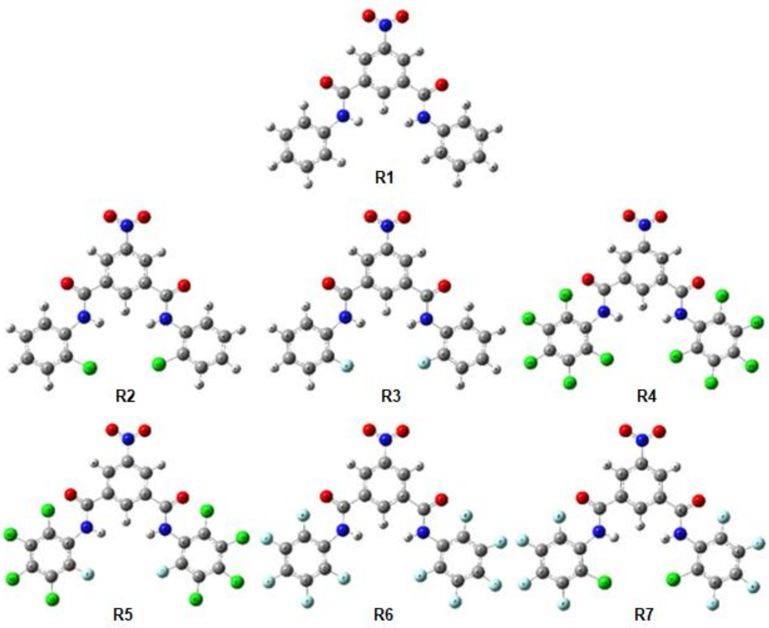

Figure 2 The B3LYP/6-31G(d,p)-optimized structures of **R1**-**R7** receptors

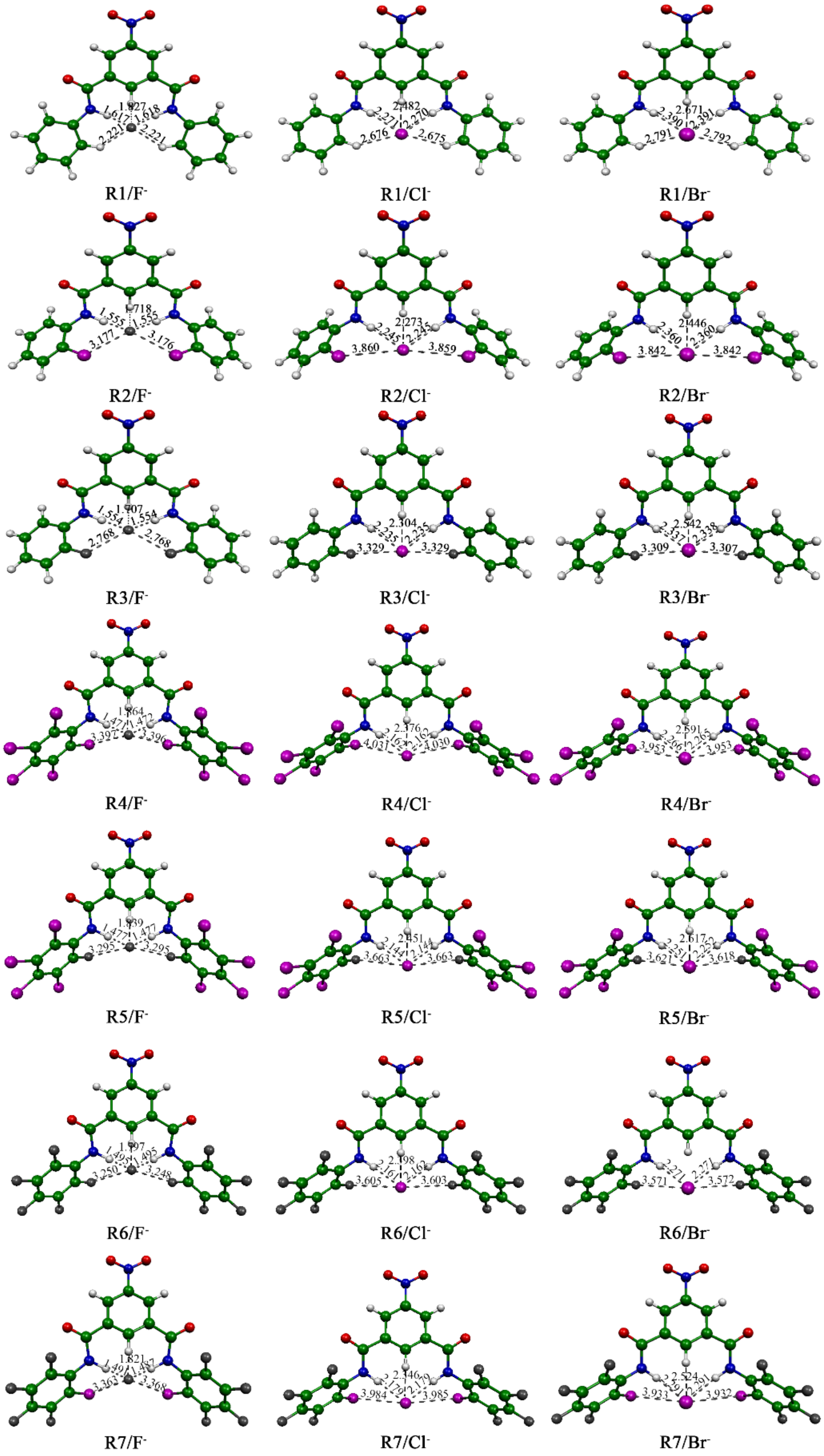

Figure 3 The B3LYP/6-31G(d,p)-optimized structures of the complexes between **R1-R7** receptors and F^-, Cl^-, and Br^- ions

3.2. Energetic and thermodynamic properties

Table 2 shows binding energy, enthalpy changes and Gibbs free energy changes of complexation between receptors and halide ions calculated using the B3LYP/6-31G(d,p) level of theory. The negative values of the binding energy indicate that the interactions between receptors and anions are energetically favourite. Likewise, the stability of the complexes and the negative values of enthalpy and Gibbs free energy changes indicate that all complexes are formed by spontaneous exothermic reaction.

The binding energies of 3 halide ions with the 7 receptors are in the range of -108.25 to -151.39 kcal/mol. Based on the binding energies of the complexes between **R1**-**R7** and 3 halide ions, the stability of the complexes follows the order as F^- > Cl^- > Br^-. This finding is in agreement with other receptors such as urea and thiourea derivative receptors including aromatic ligands reported by previous works [20], [21]. The complex with the highest stability is **R5**/F^-. F^- ion is able to form the stronger hydrogen bond with -NH of amide group of the receptors because of the high basicity of F^- [22]. The binding energy of **R5**/F^- is -151.39 kcal/mol, corresponding to the shortest hydrogen bond distance of 1.597 Å.

When considering the Gibbs free energy changes (ΔG) of the complexes between receptors and halide ions, the trend of the Gibbs free energy change is consistent with the binding energy. The fluoride ion forms the most stable complexes with the **R1**-**R7** receptors with Gibbs free energy changes of -137.20, -125.31, -124.91, -141.32, -142.30, -140.65 and -139.91 kcal/mol, respectively. On the other hand, bromide ion forms complexes with the lowest stability with **R1**-**R7** receptors with Gibbs free energy changes of -114.04, -101.75, -101.94, -117.19, -118.63, -117.51 and -116.21 kcal/mol, respectively. These findings are in line with the shortest hydrogen bond distances of the complexes **R1**/F^-, **R2**/F^-, **R3**/F^-, **R4**/F^-, **R5**/F^-, **R6**/F^- and **R7**/F^- in comparison with the complexes formed by **R1**-**R7** receptors with chloride and bromide ions.

