

Quantum Chemical Investigations on Stabilities of Protonated Species of 25,27-{2,2'-(2,2'-((2,5,8-triazanonyl)diphenoxy)diethyl)-*p*-tert-butylcalix(4)arene

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ABSTRACT Protonation on the nitrogen donor atoms of the 25,27-{2,2'-[2,2'-((2,5,8-triazanonyl)diphenoxy)diethyl]-*p*-tert-butylcalix[4]arene (L) has been investigated by quantum-chemical calculations. The optimized structures of the ligand L and its protonated species were obtained by the semi-empirical PM3 method. The stabilization energies of the protonated species of the ligand L were derived from the *ab initio* calculations with STO-3G, 3-21G and 6-31G basis sets including counterpoise correction.

KEYWORDS: *ab initio* calculations, calix[4]arene, protonation, stabilization energy, counterpoise method, equilibrium constant.

INTRODUCTION

The macrocyclic ligands containing nitrogens as donor atoms¹⁻³ and the polyaza derivatives of the calix[4] arenes⁴⁻⁵ were widely studied in terms of the basicity constants. The studies of these compounds have never given any information on the sequence of protonation on their nitrogen donor atoms. In order to get the protonation sequence on the nitrogen donor atoms of the mentioned compounds and the stability of their complexes with alkaline and alkaline earth metals,⁶⁻⁸ the quantum-chemical approach has been usually applied. The stabilization energies of the protonated species of the 1,4,7,10-tetraazacyclododecane (cyclen) were determined by the *ab initio* LCAO-MO-SCF calculations.⁸ This basic knowledge of the protonation of the cyclen which contains four nitrogen donor atoms was very useful to get understanding of the complex formations of the macrocyclic compounds containing nitrogen donor atoms such as cyclen complexes with many metal ions.⁹⁻¹¹

In this work, the quantum-chemical energies for the 25,27-{2,2'-[2,2'-((2,5,8-triazanonyl)diphenoxy)diethyl]-*p*-tert-butylcalix[4]arene¹² and its protonated species have been evaluated in order to get more understanding on the protonation mechanism. The basis set superposition error of the *ab initio* MO-SCF calculations for interaction energies of their related configurations has been substantially reduced by the procedure of the counterpoise correction.^{7,13}

METHODS

The structures of the 25,27-{2,2'-[2,2'-((2,5,8-triazanonyl)diphenoxy)diethyl]-*p*-tert-butylcalix[4]arene (L) and its protonated species were optimized by the semi-empirical PM3 method. The stabilization energies of the protonated species of the ligand L were derived from the *ab initio* MO-SCF computations employing STO-3G,¹⁴ 3-21G¹⁵ and 6-31G¹⁶ basis sets. Counterpoise correction¹³ was included into the *ab initio* calculations with STO-3G, 3-21G and 6-31G basis sets, in order to improve the interaction energy between two reactants in the protonation process. All calculations were performed on the Pentium II/350 IBM-PC-300GL of RAM 128 MB. The program Gaussian 94W¹⁷ were used for all quantum-chemical computations.

RESULTS AND DISCUSSION

The optimized structure of the ligand L obtained from the PM3 method is shown in the Figure 1. The protonations on this ligand L were taken place at the nitrogen atoms by the sequence of N_a at the first, N_c the second and N_b the third (see Figure 1) indicating by their corresponding total energies of -3144.03438, -3144.02259 and -3143.99945 hartrees (by *ab initio* calculations with 3-21G basis set) respectively. The total energies and stabilization energies of the ligand L and its protonated configurations computed by the *ab initio* calculations using STO-3G, 3-21G and 6-31G basis sets are shown

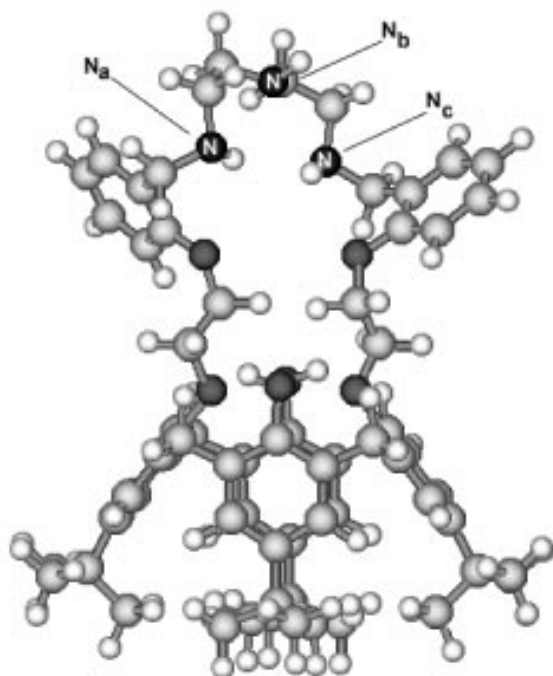
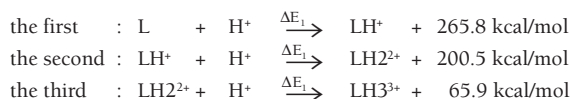


Fig 1. The optimized structure of the 25,27-[2,2'-(2,2'-((2,5,8-triazanonyl)diphenoxy)diethyl)-p-tert-butylcalix[4]arene (L) obtained from the PM3 method.

in Table 1. The *ab initio* energies with STO-3G, 3-21G and 6-31G including the counterpoise procedure to eliminate the basis set superposition error were also evaluated as shown in Table 2.

