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Complexation Energies and Electronic-Structural Properties of Adamantane Derivatives: A DFT Study

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Abstract

This article is an investigation related to the complexation energies, binding abilities, frontier molecular orbital's energy gaps and dipole moments on dimeric forms of 1-adamantanol, 1-adamantanemethylamine and 1-adamantanecarboxylic acid as the adamantane derivatives. All the optimizations, counterpoise corrections and complexation energy computations have been achieved by density functional theory with B3LYP and WB97XD functionals. In all counterpoise calculations have been used the empirical dispersion method with B3LYP and WB97XD for non-covalent interactions. The more favorable complexation energies have been obtained by B3LYP with the addition of dispersion correction. In addition, the images mapped with total density and electrostatic potential have been obtained in this study.

Keywords: Adamantane derivatives, Complexation energy, Density functional theory

Adamantan Türevlerinin Kompleksleşme Enerjileri ve Elektronik-Yapısal Özellikleri: Bir DFT Çalışması

Öz

Bu makale, adamantan türevleri olarak 1-adamantanol, 1-adamantanmetilamin ve 1-adamantankarboksilik asit yapılarının dimerik formlarında kompleksleşme enerjileri, bağlanma yetenekleri, sınır moleküler orbital enerji boşlukları ve dipol momentleri ile

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ilgilidir. Tüm optimizasyonlar, counterpoise düzeltmeleri ve kompleksleşme enerji hesaplamaları, B3LYP ve WB97XD ile yoğunluk fonksiyonel teorisi yardımıyla elde edilmiştir. Tüm counterpoise hesaplamalarında kovalent olmayan etkileşimler için B3LYP ve WB97XD ile ampirik dispersiyon metodu kullanılmıştır. B3LYP yaklaşımında dispersiyon düzeltmesinin eklenmesiyle daha uygun kompleksleşme enerjileri elde edilmiştir. Ek olarak, bu çalışmada toplam yoğunluk ve elektrostatik potansiyel ile haritalanan görüntüler elde edilmiştir.

Anahtar Kelimeler: Adamantan türevleri, Kompleksleşme enerjisi, Yoğunluk fonksiyon teori

1. Introduction

Adamantane is a crystalline, colorless compound highly soluble in hydrocarbons and it has four cyclohexane rings. Adamantane derivatives are organic compounds that are effective in medical practice, extensively [1-3]. The first adamantane-derived drug is amantadine developed for the treatment of Parkinson's and influenza diseases [4-8]. Other biological characteristics of adamantane-like compounds such as anticancer, antihypertensive, central nervous and antimicrobial activities are reported in literature [9-13]. Also, the chemical and physical characteristics of adamantane derivatives such as low surface energy, thermal stabilities and oxidative stabilities have been the focus of several scientific studies [14, 15].

Adamantane derivatives have been recently analyzed by computational approaches as potential hole transport materials for perovskite solar cells [16], porous materials for energy conversion, gas storage [17] and optical materials [18]. The crystal structure and data, electronic structure calculations, spectral analysis, molecular orbitals (MO) analysis, natural bond analysis (NBO), non-linear optical (NLO) properties, molecular docking studies and electrostatic potential analysis on the several adamantane derivatives have been the main topics of the previous studies [19−26].

Structural properties of Adamantane derivatives have been studied due to the use as technological materials in the industrial areas and the synthesis and spectroscopic analysis of very novel compounds in recent years. Hydrogen bond geometries between the hydroxyl, methylamine and carboxylic components have attracted our attention in

these dimers. The main objective is to examine the interactions that are caused by the effective hydrogen bonds in the selected dimer structures. In this research article; the dimeric forms of 1-adamantanol (AD1), 1-adamantanemethylamine (AD2) and 1-adamantane carboxylic acid (AD3) as the adamantane derivatives are optimized by computational quantum chemistry methods. AD1 and AD2 compounds are also called as 1-hydroxyadamantane and 1- (amino methyl) adamantane in literature, respectively. In addition, we aimed to obtain corrected complexation energies by using Grimme's dispersion correction in B3LYP and compare without dispersion contribution. The corrected complexation energies, dipole moments and non-covalent interactions of the adamantane derivatives are evaluated in this study.

