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Comparative semiempirical, ab initio, and DFT study of interactions between polypyrrole pentamer dication and some anions

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Abstract. Complexes between pyrrole pentameter dication and chloride, bromide, and perchlorate anions were studied using AM1, PM3, HF/3-21+G$^{(*)}$, and B3LYP/6-31+G** methods. The resulting complexation energies were in agreement with the trends in the ionic radiuses of the anions. Semiempirical methods were found to underestimate the complexation energy of the perchlorate anion and in the case of PM3 also the bromide anion. HF/3-21+G$^{(*)}$ also gave a too narrow range of complexation energies, in addition nonplanarity of the dication was not observed. The DFT B3LYP/6-31+G** method, while being most consistent, yielded some complexation energies with slightly higher BSSE than expected.

Key words: polypyrrole, anions, DFT, ab initio, AM1, PM3.

INTRODUCTION

Intrinsic conducting polymers with conjugated double bonds have been under intense investigation for more than twenty years already. Polypyrrole (PPy), together with polythiophene and polyaniline, is among the most promising candidates for wide applications for its good environmental stability, simple synthesis, and high conductivity. The applications of PPy include (but are not limited to) various sensors, functional membranes, selective coatings, polymeric batteries and capacitors, electrochromic windows and displays, etc. [1, 2].

Polypyrrole is commonly synthesized by means of the electrochemical polymerization of pyrrole from a solution of some supporting electrolyte. Both aqueous

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and nonaqueous solutions can be used. The thickness, structure, and other properties of the polymer film formed on the anode can be varied within a wide range by altering the electrodeposition conditions or the composition of the solution. The role of the anions incorporated into the polymer film in order to maintain electroneutrality is not limited to the stabilization of the opposite charge. The anions also play a key role in the formation of the structure of the polymer chains, participating therefore in the origination of the properties of the whole polymer film [1, 3–5]. Thorough understanding of the influence of anions on the structure and properties of the conducting polymers would, therefore, enable the synthesis of conducting polymers of specific predefined properties. While a wide variety of experimental methods have been applied for the investigation of the influence of dopant anions on the properties of conducting polymers [6–10], theoretical treatments are commonly limited to substituted or unsubstituted neutral oligomers [11, 12] or their cationic and anionic forms [13, 14]. Lattice simulations of the placement and movement of chloride and tetrafluoroborate anions inside polymer films [15, 16] are among the very few investigations reported.

METHODOLOGY

All oligopyrroles dications and their complexes with anions were treated as conventional closed shell systems. No solvation models were applied, as the use of continuum models can hardly be justified for polymer films containing only limited solvent molecules per chain and in the vicinity of charged electrodes. Small hard inorganic anions are known to have strong interaction with conducting polymers, and the amount of solvent inside the polymer as well as solvent movement into and out of the polymer during redox cycling is relatively limited [7–10]. There is very little experimental evidence about the actual structure, composition, and interactions inside PPy films. While most investigations presume that PPy chains always take the planar all-*anti* form, a series of STM images of PPy doped with large (polymeric) anions published already a while ago [17–19] suggest that under some conditions the helical structures, apparently formed from all-*syn* pyrrole chains, are the predominant form of the polymer. It has also been shown that the rotational barriers between pyrrole units are not very high [11, 20], therefore, only the energetically more favoured all-*syn* oligomers [21] were considered in the present study for anion-charged oligomer complexes. While the simple model used in this work cannot accurately reflect the reality in its full complexity, it is focused on the anion–polymer chain interactions. The choice of short oligomers enables the search for fully relaxed conformations with no periodic or planarity constraints using reasonably elaborate methods.

