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Topologic and spectroscopic approach of tricarbonylchromium complexes

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ABSTRACT

This papers presents a computational analysis on heptalene tri carbonyl chromium complexes containing two ligands R=H (Complex 1) and R=Me (Complex 2) in diethylether solution, using density functional theory DFT at PBE / TZP level.Frontier molecular orbitals of these compounds have been analyzed. The effect of the ligand on reactivity reveals that the reaction mechanism pathway of η^6, η^6 inter-ring haptotropic isomerization is difficult in complex 2 (Ea=72.6 Kcal.mol^{-1}) than in complex 1 (Ea=52.2Kcal.mol^{-1}). TDDFT calculations predict that the bathochromic effect of the HOMO-LUMO transition decrease when passing from the unsubstituted complex to the substituted complex.

KEY WORDS: Computational analysis, Heptalene, TD DFT, DFT, Reactivity, Haptotropic isomerization.

1. INTRODUCTION

Inter-ring haptotropic rearrangement (IRHR) is a migration of organometallic group from one of the aromatic ring to the other inπ-systems. At present, many examples of IRHR are known, such as in (naphthalene, biphenyl, biphenylene, dibenzothiophene, anthracene, phenanthrene and fluoranthrene) - tricarbonylchromium complexes and in some other $Cr(CO)_3$ complexes with polyaromatic ligands including such complex systems as coronene and nanotubes.

In 1961, Dauben and Bertelli have synthetized the bicyclid non-benzenoid hydrocarbon heptalene. The chemistry of heptalenes which are nonplanar 12π-electrons systems with localized double bonds has been studied in details. 8π- and 12π-annulenes, heptalene readily undergoes band isomerization, the kinetics of with has been studied for a series of substituted compounds.

Our aim in this work is to study and compare the structure (distances, angles and frontier molecular orbitals) of tricarbonylchromium complexes of heptalene ligand synthetized by Vogel in 1974, using the density functional theory calculation (DFT), after that we determinate the influence of the substituent on reactivity and optical properties. This study is observed in diethylether solvent.

2. MATERIALS AND METHODS

DFT calculations have been carried out with the Amsterdam Density Functional ADF program developed by Baerends (1973). Electron correlation was treated within general gradient approximation (GGA), scalar relativistic effects were considered at the level of Zero Order Regular Approximation (ZORA) with a TZP and the basis set superposition error (BSSE). The geometry optimization of the two complexes, are performed using PBE functional.

The geometrical structure of the singlet ground state and the lowest lying triplet excited state are optimized by the DFT method with time-dependent functional theory approach TDDFT/SOAP model. Solvent is treated using Conductor like Screening Model (COSMO).

3. RESULTS AND DISCUSSION

Geometrical optimization: Two models structure of heptalene tri carbonyl chromium complexes (Figure 1) containing two ligands R=H (Complex 1) and R=Me (Complex 2). η^6-structure corresponds to the 18-electrons. Geometries of these complexes are described by DFT method and with constraint of symmetry, optimized structure are given in Figure 1.

The important optimized geometry parameters are presented in Table 1. Analysis of bond orders predicts that these complexes are totally symmetric in η^6-coordinated molecules. In Table 1, we can see an increase in the Cr-C_2 and Cr-C_5 bond lengths by 0.022 Å and 0.026Å respectively, and a decrease in the Cr-C_3 and Cr-C_4 bond lengths by 0.022 Å and 0.011Å respectively passing from the un substituted complex to the substituted complex. We can see also that the angles C_1-Cr-$C_2$and Cr-C_8-O_{12} are larger in the complex 1 than in the complex 2. A large increase ofC_8-Cr-C_9 angle bond can be seen easily when going from the complex 1 to the complex 2.