2. Material and Method

Geometry optimizations of the adamantane derivatives were provided by density functional theory (DFT) [27] with Becke's three-parameter exchange function [28] along with Lee-Yang-Parr correlation exchange functional (LYP) [29] and wB97XD in combination with 6-31G (*d*, *p*) basis set. WB97XD is in the group of long range corrected functionals and includes empirical dispersion [30]. The description of atomic coordinates, initially, for all the geometry optimizations and molecular orbitals were formed by Gauss View software database [31]. All the optimizations, counterpoise (CP) corrections [32], basis set superposition error (BSSE) corrections and complexation energy computations were performed by using Gaussian 09W program package [33]. Monomer components (monomers A and B) as Gaussian fragments 1 and 2 were selected in Gauss View software. Corrected complexation energy is a value calculated by the CP approach. Raw (uncorrected) complexation energy does not contain CP correction. CP correction is a method for removing BSSE [34]. Gap between corrected and raw complexation energy is equal to BSSE energy. In all CP calculations empirical dispersion method, D2 version of Grimme's dispersion correction [35], was applied with B3LYP and WB97XD by defining the values of the functional-specific global parameters for non-covalent interactions [36, 37].

3. Results and Discussion

The modeling images of the dimeric structures are given in Fig. 1. The energies of the monomeric and dimeric structures, complexation energies and hydrogen bond geometries (H···X' distances) for AD1, AD2 and AD3 are shown in Table 1. The stronger binding abilities between the monomer components with the hydrogen bond are computed as 1.86 (H3···O2'), 2.11 (H3···N2'), and 1.62 Å (H3···O4') by WB97XD methodology for AD1, AD2 and AD3, respectively. It is noteworthy that the binding abilities with O2-H3···O4' hydrogen bond geometry and corrected complexation energies results are more effective in AD3 dimer.

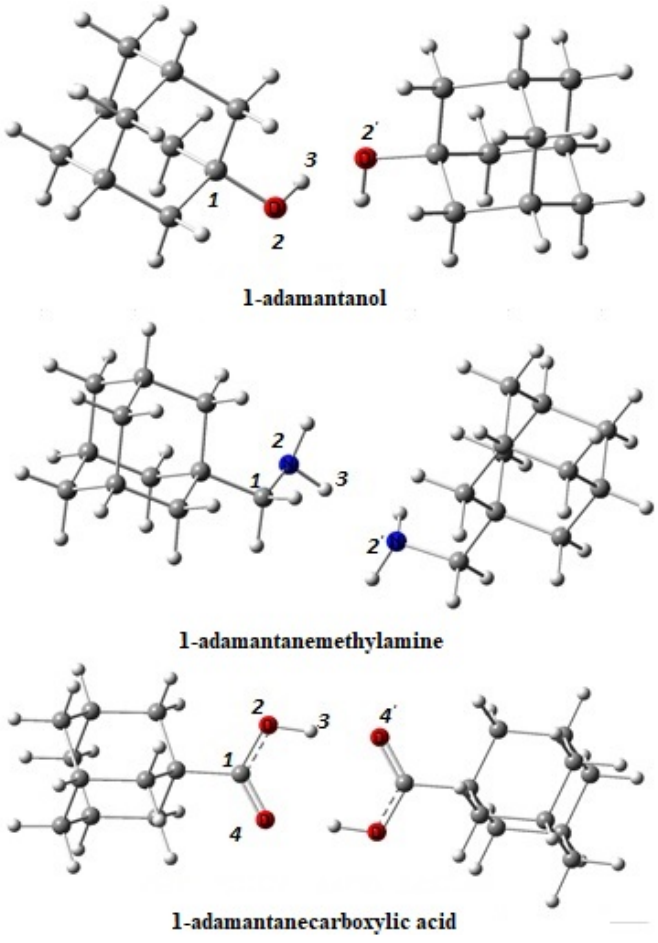

Figure 1. Dimeric forms of the adamantane derivatives

Corrected complexation energies are −4.26 (AD1), −2.60 (AD2) and −20.35 (AD3) kcal/mole without dispersion contribution in B3LYP. As shown in Table 1, corrected

complexation energies are computed as −8.61 (AD1), −6.04 (AD2) and −23.75 (AD3) kcal/mole by using Grimme's dispersion correction in B3LYP. Adding dispersion correction in WB97XD approach did not affect the complexation energies in CP calculations (Table 1). This indicates that the WB97XD function already contains dispersion correction. There are strong intermolecular hydrogen bonds in dimers. Non-covalent interactions (van der walls and steric interactions) are weak physical interactions and lower than hydrogen bonds.

