



A Semi-Empirical and Density Functional Theory Study of 2,2',3,4-Tetrahydroxy-3'-sulpho Azobenzene Derivatives and Their Zirconium Complexes

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In this study, certain theoretical properties of three tetrahydroxyazo derivatives and their zirconium complexes, such as stability, reactivity, geometry and energy have been calculated by MOPAC2009 with the PM6 method and GAUSSIAN 09 programs at the basis set B3LYP/LanL2DZ to understand the basic principles concerning their behaviour. The theoretical data was then compared with that of certain experimental results realized earlier by our group to ascertain any possible correlation.

Key Words: Tetrahydroxyazobenzene derivatives, Tetrahydroxyazon, Semi-empirical calculation, Theoretical calculation, PM6, Zirconium complexes, DFT, B3LYP.

INTRODUCTION

Azobenzene and its derivatives have attracted much attention as dyestuffs and because of their great potential in developing optical materials^{1,2}, information storage devices^{3,4} and novel nano devices in industry⁵⁻⁷. In addition, azobenzene derivatives can be used as energetic materials^{4,8}. Azobenzenes are well-known photoactive molecules, which show *trans-cis* isomerization⁹. The constrained environment of the adsorbed azobenzene molecules may strongly influence the optical and photochemical properties of azobenzene molecules¹⁰. The researchers have been focused on the development of new such compounds in recent years for this purpose¹¹.

Certain *o,o'*-azobenzene molecules such as 2,2',3,4-tetrahydroxy-3'-sulpho azobenzenes (tetrahydroxyazo) have been synthesized previously by our group. Following their structure characterization, these tetrahydroxyazo molecules were successfully used for the determination of certain metals in certified pharmaceutical suspension, granite or certain alloys by our group¹²⁻¹⁷. The molecules include different substituents on various positions of the phenyl ring. The shifts of their colour band are related to the substituents on the phenyl ring and consequently their absorption spectra are related to their molecular geometries. Thus, the azobenzene dyes are under investigation for their colour band affects the selection of the optical device¹⁸. Moreover, it is thought that a third OH-group, which is located in the *ortho* position to the azo group in the pyragallol moiety in our synthesized tetrahydroxyazo molecules gives an opportunity to react in a more acidic media,

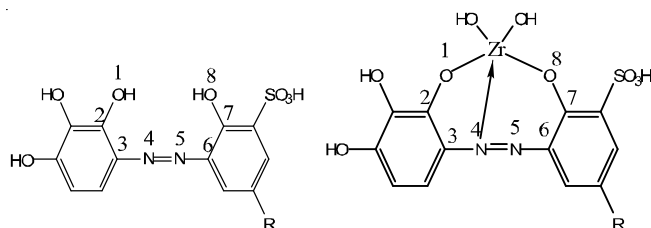
enabling the formation of metal-nitrogen bonds between the -OH group and the nitrogen atom on the azo group. The electron density between the -OH group, located in the *ortho* position and the nitrogen atom on the azo group, increases the stability of this bond^{17,19}. Thus, analytical properties of the tetrahydroxyazon complexes increase due to the tetrahydroxyazo ligand.

Zirconium widely-distributed in the earth's crust, has become an important material in different technological fields. Zirconium is used in the nuclear industry as a fuel rod cladding, as a catalyst in organic reactions and in the manufacture of water repellent textiles, in metal alloys and in dye pigments and ceramics²⁰⁻²². Salts and complexes of Zr display high reactivity towards phosphodiester cleavage of DNA or RNA^{23,24}. Skin and lung granulomas have been observed after repeated zirconium exposure²⁵. There has been such a substantial increase in the use and importance of both tetrahydroxyazo and its Zr complexes. To the best of our knowledge, no theoretical study on tetrahydroxyazo derivatives and their zirconium complexes synthesized earlier by our group exists. The goal of the present study is to calculate and evaluate certain theoretical properties, such as stability, reactivity, geometry and energy of both the three tetrahydroxyazo molecules and their zirconium complexes (Fig. 1) in liquid phase using both Density Functional Theory (DFT) at the basis set LanL2DZ and restricted Hartree-Fock level using the PM6 semi-empirical SCF-MO method and to compare with experimental results realized by our group earlier identify any possible correlation.

TABLE-1
CALCULATED THERMODYNAMIC AND PHYSICAL PARAMETERS OF THE TETRAHYDROXYAZO DERIVATIVES AND THEIR ZIRCONIUM COMPLEXES (INDICATED IN FIGURE 1) IN AQUEOUS PHASE AT 298 K ($\epsilon = 78.4$)

	ΔH_f^a	ΔH^b	ΔS^c	ΔG_f^d	ΔG^e	E_{HOMO}	E_{LUMO}	N^f	D^g
azo-H	-228.634	14268.499	157.4781	-275.562	-32,660	-9.087	-1.528	-7.559	7.269
azo-Cl	-235.017	15235.8964	167.0468	-284.797	-34.544	-9.114	-1.683	-7.431	4.752
azo-NO ₂	-233.916	16131.6412	174.6546	-285.963	-35.915	-9.197	-1.726	-7.471	3.206
azo-H-Zr	-491.815	17010.3559	180.2534	-545.531	-36.705	-8.918	-1.485	-7.433	6.714
azo-Cl-Zr	-498.799	17696.108	183.6594	-553.530	-37.034	-8.964	-1.641	-7.323	4.769
azo-NO ₂ -Zr	-503.935	18430.8114	194.2456	-561.820	-39.454	-9.03	-1.678	-7.352	7.116
ZrOCl ₂	-156.826	4411.819	83.8585	-181.816	-20.578	-10.67	-2.097	-8.573	4.033

^aHeat of formation; ^bEnthalpy; ^cEntropy; ^dFormation Gibbs free energy was calculated by the equation of $\Delta G_f = \Delta H_f - T\Delta S$; ^eGibbs free energy was calculated by $\Delta G = \Delta H - T\Delta S$; ^fHOMO-LUMO,³¹; ^gDipole moment



R:	H	NO ₂	Cl
Name-ligand:	2,2',3,4-tetrahydroxy-3'sulpho azobenzene	2,2',3,4-tetrahydroxy-3'sulpho 5'-nitro azobenzene	2,2',3,4-tetrahydroxy-3'sulpho-5'-chloro azobenzene
Abbreviation-ligand	azo-H	azo-NO ₂	azo-Cl
Abbreviation-complex	azo-H-Zr	azo-NO ₂ -Zr	azo-Cl-Zr

Fig. 1. Structures and abbreviations of the tetrahydroxyazo derivatives and their zirconium complexes

EXPERIMENTAL

The structural and geometrical features of the tetrahydroxyazo derivatives indicated in Fig. 1 and their zirconium complexes of tetrahydroxyazo derivatives are studied systematically in this work by both semi-empirical and DFT calculations. The practical numbering system adopted to carry out the calculations of the molecules analyzed is shown in Fig. 1. Theoretical calculations were carried out using the MOPAC2009 packet program at the restricted Hartree-Fock level using PM6 semi-empirical SCF-MO methods²⁶.