Semiempirical calculations with AM1 [22] and PM3 [23] methods were carried out using the Spartan program [24]. Standard ab initio (HF) calculations using the 3-21+G$^{(*)}$ [25–29] basis set (for bromine polarization functions from standard 6-31+G* basis set were added to 3-21+G basis) and density functional calculations with the B3LYP hybrid functional [30–33] and 6-31+G** [29, 34–37] basis set were performed using the Gaussian 03 [38] program package. All geometries were fully optimized and the frequencies were calculated at the respective levels. Harmonic frequency analysis indicated that all structures were minima on the potential energy surface (i.e. number of imaginary frequencies, NImag = 0). No scaling was applied to the obtained frequencies for the calculation of enthalpies and free energies. Heats of formation calculated with AM1 and PM3 methods are reported in Table 1. Total energies, enthalpies, and Gibbs free energies calculated with ab initio and DFT methods are given in Table 2.

Complexation energies were calculated in the usual way, that is as energies for reaction (1)

$$Py_5^{2+} + An^- = [Py_5An]^+, \tag{1}$$

$$E(1) = E([Py_5An]^+) - [(E\,(Py_5^{2+}) + E\,(An^-)], \tag{2}$$

where E denotes either electronic energy, enthalpy, or free energy. It is well known that complexation energies calculated in such a way may be seriously

Table 1. Heats of formation (ΔH_f, in kcal/mol) calculated with AM1 and PM3 methods

	ΔH_f(AM1)	ΔH_f(PM3)
Cl^-	−37.7	−51.2
Br^-	−20.4	−56.2
ClO_4^-	166.5	−128.1
PPy^{2+}	576.9	517.3
$PPy^{2+}–Cl^-$	352.8	277.4
$PPy^{2+}–Br^-$	372.4	291.6
$PPy^{2+}–ClO_4^-$	587.2	238.9

Table 2. Electronic energies (E), enthalpies (H), and free energies (G) calculated at the HF/3-21+G$^{(*)}$ and B3LYP/6-31+G** levels (in a.u.)

	E	H	G
HF/3-21+G$^{(*)}$			
Cl^-	−457.46831	−457.46595	−457.48333
Br^-	−2560.31135	−2560.30899	−2560.32753
ClO_4^-	−754.96998	−754.94954	−754.97947
PPy^{2+}	−1033.28705	−1032.89704	−1032.96274
$PPy^{2+}–Cl^-$	−1491.05121	−1490.65894	−1490.72663
$PPy^{2+}–Br^-$	−3593.88676	−3593.49456	−3593.56351
$PPy^{2+}–ClO_4^-$	−1788.53563	−1788.12267	−1788.19883
B3LYP/6-31+G**			
Cl^-	−460.27473	−460.27237	−460.28975
Br^-	−2571.80318	−2571.80082	−2571.81936
ClO_4^-	−760.83085	−760.81150	−760.84426
PPy^{2+}	−1045.64298	−1045.28489	−1045.35772
$PPy^{2+}–Cl^-$	−1506.21870	−1505.85770	−1505.93243
$PPy^{2+}–Br^-$	−3617.75114	−3617.39035	−3617.46545
$PPy^{2+}–ClO_4^-$	−1806.74592	−1806.36526	−1806.44749

Table 3. Calculated complexation energies (ΔE), enthalpies (ΔH), and free energies (ΔG), all in kcal/mol

	AM1	PM3	HF			B3LYP		
	ΔH	ΔH	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
PPy^{2+}–Cl^-	−186.4	−188.7	−179.8	−179.9	−170.2	−188.3	−187.9	−178.2
PPy^{2+}–Br^-	−184.1	−169.5	−172.4	−172.5	−162.9	−181.3	−181.1	−170.9
PPy^{2+}–ClO_4^-	−156.2	−150.3	−160.7	−159.1	−146.9	−167.8	−165.8	−151.1

affected by the artificial lowering of the energy of the complex due to the basis set superposition error (BSSE) (see e.g. [39], p. 172). We estimated the magnitude of the BSSE using the standard counterpoise correction method [40–41]. The size of BSSE is thought to diminish with the increase of basis set. However, in the case of the PPy–Br complex the BSSE is found to be greater at the B3LYP/6-31+G** level than at the HF/3-21+G$^{(*)}$ level, in accordance with our earlier claim that the 6-31+G* basis set for bromine is not well balanced [42]. Calculated complexation energies, enthalpies, and free energies are given in Table 3 with BSSE correction included.

