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Růžičková, Zdeňka, Holub, Josef, Melichar, Petr et al. (2016) The π Complex of the Hydronium Ion Frozen on the Pathway of Electrophilic Aromatic Substitution. European Journal of Organic Chemistry. pp. 4473-4475. ISSN: 1099-0690

https://doi.org/10.1002/ejoc.201600912

The π-complex of the Hydronium Ion Frozen on the Pathway of Electrophilic Aromatic Substitution

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Abstract: *A very rare crystal has been prepared consisting of a 2D aromatic (toluene) together with a weakly coordinating 3D aromatic (closo-1-*$CB_{11}H_{12}^{-}$*) and a hydronium ion, and this has been analyzed using X-ray diffraction and high-level quantum mechanical calculations. The nature of the crystal arrangement has made it possible to detect the frozen π-complex that would originate during the protonation of toluene by the acidic hydronium ion.*

Nonclassical, noncovalent interactions that form between X–H moieties (X = C, N, O) and π-electron clouds of 2D aromatic systems are well known as nonconventional hydrogen bonds. These interactions have been intensively studied by various spectroscopic methods and quantum mechanical (QM) calculations.[1] It has been shown that X–H⋯π interactions play an important role in structural biology.[2] However, there are very few crystalline X-ray structures which exhibit X–H⋯π interactions,[3] with literature examples limited to a calixarene ligand⋯water complex,[4] a (mercuracarborand-water)$_2$⋯benzene complex,[5] and a chloroform-benzene complex.[6] Also known are cation⋯π contacts afforded by the hydronium ion interacting with three benzene rings.[7] This structure is formed primarily because of the high acidity of the hydronium ion in the presence of the weakly coordinating *closo*-1-$CHB_{11}Cl_{11}^{(-)}$. The parent *closo*-1-$CHB_{11}H_{11}^{(-)}$ anion is also known for its weak-coordinating ability and has been isolated in complexes with a large variety of countercations.[8] Among these, $Ag^{(+)}$ has been shown to play an interesting role. An interacting crystal structure of $Ag^{(+)}CHB_{11}H_{11}^{(-)}$ complexed with $2C_6H_6$ contained $Ag^{(+)}$ pointing toward the edge of the benzene ring.[9] In order to obtain a deeper insight into the behavior of further cations in the presence of weakly coordinating *closo*-1-$CHB_{11}H_{11}^{(-)}$, we examined a crystal consisting of a 2D aromatic with a cation complemented by a *closo*-1-$CHB_{11}H_{11}^{(-)}$ counteranion. First, to prepare a diorganotin(IV) dication, we mixed two equivalents of $Ag^{(+)}CB_{11}H_{12}^{(-)}$ with $Sn[CH(SiMe_3)_2]_2Br_2$ prepared *in situ* from $Sn[CH(SiMe_3)_2]_2$ [10] and bromine in toluene in ambient air (for further details, see the Supplementary Information). Its hydrolysis and subsequent crystallization provided *closo*-1-$CB_{11}H_{11}^{(-)}$ + $CH_3C_6H_5$ + $H_3O^{(+)}$ along with $\{[Sn[CH(SiMe_3)_2](OH)]_2(\mu\text{-}O)\}$.[11]

In the crystal structure of this adduct (Figure 1a, 1b and S1), two layers of $H_3O^{(+)}$ with $CB_{11}H_{12}^{(-)}$ are sandwiched between layers of toluene molecules. All pairwise interactions in the crystal structure have been computationally characterized (Table S1). The crystal packing is dominated by the interactions of $H_3O^{(+)}$ with $CB_{11}H_{12}^{(-)}$ (about –92 kcal mol^{-1}) *via* the dihydrogen bond and with the toluene (about –19 kcal mol^{-1}). Each toluene molecule thus forms two strong and very rare O-H⋯π interactions; each $H_3O^{(+)}$ is interconnected with three $CB_{11}H_{12}^{(-)}$ *via* the dihydrogen bonds. The disordered $H_3O^{(+)}$ ion is refined as the tetrahedral species H_4O with the occupancy of each H atom being ¾. The disorder of the $H_3O^{(+)}$ ion is consistent with the weakly coordinating properties of the crystal anion *closo*-1-$CHB_{11}H_{11}^{(-)}$. The toluene ring centroid distances to the appropriate oxygen atoms [3.211(3) Å] and hydrogen atoms [2.067(3) Å; refined freely], are comparable to the average separations found for the $H_3O^{(+)}(C_6H_6)_3$ moiety reported in Reference 9.

The strong interaction of $H_3O^{(+)}$ with the 2D aromatic ring seems to be a frozen π-complex during the protonation of toluene with the electrophilic hydronium ion. We supported our hypothesis about the frozen transition state (TS) by employing QM calculations. It should be noted that the π-complex in electrophilic substitutions is defined as a TS in textbooks of computational chemistry.[12] In a similar manner to Reed *et al.*, who explained the accommodation of $Ag^{(+)}$ with respect to the 2D aromatic in terms of frontier orbitals by Fukui even without taking $CB_{11}H_{12}^{(-)}$ into consideration,[13] we started to search for a transition state using a two-component ($H_3O^{(+)}$ + toluene) input based on the X-ray geometry (the H atom of $H_3O^{(+)}$ was located above the center of the aromatic ring). Indeed, we did detect a TS, which had an imaginary frequency of –68.6 cm^{-1} when calculated using MP2/cc-pVTZ, and was –51.6 cm^{-1} using B3LYP/6-31+G*. These results support previous work[14] that MP2 and DFT model chemistries provide almost the same energetic balance when examining reaction profiles involving boron clusters. With an H atom of the hydronium ion located at a close distance of 1.77 Å to the *ortho* position of toluene (Figure 1b), this is commensurate with the *ortho*/*para* directing nature of CH_3. The imaginary frequency can be visualized as the wagging mode of the H_2O fragment. Note that the so-called elevation angles α and β (deviations of the approaching H atom toward C(*ortho*) and of the H atom bonded to C(*ortho*) from the toluene plane, respectively) are 104° and 2°, respectively. Such values are not too far from 90° and 0° associated with the ideal π-complex.[15]