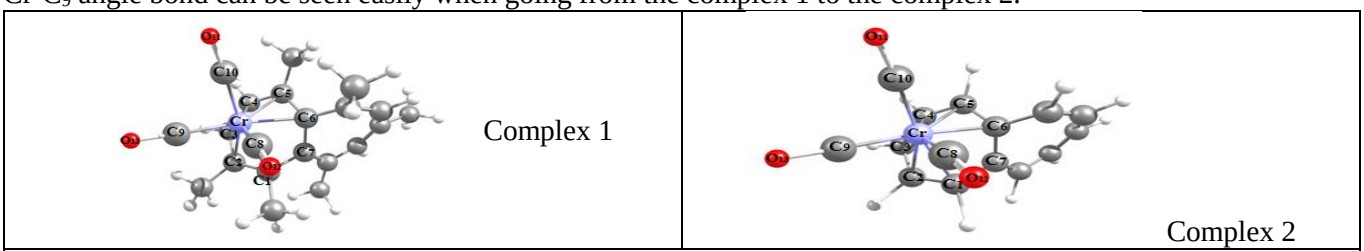

Figure.1.Optimized geometrical structures of tricarbonyl chromium complexes of heptalene ligand with R=H (Complex 1) and R=Me (Complex 2)

Table.1. Selected DFT optimized distances (Å) and angles (º)

		Complex 1	Complex 2
Bond Distances (Å)	$Cr-C_1$	2.220	2.220
	$Cr-C_2$	2.208	2.230
	$Cr-C_3$	2.264	2.242
	$Cr-C_4$	2.257	2.246
	$Cr-C_5$	2.204	2.230
	$Cr-C_6$	2.220	2.220
	$Cr-C_8$	1.865	1.852
	$Cr-C_9$	1.862	1.854
	$Cr-C_{10}$	1.862	1.863
Angles (º)	C_1-Cr-C_2	72	37
	C_8-Cr-C_9	46	87
	$Cr-C_8-O_{12}$	179	176

Frontier molecular orbitals analysis: The frontier molecular orbitals of these compounds are presented in Figure 2. The HOMO/LUMO gaps are large in the two systems respectively (1.814 eV and 2.305 eV) and predict the stability of these complexes. Furthermore, the molecular orbital diagrams indicate that the first complex contributed to the ease oxidation and reduction process with 2-electrons, but the second complex undergo only to the reduction with 2-electrons (Figure 2).

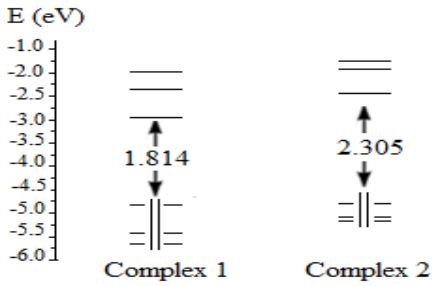

Figure.2. DFT molecular orbital diagrams of the two complexes

Mechanism of η^6, η^6 inter-ring haptotropic rearrangement: In this section, we examined the reaction of η^6, η^6 inter-ring haptotropic isomerization proposed by Ustynyuk (1994) in η^6-tricarbonylchromium complexes of heptalene (Figure 3). This reaction is observed in diethylether solvent.

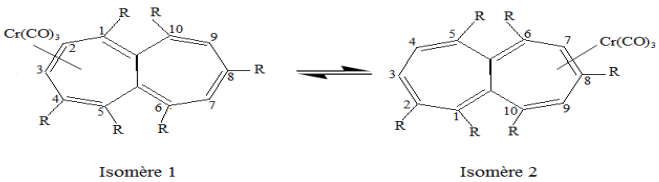

Figure.3. Haptotropic migration of $Cr(CO)_3$ group in heptalene ligand with R=H (Complex 1) and R=Me (Complex 2)

Mechanism in complex 1: The energetic profile of η^6, η^6inter-ringhaptotropic migration of $Cr(CO)_3$ fragment in un substituted complex is presented in Figure 4. The energetic barrier of this IRHR is 52.2 $Kcal.mol^{-1}$with a transition state (TS) in anη^3-coordination mode. On the other hand, we can see that the heptalene slippage taken place in this reaction pathway, when going from the non-coordinated heptalene to the coordinated heptalene, as we see on the dihedral angle (Figure 5) it decrease from 180º to 17º and to -62º passing from the non-coordinated heptalene to the reactant and to the TS respectively, and increase when going from the TS (-62º) to the product (-33º).

