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MOLECULAR MODELING OF SELECTIVITY OF ORTHO-ESTER TETRA AZOPHENYLCALIX[4]ARENE FOR METAL IONS

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ABSTRACT

The tetra azophenylcalix[4]arene with *ortho*-ester group was applied for determination of transition metal ions using spectrophotometer. In this case, the derivatives with *ortho*-ester group turned out the complexing formation selectively with transition metal ions over alkali, alkaline earth metal ions. From those, this study used the molecular mechanic method MM+ and molecular dynamic simulation, semi-empirical quantum chemical calculations (SCF AM1, PM3 and ZINDO/S) to investigate the complexes formation of metal ions with *ortho*-ester tetra azophenylcalix[4]arene. The complexes of *ortho*-ester tetra azophenylcalix[4]arene and metal ions Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} in 265 complexes in water molecules were simulated by combining molecular mechanics (MM^+) with molecular dynamic simulation (MD). The investigated structures in this work pointed out the different insight of the superior selectivity of *ortho*-ester tetra azophenylcalix[4]arene for metal ions. The stability constants of complexes host-M^{n+} correlated closely with the relative energies of them. The binding energies of those represented the stable characteristics of *ortho*-ester tetra azophenylcalix[4]arene with metal ions.

Keywords: Molecular Dynamic simulation, diazophenylcalix[4]arenes, molecular mechanics MM+, semi-empirical quantum and *ab initio* calculation Introduction

INTRODUCTION

Recent years, there are many advanced approaches for computational chemistry including supramolecular chemistry. This can lead on the deeper insight into the structural characteristics and thermodynamic properties. These characteristics involved the processes of electronic, atomic and molecular distribution in supramolecular organization. The calixarene ligands were identified for the molecular structure of some kinds. This showed a particular attraction as a fundamental key for constructing new supramolecular-structural systems. Therefore, the calixarenes have become the warmer subjects in development of new derivatives for supramolecular chemistry application. The calix[4]arene ligands presented a complexing capability with different metal ions[1-3]. Calixarenes have been synthesized in a number of sizes by the condensation reaction of *p*-substituted phenols with formaldehyde in the presence of strong base. Chemical modification of calixarenes by the alkylation of phenolic groups at the lower rim or modified upper rim by a numerous methods formed many calixarenes derivatives. Azocalixarenes, which are generated by the electrophilic substitution reaction of nitrogen atoms at the *p*- position unit of the calixarene structure, mainly studied calixarenes bridging phenylazo moieties on the upper rim and lower rim, double azocalixarenes and azocalixcrowns. These compounds consist of at least a conjugated chromophore azo (–N=N–) group in *p*-positions and two or more aromatic rings azo groups, they are an important classes of organic colorants. Those can be also used as the original structures to develop the chromoionophores in supramolecular chemistry, since these calix[4]arenes can use fruitfully in the chemical sensor techniques[4-6].

The chromoionophore derivatives can be designed by changing two different parts: the first is the distinguishing part for metal ions; the second is to transform the chemical information by ionophore-ion interaction. The *ortho*-ester diazophenylcalix[4]arene as a selective coloring sensor proposed by Kim and co-works[7-9]. This derivative also pointed out the selective capability with Pb^{2+} ion over alkali and alkaline earth metal ions. The *ortho*-carboxyl and *ortho*-ester diazophenylcalix[4]arene derivatives exhibited to be the new chromogenic agents by significantly color changes[10]. The spectroscopic results were described by absorbance magnitude of UV-vis spectrum as a function of wavelengths. Generally, these agents presented excellently selective ability for transition metal ions[1-9]. Since calix[4]arene derivatives denoted many important applications in analytical chemistry, so theoretical way is also one of necessary choices to investigate the structural properties and their stability. Recently *ab initio* calculations and molecular dynamic simulations were carried out to evaluate the properties of the complex structures such as thermodynamic properties, bond angles and bond lengths[11-13]. The *ab initio* relative energies of calix[4]arene derivatives were reached in different levels of theory RMP4 with basis sets 6-311G and 6-311G++ proposed by Rahman[13] and Rozhenko[3]. For new calix[4]arene derivatives bearing two phosphonic acid groups proposed by Plutnar and co-works, the interaction distances and bond angles of them were determined on the lower and upper rim using experimental measurements[14,15]. Complexing capability of calix[4]arene derivatives with metal ions yielded the different insights about the structural features. Complexes of *exo* and *endo* style for *p-tert*-butylcalix[4]arene and metal ions Ge, Sn were also considered by the experimental measurements. This ligand also presented significantly applications in semi-conductive techniques.

