

Theoretical analysis of the fluxional behaviour of cyclooctatetraene Ru and Ni complexes

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Abstract

Cyclooctatetraene's (COT) behaviour in some of its Ni and Ru complexes is studied by means of DFT methods (B3LYP and BLYP). The experimentally observed COT fragment conformational changes (tub-shaped or planar) are analysed, together with the different locations of metal–carbon bonds in the complexes. These phenomena are studied using both static and molecular dynamics calculations. The results allow us to predict changes in the COT fragment, which goes from aromatic to totally antiaromatic, depending on its environment. This situation favours the electronic flow through the metal atoms into the organometallic molecules, giving place to different geometries that generate the dynamic fluxional behaviour.

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1. Introduction

Cyclooctatetraene is a tub-shaped annulene that has been widely used in organic [1] and organometallic [2] synthesis. As a neutral molecule, it has been described as a hydrocarbon ring displaying Hückel antiaromaticity with eight π -electrons [3]. Upon reduction, a conformational change yields an aromatic and planar Hückel system ($4n+2$) [4]. This reduction process can be achieved by several methods, the electrochemical procedures having been the most widely studied [3]. The free dianionic species, COT^{2-} , has a rather short life-time [5], but it can bind to other moieties forming stable organic and organometallic molecules.

COT and COT^{2-} are two of the most versatile ligands found in organometallic chemistry, exhibiting a number of different coordination modes in monometallic compounds,

such as η^2 , η^4 , η^6 and η^8 [6]. They also show a wide variety of fluxional behaviours, in both their intrinsic conformation as well as in the position they keep in the framework of different molecules [7]. The term *fluxional isomerism* has been defined as the intramolecular time-averaged rearrangement of two or more possible molecular configurations [8]. The neutral COT molecule, its dianion and its radical anion as well as some of their organometallic complexes have been theoretically analysed previously [3,5,9,10]. Particular cases of fluxional isomerism for some of these organic species have been reported [11], but the case of neutral COT has not been studied. In order to reveal the factors affecting the peculiar behaviour of the COT fragment, we performed a theoretical study of the changes undergone by some COT organometallic compounds of Ni and Ru with different fluxional processes.

2. Computational methods

Full geometry optimisation for all Ni complexes were performed within Density Functional Theory (DFT) using

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the B3LYP functional with 6-31G* basis set, as implemented in Jaguar 4.0 [12]. Optimised geometries were verified with frequency calculations. GAUSSIAN98 [13] was used to optimise the molecule with Ru, at B3LYP level, with 6-31G* basis set including LAN2DZP pseudopotential for the Ru atom. Optimised geometries were also verified with frequency calculations. Wave functions and molecular orbital analyses were performed at the HF/6-31G* level in all cases. Molecular dynamics calculations for molecule **2** were performed in a DFT (BLYP) scheme as implemented in the molecular dynamics module included in the NWChem package, version 3.3.1 [14]. NICS (Nucleus Independent Chemical Shifts) is a Schleyer et al. proposition as a new aromaticity index. This index is denoted as absolute magnetic shielding and it is computed at the ring centres, which are determined by the non-weighted mean of the heavy atom coordinates. In this work, NICS calculations were performed following this technique [15] at B3LYP/6-31G** level using GAUSSIAN98. The COT⁻² ring of the molecules under study was submitted to this procedure, but the technique was validated calculating the free COT⁻² ring case obtaining a value of -13.8 very near to the same obtained by Schleyer (-13.9) [15].

3. Results and discussion

The molecules studied are shown in Figs. 1 and 2. They were chosen due to their diverse fluxionality behaviour.

Molecule **1** $\{(Bu_2PC_2H_4PBu_2)Ni\}_2(\mu-C_8H_8)$, exhibits both structural isomerism and fluxional isomerism [16]. In order to reduce the degrees of freedom in the geometry optimisation process, the methyl derivative, $\{(Me_2PC_2H_4PMe_2)Ni\}_2(\mu-C_8H_8)$, was chosen for this study. Fig. 1 shows the three possible conformers for this compound.

The COT fragment in **1a** displays its tub-shape, while it adopts a planar structure in **1b** and **1c**. **1a** is a structural isomer of both **1b** and **1c**, while **1b** and **1c** are fluxional isomers of each other. The bonding of the two nickel atoms is *cis* in **1b** and *trans* in **1c**, where the configuration is defined in terms of the participating electron pairs of the COT fragment.