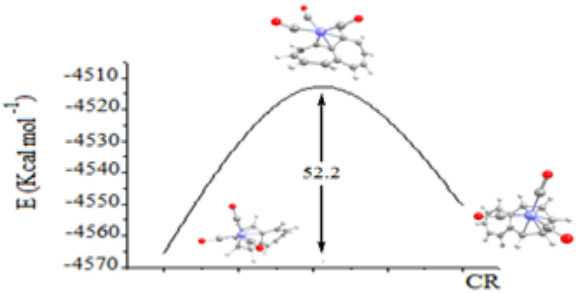

Figure.4. Energy profile of the haptotropic migration in complex 1

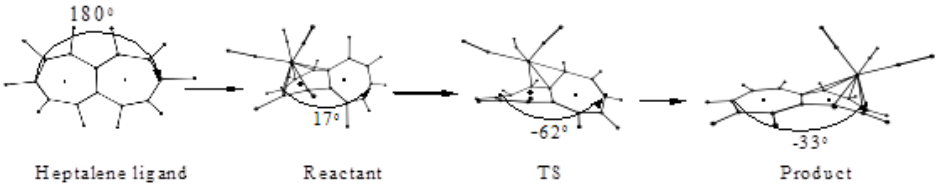

Figure.5. Dihedral angle of heptalene ligand in the mechanism 1

Mechanism in complex 2: In the substituted complex, the heptalene ligand undergoes η^6, η^6IRHR with a large activation barrier (72.6Kcal.mol^{-1}) compared to the un substituted complex (Figure 6). We found TS in a η^3-coordination fashion.

The presence of hexamethylheptalene ligand leads to the large difference in the planarity of all compounds of the reaction mechanism (reactant, TS and product). In this search, we can see a large decrease in the dihedral angle of the hexamethylheptalene ligand in the passage: non-coordinated heptalene (180º) →reactant (23º) → TS (-5º) → product (-24º) (Figure 7).

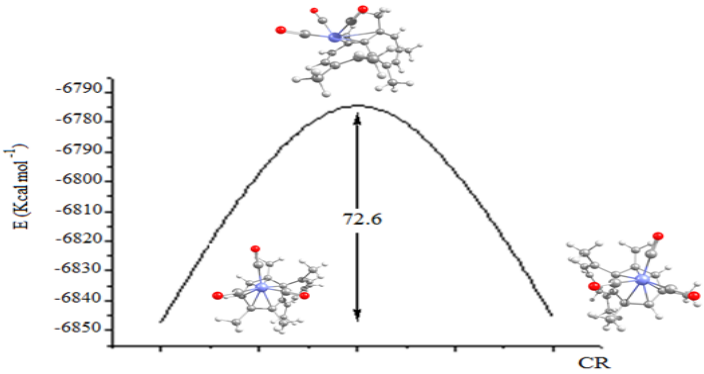

Figure.6. Energy profile of the haptotropic migration in complex 2

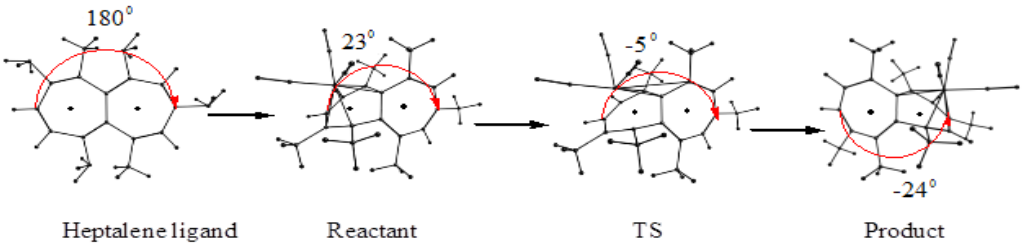

Figure.7. Dihedral angle of heptalene ligand in the mechanism 2

Acidity strength: The values of chemical descriptors [33-35] are display in Table 2. The complex 2 present a higher capacity to donate electrons than the first complex causes bythe higher HOMO energy.

Results of electrophilicity indicate that the complex 1 present a higher capacity to attract electrons.