In this present work, we report the use of the molecular mechanic method MM+ and semi-empirical quantum methods AM1, PM3 and ZINDO/S to calculate the structural conformation of complexes host *ortho*-ester tetra azophenylcalix[4]arene and ions M^{n+} (Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}). The molecular dynamic MD calculation is also used to combine with molecular mechanic MM+ method in range 20K to 300K. The selective characteristics of *ortho*-ester tetra azophenylcalix[4]arene were also investigated to have an insight fairly for complexing stability. The complexes are evaluated by the different insight of ions Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. The atomic charges, bonding lengths and the relative energies resulting from methods MM+ and MM+/MD of those are also used to consider for the stable characteristics of the complexes between host and transition metal ions. The investigated results are also compared to those from literature[8,9].

EXPERIMENTAL

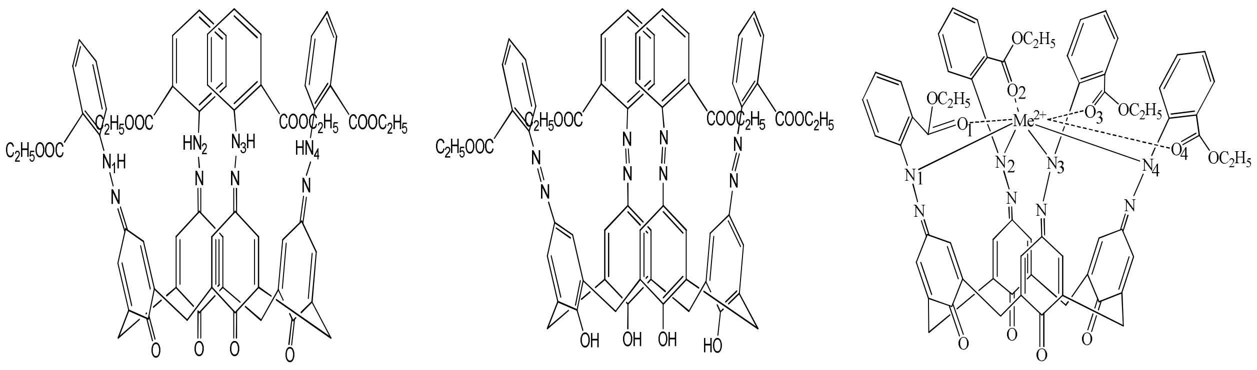
The complexing structures of host *ortho*-ester tetra azophenylcalix[4]arene and metal ions M^{n+} (Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}) were constructed by HyperChem package. The fine structures were obtained by molecular mechanics force field MM+ at gradient level 0.01. These are re-considered by combining molecular mechanics with molecular dynamic simulation MM+/MD at corresponding conditions Run Time = 60.0ps, simulation temperature = 300.0*K*, Time step = 0.0010ps and Steps to refresh = 1. The structural descriptors such as atomic charges and bonding distances were estimated by using semi-empirical quantum chemistry methods SCF AM1, PM3 and ZINDO/S. These are used here depend on the different parameters for metal cations. Method AM1 is used for calculating complexes host-K^+ and host-Na^+. Calculation PM3 is utilized for complexes host-Ca^{2+} and host-Mg^{2+}. For transition metal ions the method ZINDO/S is selected to calculate the complex properties. The total and binding energies for complexes host-ions M^{n+} resulted from those calculations after several days in the smallest convergence limit 0.01 and iteration limit. The effects of functional sites =N-NH-of phenylazo group; -C=N-N and metal cations were evaluated by atomic charges and bonding distances between metal ion and donor atoms.