The initial data for all of the geometrical optimizations was obtained using a molecular mechanic program (CS ChemOffice Pro 12.0.2.1076 for Microsoft Windows)²⁷, followed by full optimization of all geometrical variables (bond lengths, atomic charges, bond angles and dihedral angles) using PM6 quantum chemical methods by the MOPAC2009 program. An Intel(R) Core(TM) i7 X 990 @ 3.47 GHz 3.46 GHz computer was used for semi-empirical calculations.

Density functional (DFT) calculations in this work were also carried out with Lee, Yang and Parr including partially exact HF-exchange (B3LYP)²⁸ and LanL2dz basis²⁹ set using the GAUSSIAN 09 series of programs³⁰. An Intel Core i7 980X-6 core, 3.33GHz, L3 Cache 12 MB work station was used for the DFT calculations.

The optimized geometrical parameters were compared with both the available gaussian and the experimental data in order to establish accuracy for the prediction of the geometrical parameters of the ligands and the metal complexes.

RESULTS AND DISCUSSION

Semi-Empirical studies with PM6

Stability and structure of the molecules: The thermodynamic magnitudes obtained for the tetrahydroxyazo ligands and the zirconium complexes were calculated to analyze the relative stability and structures of the zirconium complexes in aqueous phase by PM6 (Table-1). The calculated thermodynamic parameters by PM6, as well as the previously studied experimental data, are also summarized in Table-2 for the tetrahydroxyazo molecules and their complexation reactions with zirconium.

TABLE-2
CALCULATED THERMODYNAMIC PARAMETERS BY PM6 AND THOSE OBTAINED FROM PREVIOUS STUDIES FOR THE COMPLEXATION REACTIONS

Complex	M + L → ML			
	RS ^a	$\delta\Delta G_{f(R)}^b$	$\delta\Delta G_{(R)}^c$	(Exp. log β^d)
azo-H-Zr	-106.355	-88.152	16.533	14.94
azo-Cl-Zr	-106.956	-86.917	18.088	17.25
azo-NO ₂ -Zr	-113.193	-94.041	17.039	19.72

^aH_f (products) - ΔH_f (reactants); ^b ΔG_f (products) - ΔG_f (reactants); ^c ΔG (products) - ΔG (reactants); ^dthe logarithm of the experimental complex formation constants of zirconium and the studied tetrahydroxyazo ligands¹⁴

Enthalpy, heat of formation and relative stability (ΔH , ΔH_f and RS): The ΔH values of the studied molecules are azo-H < azo-Cl < azo-NO₂ and azo-H-Zr < azo-Cl-Zr < azo-NO₂-Zr. All three ligands and their zirconium(IV) complexes have positive ΔH values. The ΔH_f values of the studied molecules are azo-NO₂-Zr < azo-Cl-Zr < azo-H-Zr < azo-Cl < azo-NO₂ < azo-H (Table-1). All these molecules have negative ΔH_f values. The relative stabilities were calculated regarding ΔH_f values (Table-2). The relative stabilities (RS) for the formation of all the studied ML complexes were negative. If RS is negative, the reaction is exothermic, meaning that the overall decrease in enthalpy is achieved by the generation of heat.

Gibbs free energy (ΔG and ΔG_f , $\delta\Delta G$ (R) and $\delta\Delta G_f$ (R)): As can be seen from Table-1, the stabilities of these azobenzene molecules depend on their Gibbs free energies (ΔG_f ; thermokinetic Gibbs free energy) in the aqueous phase in the following order: azo-NO₂ > azo-Cl > azo-H. It is observed that molecules having -NO₂ and -Cl group are more stable and are less reactive than those of azo-H. It is thought that the reason for this originates from the electron withdrawal

properties of these substituents. For the tetrahydroxyazo-zirconium complex structures, the order of stability is azo-NO₂-Zr > azo-Cl-Zr > azo-H-Zr. The best reactive structures are azo-H-Zr among the complexes (Table-1).

Regarding the ΔG values (thermodynamic Gibbs free energy), the order of stability is azo-NO₂ > azo-Cl > azo-H and azo-NO₂-Zr > azo-Cl-Zr > azo-H-Zr for the ligands and complexes, respectively (Table-1). The best reactive structure is azo-H-Zr among the zirconium(IV) complexes like those regarding the ΔG_f values. The order for azo-NO₂-Zr, azo-Cl-Zr, azo-H-Zr and the three complexes, azo-NO₂-Zr, azo-Cl-Zr and azo-H-Zr, is the same as those regarding the ΔG_f values.

The calculated values for the Gibbs free energy of the complexation reactions [$\Delta G_{f(R)}$ and $\Delta G_{(R)}$] in water are reported in Table-2. It is known that if $\delta\Delta G_{(R)}$ is positive, the complexation reaction is not spontaneous. The thermokinetic Gibbs free energy values of the ML complexation reactions [$\delta\Delta G_{f(R)}$] were negative. On the other hand, the thermodynamic Gibbs free energy values [$\delta\Delta G_{(R)}$] are positive. If $\delta\Delta G_{f(R)}$ is negative, the complexation reaction is spontaneous. [$\delta\Delta G_{f(R)}$] and [$\delta\Delta G_{(R)}$] do not give a meaningful correlation (not shown here) with the experimental complex formation constants ($\log \beta$). On the other hand, the negative values for the both Gibbs free energy of the complexes (ΔG_f and ΔG) show that the complexation reaction is spontaneous. The negative Gibbs free energy values for the formation reactions of the ML complexes confirm that the ML complexation reaction is favoured. The values are in good agreement with the experimental data which showed these tetrahydroxyazo-zirconium complexes have M:L: 1:1 and high complex formation constants (Table-2) by our previous experimental study^{12,14-17}. RS, ΔG_f and $\delta\Delta G$ values of the three ML complexes are given comparatively with those of the experimental complex formation constants ($\log \Delta$) in Fig. 2. $\log \beta$ gives good correlation with all RS, ΔG_f and $\delta\Delta G$ values. The best correlation with $R^2 = 0.9999$ was observed between $\log \beta$ and ΔG_f values.