Table 1. Energies and hydrogen-bond geometry of the adamantane derivatives by B3LYP and WB97XD type calculations

	Derivatives					
	AD1		AD2		AD3	
	B3LYP	WB97XD	B3LYP	WB97XD	B3LYP	WB97XD
Monomer (a.u.)	-465.96654	-465.84689	-485.40854	-485.28688	-579.31875	-579.16709
Dimer/CP corrected (a.u.)	-932.04213	-931.70840	-970.94357	-970.58679	-1158.77246	-1158.36309
Raw Complexation Energy (kcal.mole^{-1})	-12.23	-12.41	-8.14	-8.52	-27.84	-25.93
Corrected Complexation Energy (kcal.mole^{-1})	-8.61	-8.75	-6.04	-6.43	-23.75	-22.52
d(H···X')* (Å)	1.93	1.86	2.19	2.11	1.63	1.62

The relationship between the binding ability and interaction energy has been highlighted in earlier study [38]. The interaction energy was -19.815 kcal/mole as a lower level by the M06-2X of density functional than the B3LYP functional for a dimer linked with strong C-H···O interaction and N-H···O hydrogen bonds in this study [38]. In a similar study on the intermolecular interactions in aromatic amino acid residues, the binding energies have been computed at -5.8 and -6.6 kcal/mole by second-order Møller-Plesset perturbation (MP2) theory and the molecular mechanics modeling for para-cresol dimer, respectively [39].

Hydrogens interact symmetrically with atoms with higher electronegativity in AD3 dimeric form. So, it has minimum complexation energy values and stronger binding abilities with H3···O4' hydrogen bond geometry. Along with that, C1-O2-H3, C1-N2-H3 and C1-O2-H3 bond angles as (shown in Fig. 1) are respectively calculated by B3LYP as 107.37°, 110.98° and 105.71° in AD1, AD2 and AD3 monomeric forms. These angles are respectively 108.85°, 109.39° and 110.44° in AD1, AD2 and AD3 dimers as a result of intermolecular interactions. The analysis of the interaction energy and the decrease in

bridging angles are reviewed in a previous study involving the interactions of polyaniline emeraldine salt with NH_3, CO_2, and CO [40].

Table 2 includes the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and dipole moments for the monomeric and dimeric forms by B3LYP approach. As shown in the table, the minimal dipole moment is resulted in AD3 dimeric forms. The charge distribution and geometry of a molecule determines the polarity of this molecule. Polar or apolar properties of a molecule relate to electronegativity and molecular geometry. The dipole moment near zero indicates that the bond moments are of equal magnitude and opposite direction in AD3 dimeric forms.

Table 2. HOMO-LUMO energy gaps and dipole moments of the adamantane derivatives by RB3LYP /6-31G(d, p) type calculations

	HOMO-LUMO gap -monomer- (eV)	HOMO-LUMO gap -dimer- (eV)	Dipole moment -monomer - (Debye)	Dipole moment -dimer- (Debye)
AD1	8.63	8.04	1.54	2.16
AD2	8.11	7.71	1.46	2.91
AD3	7.46	7.24	1.71	0.22

HOMO-LUMO plots, molecular orbital energy levels for the AD1 dimeric form are displayed in Fig. 2. The frontier molecular orbital energy gaps (HOMO-LUMO gaps) of the AD1, AD2 and AD3 dimeric forms are calculated as 8.04, 7.71 and 7.27 eV, respectively (Table 2). The frontier molecular orbital energy gaps of the dimers are lower than those of monomers. The visuals mapped with electrostatic potential (ESP) onto AD1, AD2 and AD3 dimers are given in Fig. 3. Red, green, and blue tones represent negative, neutral and positive potential values, respectively. ESP is effectively observed onto dimer interaction regions. It is used to explore the electron richness or poorness of the molecular regions and to discuss the suitability of the electrophilic and nucleophilic attack. That is, it presents the distribution of positive and negative potentials on the molecule. The negative ESP generally refers to the lone pair of an electronegative atom [41]. In monomers, the hydroxyl, methylamine and carboxylic regions act as electrophilic attack. The regions with the positive electrostatic potential tone act as a nucleophilic attack. The surface map values are approximately -0.017 (around the oxygen), -0.013 (around the nitrogen) and -0.012 (around the symmetric atom group) for AD1, AD2 and AD3 dimeric forms, respectively.