RESULTS AND DISCUSSION

Optimization of Host and Complexes

The *ortho*-ester tetra azophenylcalix[4]arene and metal ions are host and guests, respectively. All the initial structures were built by HyperChem package. These optimized by using the force fields available MM+ with algorithm Polak-Ribiere at gradient level 0.001kcal/mol. This force field is derived from Allinger's MM2 force field (HyperChem Release 7.5, 2011). The molecular dynamic calculation MD was carried out at parameter level Run Time = 60.0 ps, Simulation Temperature = 300.0 K, Time Step = 0.0010 ps and Steps to refresh = 1 for optimizing complexing structures.

The *ortho*-ester tetra azophenylcalix[4]arene has two tautomeric isomers. These two tautomeric isomers exist in solution together, however the keto tautomeric isomer with–N=NH- group on upper rim and C=O group on lower rim can constitute the stability of color complexes with metal ions. This was proved by experimental absorption spectra for these two forms[7,8]. This is also exhibited in complex *ortho*-ester tetra azophenylcalix[4]arene (TEAC) and Th^{4+} ion[10]. This complexing structure was also determinated by FT-IR and NMR spectrums. These spectrums confirmed the existence of keto tautomeric isomer. The functional group (–N=N–) exhibited the important role and the stretching vibration at 1512 cm^{-1}. The –C=N– group was found at new band of 1639 cm^{-1} to accommodate convictive evidences connecting the bonding between nitrogen and metal ion. These isomers establish the dynamic equilibrium between two substances with same molecular formula (Figure-1).



(a) Quinon isomer (b) Hydroxyquinol isomer (c) Complexing structure

Fig.-1: Structure of ortho-ester tetra azophenylcalix[4]arene isomers and complex: a) C=O groups on lower rim and C=N-NH- groups on upper rim; b) -OH groups on lower rim and C–N=N-groups on upper rim and c) complexing structure.

These have different functional groups and exist in dynamic equilibrium with each other. Therefore, they can interconvert rapidly from one form to another. Since the stable quinon (keto) form exists in relatively higher magnitude, so the *ortho*-ester tetra azophenylcalix[4]arene structure in quinon form (keto) with C=O group on lower rim can form the stable complex with metal ions. This also was confirmed by previous articles[9,10]. These phenomena were important testimonies to indicate the interaction of TEAC with metal ion M^{n+} at –N=N- bonding site. Therefore the quinon isomer of *ortho*-ester tetra azophenylcalix[4]arene was utilized to investigate the complexing capability with metal ions using molecular mechanics MM+ and molecular dynamic calculations MD.

Table-1: Total energies (kcal/mol) of complexes between *ortho*-ester tetra azophenylcalix[4] arene and metal ions without water molecules

Complex	Methods				Stability constants $mol^{-1}.L$ [12,13]
	MM+		MM+/MD		
	E, kcal/mol	Gradient	E, kcal/mol	T/K	
Host-Na^+	350.493604	0.009240	530.4717	283.9650	ND
Host-K^+	255.267083	0.009776	424.5831	251.5860	ND
Host-Mg^{2+}	402.453066	0.009115	577.6973	252.0144	2.6×10^4

Host-Ca^{2+}	287.448361	0.009485	463.3792	238.3901	6.0×10^4
Host-Co^{2+}	482.364707	0.009229	666.1967	256.8974	6.8×10^3
Host-Ni^{2+}	493.118437	0.008609	678.4552	257.2544	3.4×10^3
Host-Cu^{2+}	476.607610	0.009849	648.9711	255.8593	6.2×10^3

The relative energies of complexes host-M^{n+} resulting from MM+ and MM+/MD method correlated tightly in value R^2 of 0.9978 was given in Figure-2a. This can also observe easily that the stability of complexes correlated also closely with the relative energies resulting from MM+ and MM+/MD method in value R^2 of 0.9964 and R^2 of 0.9855, respectively (Figure-2b).

The most stable complexes are produced by keto isomer of *ortho*-ester tetra azophenylcalix[4]arene presented in their relative energies in Table-1. Those are consistent with their stability constants from literature[8,9,10]. The correlations can be used to predict the properties of different complexes host-M^{n+} such as stability constants or energy values, respectively. The structures of complexes *ortho*-ester tetra azophenylcalix[4] arene and metal ions were illustrated in Fig.-3, after optimizing by MM+/MD method.