Based on graphs presenting the relationship between the Gibbs free energy changes and average hydrogen bond distances of the complexes, a linear relationship between the 2 variables is found in all complexes as shown in Figure 4. This linear relationship in all complexes is confirmed with the correlation coefficients of **R1**-**R7** receptors with halide ions which were 0.9992, 0.9996, 0.9995, 0.9998, 0.9987, 0.9984 and 0.9999, respectively.

The highest occupied molecular orbital energies (E_{HOMO}), lowest unoccupied molecular orbital energies, (E_{LUMO}) and energy gaps (E_{gap}) of the complexes between **R1**-**R7** receptors and halide ions are shown in Table 3. The E_{gap} of all anion complexes were within the range of 2.776-3.157, 2.367-3.456, 2.449-3.347, 2.721-4.027, 2.721-4.000, 2.667-3.810 and 2.640-3.864 eV for **R1**-**R7** receptors, respectively. The energy gaps of the complexes are slightly lower than those of their free receptors.

Since, a complex with higher energy gap has more stable structure, the complexes of fluoride ion with **R1**-**R7** receptors are more stable as compared to the complexes of other ions with **R1**-**R7** receptors, due to their higher energy gaps. The most stable complex is **R5**/F^- with the highest energy gap. The partial charge transfers (PCT) are also shown in Table 3. All of partial charge transfers of anion complexes are positive values in the range of 0.71–0.31 e, indicating the occurrence of charge transfer from halide anions to the receptors. The highest charge transfers from fluoride ion to the receptors are also observed, corresponding to the strong binding interactions [23], [24]. Therefore, the complexes of fluoride ion with **R1**-**R7** receptors having the highest PCT, are the most stable complexes compared to the complexes of other ions with **R1**-**R7** receptors [25].

Table 2 The binding energy (E_{bind}), enthalpy change (ΔH) and Gibbs free energy change (ΔG) of complexations between **R1**-**R7** receptors and halide ions (in kcal/mol)

Complexes	E_{bind}	ΔH_{298}	ΔG_{298}
R1/F^-	-148.08	-147.63	-137.20
R1/Cl^-	-127.45	-127.98	-117.71
R1/Br^-	-124.06	-124.53	-114.04
R2/F^-	-132.70	-132.84	-125.31
R2/Cl^-	-112.66	-112.34	-106.29
R2/Br^-	-108.25	-107.83	-101.75
R3/F^-	-133.94	-134.68	-124.91
R3/Cl^-	-114.64	-114.93	-106.69
R3/Br^-	-110.18	-110.40	-101.94
R4/F^-	-150.69	-151.40	-141.32
R4/Cl^-	-130.17	-130.48	-121.89
R4/Br^-	-125.59	-125.80	-117.19
R5/F^-	-151.39	-152.10	-142.30
R5/Cl^-	-131.87	-132.23	-123.35
R5/Br^-	-127.17	-127.40	-118.63
R6/F^-	-149.71	-150.46	-140.65
R6/Cl^-	-130.65	-131.03	-122.26
R6/Br^-	-125.97	-126.22	-117.51
R7/F^-	-149.20	-149.95	-139.91
R7/Cl^-	-128.88	-129.21	-120.61
R7/Br^-	-124.36	-124.57	-116.21

Table 3 The highest occupied molecular orbital energies (E_{HOMO}), the lowest unoccupied molecular orbital energies (E_{LUMO}), energy gaps (E_{gap}) (in eV) and partial charge transfers (PCT) (in e) of the complexes between **R1**-**R7** receptors and halide ions calculated at B3LYP/6-31G(d,p) level of theory