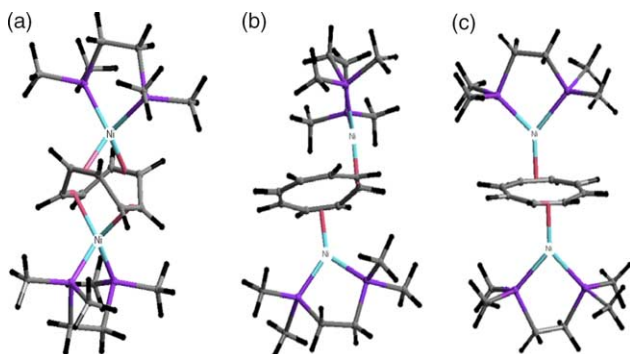


Fig. 1. Structure of the calculated conformers for Molecule 1.

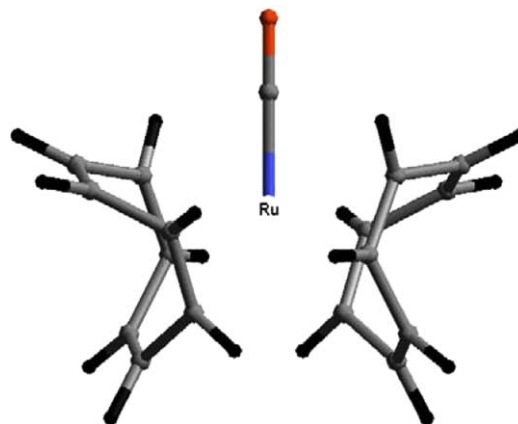


Fig. 2. Molecule 2.

It is important to note that **1a** on one hand and **1b** and **1c** on the other are synthesised using two different reaction pathways, and hence they can be seen as two independent species. Significant differences in energy are obtained for these species and the interest arise to ascertain which structure is energetically favoured.

Molecule **2** $Ru(CO)(1-4-\eta)(C_8H_8)(1,2,5,6-\eta)(C_8H_8)$ is shown in Fig. 2. It is a classical example of a metallocene. However, the COT moieties are distorted in the crystal as shown by X-ray diffraction studies [17]. The authors used NMR techniques to determine the dynamic behaviour of this species in solution. A good fit was obtained between experimental and calculated structural data for this molecule, which validates the method employed.

It is important to note that the COT ring always presents a dynamic behaviour. There is a considerable amount of research that deals with the mobility of this molecule on its own [18], fused to other organic fragments [19], and as a ligand in organometallic compounds [20].

The geometrical structure of COT and COT⁻² has been examined using the Walsh procedure [21,22], in order to analyse the variations of orbital energies when molecular distortions arise in a π framework. The conclusions drawn are that the dianion and the neutral triplet state of COT should be planar, belonging to the D_{4h} point group (the strain from D_{8h} point group is due to a Jahn–Teller mechanism), whereas the closed shell singlet state of COT should be the strongly puckered tub shape belonging to the D_{2d} point group.

The results obtained are discussed in the following two sections, which deal with the Ni and Ru compounds, respectively.

4. Ni compounds

Compounds **1a**, **1b** and **1c** were prepared and characterized by Pörschke and co-workers [16]. Several important features in this paper are worth mentioning. Both classes of compounds (**1a** on the one hand and the set **1b**, **1c** on

the other) are prepared from different reactions and an equilibrium between both sets of structures has not been detected. It seems there is some steric impediment between both conformations due to the presence of the bulky substituents of the diphosphine ligands that can interact with the tub-shaped COT in an interconversion process. The total energy difference between structures **1a** and **1b** obtained in our calculations is 4.3 kcal/mol favouring structure **1a**, i.e. the most stable structural isomer contains the tub-shaped COT ligand. The calculation of an intermediate product between **1a** and **1b**, in which the ring is distorted between the planar and the tub shape structures, was found to be 34.8 kcal/mol higher in energy. This value is an upper limit for the energy barrier between both conformational structures. This conclusion agrees with Pörschke et al. [16], who established structure **1a** as the most stable product of the reaction. Furthermore, the energy difference between **1b** and **1c** is 1.36 kcal/mol favouring **1b**.

Interestingly, the most stable isomer expected, in spite of the aromatisation undergone by the ring, is the one with the tub shape COT fragment. Pörschke proposed an explanation to this unexpected result based on the lack of distortion in

the tub conformation and in the saturation of all C=C bonds with coordinated bonds to the metal centre. Furthermore, in the tub-shaped COT containing isomer, the nickel atom adopts a tetrahedral coordination mode while with the planar COT, it lies in a trigonal plane, an uncommon coordination mode for this metal.