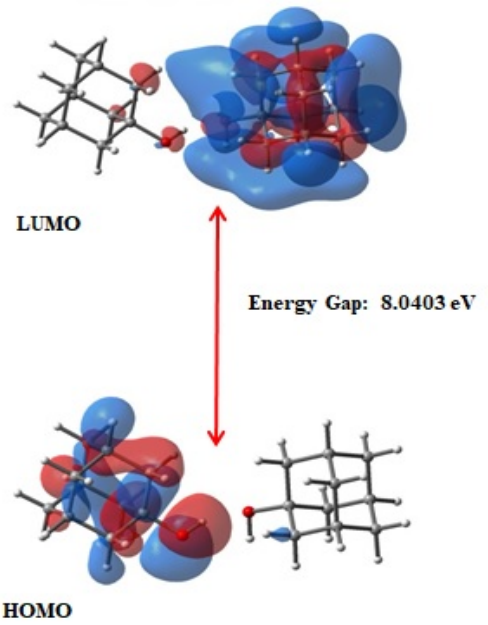

Figure 2. The frontier molecular orbitals and energy levels of 1-Adamantanol dimeric form

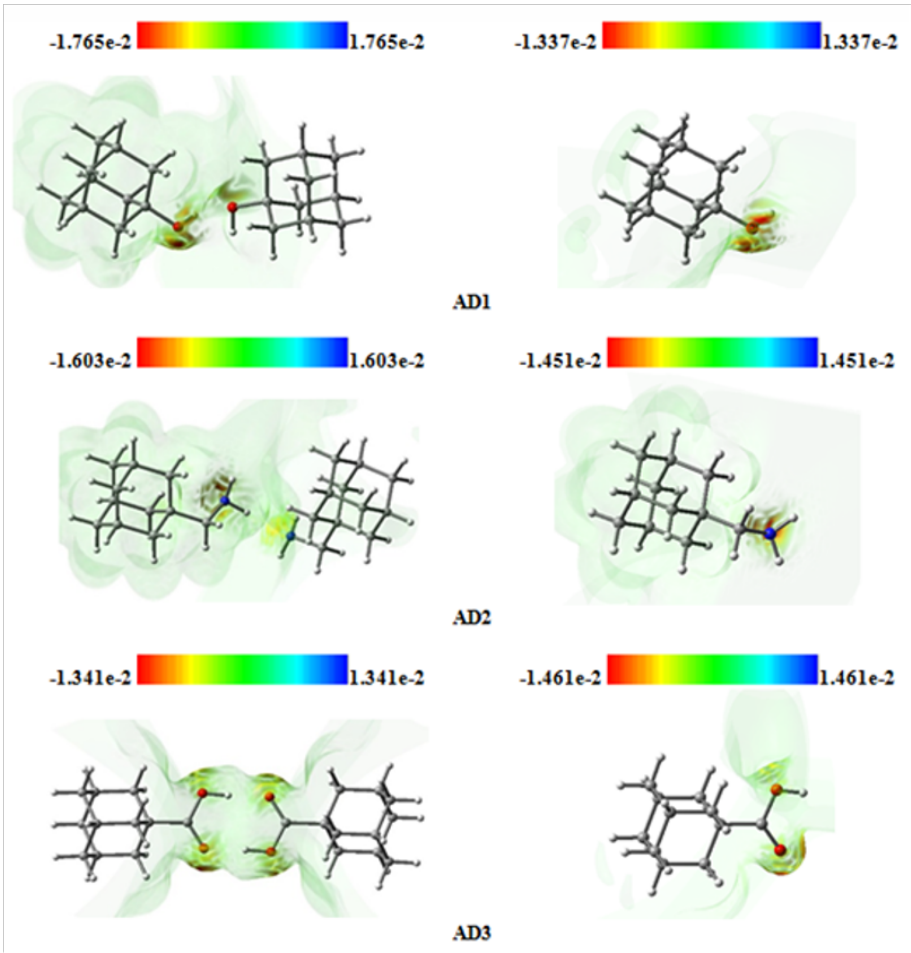

Figure 3. The visuals mapped with ESP of the dimer and monomer structures

4. Conclusions

In this study, the monomer and dimer optimizations of the adamantane derivatives have been performed via density functional theory. The binding abilities with the hydrogen bond geometries and complexation energies have been evaluated in dimer structures. Complexation energies and binding abilities with the hydrogen bond geometry are much more effective in AD3 dimer with atoms with higher electronegativity. D2 version of Grimme's dispersion correction has been tested with density functional theory for non-covalent interactions. In B3LYP the more favorable complexation energies have been obtained with dispersion correction. In all dimers the binding abilities computed by WB97XD functional are stronger for containing empirical dispersion. The energy gaps and dipole moment values for the monomeric and dimeric forms of the adamantane derivatives have been calculated. The relations of polarity and apolarity properties to electronegativity and molecular geometry have been commented. The surface map values have been calculated by ESP analysis observed onto dimer interaction regions and monomers. The hydroxyl, methylamine and carboxylic regions in dimers and monomers act as electrophilic attack.

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References

[1] Shundalau, M.B., Al-Abdullah, E.S., Shabunya-Klyachkovskaya, E.V., Hlinisty, A.V., Al-Deeb, O.A., El-Emam, A.A., Gaponenko, S.V., *Raman, infrared and DFT studies of N'-(adamantan-2-ylidene) benzohydrazide, a potential antibacterial agent*, Journal of Molecular Structure, 1115, 258-266, 2016.

[2] Lamoureux G., Artavia G., *Use of the adamantane structure in medicinal chemistry*, Current Medicinal Chemistry, 17, 2967-2978, 2010.

[3] Liu, J., Obando, D., Liao, V., Lifa, T., Codd, R., *The many faces of the adamantly group in drug design*, European Journal of Medicinal Chemistry, 46, 1949-1963, 2011.