A protonated benzene ($C_6H_7^{(+)}$) has already been found in a crystal structure and a protonated toluene ($CH_3C_6H_6^{(+)}$) has been reported[9] and also isolated as a $BF4^{(-)}$ salt.[16] The latter can be regarded as either the σ-complex or, more probably, as the σ–π continuum[15] during the entire electrophilic reaction, in which one proton from toluene is exchanged for that from $H_3O^{(+)}$. Indeed, we have not found any imaginary frequency for the $CH_3C_6H_6^{(+)}\cdots H_2O$ complex. Note that σ-complexes are not transition states during electrophilic substitutions and some of them have been detected as intermediates.[12] The respective C–H bond length computed as 1.14 Å (a larger value than that usually computed) supports the σ–π continuum concept as well the α and β values (in the presence of the outgoing H_2O) of 71° and 31°, respectively. The ideal σ-complex is characterized with α and β being 55°.[15]

The π-complex found in the reported crystal structure might be a result of the poor ligation properties of the 3D aromatic system. This has also been shown in $Ag^{(+)}CB_{11}H_{12}^{(-)}$ + $2C_6H_6$, where benzene successfully competes with the carbaborane anion for coordination to silver.[9]

Considering the hydroxylation property of the hydronium ion, rather than the proton exchange shown above, we have explored this from the position of the hydronium ion in which $O^{(+)}$ points towards the center of the aromatic ring. It should be noted that this structural arrangement has been computed to be less stable than that in which H atoms point toward the π-system (see Figure S2). The obtained TS was found to be geometrically very similar (an imaginary frequency was calculated to be –31 cm^{-1}). Protonation competes with hydroxylation, with the former process being favored.

In summary, we have studied the behavior of hydronium cation with respect to toluene in the presence of weakly-coordinating *closo*-1-$CHB_{11}H_{11}^{(-)}$. The QM analysis of the reported crystal structure has made it possible to detect the protonation-based frozen π-complex. This observation will significantly contribute towards the improved understanding of the reaction mechanism of electrophilic substitutions, such as those taught in basic organic chemistry courses.

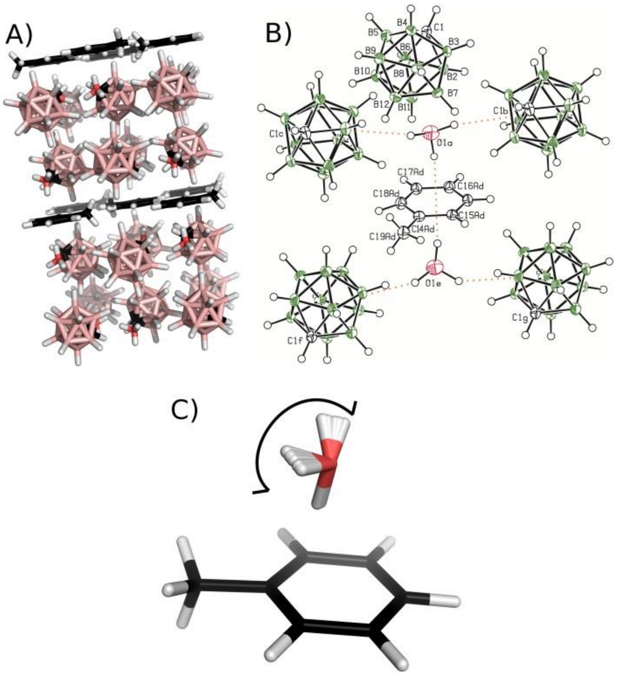

Figure 1. A) An overview of an X-ray crystal structure. B) ORTEP view (at 50% probability level) of toluene + $H_3O^{(+)}$ + $CB_{11}H_{12}^{(-)}$ adduct. C) The optimized transition state with one negative frequency, which is shown.

Experimental Section

Syntheses, X-ray diffraction analysis and QM analysis

The synthetic procedure of the ternary-complex preparation as well as X-ray diffraction and QM analyses are described in detail in the SI.

Acknowledgements

This work was supported by the research project RVO 61388963 of the Academy of Sciences of the Czech Republic. We acknowledge the financial support of the Czech Science Foundation (JF: P208/12/G016). We also thank the Gilead Sciences and IOCB Research Center for financial support.

Keywords: weakly coordinating anion • π-complex • electrophilic substitution • X-ray diffraction • QM calculations

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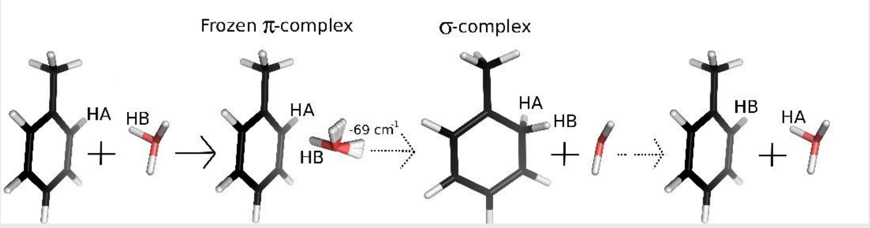

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