

Electronic Supplementary Information

Mechanistic Aspects of the Gas-Phase Coupling of Thioanisole and Chlorobenzene to Dibenzothiophene Catalyzed by Atomic Ho⁺

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Dedicated to Professor R. N. Zare, Stanford University, on the occasion of his 75th birthday.

Experimental Section and Computational Details

The experiments were carried out in a Spectrospin-CMS-47X Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer as described elsewhere¹⁻³. Holmium cations Ho⁺ were generated by laser ablation of holmium target using a Nd:YAG laser ($\lambda=1064$ nm) with helium as carrier gas; the holmium target was prepared using a pure metal foil commercially available from Sigma-Aldrich Corporation. The ions generated were transferred from the external ion source into the cylindrical ICR-cell which is fixed in a superconducting magnet field (7.05T), by using a system of electrostatic potentials and lenses. Mass selection was performed using the FERETS⁴ ion ejection protocol. Thermalization of the ions of interest has been achieved by collisions with repeatedly pulsed-in argon. Reaction efficiencies were determined via the pseudo-first-order decay of the reactant ions and are reported as percentage of the theoretical collision rate according to the average dipole orientation approximation (k_{ADO})⁵. Collision-induced dissociation experiments were performed for structural investigations via introducing argon into the ICR cell for collisions with the ion of interest; prior to that, the latter ion has been translationally excited to increase its kinetic energy.

The theoretical studies were performed using the Gaussian 09 program⁶ at the density functional theory level of theory using the B3LYP⁷⁻¹⁰ functional including DFT-D3 dispersion correction¹¹; a small-core pseudo potential¹² and the corresponding atomic natural orbital contracted valence basis sets^{13,14} were applied for holmium, and the def2-TZVP basis set¹⁵ was used for all other atoms. Stationary and saddle points were located and confirmed by vibrational frequency analysis. Intrinsic reaction coordinate¹⁶⁻¹⁸ calculations were performed to link transition structures with the respective intermediates. The Natural Bond Orbital¹⁹⁻²⁴ (NBO) analysis was performed to obtain the electronic configurations of the different structures. Finally, unscaled vibrational frequencies were used to include zero-point energy (ZPE) corrections.

Figures

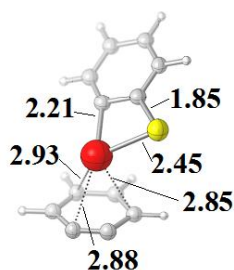


Fig. 1 Structural information of the complex of $\text{Ho}(\text{C}_6\text{H}_4\text{S})^+$ with benzyne ($[\text{Ho}(\text{C}_6\text{H}_4\text{S})(\text{C}_6\text{H}_4)]^+$). Selected bond lengths are given in Å; charges are omitted for the sake of clarity.

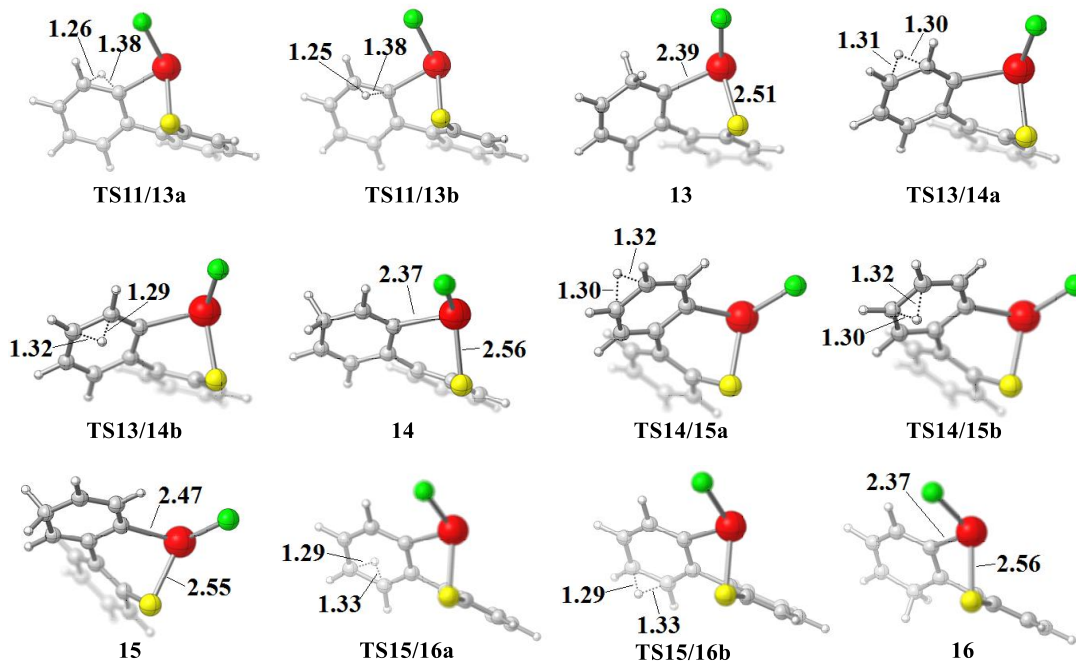


Fig. 2 Structural information of the associated coordinates for the hydrogen migration along the phenyl ring starting from intermediate **11**; the notations **a** and **b** for the transition structures stand for the migrations on both sites of the ring, respectively. Selected bond lengths are given in Å; charges are omitted for the sake of clarity.

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