Our results agree with Pörschke's proposal, and adds the finding that the planar ring is not aromatic at all. It is indeed slightly *antiaromatic* and hence there is no additional stabilisation. This argument is supported by the NICS calculations made on the COT rings belonging to **1b** and **1c** that yield NICS values of 1.60 and 1.78, respectively. These values are very far from the -13.9 value obtained by Schleyer for the dianion COT^{2-} [15]. Therefore, the stabilisation obtained for the planar COT fragments is insufficient to alter the order of stability in the complexes. Other feature that can account for the most stable species is the chelate effect since in the tub shape structure the ligand (COT) is joined to both Ni atoms, whereas in the planar shapes there are not chelates.

The molecular orbital diagrams obtained for each structural orientation of the Ni atom are compared in Fig. 3. The tetrahedral species is shown in Fig. 3(a) and

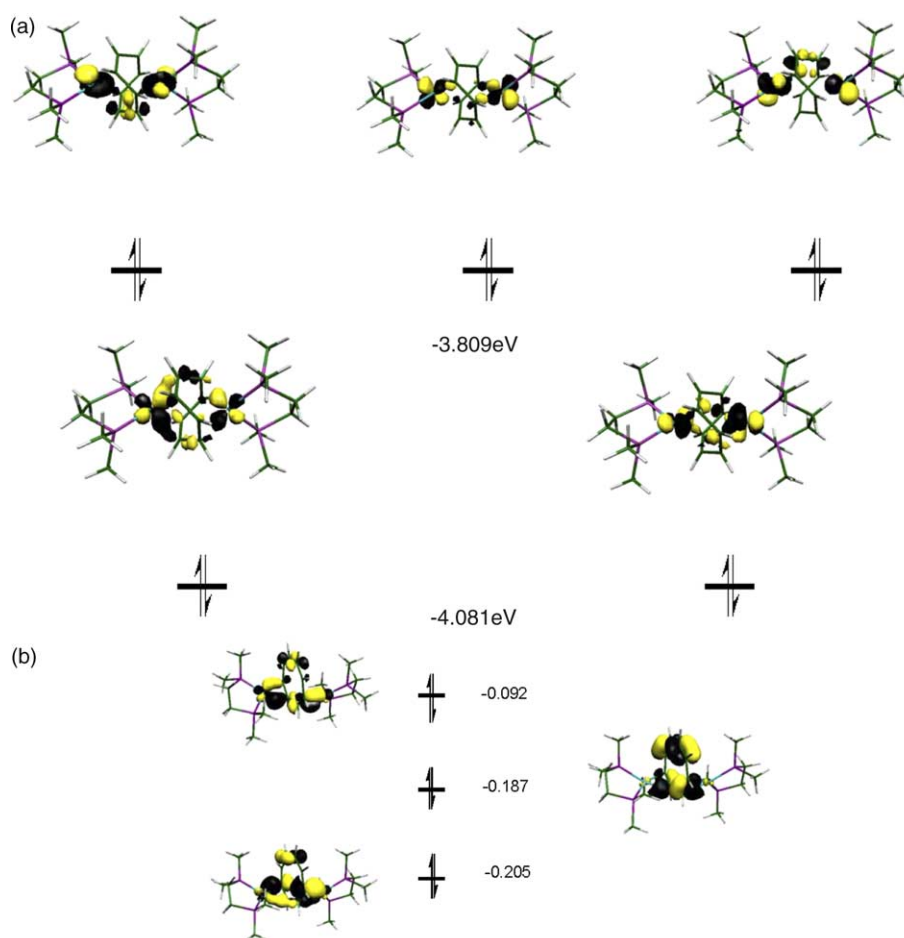


Fig. 3. Molecular orbital splitting of molecules **1** and **1b**, (the HOMO is placed as the upper figure in both cases). (a) Local tetrahedral shape around the Ni atom. (b) Local trigonal shape around the Ni atom.

the trigonal in (b). These structures show significant differences on the ordering and energy of the orbitals.