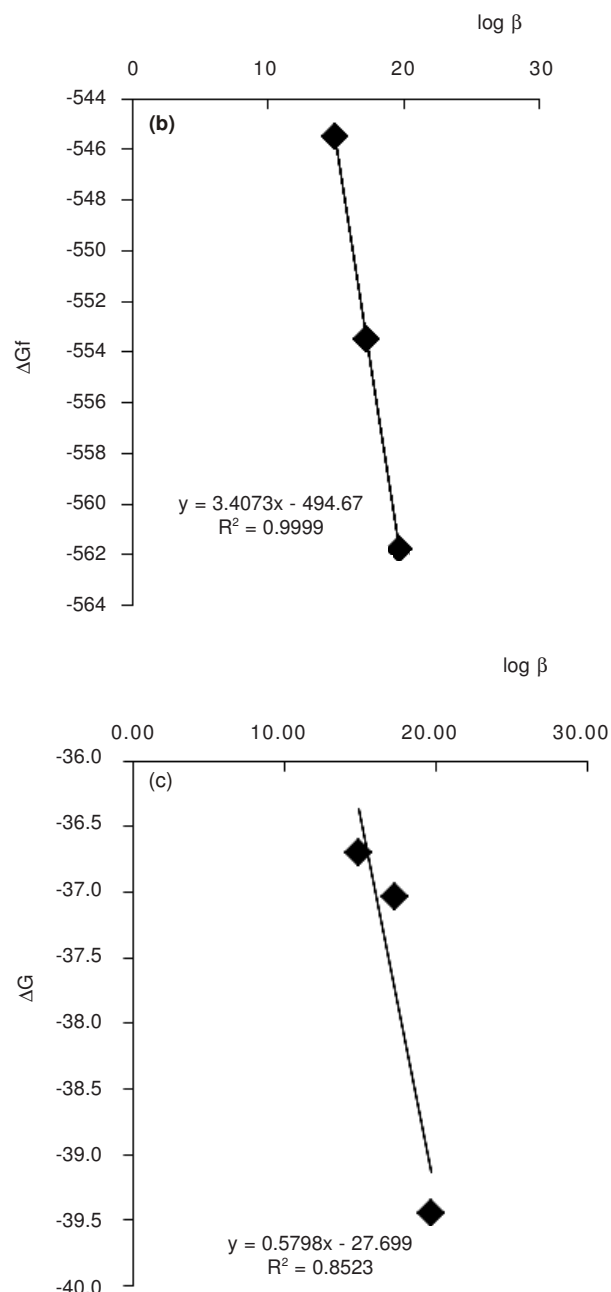
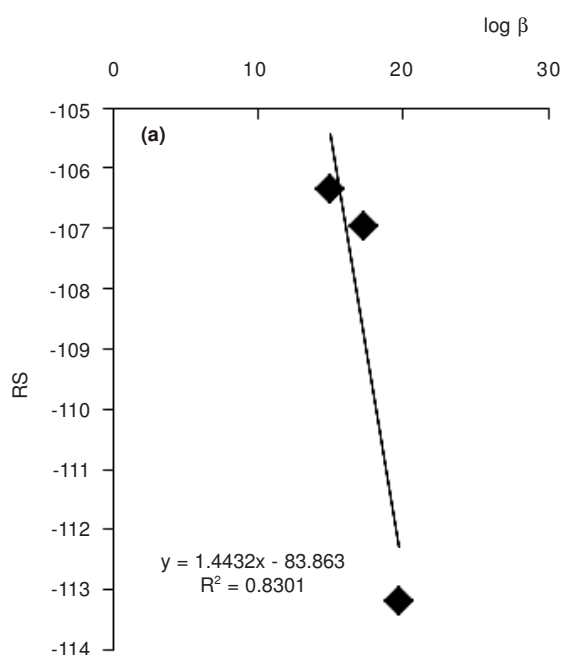


Fig. 2. Graphs complex formation constants ($\log \beta$) versus a) relative stability (RS) and b, c) Gibbs Free Energy [ΔG_f and $\delta\Delta G_{(R)}$] values of the studied ML complexes by PM6

Dipole moment: The dipole moment (D) value order is given in the following order: azo-NO₂-Zr > azo-H-Zr > azo-Cl-Zr and azo-H > azo-Cl > azo-NO₂. When (D) of the molecules was investigated, a correlation was observed between the molecule structures (dipole moments) and reactivities for the three tetrahydroxyazo ligands. Insignificant correlation could be observed between the complex molecule structures and reactivities for all of the studied molecules (Table-1). It is thought that the dipole moment does not give any important information from the viewpoint of the reactivity for these complexes in the present study. The correlation between dipole moments and complex formation constants is given in Fig. 3. A meaningful correlation was not observed between the dipole moments and the complex formation constants.

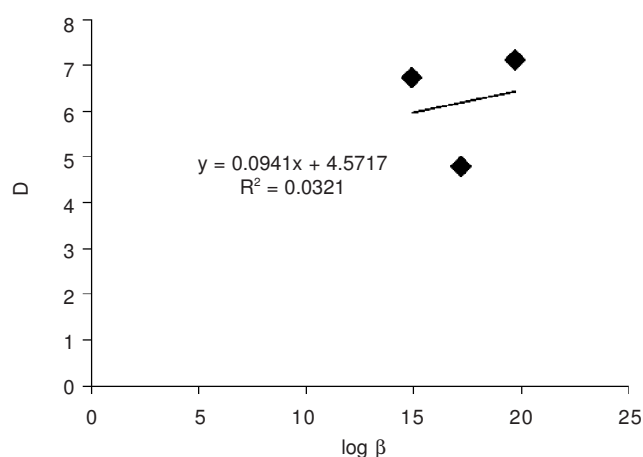


Fig. 3. Graph complex formation constants ($\log \beta$) versus dipole moment (D) values of the studied ML complexes by PM6

Nucleophilicity: The frontier orbital energies, E_{HOMO} and E_{LUMO} , are important parameters of molecular electron structure. The lower the E_{HOMO} , the weaker is the molecule donating electron ability. A higher E_{HOMO} implies the molecule is a good electron donor. E_{LUMO} appears as a molecule receiving electron^{31,32}. When the nucleophilicities ($N = E_{\text{HOMO}} - E_{\text{LUMO}}$) of the molecules are investigated, the N value order is given for both ligands and possible complex structures in the following order: azo-Cl > azo-NO₂ > azo-H and azo-Cl-Zr > azo-NO₂-Zr > azo-H-Zr. There is a parallelism between reactivity and N values for the three ligands. A meaningful correlation could not be

observed between the reactivity and the N values for the complex structures (Fig. 4). It is therefore thought that nucleophilicity does not show an important effect on the formation constants of the zirconium(IV) complexes.