Complexes	E_{HOMO}	E_{LUMO}	E_{gap}	PCT
R1	-6.395	-2.776	3.619	-
R1/F^-	-3.075	0.054	3.129	0.28
R1/Cl^-	-3.265	-0.109	3.157	0.17
R1/Br^-	-2.884	-0.109	2.776	0.20
R2	-6.585	-2.803	3.782	-
R2/F^-	-3.320	0.136	3.456	0.30
R2/Cl^-	-2.857	-0.054	2.803	0.19
R2/Br^-	-2.449	-0.082	2.367	0.21
R3	-6.476	-2.776	3.701	-
R3/F^-	-3.157	0.190	3.347	0.30
R3/Cl^-	-2.830	-0.027	2.803	0.19
R3/Br^-	-2.476	-0.027	2.449	0.22
R4	-7.320	-3.021	4.299	-
R4/F^-	-4.218	-0.190	4.027	0.31
R4/Cl^-	-3.456	-0.354	3.102	0.21
R4/Br^-	-3.075	-0.354	2.721	0.24
R5	-7.293	-3.048	4.245	-
R5/F^-	-4.191	-0.190	4.000	0.31
R5/Cl^-	-3.483	-0.381	3.102	0.21
R5/Br^-	-3.102	-0.381	2.721	0.24
R6	-7.184	-3.048	4.136	-
R6/F^-	-3.891	-0.082	3.810	0.31
R6/Cl^-	-3.374	-0.327	3.048	0.23
R6/Br^-	-2.993	-0.327	2.667	0.23
R7	-7.211	-3.048	4.163	-
R7/F^-	-3.973	-0.109	3.864	0.31
R7/Cl^-	-3.347	-0.327	3.021	0.20
R7/Br^-	-2.966	-0.327	2.640	0.23