A simplification was made in this analysis, whereby the point groups for the full molecules were not considered, but only that of the highly symmetrical metal environment. In spite of the known geometries and the respective point groups (14), i.e. distorted D_{2d} for **1a**, C_i for **1b** and C_2 for **1c**, the symmetry groups T_d and D_{3h} corresponding to the metal centre and its bonding atoms were taken into account in order to emphasise the main differences between both orbital arrangements. In the same way, a local symmetry group of D_{8h} was used for the COT fragment. Under these conditions the ordering is as it is described below:

The geometry for the T_d case is slightly distorted, so that the $d_{x^2-y^2}$ and d_{z^2} primitive atomic orbitals are found together in a degenerate set (belonging to the e irreducible representation in T_d point group) and the d_{xy} , d_{xz} and d_{yz} primitive atomic orbitals in another set (t_2 in T_d point group). A good approximation of two degenerate sets was found for this case, one with 3-fold degeneracy and another one with double degeneracy, in good agreement with the expected scheme. The first degenerate set corresponding to the HOMO is conformed by contributions of the d_{xy} , d_{xz} and d_{yz} metallic atomic orbitals (a small energy difference is observed for the d_{xy} eigenvalue attributed to the distortion that compels the ordering to that of the D_{2d} point group). The HOMO-1 is conformed by the combination of d_{z^2} and $d_{x^2-y^2}$ contributions.

A 2-fold degenerate set would be expected for the three-coordinated systems belonging to a D_{3h} symmetry. This corresponds to a combination of the $d_{x^2-y^2}$ and d_{xy} orbitals (e' irreducible representation from D_{3h} point group), followed by a single molecular orbital arising from d_{z^2} contribution (a'_1) and another degenerate set arising from d_{xz} and d_{yz} contributions (e''). The degeneracy in the first set is broken in such a way that the HOMO is made up of a pure $d_{x^2-y^2}$ contribution plus contributions of the COT π orbitals. HOMO-1 is conformed exclusively by the same π set from the COT fragment.

The shape of the HOMO wave function corresponding to molecule **1b** described above (see Fig. 3) is particularly interesting to the present study in that this is the orbital through which the migration of the ligand in the fluxional process is expected to proceed. An important π contribution can be appreciated from the original non-bonding molecular orbitals b_{1u} and b_{2u} of the COT fragment. This function interacts with the metal $d_{x^2-y^2}$ atomic orbital in order to generate the coordinated bond, but there are other free positions on the ring in which the metal can bond. Therefore, a change in bond location is possible, giving rise to the other fluxional isomer.

5. Ru compound

As has been previously suggested [17], the fluxional behaviour of molecule **2** is very complicated. A dynamical

Table 1
Selected interatomic distances (Å) for compound **2**

	This work	X-ray [17]
Ru-C(3)	2.277	2.27(1)
Ru-C(4)	2.258	2.25(1)
Ru-C(12)	2.409	2.42(1)

A comparison with experimental X-ray values is also presented.

method was hence chosen for its study. The dynamical process involves a change in hapticity which can go from bonding mode (1,2,5,6- η) to (1-4- η), as well as COT ring interchange, both inter and intramolecularly.

The optimised molecule is shown in Fig. 2. Frequency calculations show that this structure is a local minimum. It is important to note that this structure presents the COT fragments in an inverted position respect to each other. The structure modelled is in good agreement with that obtained by Bennett and co-workers [17] by X-ray diffraction studies for the PBu_3 derivative (see Table 1). Both COT rings keep a non-symmetrical position with respect to the Ru atom, being almost completely staggered with η^4 hapticity in both cases.

The main calculated bond distances and angles between the Ru atom and the different bonding carbon atoms are in good agreement with crystallographic measurements [17] (see Table 1). For example, there is an angle of 18° between the planes formed by the four bonding carbon atoms on each COT ring in the calculated structure, as compared to the 17° found in the X-ray structure. The average calculated distances between the Ru atom and the bound carbon atoms is 2.26 Å, in good agreement with the experimental value of 2.22 Å. It must be noted that the match cannot be perfect as the calculated molecule is the full geometry optimised analogue of the experimentally described molecule. A perfect match is hence not expected.

With the dynamical NWChem method we can estimate the changes in structure and energy experimented by

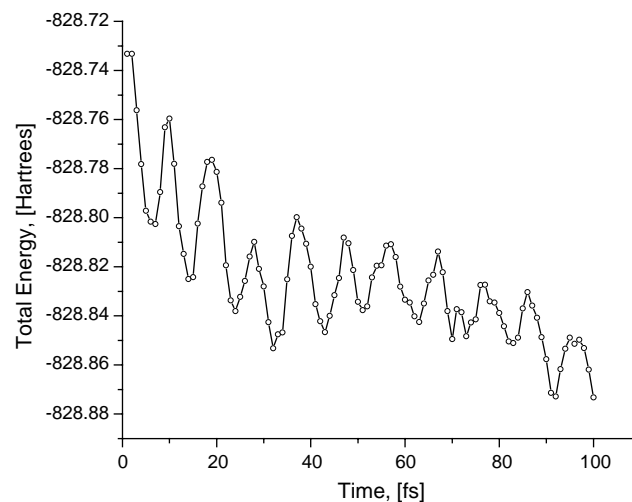


Fig. 4. Total energy vs. time plot for the dynamic fluxional process of molecule **2**.