Table.2. Overall reactivity descriptors (eV)

Complex	μ	η	ω	HOMO	LUMO
Complex 1	-3.841	0.907	8.132	-4.748	-2.934
Complex 2	-3.589	1.152	5.590	-4.742	-2.437

Optical properties: The absorption spectra of these compounds in the Et_2O solution are determinate by the TDDFT calculations. It is interesting to note that all the absorption peaks of the two complexes are observed in ultraviolet-visible regions between 200-500 nm. In complex 1, the strong absorption bond observed at 200-335 nm (Figure 9). It is dominated in the ultraviolet region and it's mixed between ligand-to-metal (LMCT), metal-to-ligand (MLCT) charge-transfer and intra charge transfer (ICT) configurations (Table 3). For the second complex, the strong absorption peak appear in the region 215-259 nm with contribution to the LMCT transition.

Our calculation predict that the main difference between these complexes appear in the absorption peak of the HOMO-LUMO transition, at 614 nm with 98% in complex 1 and at 503 nm with 97% in complex 2 (see Table 3 and Figure 8). This observation indicates that the bathochromic effect of the HOMO-LUMO transition decrease when the substitute is changed (in the passage: un substituted complex →substituted complex).

Table.3. Absorption bonds in the UV-visible region of the tow complexes in diethylether solvent

Complex	Transition	E(eV)/(nm)	Oscillator (f)	Character
Complex 1	(15%) HOMO-4→LUMO+4	5.71/217	0.047	LMCT
	(17%) HOMO-4→LUMO+1	4.84/256	0.050	ICT
	(35%) HOMO-4→LUMO	4.31/288	0.113	LMCT
	(27%) HOMO→LUMO+7	4.02/308	0.175	MLCT
	(32%) HOMO-2→LUMO+1	3.26/380	0.087	MLCT
	(94%) HOMO→LUMO+2	3.04/407	0.016	LMCT
	(73%) HOMO-2→LUMO	2.74/452	0.048	MLCT
	(98%) HOMO→LUMO	2.02/614	0.002	LMCT
Complex 2	(25%) HOMO-4→LUMO+5	4.70/233	0.018	LMCT
	(36%) HOMO-6→LUMO	4.60/269	0.114	ICT
	(26%) HOMO-3→LUMO+2	3.95/313	0.072	ICT
	(43%) HOMO-3→LUMO+1	3.75/330	0.060	MLCT
	(24%) HOMO-2→LUMO+1	3.48/356	0.052	MLCT
	(53%) HOMO-1→LUMO+1	3.31/375	0.038	MLCT
	(96%) HOMO-2→LUMO	2.88/430	0.007	MLCT
	(94%) HOMO-1→LUMO	2.80/443	0.008	MLCT
	(97%) HOMO→LUMO	2.46/503	0.010	LMCT

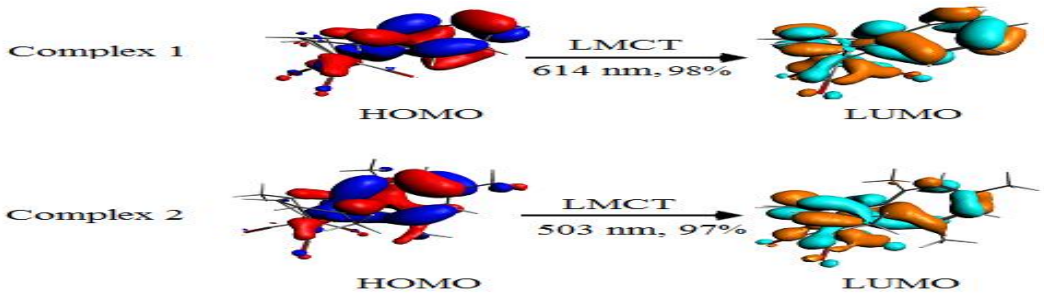

Figure.8. HOMO-LUMO transition in the two complexes according to TDDFT calculations in Et_2O solvent.