Quantum Calculations

To investigate the interaction between a ligand *ortho*-ester tetra azophenylcalix[4]arene and a cation, it is necessary to know the electronic distribution, bonding distances in donor atoms, and metal cation. Quantum calculations can be used to calculate those. Because of the size of calixarenes cannot be solved analytically, semiempirical quantum mechanical methods that describe the electronic distribution in Mulliken charges on each atom. The structural forms of host and complexes in lowest energy derived from the MM+ optimized processes were used to calculate the binding energies and structural properties. The default options are used for SCF RHF involved total charge 0,0; spin multiplicity 1 for neutral molecules in which the spin multiplicity depends on the total charge of host molecule and metal ion, respectively. The Mulliken atomic charges on donor atoms N_1, N_2, N_3, N_4, O_1, O_2, O_3 and O_4 of *ortho*-ester tetra azophenylcalix[4]arene were resulted from semi-empirical quantum calculations congruenting with metal ion in complex host-M^{n+} (Fig.-1 and Table-2). The method AM1 used to calculate for alkali ions $Na^+$and K^+; method PM3 used to calculate for alkaline earth ions $Ca^{2+}$and Mg^{2+}; method ZINDO/S used for transition metal Co^{2+}, Ni^{2+}, Cu^{2+} ions.

The calix[4]arene derivatives with various functional groups showed the different complexing capability with metal ions. The *ortho*-ester tetra azophenylcalix[4]arene derivative displayed an applicability in analytical chemistry. However it also depends on groups OH on lower rim of them. The hydrogen bonds among OH groups can be reacted with water molecules. The C-OH groups on benzene ring can be changed into C=O groups in the cause of intramolecular hydrogen bonds. This also causes the change -N=N- into =N-NH- group. The bond N-H of =N-NH- group is ruptured readily. Therfore, the metal ion M^{n+} can attach propitiously to nitrogen atom of =N-NH- group. The cone conformers of *ortho*-ester tetra azophenylcalix[4]arene rendered to be the most stable forms. This can be proved by using semiempirical quantum calculations.

The complexing structures showed the guest-metal ions, ligated-nitrogen and ligated-oxygen atoms of *ortho*-ester tetra azophenylcalix[4]arene were demonstrated in Figures- 1 to 3. The calculated-proximate distances between donor-atoms (N and O) and guest (M^{n+}) as well as atomic charges were calculated by semiempirical quantum methods. The atomic charges and distances between guest-metal ions and donor nitrogen and oxygen atoms of group =N-NH- and ester group $-COOC_2H_5$ on upper rim were given in Table 2. For complexes host-M^+ (K^+ and Na^+) the bonding distances M^+-N and M^+-O are in range 2.2612Å to 2.3018Å and 2.1862Å to 2.1962Å for host-Na^+ and in range 2.7221Å to 2.7270Å and 2.6408Å to 2.6607Å for host-K^+, respectively. Those were calculated by semiempirical method AM1. But binding energies of these are equal to -14641.24 kcal.mol^{-1} and -14858.85 kcal.mol^{-1}, respectively. So the complex K^+ pointed out to be more stable than complex Na^+. Similarly for the complexes host-Mg^{2+} and host-Ca^{2+} the bonding distances M^{2+}-N and M^{2+}-O are in range 2.1131Å to 2.2397Å and 2.0293Å to

2.0492Å for host-Mg^{2+} and in range 2.4560Å to 2.4630Å and 2.3664Å to 2.3844Å for host-Ca^{2+}, respectively. Accordingly the complexes host-Mg^{2+} and host-Ca^{2+} pointed out to be more stable than complexes host-Na^+ and host-K^+. The distances between ligand and cation M^{n+} in X-ray crystal structures of complexes calixarene and cation are available from Cambridge Crystallographic Data. This showed that the distances of cation Na^+, K^+ and Ca^{2+} to ligand calixarene are equal to 2.34 ± 0.01Å, 2.66 ± 0.02Å and 2.31 ± 0.03Å, respectively. These are approximate to those from semiempirical quantum calculations, as given in Table-2.

