

A theoretical study of aromaticity in 1,2-diaza and 1,2-diphospha-cyclooctatetraenes and their role as ligands in organometallic compounds

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Abstract

Eight member rings with two adjacent pnictogen heteroatoms are analysed from a theoretical point of view. 1,2-diaza-cyclooctatetraene presents a distorted structure when it has a double negative or double positive charge. On the other hand, 1,2-diphospha-cyclooctatetraene is a perfect planar (presumably aromatic) structure when the global charge is -2 or $+2$. The capability of these rings to bond to a Cr(0) carbonyl fragment is also analysed.

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1. Introduction

Compounds with cyclopentadienyl ligands with n -hapto coordination, as well as the reactivity of charged compounds with cyclooctatetraene and metals with d or f orbitals, are topics that have been studied for several years [1]. In particular, the capability of cyclooctatetraene (COT) to form organometallic complexes has been widely studied [3]. It has been observed that the perfluorination of the cyclooctatetraene ligand produces a significant improvement in the thermal and air stability of the η^6 -complexes [4]. This result indicates the capability of COT to present the inductive effects from further nucleophilic attacks and consequently to also handle different changes in charge and electron mobility. Besides, previous ab initio calculations of annelated COTs [5] reported the planar conformation as the most stable structure with delocalised diradicals. However, it is not clear whether the planar conformation will remain for COT with other substituents or for COT with one or more heteroatoms. In fact, the study on the stability and the reactivity of the heterocyclic (i.e. cyclooctatetraene rings containing one or more heteroatoms) counterparts has not been analysed, nor their hypothetical derivatives. The chemical properties of these compounds are not known, and thus it is an important matter of study that should be explored.

One of these important ligands, the 1,2-diaza-cyclooctatetraene [2] (DCOT) (Fig. 1), has been experimentally prepared by several authors. It has been reported that DCOT does not show valence tautomerism. It has also been established, by NMR ^{13}C and calorimetry determinations (enthalpies of formation) [2], that the tub conformation is the most stable structure since with this conformation, the electronic lone-pair of the nitrogen atoms (and their corresponding occupied orbitals) are perpendicular to the nitrogen carbon double bond plane (Fig. 1(b)).

Furthermore, the NMR ^{13}C studies show that in the ground state, the molecule of DCOT does not show electronic delocalisation. The double bonds are localized and the tub shape produces a molecule with very low flexibility. The two possible conformations are shown in Fig. 2, a being the most stable conformation, as the NMR studies indicate.

The reactivity of this molecule is different when it is not neutral. The double charged species, either negative or positive, should present the configuration of an aromatic ring, consequently adopting the planar structure as the most stable one.

In previous works, we studied the aromaticity of heterocyclic rings and its connection with the molecular charge, in particular, aromatic heterocyclic rings bigger than pyridine and its analogues [6]. To continue the analysis of the aromaticity in this type of compounds, and considering the DCOT as the model, we performed a theoretical study of heterocyclic rings with two adjacent heteroatoms, as a means to analyse the most stable structure and the most stable electronic configuration.

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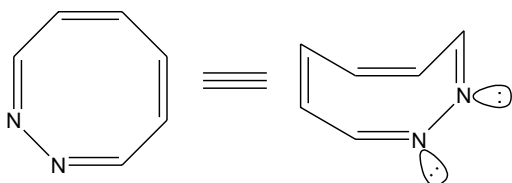


Fig. 1. (a) DCOT planar view; (b) DCOT tub conformation.

The analysis of the bonds and the stability of these compounds allowed us to establish some issues related to their reactivity with some organometallic fragments. In this study, we analysed the geometric and electronic configuration of DCOT and its phosphorus analogue (DPCOT) 2, as aromatic fragments and as chelating agents. This study models the isolated rings in different ionisation states, as well as some molecules with these rings as substituents on Cr(0) carbonyl fragments. Most stable structures, nucleus independent chemical shifts (NICS) to analyse the aromaticity, natural bond orbital (NBO) to obtain the atomic charges, and molecular orbital pictures are reported for these systems.

2. Computational details

All calculations have been performed with the Gaussian 98 program [7]. Full geometry optimisations without symmetry constraints were carried out using density functional (DF) calculations. Becke's gradient corrections [8] for exchange and Perdew-Wang's for correlation [9a] were used for the optimisation and total energy evaluation, therefore the correspondent functional is the BPW91 that has shown excellent performance in this kind of systems [9b,c]. All calculations were performed using the 6-31-G** basis set for C, N, H and P and 3-21-G* basis set for Cr and Fe.