[4] Al-Wahaibi, L.H., Hassan, H.M., Abo-Kamar, A.M., Ghabbour, H.A. and El-Emam, A.A., *Adamantane-ısothiourea hybrid derivatives:synthesis, characterization, in vitro antimicrobial, and in vivo hypoglycemic activities*, Molecules, 22, 710, 2017.

[5] Davies, W.L., Grunnert, R.R., Haff, R.F., McGahen, J.W., Neumeyer, E.M., Paulshock, M., Watts, J.C., Wood, T.R., Hermann, E.C., Hoffmann, C.E., *Antiviral activity of 1-adamantamine (amantadine),* Science, 144, 862–863, 1964.

[6] Togo, Y., Hornick, R.B., Dawkins, A.T., *Studies on induced influenza in man: I. double blind studies designed to assess prophylactic efficacy of amantadine hydrochloride against A2/Rockville/1/65 strain*, Journal of the American Medical Association, 203, 1089–1094, 1968.

[7] Wendel, H.A., Snyder, M.T., Pell, S., *Trial of amantadine in epidemic influenza*, Journal of Clinical Pharmacy and Therapeutics, 7, 38–43, 1966.

[8] Schwab, R.S., England, A.C., Poskanzer, D.C., Young, R.R., *Amantadine in the treatment of Parkinson's disease*, Journal of the American Medical Association, 208, 1168–1170, 1969.

[9] Sun, S.Y., Yue, P., Chen, X., Hong, W.K., Lotan, R., *The synthetic retinoid CD437 selectively induces apoptosis in human lung cancer cells while sparing normal human lung epithelial cells*, Cancer Research, 62, 2430-2436, 2002.

[10] Nakamura, Y., Fujimoto, T., Ogawa, Y., Namiki, H., Suzuki, S., Asano, M., Sugita, C., Mochizuki, A., Miyazaki, S., Tamaki, K., Nagai, Y., Inoue, S., Nagayama, T., Kato, M., Chiba, K., Takasuna, K., Nishi, T., *Lead optimization of 5-amino-6-(2,2-dimethyl-5-oxo-4-phenylpiperazin-1-yl)-4-hydroxyhexanamides to reduce a cardiac safety issue: discovery of DS-8108b, an orally active renin inhibitor*, Bioorganic & Medicinal Chemistry, 21, 3175-3196, 2013.

[11] Abou-Gharbia, M. A., Childers, W. E., Fletcher, H., McGaughey, G., Patel, U., Webb, M. B., Yardley, J., Andree, T., Boast, C., Kucharik, R.J., Marquis, K., Morris, H., Scerni, R., Moyer, J.A., *Synthesis and SAR of adatanserin: novel adamantyl aryl- and heteroarylpiperazines with dual serotonin 5-HT(1A) and 5-HT(2) activity as potential anxiolytic and antidepressant agents*, Journal of Medicinal Chemistry, 42, 5077-5094, 1999.