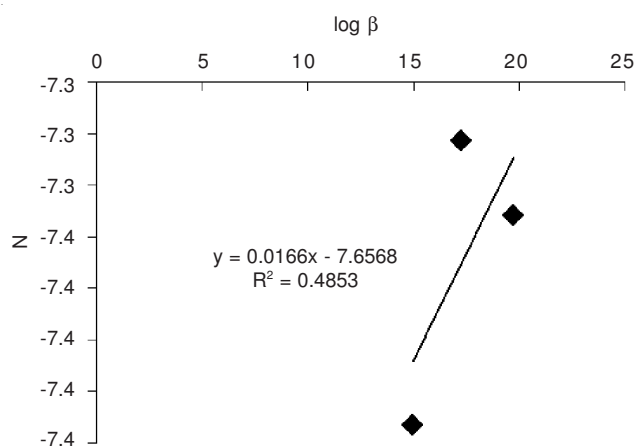


Fig. 4. Graph complex formation constants ($\log \beta$) versus nucleophilicity (N) values of the studied ML complexes by PM6

Molecular structure of the ligands and the zirconium complexes [Atomic charges, bond lengths and angles and dihedral angles] by PM6: Table-3 shows selected geometrical parameters calculated with PM6 for the studied ligands and their zirconium(IV) complexes to investigate the changes during complexation reactions. As seen in Table-3, all the selected

TABLE-3
SELECTED ATOMIC CHARGES, BOND LENGTHS (ATOM DISTANCES), BOND ANGLES AND DIHEDRAL ANGLES OBTAINED FROM PM6 CALCULATIONS

Bond angles, BA (°)	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O-2C-3C	124.028	124.111	124.063	120.444	2.890	120.657	2.783	120.397	2.954
2C-3C-4C	113.315	113.792	113.413	113.379	0.057	125.942	10.678	113.413	0.000
3C-4C-5C	119.239	119.039	119.327	117.413	1.531	121.171	1.791	119.327	0.000
4N-5N-6C	117.757	117.802	117.683	120.399	2.244	116.290	1.284	120.338	2.256
5N-6C-7C	127.240	127.197	127.169	126.072	0.919	113.051	11.121	127.169	0.000
6C-7C-8O	116.727	115.622	116.537	120.239	3.008	119.511	3.363	116.537	0.000
Bond lengths, BL (Å)	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O-2C	1.363	1.364	1.363	1.312	3.740	1.304	4.426	1.312	3.737
2C-3C	1.420	1.421	1.421	1.432	0.801	1.428	0.474	1.432	0.795
3C-4N	1.425	1.423	1.423	1.430	0.378	1.409	0.976	1.428	0.372
4N-5N	1.255	1.255	1.255	1.264	0.731	1.267	0.921	1.264	0.712
5N-6C	1.434	1.437	1.436	1.422	0.869	1.439	0.191	1.424	0.811
6C-7C	1.440	1.445	1.445	1.437	0.259	1.456	0.790	1.439	0.423
7C-8O	1.329	1.327	1.327	1.292	2.792	1.284	3.270	1.290	2.746
Atomic charges, AC	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O	0.475	0.470	0.472	0.505	6.448	0.477	1.375	0.505	6.893
4N	0.147	0.123	0.131	0.0573	61.016	0.086	30.079	0.068	47.784
5N	0.117	0.121	0.124	0.123	5.642	0.031	74.505	0.131	5.242
8O	0.480	0.437	0.468	0.502	4.586	0.488	11.566	0.497	6.043
Dihedral angles, DA (°)	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O-2C-3C-4C	0.220	1.689	0.434	0.255	16.247	1.689	0.000	0.334	22.883
2C-3C-4N-5N	178.884	179.799	178.179	169.140	5.447	4.981	97.230	168.875	5.221
3C-4N-5N-6C	179.987	177.366	179.862	176.282	2.059	177.366	0.000	176.134	2.073
4N-5N-6C-7C	4.699	169.548	5.521	6.525	38.866	169.548	0.000	7.220	30.779
5N-6C-7C-8O	1.282	0.105	1.120	2.592	102.154	0.105	0.000	3.083	175.221

TABLE-4
CALCULATED THERMODYNAMIC AND PHYSICAL PARAMETERS OF THE TETRAHYDROXYAZON DERIVATIVES
AND THE POSSIBLE ZIRCONIUM COMPLEXES (Fig. 1) BY DFT IN AQUEOUS PHASE

	$E_{\text{elec+ZPE}}^a$	$E_{\text{elec+thermal}}^b$	$H_{\text{elec+thermal}}^c$	$G_{\text{elec+thermal}}^d$	E_{total}	HOMO	LUMO	N^e	D^f	Exp. \log^{pg}
azo-H in aqueous phase	-1108.87308	-1108.85255	-1108.852	-1108.92364	148.861	-0.23210	-0.11116	-0.121	7.709	-
azo-Cl in aqueous phase	-1123.21403	-1123.19217	-1123.191	-1123.26628	143.397	-0.23446	-0.11604	-0.118	4.486	-
azo-NO ₂ in aqueous phase	-1313.33822	-1313.31509	-1313.314	-1313.392759	151.518	-0.23648	-0.13729	-0.099	5.435	-
azo-H-Zr in aqueous phase	-1306.22998	-1306.20441	-1306.203	-1306.28405	154.566	-0.23002	-0.12236	-0.108	7.803	14.94
azo-Cl-Zr in aqueous phase	-1320.57128	-1320.54451	-1320.544	-1320.627015	149.174	-0.23175	-0.12739	-0.104	5.128	17.25
azo-NO ₂ -Zr in aqueous phase	-1510.58472	-	-1510.555	-1510.643032	155.488	-0.23228	-0.12719	-0.105	4.819	19.72
ZrOCl ₂ in aqueous phase	-150.728126	1510.556115	-150.7243	-150.756515	9.181	-0.21627	-0.03284	-0.183	-	-
ZrOCl ₂ in gas phase	-4510.26998	-4510.26712	-4510.266	-4510.298374	9.066	-0.35485	0.03171	-0.387	-	-