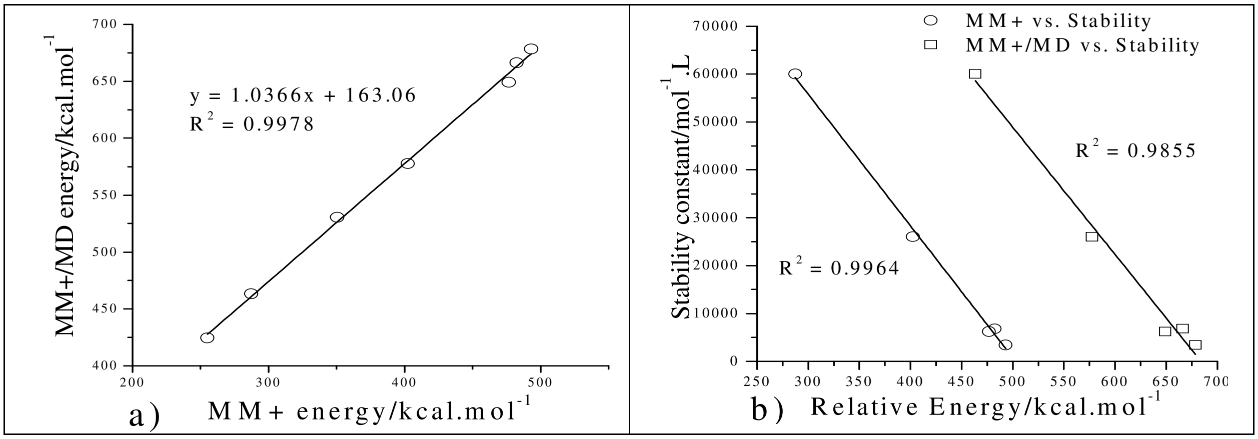
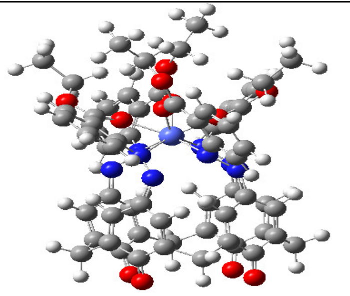
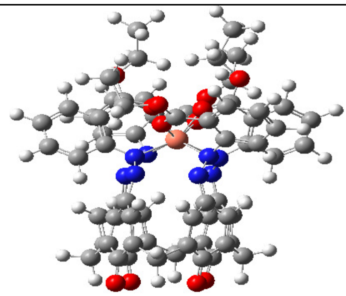
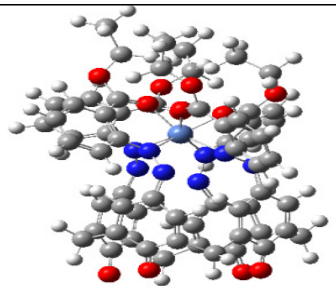
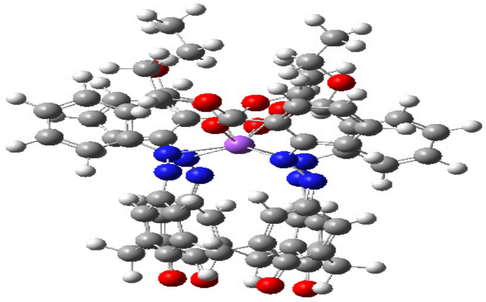


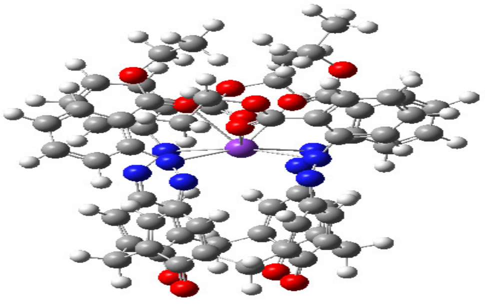
Fig.-2: Correlation between MM+ (a) and MM+/MD relative energy (b), and stability constants/mol^{-1}.L *vs.* MM+ and MM+/MD relative energies/ kcal.mol^{-1} for keto isomer of *ortho*-ester tetra azophenylcalix[4]arene and metal cations.