[12] Al-Abdullah, E.S., Asiri, H.H., Lahsasni, S., Habib, E.E., Ibrahim, T.M., El-Emam, A.A., *Synthesis, antimicrobial, and anti-inflammatory activity, of novel S-*

substituted and N-substituted 5-(1-adamantyl)-1,2,4-triazole-3-thiols, Drug Design Development and Therapy, 8, 505-518, 2014.

[13] Al-Abdullah, E.S., Al-Tuwaijri, H.M., Hassan, H.M., Haiba, M.E., Habib E.E., El-Emam, A.A., *Antimicrobial and hypoglycemic activities of novel N-Mannich bases derived from 5-(1-Adamantyl)-4-substituted-1,2,4-triazoline-3-thiones*, International Journal of Molecular Sciences, 15, 22995-23010, 2014.

[14] Fort, R.C., Schleyer, P.R., *Adamantane: consequences of the diamondoid structure*, Chemical Reviews., 64, 277-300, 1964.

[15] Marsusi, F., Mirabbaszadeh, K., Mansoori, G.A., *Opto-electronic properties of adamantane and hydrogen-terminated sila- and germa-adamantane: A comparative study*, Physica E, 41, 1151-1156, 2009.

[16] Gapol, M.A.B., Kim, D.H., *Novel adamantane-based hole transport materials for perovskite solar cells: a computational approach*, A European Journal of Physical Chemistry Chemical Physics, 21, 3857-3867, 2019.

[17] Nasrallah, H., Hierso, J., *Porous Materials Based on 3-Dimensional Td-Directing Functionalized Adamantane Scaffolds and Applied as Recyclable Catalysts*, Chemistry of Materials, 31, 619-642, 2019.

[18] Elavarasi, S.B., Mariam, D., Momeen, M.U., Hu, J., Guin, M., *Effect of fluorination on bandgap, first and second order hyperpolarizabilities in lithium substituted adamantane: A time dependent density functional theory*, Chemical Physics Letters, 715, 310-316, 2019.

[19] Myint, M.A., Blackmanx, A.G., Tan, E.W., *(±)-Adamantane-1,2-diyl diacetate*, Acta Crystallographica, E61, o3154–o3155, 2005.

[20] Pirali O., Goubet M., Boudon, V., D'Accolti, L., Fusco, C., Annese, C., *Characterization of isolated 1-aza-adamantan-4-one (C9H13NO) from microwave, millimeter-wave and infrared spectroscopy supported by electronic structure calculations*, Journal of Molecular Spectroscopy, 338, 6–14, 2017.

[21] Shundalau, M.B., Al-Abdullah, E.S., Shabunya-Klyachkovskaya, E.V., Hlinisty, A.V., Al-Deeb, O.A., El-Emam, A.A., Gaponenko, S.V., *Raman, infrared and DFT studies of N'-(adamantan-2-ylidene) benzohydrazide, a potential antibacterial agent*, Journal of Molecular Structure, 1115, 258-266, 2016.

[22] Saeed, A., Ashraf, Z., Erben, M.F., Simpson, J., *Vibrational spectra and molecular structure of isomeric 1-(adamantan-1-ylcarbonyl)-3-(dichlorophenyl)thioureas*, Journal of Molecular Structure, 1129, 283–291, 2017.

[23] Haress, N.G., Alomary, F.A.M., El-Emam, A.A., Mary, Y.S., Panicker C. Y., Al-Saadi, A.A., War, J.A., Alsenoy, C.V., *Spectroscopic investigation (FT-IR and FT-Raman), vibrational assignments, HOMO-LUMO analysis and molecular docking study of 2-(Adamantan-1-yl)-5-(4-nitrophenyl)-1,3,4-oxadiazole*, Spectrochimica Acta Part A, Molecular and Biomolecular Spectroscopy, 135, 973-983, 2015.

[24] Almutairi, M.S., Alanazi, A.M., Al-Abdullah, E.S., El-Emam, A.A., Pathak, S.K., Srivastava, R., Prasad, O., Sinha, L., *FT-IR and FT-Raman spectroscopic signatures, vibrational assignments, NBO, NLO analysis and molecular docking study of 2-{[5-(adamantan-1-yl) - 4-methyl - 4H - 1,2,4-triazol-3-yl]sulfanyl}-N,N-dimethylethanamine*, Spectrochimica Acta Part A, Molecular and Biomolecular Spectroscopy, 140, 1–14, 2015.