^aElectronic energy + zero point energy, ^bElectronic energy + thermal energy, ^c $H = E + RT$, ^dElectronic energy + thermal Gibbs free energy, ^e $N = \text{HOMO-LUMO}$, ^fDipole moment, ^gThe logarithm of the previously studied experimental complex formation constants of zirconium and the studied tetrahydroxyazo ligands.¹⁴

bond lengths (BL) in all the three ligands range from 1.255 to 1.445 Å. The bond lengths range from 1.284 to 1.456 Å for the complex structures. Differences between the complexes and the ligands are observed in the equivalent distances and these differences in the distances ($[(BL_{\text{complexes}} - BL_{\text{ligands}}) / BL_{\text{ligands}}] \times 100$), e.g. $[(BL_{\text{azo-H-Zr}}) - (BL_{\text{azo-H}})] / (BL_{\text{azo-H}}) \times 100$ range from 0.259 to 4.426 %. In all three complexes, the bond lengths between the (1O)-(2C) and (7C)-(8C) atoms are shorter than those of their ligands. This can be explained by the fact that zirconium can be bound to the ligands on the above-mentioned atoms. This PM6 calculation finding supports previously studied experimental data where it was thought that the atoms which are indicated (1-O) and (8-O) (the oxygen atoms) in Table-3 were bonded directly to the zirconium atom. It was also observed that (5N)-(6C) bond lengths for the azo-H-Zr and azo-Cl-Zr complexes are shorter than those of their ligands. It was also observed that (4N)-(5N) bond lengths for all the complexes are longer than those of their ligands because of the coordinate covalent bond formation between Zr and (4N)-(5N). (3C)-(4N) bond lengths for the azo-H-Zr and azo-Cl-Zr complexes are longer than those of their ligands. It is thought that the reason for this increase of bond lengths in these complexes could be coordinate covalent bond formation with Zr on the 4C atom. The (2C)-(3C) bond lengths for all the complexes are longer than those of their ligands.

The selected angles (BA) range from 113.315° to 127.169°; and from 113.051° to 127.169° in the studied ligands and their complexes, respectively. Differences are observed in the equivalent angles and these differences in the angles ($[(BA_{\text{complexes}} - BA_{\text{ligands}}) / BA_{\text{ligands}}] \times 100$), e.g. $[(BA_{\text{azo-H-Zr}}) - (BA_{\text{azo-H}})] / (BA_{\text{azo-H}}) \times 100$ range from 0.000 to 10.678. During the complexation reaction, no important change was observed on the bond angles except for the azo-NO₂-Zr complex in the (2C)-(3C)-(4N) angle due to the nitro substituent, which is the biggest atom in respect of the -H and -Cl substituents. In all the complexes, the bond angles between the (1O)-(2C)-(3C) atoms (Table-3 and Fig. 1) are smaller than those of the

their ligands. It is also observed that the (5N)-(6C)-(7C) bond angles for the azo-H-Zr and azo-NO₂-Zr complexes are smaller than those of their ligands. On the other hand, the bond angles between (2C)-(3C)-(4N) and (6C)-(7C)-(8O) for the azo-H-Zr and azo-NO₂-Zr complexes are greater than those of their ligands.

All the selected atomic charges (AC) range from 0.117 to 0.480 for all three ligands and from 0.031 to 0.505 for the complexes. Differences between the complexes and the ligands are observed in the equivalent atomic charges and these differences in the distances ($[(AC_{\text{complexes}} - AC_{\text{ligands}}) / AC_{\text{ligands}}] \times 100$), e.g. $[(AC_{\text{azo-H-Zr}}) - (AC_{\text{azo-H}})] / (AC_{\text{azo-H}}) \times 100$ range from 1.375 to 61.016 %. The smallest deviation was observed on 1O atom for the azo-NO₂-Zr complex. The greatest deviation was observed on the 4N atom for the azo-H-Zr complex. The atomic charges on (4N) atoms in all three complexes are smaller than those of their ligands. On the other hand, the atomic charges on the (1O) and (8O) atoms of the three complexes are greater than those of their ligands.

The dihedral angles (DA) range from 0.105 to 179.987 for all three ligands and from 0.105 to 177.366 for the complexes. The deviations from their ligands ($[(DA_{\text{complexes}} - DA_{\text{ligands}}) / DA_{\text{ligands}}] \times 100$), e.g. $[(DA_{\text{azo-H-Zr}}) - (DA_{\text{azo-H}})] / (DA_{\text{azo-H}}) \times 100$ were from 0 to 175.

Density functional theory studies: The nucleophilicity (N) and the energies for zirconium, the three ligands and the three complexes using the DFT method were calculated at the (B3LYP) level of theory using the LanL2dz basis sets to investigate any possible correlation.

Gibbs free energy [ΔG , $\delta\Delta G_{(R)}$]: The electronic energy (E_{elec}), zero point energy (E_{ZPE}), thermal energy (E_{thermal}), total energy ($E_{\text{total}} = E_{\text{elec}} + E_{\text{ZPE}} + E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}}$), electronic and thermal Gibbs free energy ($G_{\text{elec+thermal}}$) and nucleophilities (N) of the azobenzene ligands and zirconium complexes are given in Table-4. The stabilities of these azobenzene molecules depend on their Gibbs free energies (ΔG) by DFT in the aqueous phase in the following order:

azo-NO₂ > azo-Cl > azo-H (Table-3). This order is the same as those achieved by PM6. For the tetrahydroxyazo-zirconium complexes, the order of stability by DFT is azo-NO₂-Zr > azo-Cl-Zr > azo-H-Zr. The best reactive structure is azo-H-Zr among the complexes. A parallelism can be observed between the order of stability for the complexes achieved by both the PM6 and the DFT methods.