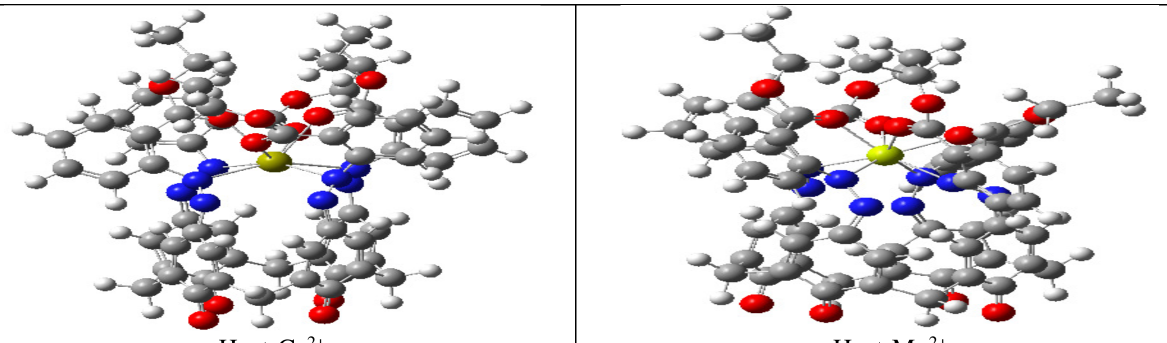

Host-Co^{2+}
E,*kcal/mol*= 666.1967


Host-Cu^{2+}
E,*kcal/mol*= 648.9711


Host-Ni^{2+}
E,*kcal/mol*= 678.4552


Host-Na^+
E, *kcal/mol* = 530.4717


Host-K^+
E, *kcal/mol* = 424.5831



Host-Ca^{2+}
E, *kcal/mol* = 463.3792

Host-Mg^{2+}
E, *kcal/mol* = 577.6973

Fig.-3: The optimal structures and MM+/MD relative energy of complexes *ortho*-ester tetra azophenylcalix[4]arene and metal cations.

Table-2: The Mulliken charge of metal ions, donor atoms and distances of the optimised M^{n+} position in complexes *ortho*-ester tetra azophenylcalix[4]arene and metal ions resulted from semiempirical quantum calculations, respectively

Structural Properties	*ortho*-ester tetra azophenylcalix[4]arene (host) with metal ions						
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
	Semi-empirical quantum calculation						
	AM1	AM1	PM3	PM3	ZINDO/S	ZINDO/S	ZINDO/S
$E_{binding}$/ kcal.mol^{-1}	-4641.24	-14858.85	-14615.33	-15445.15	-81374.47	-84527.12	-87314.73
M^{n+}	0.1033	0.3365	0.4529	0.4998	0.3678	0.3577	0.4028
N_1	0.3831	0.1317	-0.1606	-0.1145	-0.3164	-0.3476	-0.3994
N_2	-0.0965	-0.3342	0.2128	0.3113	-0.2368	-0.2015	-0.3613
N_3	0.0571	0.0394	-0.1520	-0.3448	-0.1872	-0.2630	-0.1955
N_4	-0.3111	-0.3099	-0.1693	-0.2623	-0.2236	-0.0928	-0.2527
O_1	-0.2633	-0.2714	-0.3207	-0.2889	-0.3644	-0.3962	-0.2633
O_2	-0.3195	-0.3292	-0.3281	-0.3775	-0.3239	-0.3285	-0.2813
O_3	-0.1774	-0.2405	-0.2858	-0.4098	-0.3761	-0.4051	-0.4295
O_4	-0.3181	-0.3371	-0.2388	-0.2608	-0.3916	-0.3975	-0.3301
Average	*-0.1307*	*-0.2064*	*-0.1803*	*-0.2184*	*-0.3025*	*-0.3040*	*-0.3141*
M^{n+}-N_1	2.3018	2.7270	2.2397	2.4630	2.1021	2.1113	2.1093
M^{n+}-N_2	2.2302	2.7250	2.0745	2.4561	2.0871	2.0136	2.0935
M^{n+}-N_3	2.2963	2.7212	2.2080	2.4563	2.0939	2.0994	2.1004
M^{n+}-N_4	2.2612	2.7221	2.1131	2.4560	2.0909	1.9212	2.0974
M^{n+}-O_1	2.1962	2.6607	2.0492	2.3844	1.9588	1.9689	1.9554
M^{n+}-O_2	2.1825	2.6545	2.0323	2.3604	1.8496	1.8635	1.8569
M^{n+}-O_3	2.1797	2.6586	2.0290	2.3874	2.0096	1.8934	2.0137
M^{n+}-O_4	2.1862	2.6408	2.0293	2.3664	1.8765	1.8919	1.8826
Average	*2.2293*	*2.6887*	*2.0969*	*2.4162*	*2.0086*	*1.9704*	*2.0137*