[25] Sebastian, Sr.S.H.R., Attia, M.I., Almutairi, M.S., El-Emam, A.A., Panicker, C.Y., Alsenoy, C.V., *FT-IR, FT-Raman, molecular structure, first order hyperpolarizability, HOMO and LUMO analysis, MEP and NBO analysis of 3-(adamantan-1-yl)-4-(prop-2-en-1-yl)-1H-1,2,4-triazole-5(4H)-thione, a potential bioactive agent*, Spectrochimica Acta Part A, Molecular and Biomolecular Spectroscopy, 132, 295-304, 2014.

[26] Al-Tamimi, A.S., El-Emam, A.A., Al-Deeb, O.A., Prasad, O., Pathak, S.K., Srivastava, R., Sinha, L., *Structural and spectroscopic characterization of a novel potential anti-inflammatory agent 3-(adamantan-1-yl)-4-ethyl-1H-1,2,4-triazole-5(4H)thione by first principle calculations*, Spectrochimica Acta Part A, Molecular and Biomolecular Spectroscopy, 124, 108–123, 2014.

[27] Grimme, S., *Semiemprical GGA-Type density functional constructed with a long-range dispersion correction*, Journal of Computational Chemistry, 27, 1787-1799, 2006.

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

[29] Lee, C., Yang, W., Parr, R.G., *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density*, Physical Review, B37, 785-789, 1988.

[30] Chai, J.D., Head-Gordon, M., *Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections*, A European Journal of Physical Chemistry Chemical Physics, 10, 6615-6620, 2008.

[31] Dennington, R., Keith, T., Millam, J., GaussView, Version 5.0.9, Semichem Inc., Shawnee Mission, KS, 2009.

[32] Boys, S.F., Bernardi, F., *The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors*, Molecular Physics, 19, 553-566, 1970.

[33] Frisch, M.J., Trucks, G.W., …, and Fox, D.J., Gaussian 09, Revision D.01. Gaussian, Inc., Wallingford CT, 2009.

[34] Sherrill, C.D., *Counterpoise Correction and Basis Set Superposition Error*, Georgia Institute of Technology, 1-6, 2010.

[35] Grimme, S., *Semiempirical GGA-type density functional constructed with a long-range dispersion correction*, Journal of Computational Chemistry, 27, 1787-1799, 2006.

[36] Raju, R.K., Bloom, J.W., An, Y., Wheeler, S.E., *Substituent effects on non-covalent interactions with aromatic rings: insights from computational chemistry*, A European Journal of Physical Chemistry Chemical Physics, 12, 3116-3130, 2011.

[37] Cortopassi, W.A., Kumara, K., Paton, R.S., *Cation–π interactions in CREBBP bromodomain inhibition: an electrostatic model for small-molecule binding affinity and selectivity*, Organic and Biomolecular Chemistry, 14, 10926-10938, 2016.

[38] Karakaya, M., Sert, Y., Sreenivasa, S., Suchetan, P.A., Çırak Ç., *Monomer spectroscopic analysis and dimer interaction energies on N-(4-methoxybenzoyl)-2-methylbenzenesulfonamide by experimental and theoretical approaches*, Spectrochimica Acta Part A, 169-177, 2015.

[39] Gervasio, F.L., Chelli, R., Procacci, P., Schettino, V., *The nature of intermolecular interactions between aromatic amino acid residues*, Proteins, 48, 117-125, 2002.

[40] Ullah, H., Shah, A.A., Bilal, S., Ayub, K., *DFT study of polyaniline NH_3, CO_2, and CO gas Sensors: comparison with Recent Experimental Data*, Journal of Physical Chemistry C, 117, 23701−23711, 2013.

[41] Almutairi, M.S., Xavier, S., Sathish, M., Ghabbour, H.A., Sebastian, S., Periandy, S., Al-Wabli, R.I., Attia, M.I., *Spectroscopic (FT-IR, FT-Raman, UV, 1H and 13C NMR) profiling and computational studies on methyl 5-methoxy-1H-indole-2-carboxylate: A potential precursor to biologically active molecules*,. Journal of Molecular Structure, 1133, 119−210, 2017.