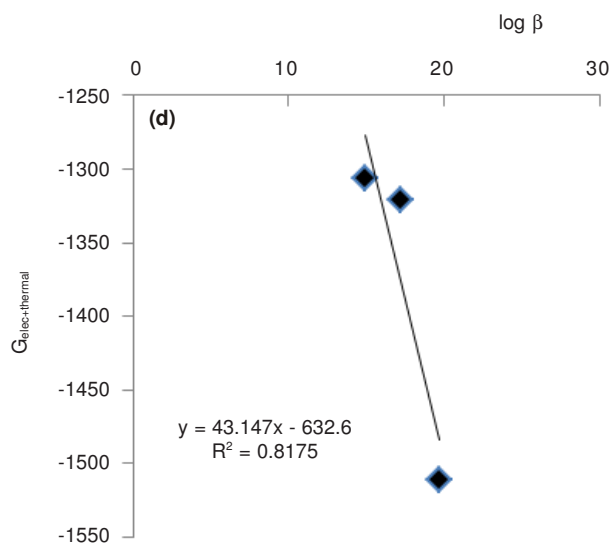
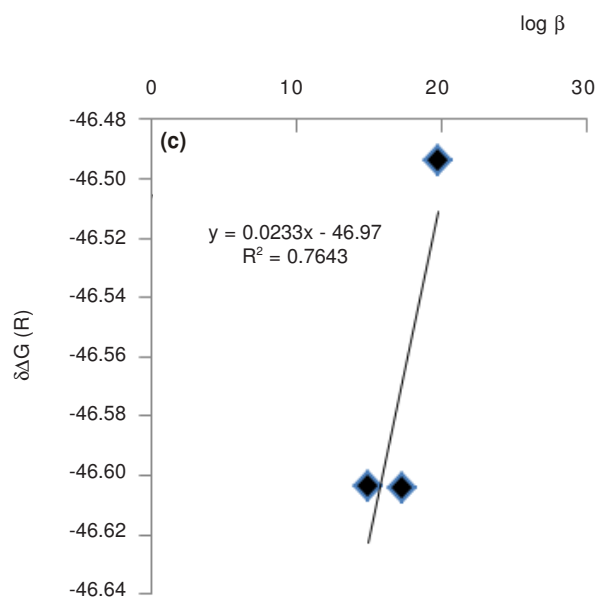
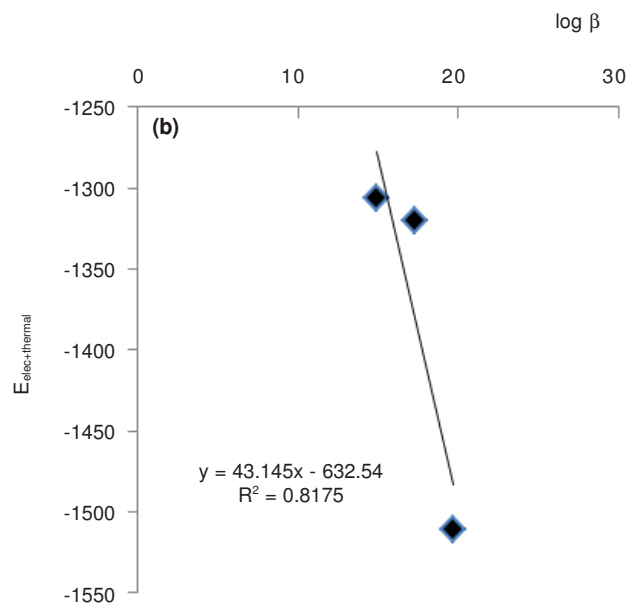
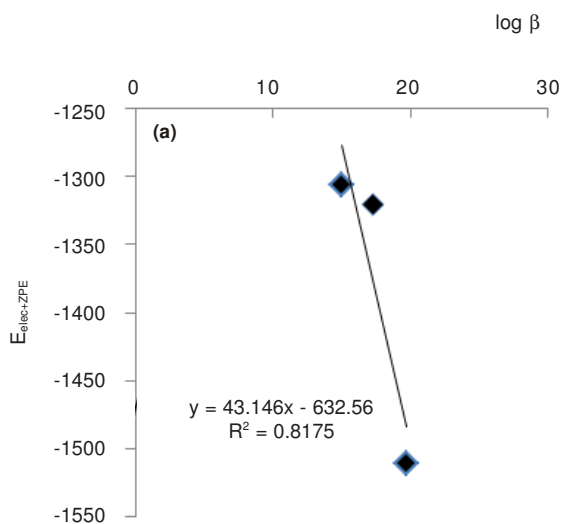
Calculated values for the Gibbs free energy of the complexation reactions [$\delta\Delta G_{(R)}$] by DFT in water are reported in Table-5. The $\delta\Delta G_{(R)}$ values of the three complexes are negative meaning that these complexation reactions are favoured. The negative $\delta\Delta G_{(R)}$ values and the experimental complex formation constants $\log \beta$ for the formation reactions of the ML complexes confirm that the ML complexation reactions are spontaneous. The $\delta\Delta G_{(R)}$ values of the azo-H-Zr and azo-Cl-Zr are close to each other. The $\delta\Delta G_{(R)}$ value for the azo-NO₂-Zr complex is slightly higher than these two values.

TABLE-5
CALCULATED THERMODYNAMIC PARAMETERS BY THE DFT AND OBTAINED FROM PREVIOUS STUDIES FOR THE COMPLEXATION REACTIONS

M + L → ML		
Complex	$\delta\Delta G_{(R)}$ ^a	Exp. $\log \beta$ ^b
azo-H-Zr	-46.60390	14.94
azo-Cl-Zr	-46.60423	17.25
azo-NO ₂ -Zr	-46.49376	19.72

^a ΔG (products) - ΔG (reactants); ^bThe logarithm of the experimental complex formation constants of zirconium and the studied tetrahydroxyazo ligands¹⁴

The $\delta\Delta G_{(R)}$, the energies ($E_{\text{elec+ZPE}}$, $E_{\text{elec+thermal}}$), enthalpy ($H_{\text{elec+thermal}}$), Gibbs free energy ($G_{\text{elec+thermal}}$), thermal total energy (E_{total}) (Table-4) values of the three ML complexes are given comparatively with those of the experimental complex formation constants ($\log \beta$) in Fig. 5. The three energies, the total of electronic and zero point energy ($E_{\text{elec+ZPE}}$), the total of electronic and thermal energy ($E_{\text{elec+thermal}}$) and the total of electronic and thermal Gibbs free energy ($G_{\text{elec+thermal}}$) have the same good correlation with $R^2 = 0.8175$. On the other hand, the total energy (E_{total}) has the smallest correlation with $R^2 = 0.0238$.



