



Cation- π interaction of Tl^+ with [6]helicene: Experimental and DFT study



Emanuel Makrlík ^{a,*}, David Sýkora ^b, Stanislav Böhm ^b, Petr Vaňura ^b, Vladimír Církva ^c, Jan Storch ^c, Miroslav Polášek ^d

^a Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Kamýcká 129, 165 21 Prague 6, Czech Republic

^b Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

^c Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 2/135, 165 02 Prague 6, Czech Republic

^d J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejšková 2155/3, 182 23 Prague 8, Czech Republic

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ABSTRACT

By using electrospray ionization mass spectrometry (ESI-MS), it was proven experimentally that the univalent thallium cation forms with [6]helicene ($C_{26}H_{16}$) the cationic complex species $[Tl(C_{26}H_{16})]^+$ in the gas phase. Further, applying quantum mechanical DFT calculations, the most probable structure of the $[Tl(C_{26}H_{16})]^+$ complex was derived. In the resulting complex, the “central” cation Tl^+ is bound by six bonds to six carbon atoms from the two terminal benzene rings of the parent [6]helicene ligand via cation- π interaction. Finally, the interaction energy, $E(int)$, of the considered cation- π complex $[Tl(C_{26}H_{16})]^+$ was found to be -144.8 kJ/mol, confirming the formation of this cationic complex species as well.

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1. Introduction

Helicenes are polycyclic aromatic compounds consisting of *ortho*-fused benzene rings with nonplanar topology with C_2 -symmetric axis perpendicular to the axis of helicity as a result of the steric repulsive interaction between terminal aromatic rings [1–3]. This makes them chiral even though they have no center of chirality. The highly delocalized large π -electron system of fully aromatic helicenes along with the previously mentioned inherent chirality predetermines their unique optical [4] and electronic [5] properties, as well as their use in many fields of research, including supramolecular chemistry [6], molecular recognition [7,8], and asymmetric organo- or transition metal catalysis [9,10]. Since helicenes are commercially available, their derivatization studies have emerged [11].

Cation- π interaction refers to the noncovalent attraction between a cation (e.g., Li^+ , Na^+ , or K^+) and a π -system (e.g., benzene) [12]. Its strength is often comparable with the interaction between a cation and traditional ligands, including water, alcohols, and

amines. As a result of the cation- π interaction, there are extraordinarily important driving forces in molecular recognition processes in many biological and artificial systems [13–16]. The cation- π interaction is a well established phenomenon in the gas phase, as well as in the solid state [17–23], and is known to play an important role in the stabilization of tertiary structures of various proteins [24].

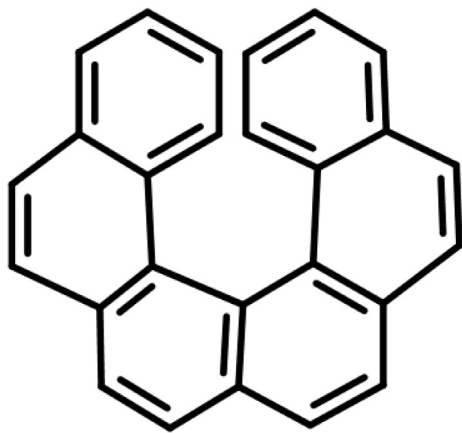
In the current work, electrospray ionization mass spectrometry (ESI-MS) was used as an experimental technique for characterization of the cation- π interaction between the univalent thallium cation (Tl^+) and the electroneutral [6]helicene ($C_{26}H_{16}$; see Scheme 1) ligand in the gas phase. At this point it should be noted that the numerous arene complexes of $Tl(I)$ have been described in the solid state [25], however, up to now, a cation- π complex with [6]helicene has not been proven. Moreover, applying quantum mechanical DFT calculations, the most probable structure of the experimentally proven cationic complex $[Tl(C_{26}H_{16})]^+$ was predicted.

2. Experimental

[6]Helicene (puriss., $\geq 99\%$) was purchased from Lach-ner, Czech Republic, while thallium(I) trifluoromethanesulfonate (puriss.,

* Corresponding author.

E-mail address: makrlik@centrum.cz (E. Makrlík).



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Scheme 1. Structural formula of [6]helicene ($C_{26}H_{16}$).

$\geq 99\%$), $TlCF_3SO_3$, was supplied by Fluka. In this context it should be emphasized that thallium has two stable isotopes, i.e., ^{203}Tl (natural abundance: 29.524%) and ^{205}Tl (natural abundance: 70.476%). The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity.

The experiments were carried out with a 3200 Q TRAP (AB Sciex, Canada) mass spectrometer fitted with an electrospray ionization source. A mixture of [6]helicene and $TlCF_3SO_3$ (both ~ 2.5 mg/L) dissolved in acetonitrile/chloroform (1:1) was introduced into the ESI source via a PEEK capillary at a flow rate of $10 \mu L/min$. Nitrogen was used as a nebulizer gas. The operating conditions for the mass spectrometer were set as follows: ionspray voltage 5.5 kV; curtain gas 10, ion source gas(1) 18, and ion source gas(2) 0 arbitrary units; ion source temperature ambient; declustering potential 70 V, entrance potential 10 V. Mass spectra were recorded from m/z 100 to 1000.

The collision induced dissociation (CID) mass spectra were measured on the Quattro Premier XE quadrupole tandem mass spectrometer (Waters, UK) equipped with an electrospray ion source. A mixture of [6]helicene and $TlCF_3SO_3$ was introduced into the ESI source at a flow rate of $20 \mu L/min$. The operating conditions of the ion source were as follows: capillary voltage 3.0 kV, cone voltage 40 V, extraction voltage 5 V, source temperature $100^\circ C$, desolvation gas (nitrogen) temperature $200^\circ C$, desolvation gas flow rate 100 L/h. In the CID experiments, argon was used as a collision gas at the pressure of 1×10^{-2} mbar. The laboratory frame collision energy was set to 15 eV.

