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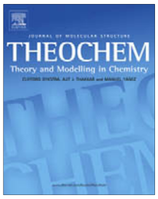

A computational study of a novel seven-membered cyclic diyne and its cobalt–carbonyl complex

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ABSTRACT

The relative thermodynamic stability of a novel seven-membered cyclic diyne and a strain-free isomer of the diyne was assessed using density functional theory (DFT) at the B3LYP/6-31G(d) level of theory. The computed optimized structure, IR harmonic vibrational frequencies, NMR chemical shifts and TD-DFT properties of the cyclic diyne, which has not been isolated experimentally, were compared with the corresponding structure and properties of a dicobalt–carbonyl coordinated complex of the diyne, which has been previously synthesized and characterized experimentally.

1. Introduction

Small carbon clusters have attracted much attention from theoretical chemists over the last decade or so [1–5]. The existence of unusual carbon-based structures in space was proposed on the basis of calculated spectra [6]. Carbocycles also have practical applications as intermediates during the formation of novel nanostructured materials, such as fullerenes and carbon nanotubes [5,7]. Moreover, a bicyclo[7.3.0]dodecadiyne core was recently recognized as a chromophore moiety in several bio-active compounds leading to the development of the synthesis of such a strained diyne [8]. The study of small cyclic molecules has proven to be a fertile area for the development of various theories discussing strain in such systems. Theoretical methods have been successfully applied to carbon-based cyclic systems, such as cyclopropanes, cubanes and larger cycles, and also to strained cycles containing other elements, such as nitrogen [9–13]. Nonetheless, systems containing rigid triple bonds within a small cycle have not been widely studied theoretically, though examples of such cycles have been reported before [8,9,14,15].

Free strained cyclic diynes constitute a "terra incognito", with the notable exception of several recently reported examples (Fig. 1) [16–19]. Small cycloynes are often stabilized within organometallic complexes, where they act as ligands coordinated to transition metals (Fig. 2) [20,21]. The formation of a novel seven-membered cyclic diyne, stabilized by dicobalt–carbonyl moieties coordinated to both triple bonds (Fig. 2b), has been reported in the literature [21]. However, all attempts to remove the cobalt–carbonyl groups and to isolate the free seven-membered cyclic diyne have proven to be unsuccessful. This is not surprising since isolation or detection of small cycloynes, such as cycloheptyne, cyclohexyne and cyclopentyne, requires the use of low temperatures or inert matrices [9]. This has prompted the current theoretical inquiry into the stability and properties of the isolated cyclic diyne and the dicobalt complex of this diyne. A strain-free isomer of the cyclic diyne (i.e., a product of the double dehydration of bispropargyl alcohol $HOMe_2CC{\equiv}C{-}C{\equiv}C{-}CCMe_2OH$) was also computed and found to be more thermodynamically stable than the cyclic species. This isomer is a dimethyl-substituted derivative of 1,7-octadiene-3,5-diyne called diisopropenyldiacetylene. This suggests that coordination to the dicobalt–carbonyl moieties strongly stabilizes the cyclic diyne favouring its formation and may also explain why the free cyclic ligand could not be isolated experimentally, despite being found computationally to be a minimum on the potential energy surface.

In this paper we computed the relative stability of the cyclic and straight-chain diynes and also the stability of the dicobalt–carbonyl complex of the cyclic diyne with respect to fragmentation to the free ligand and the free cobalt and carbonyl species. Equilibrium structures (gas phase) were computed, as well as the harmonic vibrational frequencies, NMR shielding constants and the relative energies of excited electronic states for the free cyclic diyne and its dicobalt–carbonyl complex. The bonding

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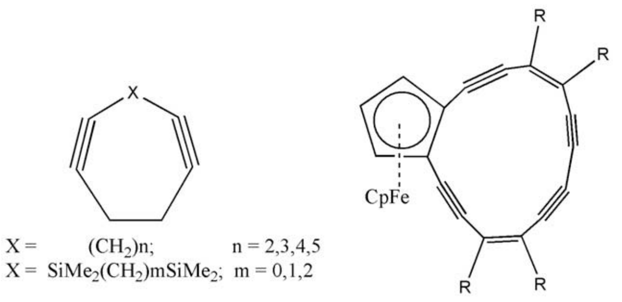

Fig. 1. Examples of uncomplexed cyclic diynes.

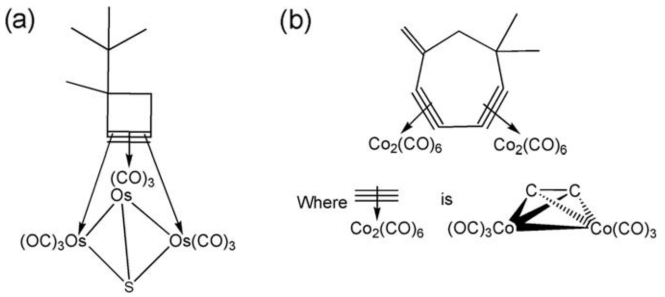

Fig. 2. Examples of complexes containing cycloyne ligands.

characteristics of these two species were also determined *via* the natural bond order (NBO) method [22]. Hence, the changes in the free cyclic diyne on complexation to the dicobalt–carbonyl moieties can be assessed. As far as the authors are aware this is also the only known computational study of these two novel compounds.