For complexes of *ortho*-ester tetra azophenylcalix[4]arene with transition metal ions Co^{2+}, Ni^{2+} and Cu^{2+} showed in Fig.-3, the structural descriptors involving atomic charges and optimized distances were calculated by semiempirical quantum method ZINDO/S, as given in Table 2. All the bonding distances are less than 2.1Å. The derivative *ortho*-ester tetra azophenylcalix[4]arene was also able to form the stability complexes with transition metal ions. In this case the selectivity of *ortho*-ester tetra azophenylcalix[4]arene for transition metal ions Co^{2+}, Ni^{2+} and Cu^{2+} seem to be most stable for ion Cu^{2+}, as exhibited in in Figs.-4a and b. This also showed for the binding energy of the optimized complexes, as in given Table- 2 and Fig.-4. The calculation results here are consistent with the stability constants from literature[8,10] and optimized distances of cation to donor atoms from Cambridge Crystallographic Data, respectively.

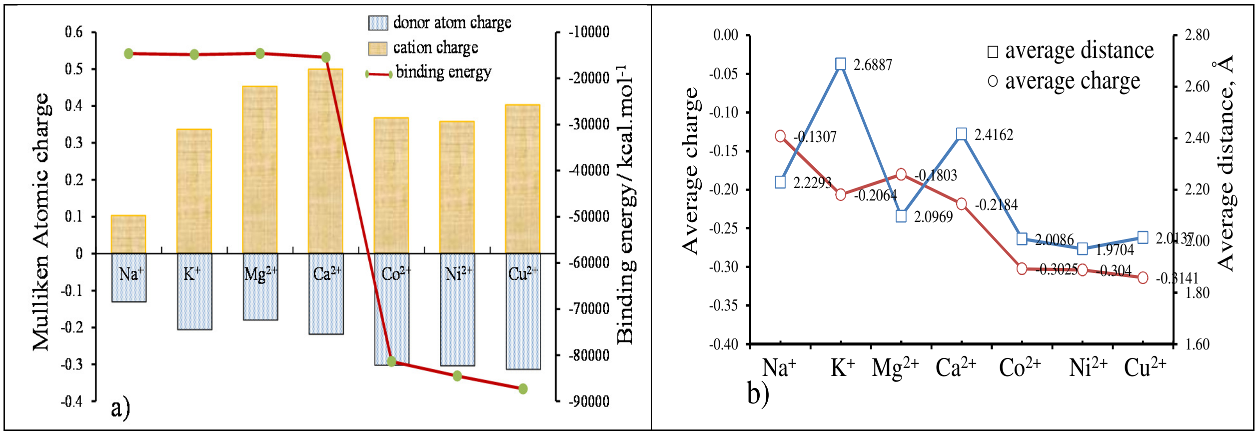


Fig.-4: The relationship between molecular properties: a) changes of cation and donor atomic charges with binding energy in complexes; b) changes of average charge and average distances from cation to donor atoms resulting from calculations AM1, PM3 and ZINDO/S.

