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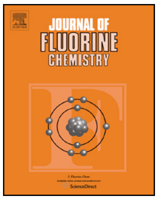

Pseudorotation as a mechanism for intramolecular electron density transfer. Fragmentation of the octafluoronaphthalene radical anion

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ABSTRACT

Adiabatic potential energy surface (PES) of the octafluoronaphthalene radical anion (RA) has been investigated with the B3LYP/6–31 + G* calculations for the gas phase and polar media. In spite of the low symmetry of the RA its PES has been found to be the surface of pseudorotation. The pseudorotation is a way of intramolecular electron density transfer and so played the key role in regioselectivity of the RA fragmentation through the fluoride ion elimination. Transition states for α and β C–F bond cleavage in the polar solvent were located. The noticeably lower energy barrier for the β C–F bond cleavage explains the observed regioselectivity of the octafluoronaphthalene reductive defluorination.

1. Introduction

Radical anions (RAs) are known to be the key intermediates of polyfluoroarenes reductive defluorination [1,2]. Regioselectivity of this reaction is determined by ability of the RA to eliminate fluoride ion from different positions of aromatic skeleton. The C–F bonds bearing the most unpaired electron density are usually supposed to be broken. However, reductive defluorination of octafluoronaphthalene by zinc in aqueous ammonia yields only the product of β-defluorination [3] that conflicts with the well known prevail location of the naphthalene LUMO in α positions (see for example [4]).

Octafluoronaphthalene RA, $C_{10}F_8^{-}\bullet$, was registered by ESR [5,6]. Sufficiently large values of hyperfine coupling (hfc) constants observed, $a_F = 22.1|(4F)$ and $28.5|(4F)$ G, testify to non-planar RA structure [7], though no theoretical analysis of hfc parameters was performed. However, geometry optimization at the B3LYP/DZP++ level of calculations has led to the structure of C_{2h} symmetry with the fluorine atoms deviated from rings plane by the value about 5–6 degrees [8]. Note that out-of-plane distortions possess the mirror symmetry, so the PES has certainly more than one minimum.

The general aim of our investigations is to establish the relation between the PES structure of the fluoroarene RAs and their spectral and chemical properties. Here we have performed detailed quantum chemical study of adiabatic PES for $C_{10}F_8^{-}\bullet$ in the gas phase and polar media and applied the obtained results for interpretation the hfc parameters of the RA and its reactivity toward the fluoride ion elimination including the reaction regioselectivity. As we know, position selectivity of polyfluoroarene anions cleavage has not been investigated earlier by the quantum chemical methods.

2. Computational details

The PES study was performed at the ROHF/6–31G* and UB3LYP/6–31 + G* calculation levels. Stationary PES points were located and their types were determined by the normal vibrations analysis. Interrelations between transition states (TS) and minima on the PES were established by the intrinsic reaction coordinate (IRC) technique. We used the polarizable continuum model (PCM) to treat the solvent effects for model H_2O solvent. For the clear understanding of the stationary RA structures origin we fulfilled the ROHF/6–31G* calculations of lower anion states for the planar D_{2h} structure of the neutral $C_{10}F_8$. The HF solutions for the states of different symmetry were obtained by changing the initial guess. All calculations were done with the GAMESS package [9]. The structure images and molecular orbital (MO) plots were made by the MOLDEN program [10].

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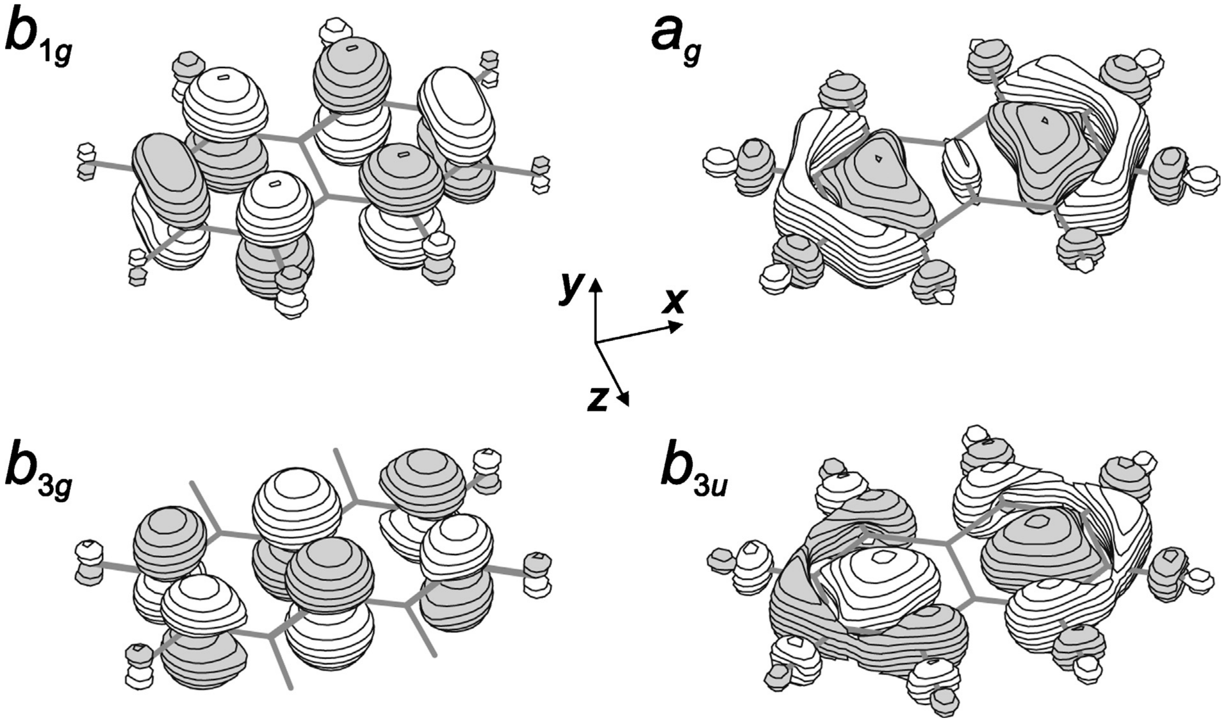