3. Results and discussion

Fig. 1 shows an ESI mass spectrum obtained in a positive mode for a mixture of [6]helicene with $TlCF_3SO_3$ in an acetonitrile/chloroform (1:1) solution. The peak observed at m/z 531.1 belongs to the cationic complex $[Ti(C_{26}H_{16})]^+$, the ion radical $[C_{26}H_{16}]^{+\bullet}$ can be seen at 328.1, while the peaks at m/z 203.0 and 244.0 correspond to the cations Tl^+ and $[Ti(CH_3CN)]^+$, respectively. In this context it is necessary to emphasize that under the present experimental conditions, the $[Ti(C_{26}H_{16})]^+$ cationic complex species was proven quite unambiguously in the gas phase. No other [6]helicene complexes with Tl^+ were found by using this experimental method.

Fig. 2a shows a CID mass spectrum of the ions $[^{203}Ti(C_{26}H_{16})]^+$ (m/z 531), where the only one significant fragment ion signal was

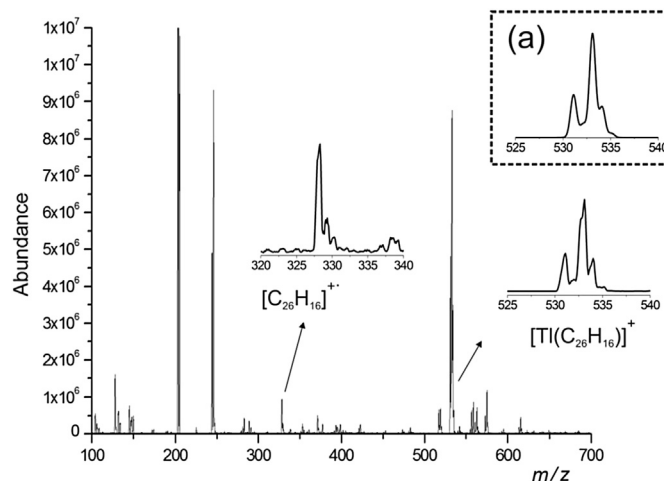


Fig. 1. Positive mode ESI mass spectrum of a mixture of [6]helicene and $TlCF_3SO_3$ (both ~ 2.5 mg/L) in acetonitrile/chloroform (1:1). The insets show the isotope patterns of the $[Ti(C_{26}H_{16})]^+$ complex and the cation radical $[C_{26}H_{16}]^{+\bullet}$ on an expanded mass scale. The inset (a) provides the calculated isotope pattern of the considered $[Ti(C_{26}H_{16})]^+$ complex.

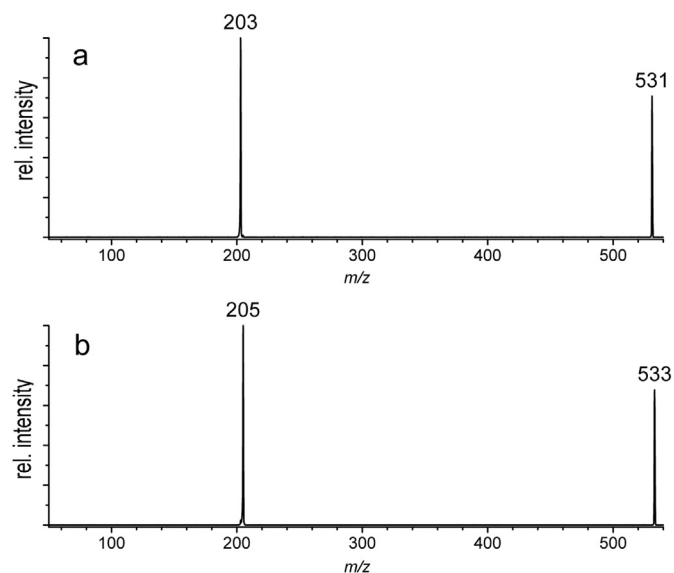


Fig. 2. CID mass spectra of (a) $[^{203}Ti(C_{26}H_{16})]^+$ and (b) $[^{205}Ti(C_{26}H_{16})]^+$ ions obtained with argon (1×10^{-2} mbar) at collision energy of 15 eV (laboratory frame).

observed at m/z 203. Similarly, in a CID mass spectrum of $[^{205}Ti(C_{26}H_{16})]^+$ (m/z 533, Fig. 2b), the sole fragment ions at m/z 205 were found. These facts clearly indicate that the only significant fragmentation channel in the investigated complex $[Ti(C_{26}H_{16})]^+$ is the loss of one electroneutral [6]helicene ligand.

Fragmentation behavior of this $Tl(I)$ complex can be explained in terms of generalized Stevenson's rule [26]. The ionization energy of [6]helicene is 7.37 eV [27]. On the other hand, the ionization energy of the Tl atom is 6.10829 eV [28], and thus the elimination of [6]helicene from the cationic complex $[Ti(C_{26}H_{16})]^+$ connected with the following formation of the Tl^+ cation is energetically favored over the other possible fragmentation channels.

In summary, we have proven experimentally that the cationic complex $[Ti(C_{26}H_{16})]^+$ exists in the gas phase, and when this complex is collisionally activated, it decomposes almost exclusively via elimination of the electroneutral [6]helicene molecule (i.e., $C_{26}H_{16}$), while the charge is retained on the thallium atom in the

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