In order to have a more insight for selectivity of *ortho*-ester tetra azophenylcalix[4]arene with metal ions, the caculation of electrostatic interaction of metal cations with donor nitrogen atoms of groups =N-N- and oxygen atoms of groups $–COOC_2H_5$ was performed. The charge values and bonding distances resulted from semiempirical quantum calculation methods pointed out the corresponding changes to each other. Consequently, the average partial charges of four donor nitrogen atoms and four donor oxygen atoms bonding metal ions can utilize the interpretation of electrostatic interaction of cation to ligand. The average charge value of -0.1307 for four nitrogen and four oxygen atoms bonding in complexe host-Na^+ is less negative than average value -0.2064 of complex host-K^+ (Table-1). The interaction of Na^+ ion for nitrogen and oxygen donor atoms is weaker than that of K^+ ion. The complex host-Na^+ is not stable than the complex host-K^+. The total energy and binding energy was shown in Table-1 and 2. Similarly, the interaction of transition metal ions with four donor atoms in ligand seems also to be stronger. This could show in binding energies and atomic-charge changes (Figure-4). It is also satisfied with the stability evaluation upon bonding distances. Therefore, the M^{n+} ion can move through the *ortho*-ester groups of upper rim. The complexes host-M^{n+} are formed in cone form and M^{n+} ion lies in cavity in which it bonds with nitrogen and oxygen atoms donor N_1, N_2, N_3 and N_4, and O_1, O_2, O_3 and O_4.

CONCLUSION

In this study, the quantum calculations at different theory levels has successfully used to calculate the structural properties for complexes *ortho*-ester tetra azophenylcalix[4]arene with metal ions such as: Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. The atomic charges of M^{n+} ions and donor atoms (nitrogen and oxygen) bonding M^{n+} ion and average distances between them displayed clearly the complex nature. The selectivity of *ortho*-ester tetra azophenylcalix[4] arene for metal ions Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} are found towards the transition metal ions. The stability of the complexes between ions and ligand indicated in following order: $Na^+ < K^+ < Ca^{2+} < Mg^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$. Moreover, the molecular mechanics MM+ and molecular dynamic simulations MD were used to optimize the complex conformations in environment without solvent. The molecular dynamic simulation results are also expressed the stable complexes of ligand-transition metal ions. The calculation methods denoted usefully in assessment of complex stability of *ortho*-ester tetra azophenylcalix[4]arene with metal ions. This imparted the insight of selectivity of *ortho*-ester tetra azophenylcalix[4]arene for metal ions.

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REFERENCES

1.W. Sliwa and M. Deska, *Arkivoc,* **1** ,87 (2008).
2. R.McLellan, K.M. Kennedy, M.Denis, R.D.McIntosh, E.K. Brechin and S.J.Dalgarno, *Polyhedron,* **64**, 388 (2013).
3. A.B.Rozhenko, W.W.Schoeller, M.C.Letzel, B.Decker, C.Agena and J.Mattay, *J. of Molecular Structure: THEOCHEM* ,**732**, 7 (2005).
4. F.Karcı, İ.Şener and H.Deligöz, *Dyes and Pigments* ,**59**, 53 (2003).
5. H. Deligöz and N. Ercan, *Tetrahedron,* **58**, 2881 (2002).
6. İ. Şener, F. Karcı, E. Kılıç and H .Deligöz, *Dyes and Pigments,* **62** ,141 (2004).
7. T.H .Kim, S.H. Kim, L.V. Tan, Y.J .Seo, S.Y. Park, H .Kim and J.S. Kim, *Talanta,* **71**, 1294 (2007).
8. T.H. Kim, S.H.Kim, L. V. Tan, Y.Dong, H.Kim and J.S. Kim, *Talanta*, **74**, 1654 (2008).
9. L.V. Tan, D.T. Quang, M.H. Lee, T.H. Kim, H.Kim and J.S.Kim, *Bull. Korean Chem. Soc.,* **28**, 791 (2007).
10. T.Q. Hieu, N.N. Tuan, L.N. Tu and L.V.Tan, *International J. of Chemistry*, **3**, 97 (2011).
11. J.I Choe and D.S Oh, *Bull. Korean Chem. Soc.,* **25** ,847 (2004).
12. J.I Choe, K,Kim and S.K Chang, *Bull. Korean Chem. Soc.,* **21**, 201 (2000).
13. A. Rahman, S.H.Amri, T.Maria and C. Erhard, *World J. Chem.,* **4**,52 (2009).
14. J, Plutnar, J, Rohovec, J, Kotek, Z, Žák and I, Lukeš, *Inor. Chimica. Acta.*, **335**, 27 (2002).
15. T. Hascall, K. Pang and G. Parkin, *Tetrahedron* ,**63**, 10826 (2007).

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