Atomic charges were evaluated through the NBO [10] model with 6-311-++G* basis set. The NBO (natural bond orbital) method for atomic charge calculations was chosen considering the correlation with the Lewis structure representation. It is well known that this model appropriately describes the molecular environment and consequently the electron density. NICS (NICS) is a technique proposed by Schleyer [11] as an aromaticity index. Following the methodology of Schleyer, we obtained the absolute magnetic shielding at the centre of the rings, which is determined by the non-weighted mean of the heavy atom coordinates, these calculations were carried out at 6-31+G* level as it was recommended by Schleyer.

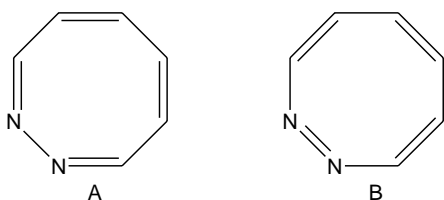


Fig. 2. Rigid conformations of DCOT.

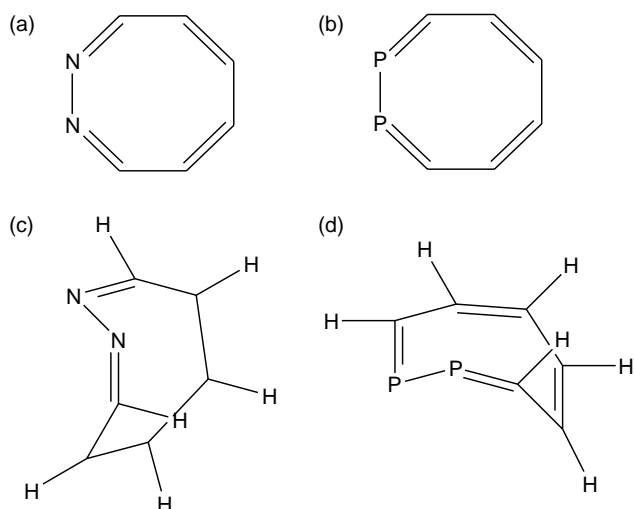


Fig. 3. (a) and (c) 1,2-diaza-cyclooctatetraene (planar and tub-shape conformation, respectively); (b) and (d) 1,2-diphospha-cyclooctatetraene (planar and tub-shapes conformation, respectively).

3. Results and discussion

Optimised planar and tub shape structures of the rings are shown in Fig. 3. The optimised model of an organometallic molecule is reported in Fig. 4.

The most stable structure of the compound with nitrogen atoms shows the predicted tub shape. Other calculations, considering different charges as +1 or -1 merely produce irregular distortions. However, the most stable structures with +2 or -2 charges are planar. A slightly different situation is found in the case of the ring with phosphorus. The neutral, the mono and di-cation, and the anion most stable structures are similar to the compounds with nitrogen. In all these cases, the tub or distorted shapes are the ground states. With phosphorus, the planar structure is more stable only when the charge is equal to -2. It is important to say that the eigenvalues of the frontier orbitals of the di-anion compounds are positive, indicating that the electrons are not attached to the molecule. Therefore, it will be difficult find these species isolated in gas phase.

The NICS [11] analysis was performed in both anionic structures with very interesting results, even though the ring with nitrogen atoms does not show large aromaticity (the NICS

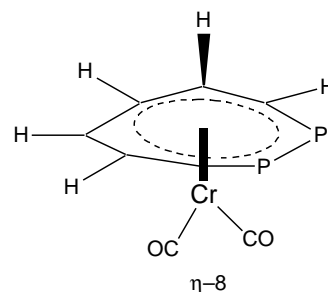


Fig. 4. Complex of di-carbonylCr(0) with 1,2-diphospha-cyclooctatetraene showing a η^8 coordination.

value is 5.05). However, the compound with phosphorus shows a very defined aromatic nature (the NICS value is -12.7). The explanation for this phenomenon is based on the nature of the multiple bond between N–N and P–P. The flexibility of the N–N bond in this molecule is so low, indeed, it has been proposed that the double bonds in the ring are static, therefore it is not possible to find a double bond between both nitrogen atoms (i.e. there is not resonance) [2a,d]. On the other hand, phosphorus, although it belongs to the same family, is less rigid than its nitrogen counterpart allowing many different kinds of bonds. In addition, this phenomenon arises from the intrinsic electronegativity difference between both elements (N and P) since electronegativity of nitrogen is 2.93, whereas, for phosphorus, it is 2.16 (Sanderson scale [12]). Therefore, with phosphorus there is a higher movement of electrons than with nitrogen. Thus, the ring containing phosphorus shows resonance and indeed aromaticity.