2. Computational procedure

Quantum chemical computational methods based on density functional theory (DFT) [23] are now routinely used for the study of molecular structure and properties since DFT is comparable in accuracy with *ab initio* methods like second-order Møller–Plesset (MP2) perturbation theory for the prediction of reliable optimized structures and vibrational frequencies. DFT methods using high-quality basis sets also seem capable of accurately computing magnetic properties like NMR shielding constants, and owing to their favourable scaling properties with molecular size, are more attractive for this reason than other relatively more expensive correlated methods.

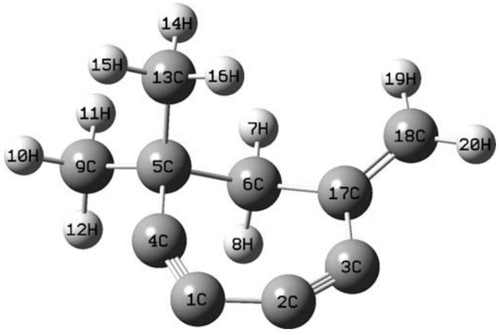

Fig. 3. Optimized structure of cyclic diyne.

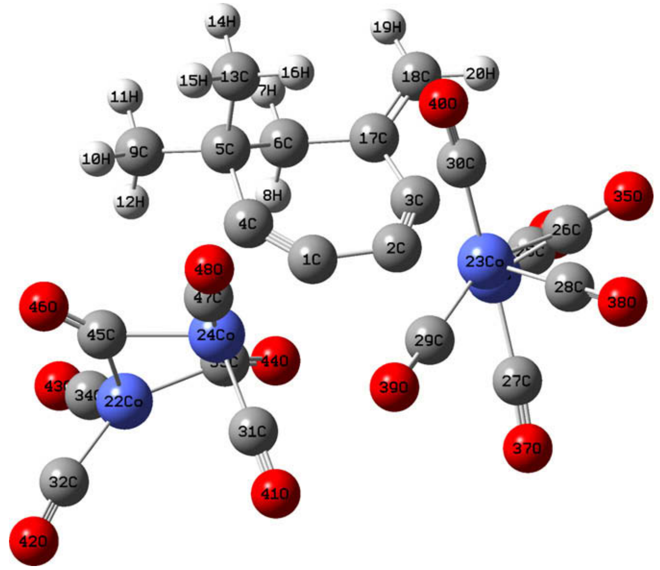

Fig. 4. Optimized structure of dicobalt-carbonyl coordinated complex of the cyclic diyne.

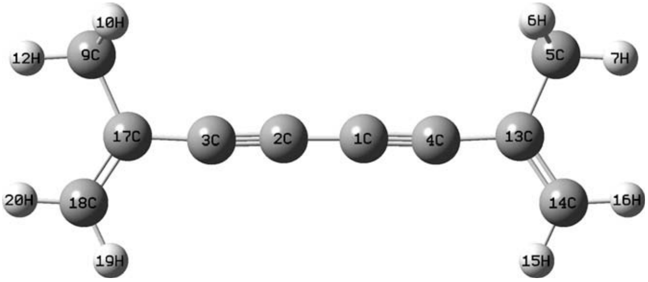

Fig. 5. Optimized stucture of non-cyclic diyne (diisopropylenediacetylene).

All calculations were performed at the B3LYP/6-31G(d) level of theory using Gaussian 03 [24]. The 6-31G(d) basis set is of moderate size. This is the smallest basis set which would be feasible for performing the calculations with the computational resources available to the authors, especially for the large dicobalt–carbonyl complex, which required 674 basis functions. The cyclic diyne was optimized to the structure shown in Fig. 3 and the dicobalt–carbonyl complex to the structure shown in Fig. 4. Fig. 5 shows the optimized geometry of the strain-free isomer.

Table 1 shows selected bond lengths, bond angles and the total energies for the three molecules, while Table 2 shows relative energies. The NBO method [22] was used to determine the Wiberg bond index (Table 3) and the orbital occupancy of selected orbitals (Table 4) of the two species. The Wiberg bond index gives information about the bond orders of the selected bonds.

The harmonic vibrational frequencies (ω) of the molecules confirm that the optimized structures are true minima (no imaginary frequencies), and these results for the cyclic diyne and the cobalt complex are in Table 5. The ^{1}H and ^{13}C NMR chemical shifts were computed using the gauge-invariant atomic orbital (GIAO) method [25], implemented in Gaussian 03. The GIAO absolute isotropic shielding constants (σ) were computed, from which the chemical shifts with respect to tetramethylsilane (TMS) were determined. These results are in Table 6. Time-dependent density functional theory (TD-DFT) was used to model the electronic excited states of the cyclic diyne and the cobalt complex and these results are in Table 7.