Fig. 5. Geometrical changes undergone by molecule **2** during the molecular dynamics process; the COT ring tends to adopt the planar shape at the fluxional change.

the molecule in predetermined conditions (300 K) as a function of time. Fig. 4 shows the energy vs. time (femtoseconds) plot and Fig. 5 shows the consecutive changes in shape that molecule **2** undergoes during the elapsed time.

The COT ring undergoes an interesting and peculiar distortion. The fragment is initially η^4 as pointed above. The first vibrations tend to change the hapticity to η^6 , but later both COT fragments separate considerably from the metal atom adopting a planar configuration (tendency to aromatisation). However, this process can be seen as a dissociation of the molecule into a Ru–CO fragment and free COT rings (maybe neutral triplets). This possibility is confirmed with the large exothermic values obtained (see below) for this process. Unfortunately, the association reaction is not observed with our calculations because it is necessary to include two Ru centers. Work is on progress

concerning the simulation for this process with several molecules.

A very interesting point is that the COT fragment has a short time in which the vibrations induce a change in the hapticity of the molecule. This process was experimentally explored by Bennett and co-workers [17] by ^{13}C NMR at 100.62 MHz in CD_2Cl_2 . They obtained an activation energy value of 12.8 kcal/mol for the ring interchange process. In this work, we estimated the energy differences between the local minimum of compound **2** and the important points in which the molecule seems to reach relative stability. Therefore the energy changes considered in the fluxional process are as follows: The change in hapticity from η^4 to η^6 involves an energy value of 17.5 kcal/mol, whereas the energy value for the change from η^4 to η^8 is 38.2 kcal/mol. The full rupture of the bonds between the Ru atom and the COT rings involves an energy value of 45.1 kcal/mol.

The frontier molecular orbitals and the HOMO-1 for molecule **2** are shown in Fig. 6. The LUMO is an antibonding function in which the d_{z^2} atomic orbital from the Ru atom interacts with the π cloud of the COT double bonds. HOMO and HOMO-1 functions conform an almost degenerate set in which there is a weak interaction between the Ru d_{xz} and d_{yz} atomic orbitals and the π bonding orbitals of the COT fragment. The weakness of the bond suggests that the union could be flexible, and therefore a good target for the fluxional process.

6. Conclusions

Theoretical calculations have been performed on molecules bearing the COT fragment and have been characterised as fluxional dynamics species. The eight-membered ring exhibits aromatic and antiaromatic behaviour when facing the different metal atoms. This feature induces different electronic flows that promote the formation of tub shape and planar isomers (with different bonding positions) in the case of the nickel compounds, whereas in the case of the Ru compound there is an interchange of rings. The fluxional behaviour in both cases can be explained in terms of frontier molecular orbitals.

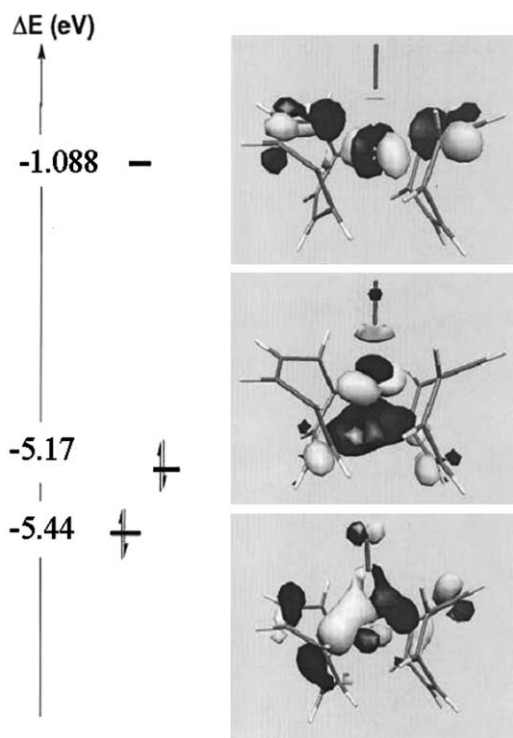


Fig. 6. Frontier molecular orbitals of molecule **2**.

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