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Calix[4]pyrrole錯体におけるハロゲン化物アニオン認識 によるイオンペア形成に関する計算

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Calix[4]pyrrole (C4P) is an organic macrocycle made of four pyrrole units connected to each other via a carbon bridge. C4P has the ability to interact with halide anions through the formation of four equivalent N-H...X⁻ hydrogen bonds. Although a wide number of experimental and theoretical studies have been carried out, the mechanism of selective anion recognition is still a matter of debate [1]. In this poster we investigate the effect of ion-pair formation on the recognition of halide anions by C4P. The starting point of our study is represented by the experimental crystal structure of the ternary complex Cl⁻:C4P:⁺N(*n*-butyl)₄ (CSD refcode: TEQKIJ) [2] shown in Figure 1. The asymmetric unit cell of the complex contains also a molecule of CH₂Cl₂ which was used as solvent. The solvent, however, does not have strong interactions with the complex and, hence, we did not include it explicitly in our subsequent quantum chemistry calculations.

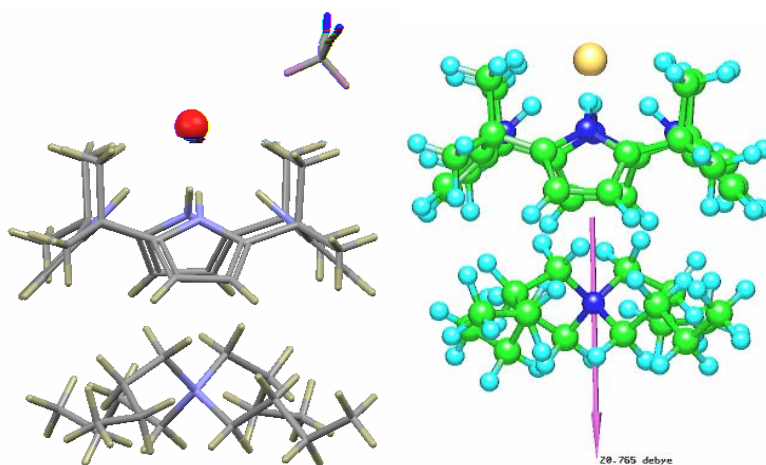


Figure 1. Crystal structure (left) and optimized geometry (right) of the Cl⁻:C4P:⁺N(*n*-butyl)₄ complex.

The geometry of the Cl⁻ complex was optimized with the AM1-COSMO method so as to model a water solution environment. The optimized structure of this complex is shown in Figure 1. As seen in this figure, the dipole moment vector is directed along the direction connecting the H-bonded halide anion and the N atom of the counterion. Next, we replaced the Cl⁻ anion with F⁻, Br⁻, and I⁻ anions and repeated the geometry optimizations. Table 1 summarizes the results of the AM1-COSMO calculations performed on the four halide complexes. The computed heats of formations (HOF) are all positive. The dipole moments increase from 18.51 D (F⁻) to 22.77 D (I⁻). The net charge of the anions is lower

than 1- since there is some charge transfer upon formation of four H-bonds with the pyrrole units of C4P. Interestingly, the Mulliken charge of the N atom in the quaternary ammonium ion is constant in all complexes thus indicating that there is not significant charge transfer between ${}^+\text{N}(n\text{-butyl})_4$ and C4P.

Table 1. Results from AM1-COSMO calculations.

X	HOF (kcal/mol)	IP (eV) ^a	H-L (eV)	Dipole (Debye)	q(X ⁻)	q(N ⁺)
F ⁻	39.456729	8.18	8.363	18.51	-0.788	0.040
Cl ⁻	20.042730	8.24	8.383	20.77	-0.819	0.041
Br ⁻	42.407855	8.26	8.386	21.50	-0.794	0.040
I ⁻	67.866482	8.29	8.411	22.77	-0.801	0.041

^aFrom the Koopmans theorem.

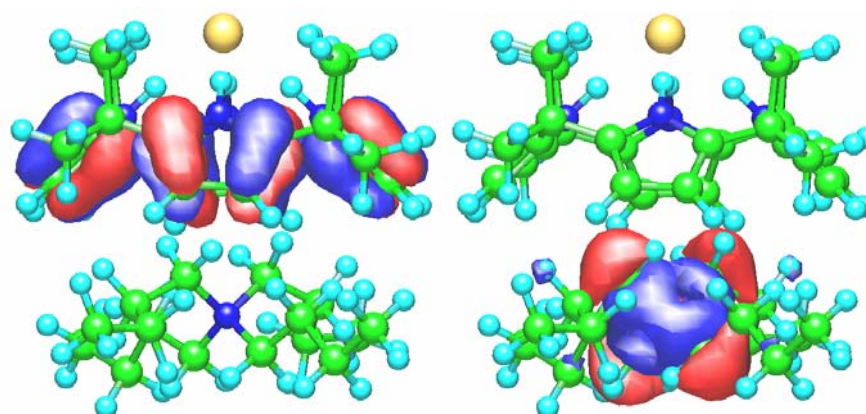


Figure 2. Frontier orbitals HOMO (left) and LUMO (right) of the Cl⁻:C4P:⁺N(*n*-butyl)₄ complex.

Figure 2 shows the frontier orbitals HOMO and LUMO of the Cl⁻ complex. This result indicates that, if the complex is irradiated with UV-vis light, valence electrons are expected to be transferred from C4P to ${}^+\text{N}(n\text{-butyl})_4$ while leaving the anion undisturbed. We also investigated the electronic structure of the four complexes using DFT methods. The structures of these complexes were fully optimized at the MPWB1K/3-21G level of theory. Our DFT results are in good agreement with the results of semiempirical MO calculations and they indicate that the negative charge is concentrated mainly on the chloride anion whereas positive charge is delocalized all over the N(*n*-butyl)₄ cation.

[1] F. Pichierri, *Theochem* 581 (2002) 117.

[2] P.A. Gale et al. *J. Am. Chem. Soc.* 118 (1996) 5140.