Fig. 1. SOMO plots of the lowest π and vibronically active σ states for the D_{2h} ($^2B_{1g}$) structure of $C_{10}F_8^{-}\bullet$ (ROHF/6–31G*).

3. Results and discussion

3.1. The Hartree–Fock calculations

First, we consider the ROHF/6–31G* calculation results as a useful starting point for investigation of the $C_{10}F_8^{-}\bullet$ PES formation. Fig. 1 shows single occupied MOs (SOMOs) for the lower anion states of the $C_{10}F_8$ molecule (D_{2h} symmetry). The $C_{10}F_8^{-}\bullet$ PES structure is determined by avoided crossing of the $^2B_{1g}$ and $^2B_{3g}$ π states. There are two stationary structures on the PES, D_{2h} ($^2B_{1g}$) and D_{2h} ($^2B_{3g}$), corresponding to a minimum and TS, respectively. Note that at this level of calculation both the π structures are stable toward out-of-plane distortions that conflicts with the ESR data [5,6].

Energy difference between the TS and minimum structures is equal to 6.6 kcal/mol. Descent from the TS in both directions of the active b_{2g} coordinate leads to the D_{2h} ($^2B_{1g}$) minimum so the PES has

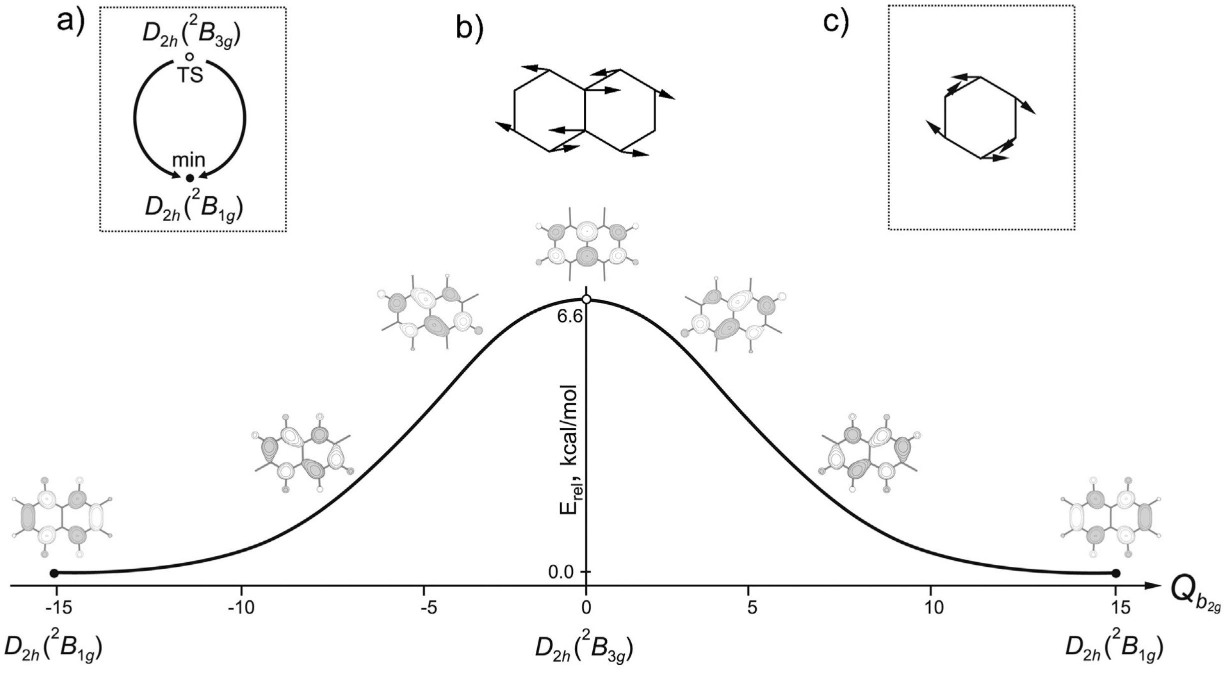

Fig. 2. (a) The scheme of $C_{10}F_8^{-}\bullet$ PES by the data of ROHF/6-31G* calculations. (b) The PES section along the active Q_{b2g} coordinate (IRC points) with the respective SOMO evolution. The active b_{2g} mode is shown on the top. c) The pseudorotational b_{2g} mode for $C_6H_6^{-}\bullet$.