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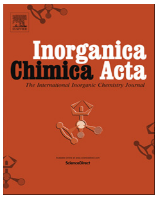

Research paper

Bonding modes in bis(benzene)beryllium(0): A density functional and Møller-Plesset computational investigation

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ABSTRACT

Density functional calculations at the B3LYP/6-311+G** and ωB97X-D/6-311+G** levels of theory and Møller-Plesset calculations at the MP2/6-311+G** level of theory predict that bis(benzene)beryllium(0) may adopt three different structures: *syn*- and *anti*-bis(1,2-η^2-benzene)beryllium(0) and (1,2-η^2-benzene)(1,2,3,4-η^4-benzene)beryllium(0); the latter is the most stable structure. Significant charge transfer from the beryllium atom to the benzene rings is observed in all structures. Due to the relatively large energy differences between the three different structures, the molecules are unlikely to be fluxional at room temperature.

1. Introduction

Recently [1], the structures and properties of benzene sandwich complexes containing triangular triberyllium clusters were reported. In that report, the calculated results indicated that the benzene rings could bond to the beryllium atoms of the triangular beryllium clusters with a number of different hapticities, including η^1-, η^2-, and η^3-arrangements. (No higher hapticities were noted in these molecules.) The small size of a beryllium atom—the metallic radius [2] of beryllium is 112 pm and the atomic radius [3] is 124.4 pm—and the Be–Be distances in the Be_3 clusters [1] may have prevented the adoption of η^4-, η^5-, or η^6-arrangements in the triberyllium sandwich compounds with benzene. However, such higher hapticity structures might be possible in bis(benzene)beryllium(0), despite the small size of a neutral beryllium atom.

Unfortunately, there are no reports of any experimental attempts to synthesize benzene or other arene complexes of neutral beryllium atoms. The only theoretical investigation reported is a computational study using the semiempirical MNDO (modified neglect of diatomic overlap) method [4]. However, some theoretical investigations of the interactions of a *cationic* beryllium center—Be^{2+}—with benzene or substituted derivatives have been reported. Density functional and Møller-Plesset calculations indicated that the bonding between Be^{2+} and benzene was attributable to *s*-π and *p*-π interactions, and that electrostatic interactions were not dominant [5]. Additional MP2 investigations [6] compared alkali and alkaline earth cationic complexes of benzene and concluded that polarization and charge transfer effects dominate the alkaline earth cation interactions with benzene. Somewhat more recent density functional calculations [7] indicated that Be^{2+} strongly interacted with a benzene system, and that the interactions were weakened when electron-withdrawing substituents were present on the arene and were strengthened when electron-donating substituents were present.

While the syntheses of arene complexes of beryllium have not been reported, beryllocene, bis(cyclopentadienyl)beryllium(II), has been known since 1959 [8]. However, due to the highly fluxional nature of beryllocene [9,10], the structure of the system was not firmly established until somewhat later: The accepted η^1,η^5-structure may be the result of the opposing factors of the delocalization energy of the cyclopentadienyl group and the strength of the Be—C σ-bond, neither of which are dominant [11] in the five-membered ring-containing structure. Gas-phase structural determinations [12] and solid-state investigations [13,14] generally indicate that the molecule contains both η^5- and η^1-bound C_5H_5 rings which rapidly interconvert; computational results [15–17] support such a fluxional description of the molecule.

Density functional methods appear to be successfully applicable to the investigation of beryllium-containing molecular systems.

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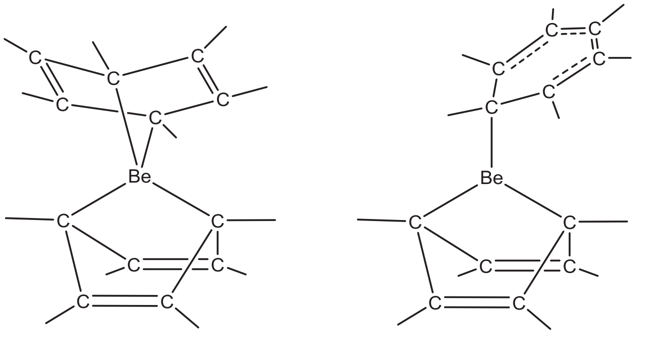
The B3LYP method has been shown to demonstrate good agreement with the G4 composite *ab initio* method [18], although the *ab initio* MP2 and CCSD(T) methods have also been employed with success [19]. In addition to extensive computational work on systems containing beryllium bonds [20,21], a modest number of additional reports of the use of density functional methods to investigate the structures and properties of beryllium-containing molecules have been reported, including beryllium carbonate complexes of noble gases [22], and Be^{2+} complexes of *N*,*O*-chelate ligands [23] and cyclic polyalanine peptides [24].

Beryllium-cyclobutadiene multidecker sandwich and inverse sandwich complexes have also been computationally investigated using a broad array of density functional methods (B3LYP, BHHLYP, BLYP, M06, CAN-B3LYP, B2LYP). The cyclobutadiene moieties in these complexes do not appear to deform from planarity upon complexation [25]. Computational methods have also been used to determine the structures of larger beryllium clusters such as the hydrogen-stabilized CBe_5H_n, $n = 2–5$, complexes, based on the isoelectronic relationship between Al and BeH [26] and the previously-investigated CAl_5^+ cluster [27]. Polyberyllium nanoribbons have also been the subject of computational investigations, wherein zig-zag chains of beryllium atoms, stabilized by planar, pentacoordinate carbon atoms, are reported to exhibit “ribbon aromaticity” [28]. Diberyllium systems containing ultrashort Be—Be bonds (172.8–186.6 pm) have also been computationally investigated [29]; the authors propose a “chemically viable” molecule in which the Be–Be moiety is supported by two “IDip”—1,3-bis(2,6-di-isopropylphenyl)imidazole-2-ylidene—ligands [29].