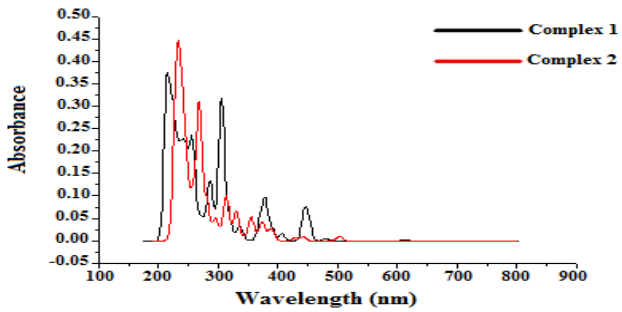

Figure.9.UV/vis absorption spectra of complex 1 and 2 in diethylether solution

4. CONCLUSION

The computational analysis of the geometric parameters using DFT calculations predicts that these complexes are found in anη^6-coordination mode.

Results obtained by DFT study shows a quiet and a large difference between the dihedral angles of the heptalene ligand in all compounds of the reaction mechanisms pathway. These results have significant effect on the reaction mechanisms pathway of the two complexes, when the activation barriers are very large (Ea=52.2 Kcal.mol^{-1} for the first complex and Ea=72.6 Kcal.mol^{-1} for the second complex).

Concerning the UV-Vis absorption obtained by TDDFT calculations, we have note that the bathochromic effect of the HOMO-LUMO transition decrease when going from the un substituted complex to the substituted complex.

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REFERENCES

Albright TA, Hoffmann P, Hoffmann R, Lillya OP, and Dobosh PA, Haptotropic rearrangements of polyene-ML_n complexes, II. Bicyclic polyene- MCp, -$M(CO)_3$ systems, J. Am. Chem. Soc., 105, 1983, 3396-3411.

Baerends EJ, Ellis DE, Ros P, Self-consistent molecular Hartree-Fock-Slater calculations I, The computational procedure**,** Chem. Phys, 2, 1973, 41-51.

Bauernschmitt R, Ahlrichs R, Stability analysis for solutions of the closed shell Kohn-Sham equation, J. Chem. Phys, 104, 1996, 9047-9052.

Bernhard W, Brugger P, Daly JJ, Englert G, Schonholzer P, Hansen H.J, σ-skeletal-rearrangement of heptalenes: thermal transformation of heptalene-1,2-dicarboxylates into heptalene-1,3-dicarboxylates, Helv. Chim. Acta, 68, 1985, 1010-1024.

Casida ME, In Recent Advances in Density Functional Methods, Chong, D P Ed, World Scientific, Singapore, 1995, 155-193.

Dauben HJ, Bertelli DJ, Heptalene. J. Am. Chem. Soc, 83, 1961, 4659-4660.

Geerlings P, De Proft F, Langenaeker W, Conceptual Density Functional Theory, Chem. Rev, 103, 2003, 1793-1874.

Gottarelli G, Hansen HJ, Spada GP, Weber RH, A liquid-crystal study of heptalene, Helv. Chim. Acta, 70, 1987, 430-435.

Gross EKU, Kohn W, Time-Dependent density functional theory, AdV. Quantum Chem, 21, 1990, 255-291.

Gross EUK, Dobson JF, Petersilka M, Density Functional Theory, In Springer Series, Topics in Current Chemistry, Nalewajski, R F Ed, Springer, Heidelberg, 1996.

Hafner K, Hock N, Knaup Gk, Meinhardt KP, Synthesis of di- tetra- and penta-methyl-heptalenes, Tetrahedron Lett., 27, 1986, 1669-1672.

Hafner K, Knaup GL, Lindner HJ, Floter HC, Synthese und dynamische Eigenschaften chiraler heptalene, Angew. Chem. Int. EEl. Engl, 24, 1985, 212-214.

Hafner K, Knaup GL, Lindner HJ, Syntheses and Dynamic Behavior of Chiral Heptalenes, Bull. Chem. Soc. Jpn, 61, 1988, 155-163.

Hafner K, Knaup GL, Synthesis and dynamic properties of 1, 2, 5, 6, 8, 10-hexamethyl-heptalene, Tetrahedron Lett., 27, 1986, 1665-1668.

