

The nature of the interactions between Ag^+ and benzene

Sérgio Emanuel Galembeck

Departamento de Química, FFCLRP, Universidade de São Paulo, 14040-901, Ribeirão Preto – SP, Brazil.

Abstract: The interaction of transition metal cations with aromatic compounds is of utmost importance to modulate the properties of materials or to modify the action of biomolecules. There are few works that study the interaction of Ag^+ with benzene, the standard aromatic compound. None of them explore the nature of this interaction. In this work all conformations of the Ag^+ - benzene system was determined, and for each the nature of cation-pi interactions was analyzed by energy decomposition and by electron density techniques of analysis.

The geometry optimization and vibrational frequency analysis were made by MP2/def2-TZVPP-SDD computational model, by using Orca 4.0.0 software. Some tests were made with DKH2 relativistic approximation, but results are similar to those obtained with SDD ECP. Single point calculations were made with CCSD(T)/def2-QZVPP-SDD, using Turbomole 6.3. NBO analysis was obtained by NBO 6.0 interfaced with Orca 4.0.0 by B3LYP/def2-TZVPP-SDD. AIMAll (17.01.25) was used for QTAIM and interacting quantum atoms (IQA) analysis. SAPT2+(CCD)/TZP was made by PSI4 1.1. After an extensive search in the potential energy surface, there are three structures for the complexation of Ag+ with benzene, η^2 , η^3 and η^6 , Figure 1. Kim et al. found also a η^1 complex [1], in contrast with our results.



Our best results indicate that the interaction energy is around 41 kcal/mol, and the complexes are nearly isoenergetic. The difference between η^2 and η^3 is only 0.05 kcal/mol, and for η^2 and η^6 , 0.42 kcal/mol. All methods indicate a donation of electron density from the pi system of benzene to the cation. According to NBO, the main interaction is $\pi(C-C) \rightarrow s(Ag)$. A d(Ag) $\rightarrow \pi^*(C-C)$ is also observed, but is much less important. NRT indicates secondary quinoidal dipolar resonance structures, instead of Dewar structures. The molecular graphs obtained by QTAIM show that all bond paths (BP) are topologically unstable, because they are curved and the ellipticities are very



12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

high. Parameters of the bond critical point (BCP), as the electron density and its Laplacian indicate that Ag-C are closed shell interactions. In contrast, the total electron density and its components reveal that Ag-C interaction for η^1 is covalent, or at least with a large covalent character, and closed shell for η^2 and η^6 , with a very small covalent character. The largest component of E_{IQA} is the exchange-correlation, not the classical energy. This suggests that all Ag-C interactions have a polar and covalent character. The largest stabilizing components of SAPT2+(CCD) are electrostatic, and dispersion. This shows that metal-carbon contacts have ionic and covalent components, and this is confirmed by sizable charge transfer energies.

In conclusion an extensive search in the potential energy surface indicates that there are three Ag^+ -benzene complexes, nearly isoenergetic. The metal-carbon interactions are polar, with a covalent component.

Key-words: cation-pi interactions, EDA, NBO, QTAIM, SAPT.

Support: This work has been supported by CAPES, CNPq (Grants 304447/2010-2 and 308254/2016-3), FAPESP (Grants 2008/02677-0 and 2014/50265-3).

References:

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