RESULTS AND DISCUSSION

Energies

Ab initio and DFT complexation energies, given in Table 3, agree reasonably well with each other. The trend in complexation energies calculated at that level follows reasonably well the ionic radiuses (1.67, 1.92, and 2.40 Å for chloride, bromide, and perchlorate, respectively [43]) of the studied ions (Fig. 1), indicating that the interaction between cations and the pyrrole pentamer dication is mainly ionic. The semiempirical AM1 and PM3 methods give the same complexation energy order as ab initio and DFT calculations, while the differences between complexation energies of different anions do not follow those calculated at higher levels so closely. It seems that both semiempirical methods underestimate the complexation energies for the perchlorate anion (probably due to the lack of d-functions and consequent rigidity of the basis set).

The difficulties with semiempirical methods became especially clear when comparing relative complexation energies (see Table 4). It is apparent that both the ab initio and DFT methods used give these in good accordance, while the results of AM1 and PM3 methods differ considerably among themselves and also from the results of the ab initio and DFT calculations. The discrepancies among the semiempirical results are largest for the case of bromide anions, where the PM3 parametrization largely underestimates the complexation energies of the bromide anion. Compared to the semiempirical and DFT methods, the HF/3-21+G$^{(*)}$ method somewhat underestimates the differences in complexation energies between the oligomer dication and different anions.

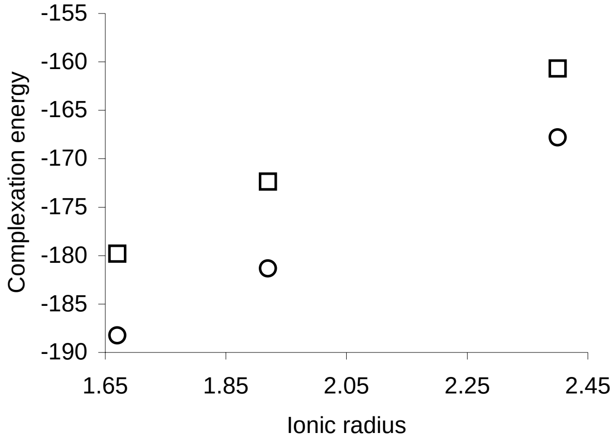


Fig. 1. Dependence of the complexation energies (kcal/mol) calculated at HF/3-21+G$^{(*)}$ (□) and B3LYP/6-31+G** (○) levels from ionic radiuses (Å, [43]).

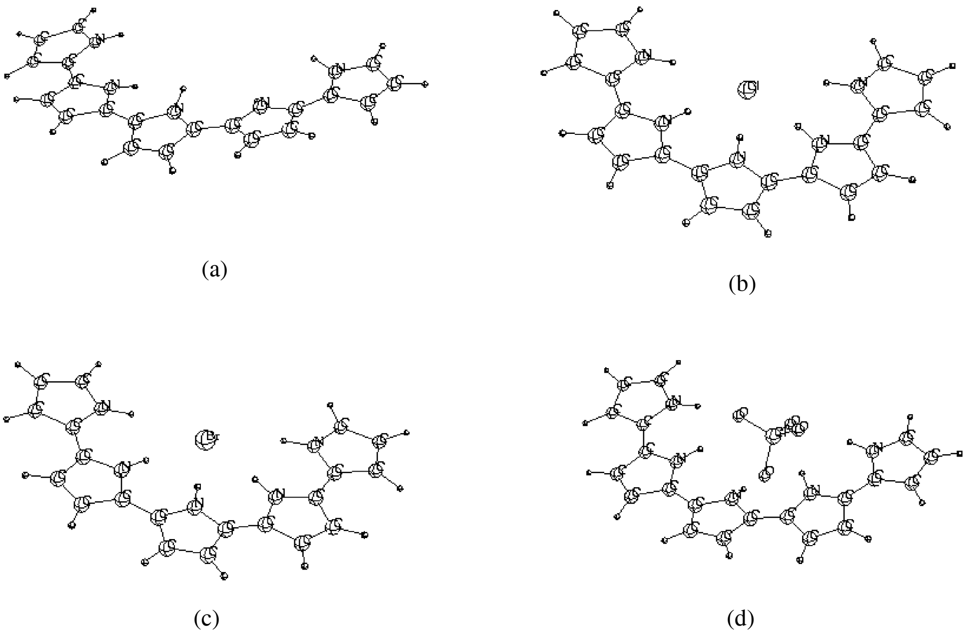
Table 4. Relative complexation enthalpies (ΔΔH, relative to PPy^{2+}–Cl^{-}, in kcal/mol)