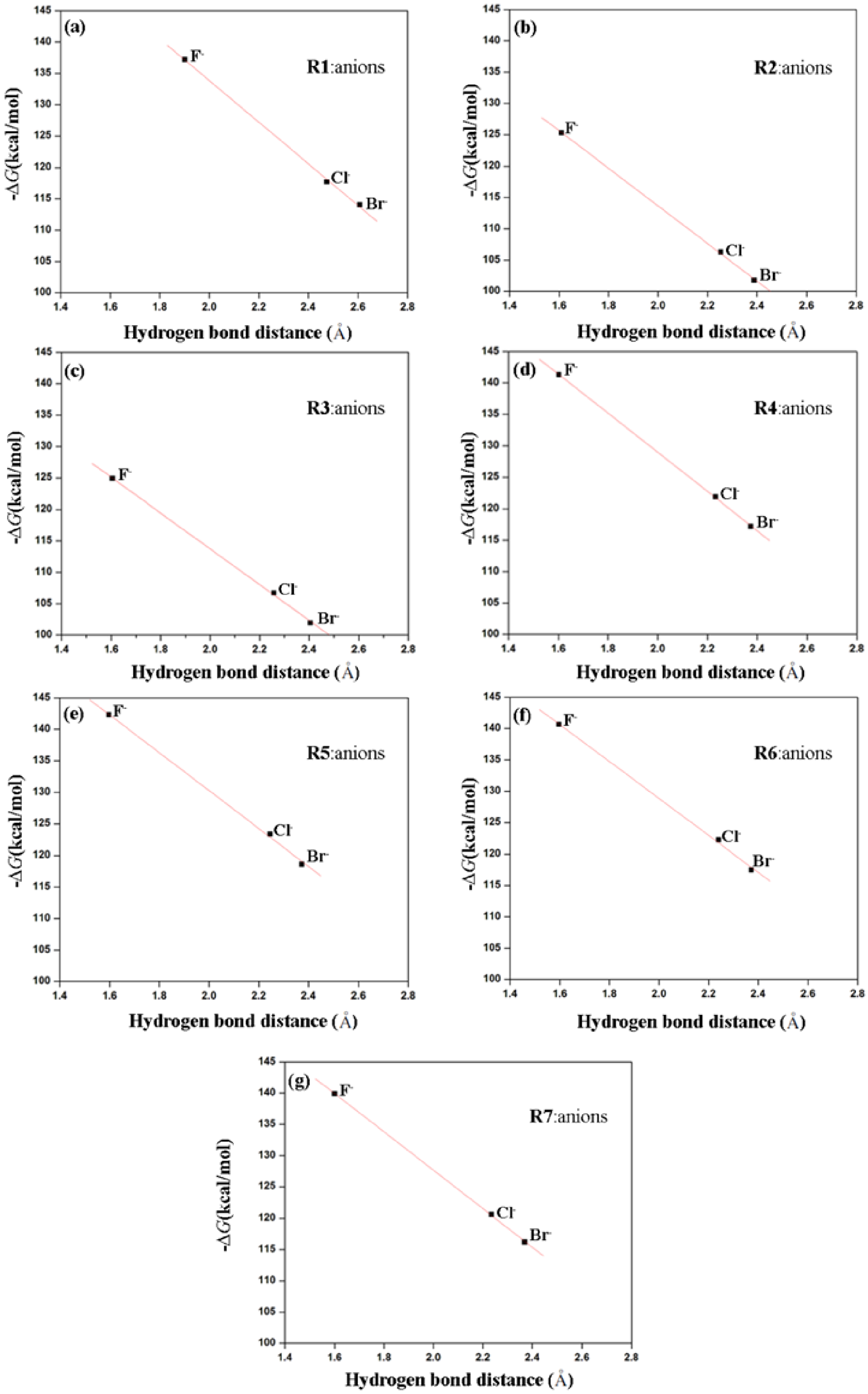

Figure 4 Relationship between Gibbs free energy changes and average hydrogen bond distances of the complexes between anions and receptors (a) **R1**, (b) **R2**, (c) **R3**, (d) **R4**, (e) **R5**, (f) **R6**, and (g) **R7**

4. Conclusion

Complexes of 7 amide derivative receptors (**R1-R7**) and 3 halide ions (F^-, Cl^- and Br^-) were studied using DFT with B3LYP/6-31G (d,p) level. The results show that the complexes between the receptors and halide ions are formed through the hydrogen bond for **R1** receptor and hydrogen bond augmented with halogen bond for **R2-R7** receptors. These reactions are spontaneous exothermic. The stability of the complexes of **R1-R7** receptors and halide ions follows the aoder as $F^- > Cl^- > Br^-$. Furthermore, fluoride ion has the strongest binding with all the receptors due to its strongest basicity. The highest stable complex is **R5**/F^- with binding energy of -151.39 kcal/mol. The Gibbs free energy changes of **R1-R7** receptors with F^- are -137.20, -125.31, -124.91, -141.32, -142.30, -140.65 and -139.91 kcal/mol, respectively. Fluoride ion, in comparison with other types of ions, produces the high PCT to the receptors, making it to have the strong interactions with the receptors. On the other hand, complexes of the receptors formed with bromide ion, having the lowest basicity, have the lowest stability. The Gibbs free energy changes of the complexation are linearly correlated with those of halide ions with the correlation coefficients of 0.9992, 0.9996, 0.9995, 0.9998, 0.9987, 0.9984 and 0.9999 for **R1-R7** receptors, respectively.

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6. References

[1] Nocentini, A. and et al. 2021. Reconsidering anion inhibitors in the general context of drug design studies of modulators of activity of the classical enzyme carbonic anhydrase. **Journal of Enzyme Inhibition and Medicinal Chemistry.** 36(1): 561-580.

[2] Liu, Y. and et al. 2019. Recent advances in anion-doped metal oxides for catalytic applications. **Journal of Materials Chemistry A.** 7(13): 7280-7300.

[3] Gale, P.A. and et al. 2018. Anion receptor chemistry: Highlights from 2016. **Coordination Chemistry Reviews.** 375: 333-372.

[4] Zhao, L. and Damodaran, S. 2019. Hofmeister order of anions on protein stability originates from Lifshitz-van der Waals dispersion interaction with the protein phase. **Langmuir.** 35(40): 12993-13002.

[5] Kayal, S., Manna, U. and Das, G. 2019. Fixation of atmospheric CO_2 and recognition of anions/hydrated anions: Differential binding mode in protonated vs. neutral tripodal urea/thiourea receptors. **Inorganica Chimica Acta.** 486: 576-581.