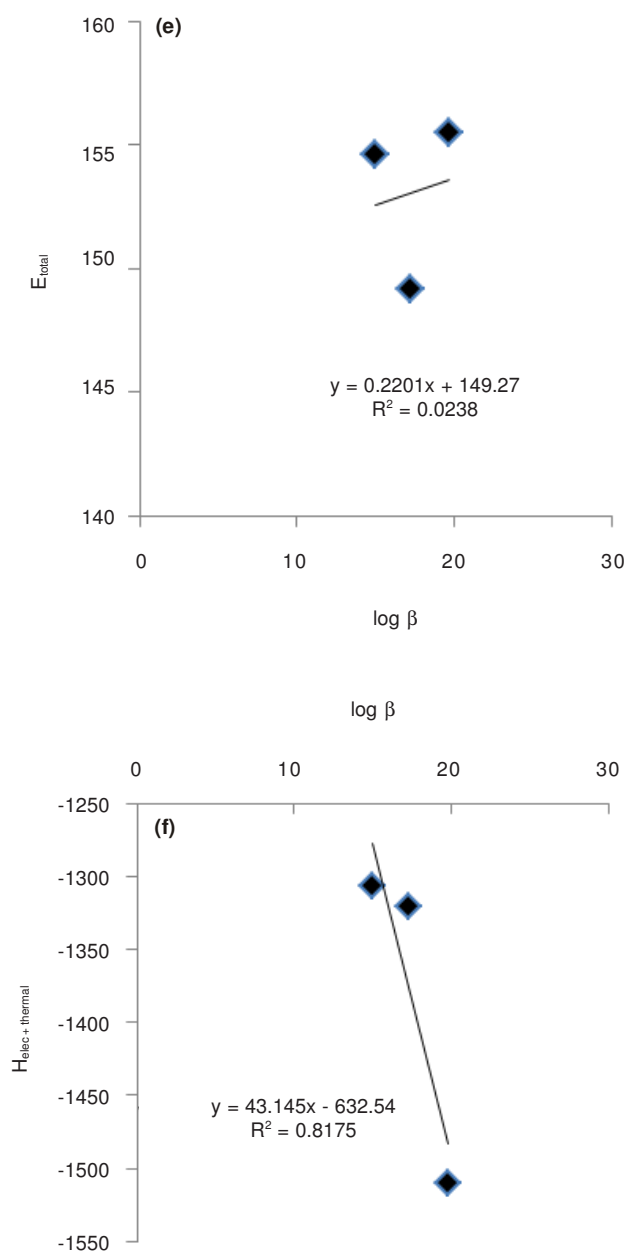


Fig. 5. The graphs complex formation constants ($\log \beta$) versus a) the electronic and zero-point energy ($E_{\text{elec+ZPE}}$), b) electronic and thermal energy ($E_{\text{elec+thermal}}$), c) Gibbs free energy [$\delta\Delta G_{(R)}$], d) the total of electronic and thermal Gibbs free energy ($G_{\text{elec+thermal}}$), e) total energy ($E_{\text{total}}: E_{\text{elec}} + E_{\text{ZPE}} + E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}}$), f) the total of electronic and thermal enthalpy ($H_{\text{elec+thermal}}$) (indicated in Tables 4 and 5) values of the studied ML complexes by DFT

Nucleophilicity: When the nucleophilicities (N) of the molecules with DFT are investigated, the N value order is given for both ligands and their zirconium(IV) complex structures in the following order: azo-NO₂ > azo-Cl > azo-H and azo-Cl-Zr > azo-NO₂-Zr > azo-H-Zr (Table-4). The same order for the three ligands could not be observed between the complex formation constants ($\log \beta$) and the nucleophilicities (N) of the molecules obtained by the PM6 method and those with the DFT are investigated. There is a parallelism for azo-Cl-Zr, azo-NO₂-Zr and azo-H-Zr molecules between the complex formation constants ($\log \beta$) and the nucleophilicities (N) of these complexes obtained by PM6 and those with DFT are

investigated. However, a meaningful correlation could not be observed between $\log \beta$ and N values for the complexes (Fig. 6).

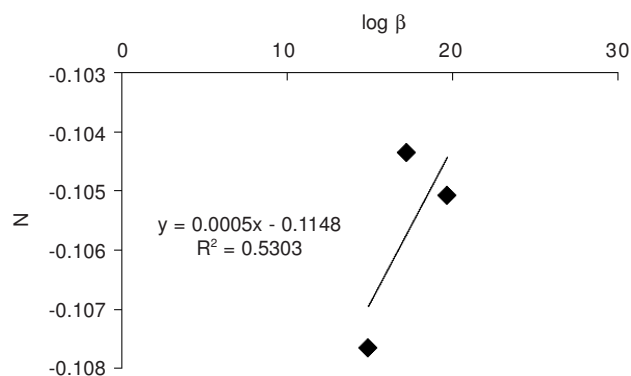


Fig. 6. Graph complex formation constants ($\log \beta$) versus nucleophilicity (N) values of the studied ML complexes by DFT

Dipole moment: The dipole moment (D) value order is given in the following order: azo-H-Zr > azo-Cl-Zr > azo-NO₂-Zr and azo-H > azo-Cl > azo-NO₂. When (dipole-moment) of the molecules was investigated, a correlation was observed between the molecule structures (dipole moments) and the reactivities for the three tetrahydroxyazon ligands. The order of dipole-moment values is the same as those by PM6 for the three ligands. No significant correlation could be observed between the complex molecule structures and the reactivities for all of the studied molecules (Table-4). The order of dipole-moment values by the DFT method is not the same as those values calculated by the PM6 method. It is thought that the dipole moment does not give any important information from the viewpoint of the reactivity for these complexes in the present study. The correlation between the dipole moments and the complex formation constants is given in Fig. 7.

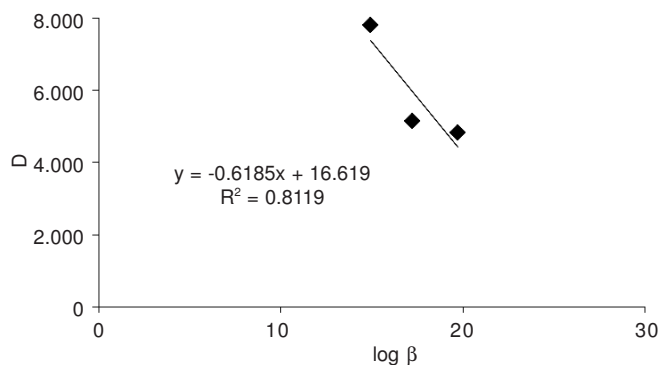


Fig. 7. Graph complex formation constants ($\log \beta$) versus dipole moment (D) values of the studied ML complexes by DFT

Molecular structure of the ligands and the zirconium complexes [Atomic charges, bond lengths and angles and dihedral angles] by DFT: The selected geometrical parameters calculated with DFT at the (B3LYP) level of theory using LanL2dz basis geometry for the studied ligands and their zirconium complexes are summarized in Table-6 to investigate the changes during complexation reactions. As seen in Table-6, all the selected bond lengths in all three ligands range from 1.291 to 1.442 Å. The bond lengths range from 1.299 to 1.437 Å for the three complexes. The ranges for both ligands and

TABLE-6
SELECTED ATOMIC CHARGES, BOND LENGTHS AND ANGLES AND DIHEDRAL ANGLES
OBTAINED FROM QUANTUM CHEMICAL CALCULATIONS BY THE DFT