	AM1	PM3	HF	B3LYP
PPy^{2+}–Br^{-}	−2.3	−19.2	−7.4	−6.8
PPy^{2+}–ClO$_4^{-}$	−30.2	−38.4	−20.8	−22.1

Geometries

The geometries of PPy pentamer and its complexes are given in Fig. 2. The most striking feature of structures in Fig. 2 is the nonplanarity of the N–H bonds of pyrroles with the rest of pyrrole ring in free pentamer dication, observed at the B3LYP/6-31+G** level. The nonplanarity is greatest at the central pyrrole unit and diminishes towards the ends of the PPy chain. The pyrrole units in the PPy pentamer dication were found to be twisted with respect to each other at the B3LYP/6-31+G** level. Similar nonplanarity of the N–H bond in pyrrole fragments, but only for the central fragment, was observed also at the AM1 and PM3 levels of calculations. The HF/3-21+G$^{(*)}$ calculations yielded a perfectly planar pentamer.

Upon complexation with an anion the PPy pentamer dication becomes planar to allow better interaction with the anion. The only exception here is the complex of the PPy pentamer dication with the perchlorate anion, where the N–H bond of the central pyrrole unit is again out of the plane defined by the rest of the PPy pentamer dication.



(a) (b) (c) (d)

Fig. 2. Structure of pentapyrrole dication (a) and its complexes with chloride (b), bromide (c), and perchlorate (d) anions calculated at the B3LYP/6-31+G** level.

CONCLUSIONS

The complexes of pyrrole oligomer dications with three inorganic anions were studied using semiempirical, HF, and DFT methods. The resulting complexation energies are in agreement with the ionic radiuses of the anions. The geometries of the dication and of the complex with the perchlorate anion were found to be nonplanar according to DFT calculations. Such calculations of relatively nontrivial systems should always be done using several computational methods as the results of different methods are seldom matching. In the present case, semiempirical methods underestimated the complexation energy of the perchlorate anion and in the case of PM3 also the bromide anion. HF/3-21+G$^{(*)}$ has a limited range of complexation energies, making them look more similar; besides, nonplanarity of the dication is not observed. The DFT B3LYP/6-31+G** method, while being most consistent, yields some complexation energies with a slightly higher BSSE than expected.

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Polüpürrooli pentameeri dikatiooni ja mõningate anioonide vaheliste interaktsioonide võrdlev poolempiiriline, *ab initio* ja DFT-uurimus

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Polüpürrooli pentameeri dikatiooni ning kloriid-, bromiid- ja perkloraatanioonide vahelisi interaktsioone on uuritud AM1-, PM3-, HF/3-21+G$^{(*)}$- ja B3LYP/6-31+G**-meetoditega. Saadud kompleksseerumisenergiad olid heas kooskõlas anioonide raadiuste kasvuga reas Cl^-, Br^-, ClO_4^-. Poolempiirilised AM1- ja PM3-meetodid alahindasid perkloraataniooni kompleksseerumisenergiat, samuti alahindas PM3-meetod ka bromiidaniooni kompleksseerumisenergiat. Ka HF/3-21+G$^{(*)}$-meetodi korral olid leitud kompleksseerumisenergiad suhteliselt kitsas vahemikus. Kasutatud meetoditest andis parimaid tulemusi B3LYP/6-31+G**, samas olid selle meetodi korral baasi superpositsiooni vead oodatust suuremad.