[6] Liu, Y. 2015. Designation and exploration of halide-anion recognition based on cooperative noncovalent interactions including hydrogen bonds and anion-π. **The Journal of Physical Chemistry A.** 119(22): 5842-5852.

[7] Montis, R. 2019. Fluoride binding by an anionic receptor: tuning the acidity of amide NH groups for basic anion hydrogen bonding and recognition. **Chemical Communications.** 55(19): 2745-2748.

[8] Borissov, A. 2019. Anion recognition in water by charge-neutral halogen and chalcogen bonding foldamer receptors. **Journal of the American Chemical Society.** 141(9): 4119-4129.

[9] Turner, G., Docker, A. and Beer, P.D. 2021. Anion recognition by halogen bonding and hydrogen bonding bis(triazole)-imidazolium [2] rotaxanes. **Dalton Transactions.** 50(37): 12800-12805.

[10] Pancholi, J. and Beer, P.D. 2020. Halogen bonding motifs for anion recognition. **Coordination Chemistry Reviews.** 416: 213281.

[11] Yu, D. and Bai, X. 2023. Integrated in silico-in vitro molecular modeling and design of halogenated phenylalanine-containing anti-hypertensive peptide inhibitors with halogen bonds to target human angiotensin-I-converting enzyme. **Chemical Physics.** 565: 111732.

[12] Frisch, M.J. and et al. 2009. **Gaussian 09.** Wallingford: Gaussian, Inc.

[13] Becke, A.D. 1988. Density-functional exchange-energy approximation with correct asymptotic behavior. **Physical Review A.** 38(6): 3098-3100.

[14] Lee, C., Yang, W. and Parr, R.G. 1988. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. **Physical Review B.** 37(2): 785-789.

[15] Becke, A.D. 1992. Density-functional thermochemistry. I. The effect of the exchange-only gradient correction. **The Journal of Chemical Physics.** 96(3): 2155-2160.

[16] Eytel, L.M. and et al. 2019. The road to aryl CH···anion binding was paved with good intentions: fundamental studies, host design, and historical perspectives in CH hydrogen bonding. **Chemical Communications.** 55: 5195-5206.

[17] Mondal, D. 2022. Anion recognition through multivalent C–H hydrogen bonds: Anion-Induced Foldamer formation and transport across phospholipid membranes. **The Journal of Organic Chemistry.** 87(1): 10-17.

[18] Tresca, B.W. and et al. 2015. Substituent effects in CH hydrogen bond interactions: Linear free energy relationships and influence of anions. **Journal of the American Chemical Society.** 137(47): 14959-14967.

[19] Arunan, E. and et al. 2011. Definition of the hydrogen bond (IUPAC Recommendations 2011). **Pure and Applied Chemistry.** 83(8): 1637–1641.

[20] Manna, U. and et al. 2021. Anion binding studies of urea and thiourea functionalized molecular clefts. **Frontiers in Chemistry.** 8: 575701.

[21] Malenov, D.P. and Zaric, S.D. 2021. New Type of aromatic π-systems for anion recognition: Strong anion-π and C–H···Anion interactions between halides and aromatic ligands in Half-Sandwich compounds. **Chemistry A European Journal**. 27(71): 17862-17872.

[22] Russ, T.H. and et al. 2012. A quinoline based bis-urea receptor for anions: a selective receptor for hydrogen sulfate. **Natural Product Communications.** 7(3): 301-304.

[23] Barabas, J. and et al. 2019. Non-covalent interactions and charge transfer between propene and neutral Yttrium-doped and pure gold clusters. **Chemistry A European Journal.** 25(69): 15795-15804.

[24] Panda, P.K. and et al. 2022. Contact electrification through interfacial charge transfer: a mechanistic viewpoint on solid–liquid interfaces. **Nanoscale Advances.** 4(3): 884-893.

[25] Toupkanloo, H.A. and Rahmani, Z. 2018. An in-depth study on noncovalent stacking interactions between DNA bases and aromatic drug fragments using DFT method and AIM analysis: conformers, binding energies, and charge transfer. **Applied Biological Chemistry.** 61(2): 209-226.