Bond angles a, (°)	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O-2C-3C	120.690	121.002	120.790	120.163	0.436	120.602	0.330	120.244	0.452
2C-3C-4C	111.221	111.614	111.298	113.405	1.964	113.687	1.858	113.620	2.086
3C-4C-5C	118.620	118.554	118.758	115.925	2.272	116.348	1.861	115.906	2.402
4N-5N-6C	117.293	116.830	116.816	121.173	3.308	120.403	3.058	121.034	3.610
5N-6C-7C	127.591	127.439	127.721	126.004	1.244	126.335	0.866	126.065	1.297
6C-7C-8O	120.561	120.015	120.520	123.377	2.336	123.663	3.040	123.339	2.339
Bond lengths d, (Å)	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O-2C	1.386	1.384	1.3848	1.366	1.440	1.366	1.342	1.365	1.452
2C-3C	1.421	1.422	1.422	1.419	0.178	1.422	0.046	1.420	0.122
3C-4N	1.403	1.399	1.400	1.417	1.014	1.412	0.949	1.415	1.038
4N-5N	1.291	1.292	1.291	1.300	0.713	1.299	0.591	1.301	0.717
5N-6C	1.423	1.423	1.423	1.404	1.366	1.407	1.157	1.404	1.375
6C-7C	1.438	1.442	1.439	1.437	11.293	1.439	0.238	1.436	0.161
7C-8O	1.371	1.358	1.369	1.334	2.677	1.326	2.402	1.332	2.760
Atomic charges	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O	-0.0798	-0.075	-0.076	-0.608	-	-0.333	-	-0.373	-
4N	-0.1173	-0.107	-0.112	-0.285	-	0.012	-	-0.284	-
5N	-0.1361	-0.136	-0.138	-0.089	-	-0.096	-	-0.09	-
8O	-0.032	-0.059	-0.023	-0.581	-	-0.561	-	-0.571	-
Dihedral angles	azo-H	azo-NO ₂	azo-Cl	azo-H-Zr	(a) %	azo-NO ₂ -Zr	(b) %	azo-Cl-Zr	(c) %
1O-2C-3C-4C	0.207	0.793	0.482	0.622	200.710	0.258	67.447	0.662	37.436
2C-3C-4N-5N	179.272	178.458	179.254	175.886	1.889	176.657	1.009	176.046	1.790
3C-4N-5N-6C	179.956	179.870	179.955	178.014	1.079	176.772	1.722	176.952	1.669
4N-5N-6C-7C	2.349	11.072	5.410	2.241	4.608	4.176	62.288	3.872	28.441
5N-6C-7C-8O	0.769	2.111	1.026	0.880	14.460	1.790	15.171	0.599	41.559

the complexes by DFT are similar to those by PM6. These deviations in the distances as % $\left(\frac{[(BL_{\text{complexes}} - BL_{\text{ligands}})/BL_{\text{ligands}}] \times 100}{[(BL_{\text{azo-H-Zr}}) - (BL_{\text{azo-H}})] / (BL_{\text{azo-H}})} \times 100\right)$ range from 0.046 to 11.293. In all the complexes, the four bond lengths between (1O)-(2C), (2C)-(3C), (5C)-(6C) and (7C)-(8C) atoms (Table-6 and Fig. 1) are shorter than those of their ligands. The same trend for the two bond lengths, (1O)-(2C) and (7C)-(8C), in all the complexes was observed by PM6 (Table-3). These findings achieved by both PM6 and DFT support our previous studied experimental data where it was thought that the atoms which are indicated (1O) and (8O) (the oxygen atoms) (Fig. 1) were bonded directly to the zirconium atom in the proposed complex structure. The (3C)-(4N) and (4N)-(5N) bond lengths for all the complexes are longer than those of their ligands, show parallelism with the PM6 data because of coordinate covalent bond formation between Zr and (4N) - (5N).

There is almost the same angle range from 111.221 to 127.721° and 113.405 to 126.335° in the studied ligands and their complexes, respectively, was observed with respect to those by PM6. The deviation, $\left(\frac{[(BA_{\text{complexes}} - BA_{\text{ligands}}) / BA_{\text{ligands}}] \times 100}{[(BA_{\text{azo-H-Zr}}) - (BA_{\text{azo-H}})] / (BA_{\text{azo-H}})} \times 100\right)$, ranges from 0.330 to 3.610. These deviations are smaller than those by PM6 (0.000 to 10.678). The greatest deviation of 3.610 was observed for (4N)-(5N)-(6C) in the azo-Cl-Zr complex. In all the complexes, the bond angles between (1O)-(2C)-(3C), (3C)-(4N)-(5N), (5N)-(6C)-(7C) atoms (Table-6) are smaller than those of their ligands. The same trend was observed just for the (1O)-(2C)-(3C) bond angles in the whole complexes by PM6. On the other hand, the bond angles between (2C)-(3C)-(4C) and (4N)-(5N)-(6C) in the three complexes are greater than those of their corresponding ligands. The same

trend has been observed for (2C)-(3C)-(4N) in the azo-H-Zr and azo-NO₂-Zr complexes by PM6. During the complexation reaction, deviations (not shown in Table-6) on all the atomic charges (AC), between the ligands and their complexes, were greater than predicted by DFT. No parallelism for those atomic charges between by DFT and PM6 calculations could be observed. The DFT method is less successful than the PM6 from the viewpoint of atomic charges in explaining the complex structures.

The dihedral angles (DA) range from 0.207 to 179.955 for all three ligands and from 0.258 to 178.014 for the complexes. The deviations from their ligands $\left(\frac{[(DA_{\text{complexes}} - DA_{\text{ligands}}) / DA_{\text{ligands}}] \times 100}{[(DA_{\text{azo-H-Zr}}) - (DA_{\text{azo-H}})] / (DA_{\text{azo-H}})} \times 100\right)$ were from 1.1 to 200.

Conclusion

Certain theoretical properties of the three tetrahydroazo derivatives and their zirconium complexes have been calculated by MOPAC2009 using the PM6 method and GAUSSIAN 09 programs at the basis set LanL2DZ.

The negative relative stabilities of all the studied ML complexes show that the complexation reactions were exothermic. The same order of stability for the complexes was achieved: azo-NO₂-Zr > azo-Cl-Zr > azo-H-Zr by both the PM6 and the DFT methods regarding Gibbs free energy. It is found that all the complexation reactions are favoured by both PM6 and DFT. This result is consistent with the very high experimental complex formation constants (log β) for the formation reactions of the ML complexes. There is a parallelism for the three ligands between the complex formation constants (log β) and the nucleophilicities (N) of these complexes by the PM6 and DFT methods. A meaningful correlation could not be observed between the log β and N values for the complexes

by the two methods. The bond lengths between (1O)-(2C) and (7C)-(8C) atoms in all three complexes are shorter than those of their ligands and can be explained by the fact that zirconium can be bound to the ligands on the mentioned atoms by both the PM6 and DFT methods. This means that these findings are in agreement with our previous experimental data where it was thought that the (1O) and (8O) atoms were bonded directly to the zirconium atom. The increase on (4N)-(5N) bond lengths for all the complexes by both the PM6 and DFT methods compared to their ligands explains the coordinate covalent bond formation between Zr and (4N)-(5N). This result also complies with the previous experimental study. The PM6 method gives slightly better results than those using the DFT method. No parallelism for those atomic charge between by the DFT and the PM6 calculations could be observed.

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