The MNDO semiempirical report of $(CH)_n$ carbocycles [4] detailed two structures of interest (Fig. 1) to the current investigation of bis(benzene)beryllium(0): Both $(1,4\text{-}\eta^2\text{-}C_6H_6)_2Be(0)$ and $(\eta^1\text{-}C_6H_6)(1,4\text{-}\eta^2\text{-}C_6H_6)Be(0)$ were reported to be stable minima on the MNDO potential energy surface. However, no other bis(benzene)beryllium(0) structures were described in that article. Herein is reported a comprehensive investigation of the bis(benzene)beryllium(0) family of complexes (including the investigation of the two molecules in Fig. 1) and the report of those complexes which were determined to be stable minima on the potential energy surfaces at the B3LYP/6-311+G** and the ωB97X-D/6-311+G** levels of density functional theory and the MP2/6-311+G** level of Møller-Plesset theory.

2. Computational methods

The structures and properties of all molecules were determined at the restricted B3LYP/6-311+G** [30–33] density functional level of theory, which includes polarization functions [34] on all atoms and diffuse functions on all non-hydrogen atoms [35]. All molecules were also optimized at the ωB97X-D/6-311+G** [36] density functional level of theory, which uses the range-separated-hybrid generalized gradient approximation (GGA), and has been reported to produce results that match experimental data better than does B3LYP [37,38]. In addition, the molecules were optimized at the Møller-Plesset MP2/6-311+G** level of theory [39–42]. The *Spartan ’14* program package [43] was used for all calculations without the use of symmetry during the optimization of the molecules. Vibrational frequencies were calculated and the stability of the final wave function was determined for all molecules at each level of theory.



$(1,4\text{-}\eta^2\text{-}C_6H_6)_2Be$ $(\eta^1\text{-}C_6H_6)(1,4\text{-}\eta^2\text{-}C_6H_6)Be$

Fig. 1. The bis(benzene)beryllium(0) structures calculated at the semiempirical MNDO level of theory [4].

3. Results and discussion

The plethora of possible bonding mode combinations (21 in all) for bis(benzene)beryllium(0)—from η^1-,η^1-; η^1-,η^2-; η^1-,η^3-; through η^5-,η^5-; η^5-,η^6-; and η^6-,η^6-—coupled with the multiple conformations that could be exhibited by each bonding mode combination appeared to make the computational investigation of bis(benzene)beryllium(0) a complicated task. However, most combinations and the associated conformations were not found to be minima on the B3LYP, ωB97X-D, or MP2 potential energy surfaces. Rather, regardless of the computational method, the bonding mode combinations investigated either transformed into one of three stable minima, failed to converge, optimized with multiple imaginary frequencies, or optimized with an unstable wave function.

Contrary to the MNDO results [4], no minima were found that contained either η^1- or 1,4-η^2-bound benzene rings. Molecules with the former bonding mode as the initial trial geometry generally transformed smoothly into 1,2-η^2-benzene systems, while initial trial geometries with the latter structures generally rearranged into the 1,2,3,4-η^4-bound system. In addition, no stable molecules containing η^3-, η^5-, or η^6-benzene rings complexed to a neutral beryllium atom could be identified, regardless of the η^3-bonding indications observed for the triberyllium sandwich complexes with benzene [1]. While the η^1- and η^3-bonding modes might be expected based on the small size of a neutral beryllium atom and the presence of η^1-bonding in beryllocene (*vide supra*), the η^5- and η^6-bonding modes may have been precluded by the small size of a neutral beryllium atom. Despite the multitude of potential bonding possibilities, only three structures were ultimately identified for the molecule; the calculated electronic properties of these structures are detailed in Table 1.

3.1. Bis(1,2-η^2-benzene)beryllium(0) conformers **1s** and **1a**

Of the three structural minima identified, two were rotational conformers in which both benzene rings were bound in an η^2-fashion. These conformers were the more stable *syn*-bis(1,2-η^2-benzene)beryllium(0), **1s**, Fig. 2, and the less stable *anti*-bis(1,2-η^2-benzene)beryllium(0) conformer, **1a**, Fig. 3. The calculated energy differences between **1s** and **1a** range from 4.30 kJ/mol (B3LYP) to 21.00 kJ/mol (ωB97X-D) to 33.40 kJ/mol (MP2).

In the structures of **1s** and **1a**, the hydrogen atoms bound to the η^2-carbon atoms of the benzene rings are bent out of the plane of the ring by about 20° at all three levels of theory. A “bend-back” angle of this magnitude is within the normal range for alkene complexes (of transition metals), as is the C—C distance [44]. With the exception of the aforementioned two hydrogen atoms, the carbon and hydrogen atoms in the benzene rings remain essentially planar in both **1s** and **1a**. However, the non-bonded C—C bonds within the rings exhibit modest bond alternation, although all of the bond distances remain shorter than C—C single bond distances [45]. At

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