Joistgen O, Pfletschinger A, Ciupka J, Dolg M, Nieger M, Schnakenburg G, Frohlich R, Kataeva O, Dotz KH, P-coligand tuning of the haptotropic metal migration in phenanthrene chromium complexes, Organometallics, 28, 2009, 3473-3484.

Klamt A, Schüürmann G, COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. Perkin Trans., J. Chem. Soc., 2, 1993, 799-805.

Li J, Li H, Liang X, Zhang S, Zhao T, Xia D, Wu Z, First principles study on the diffusion of alkali-metal ions on the armchair single-wall nanotubes, J. Phys. Chem, A. 113, 2009, 791-6.

Lindner HJ, Kitshke B, Cyclo additions reaktionen des pentalens und azulens, eineeinfache heptalen-synthese, Angew. Chem. Int. Ed. Engl, 15, 1976, 104-106.

Oprunenko YF, DSc Thesis (Chem.), M.V. Lomonosov Moscow State Univ., Moscow, 1999.

Oprunenko YF, Gloriozov IP, Theoretical DFT studies of chromium tricarbonyl complexes with polycyclic aromatic ligands, J. Organomet. Chem, 694, 2009, 1195-1211.

Oprunenko YuF, Inter-ring haptotropic rearrangements in π-complexes of transition metals with polycyclic aromatic ligands, Usp Khim, 69, 2000, 744-766.

Oth JFM, Mullen K, Konigshofen H, Wassen J, Vogel E, The dianion of heptalene, Helv. Chim. Acta, 57, 1974, 2387-2398.

Parr PG, Pearson RG, Absolute hardness:companion parameter to absolute electronegativity, J. Am. Chem. Soc, 105, 1983, 7512-7516.

Parr RG, Szentpaly L, Liu S, Electrophilicity Index, J. Am. Chem. Soc., 121, 1999, 1922-1924.

Perdew JP, Burke K, Ernzerhof M, Emission in symmetric heavy ion reactions at subthreshold energies, Phys. Rev. Lett, 78, 1997, 1396.

Perdew JP, Burke K, Ernzerhof M, Generalized gradient approximation made simple, Phys. Rev. Lett, 77, 1996, 3865-3868.

Schipper PRT, Gritsenko OV, van Gisbergen SJA, Baerends EJ, Molecular calculations of excitation energies and (hyper) polarizabilities with a statistical average of orbital model exchange-correlation potentials, J. Chemical. Physics, 112, 2000, 1344-1352.

Stegemann J, Lindner HJ, The crystal and molecular structure of dimethyl-3.8-hepalene dicarboxylate, Tetrahedron Lett., 1977, 2515-2616.

Turker L, Gumus S, DFT studies on η^6-coronene-$Cr(CO)_3$ complexes, Acta Chim. Slov, 56, 2009, 246-253.

Ustynyuk YA, Trifonova OI, Yatsenko AV, Borisenko AA, Hansen HJ, Uebelhart P, Synthesis, structure, and rearrangements of new tricarbonylchromium complexes of substituted heptalenes, Russ. Chem. Bull, 43, 1994, 2100-2106.

Verluis L, Ziegler T, The Determination of molecular Structures by density functional theory, The evaluation of analytical energy gradients by numerical integration, J. Chem. Phys, 88, 1988, 322-328.

Vogel E, Kerimis D, Allison NT, Zellerhoff R, Wassen J, Heptalenebis (tricarbonyliron), Angew. Chem. Int. Ed. Engl, 18, 1979, 545-546.

Vogel E, Konsigshofen H, Wassen J, Mullen K, Oth JFM, A heptalene synthesis from 1,6-methano[10]annulene; evidence for a fast π-bond shift, Angew. Chem. Int. Ed. Engl, 13, 1974, 732-734.

Weber RH, Brugger P, Arnold W, Schonholzer P, Hansen HJ, Formation of cyclic `ortho´-anhydrides of heptalene-1,2-dicarboxylic acids, Helv. Chim. Acta, 70, 1987, 1439-1460.

Weber RH, Brugger P, Jenny TA, Hansen HJ, Light-induced, thermal, and acid-catalyzed p-skeletal rearrangements of five-ring-annelated heptalenes, Helv. Chim. Acta, 70, 1987, 742-759.