This idea can be proved by analysing the NBO charge values and the nature of the frontier molecular orbitals. The NBO charge values are shown in Table 1 for both di-anions, one with the P–P unity and the other one with the N–N fragment. In the case of phosphorus, the negative charge is distributed in all atoms of the ring, although the carbon atoms directly joined to the heteroatoms have some preference. However, in the case of nitrogen, practically all the negative charge is localised on the same carbon atoms, whereas the other six heavy atoms are almost neutral. Therefore, there is an electronic resonance in the first case but not in the second one. The shapes of the HOMO and HOMO-1 for the compound with phosphorus heteroatoms are shown in Fig. 5. They suggest that there should be an electronic delocalisation. The energy difference between both orbitals is only 0.54 eV.

The capability of these rings as organometallic ligands can be analysed taking these properties in consideration. The compound with nitrogen atoms is definitively a bad target for the formation of a ferrocene-like compound, because the electronic delocalisation (aromaticity) and the adequate molecular orbitals needed for making the delocalised π bond do not exist. However, it is important to highlight that the localization of bonds suggested by Trost and co-workers [2d] can be achieved, so this molecule can effectively bind to a metal ion by a localised π bond as an olefin. The case of the compound with phosphorus is very different, because this ion has the appropriate characteristics to be a ligand like the cyclopentadiene anion. However, a major issue is whether

Table 1
NBO charge values for 1 and 2

1		2	
N1	-0.0781	P1	-0.1045
C3	-0.8882	C3	-0.5737
C5	-0.1149	C5	-0.2962
C7	-0.1188	C7	-0.3070

The order of the carbon atoms is denoted by each number. In this sense, C3 is bonded to the heteroatom, C5 is bonded to C3 and C7 is bonded to C5. The other half of the molecule yields the same values.

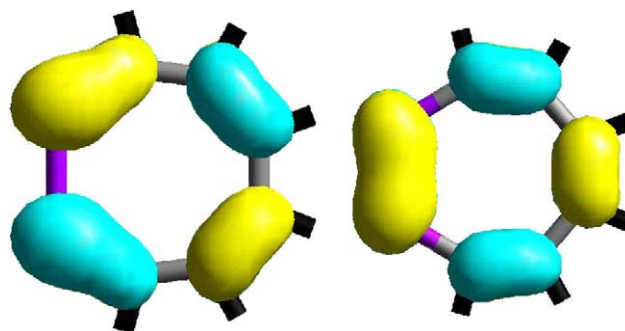


Fig. 5. Frontier occupied molecular orbitals of compound with phosphorus.

the electronic delocalisation is enough to bind a metal in an aromatic fashion and generates a η^8 -complex. According to our data it is not enough due to the fact that the trend of the phosphorus to react through its lone-pair. Furthermore, the tendency to localise the negative charge on the carbon atoms close to the phosphorus atoms, suggests that this electronic delocalisation is very weak and can be deflected to a specific region of the ring.

The calculation of the modelled organometallic compounds reinforce this idea. The organometallic species present an interesting behaviour. In both cases, the molecules have non-planar rings (the corresponding scheme for the 1,2-diphosphacyclooctatetraene carbonyl complex is shown in Fig. 6) but tub shaped. It seems that the electronic transfer from the ring to the metallic centre is crucial for a lack of important delocalised electrons on the resonance process of the ring. The result is a structure similar to the neutral molecule. However, it has a η^4 configuration, and the carbon atoms involved in the bonds to the metal are not contiguous to the phosphorus atoms, they are those that complete the ring and are far from the P–P bond. The analysis of charges and molecular orbitals of this species indicates a very good π delocalisation on the four carbon atoms fragment. In such a way, they can develop a π arene-like compound. Chen and his co-workers reported that the Jahn Teller distortion is expected to occur so as to relieve the electronic degeneracy [13]. Comparing the eigenvalues of the planar structure with the eigenvalues of the distorted structure, there is no electronic degeneracy in the planar structure and therefore, we could not explain the distortion of the structure with the Jahn Teller effect.

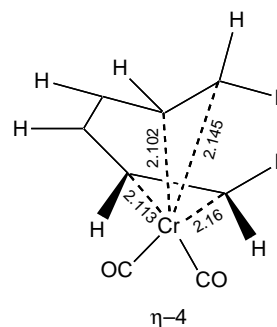


Fig. 6. Optimised geometry of complex three showing a η^4 coordination.

4. Conclusions

Eight-member rings with two heteroatoms can change their conformation from tub shape to planar on acquiring negative double charge. However, only the case of phosphorus results in an aromatic compound. Both rings can bind an organometallic fragment in π fashion, but the ring loses the planar form to adopt again the tub-shape and yielding an η^4 complex.

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