The stabilization energies of the first (ΔE_1), the second (ΔE_2) and the third (ΔE_3) obtained from the *ab initio* calculations with 6-31G basis set including the counterpoise correction, correspond to the stepwise interaction as shown below,



The optimized distances of hydrogen bonds between proton and N_a , N_b and N_c are 1.0457 1.0192 and 1.0263 Å respectively. The *ab initio* energies of whether obtained by the *ab initio* calculations with 6-31G basis set or with the less accurate basis set such as the 3-21G and STO-3G are acceptable sequences, since their relative values were considered. The most accurate result of the stabilization energies derived from the *ab initio* calculations with 6-31G including the counterpoise procedure has been expected (ΔE_1 , ΔE_2 and ΔE_3 are -265.8, -200.5 and -65.9 kcal/mol). These energies values derived from the *ab initio* calculations using 6-31G basis set with and without the counterpoise

Table 1. The total energies from *ab initio* calculations and DE stabilization energies of the related configurations of the 25,27-[2,2'-(2,2'-((2,5,8-triazanonyl)diphenoxy)diethyl)-p-tert-butylcalix(4)arene and its protonated species.

Configuration	HF / STO-3G // PM3		HF / 3-21G // PM3		HF / 6-31G // PM3	
	Total Energy (hartrees)	ΔE (kcal/mol)	Total Energy (hartrees)	ΔE (kcal/mol)	Total Energy (hartrees)	ΔE (kcal/mol)
L	-3122.55187	-	-3143.61589	-	-3159.85309	-
LH ⁺	-3123.02153	-294.7	-3144.03438	-262.6	-3160.26924	-261.1
LH ₂ ²⁺	-3123.38381	-227.3	-3144.35530	-201.4	-3160.58831	-200.2
LH ₃ ³⁺	-3123.52025	-85.6	-3144.46455	-68.6	-3160.68903	-63.2

Table 2. The *ab initio* energies with STO-3G, 3-21G and 6-31G including the counterpoise procedure of the corresponding subsystem A, B and protonation system (AB), and DE stabilization energy of the related configurations of the 25,27-[2,2'-(2,2'-((2,5,8-triazanonyl)diphenoxy)diethyl)-p-tert-butylcalix(4)arene. A, B and AB denote subsystem of reactance A and B (proton), and system of protonation, respectively.

System of A/B	HF / STO-3G // PM3			HF / 3-21G // PM3			HF / 6-31G // PM3		
	E_A (hartrees)	E_{AB} (hartrees)	ΔE (Kcal/mol)	E_A (hartrees)	E_{AB} (hartrees)	ΔE (Kcal/mol)	E_A (hartrees)	E_{AB} (hartrees)	ΔE (Kcal/mol)
L/H ⁺	-3122.55558	-3123.02153	-292.4	-3143.61064	-3144.03438	-265.9	-3159.84565	-3160.26924	-265.8
LH ⁺ /H ⁺	-3123.03043	-3123.38381	-221.8	-3144.03829	-3144.35530	-198.9	-3160.26873	-3160.58831	-200.5
LH ₂ ²⁺ /H ⁺	-3123.39859	-3123.52025	-76.3	-3144.36124	-3144.46455	-64.8	-3160.58407	-3160.68903	-65.9

EB = EH⁺ = 0

correction are hardly ever different and can be averaged as -263.5 ± 2.4 , -200.3 ± 0.2 and -64.5 ± 1.4 kcal/mol. If the counterpoise correction was applied to the *ab initio* calculations with 3-21G and 6-31G, the same results of the stabilization energies may be obtained. It seems to be that the basis set superposition error has fairly affected on the calculations using the 3-21G and 6-31G basis sets. The *ab initio* energies with the extended basis set of this work (3-21G and 6-31G) and their including the counterpoise method are quite higher than that of the *ab initio* HF-SCF-LCGO energies of the monoprotonation (the first) on the nitrogen of ammonia with the basis sets of subminimal¹⁸ (-252.1 kcal/mol), minimal¹⁹ (-190.0 kcal/mol), minimal with the counterpoise method¹⁹ and extended²⁰ (-216.9 kcal/mol) basis set (the observed energy = -202.0 kcal/mol). The *ab initio* energy with GLO basis set of the first protonation of the cyclen⁸ ($\Delta E_1 = -257.3$ kcal/mol) indicate that the stabilization energy of the first protonation of this work is acceptable result.

The results of the total energies of the ligand L's protonated species correspond to the protonation constants (K) obtained from the previous work.⁵ According to the thermodynamic formulae of the reaction enthalpy ($\Delta H = \Delta G + T\Delta S$) and the dependent of ΔG on the Gibb's free energy ($\Delta G = -2.303RT \log K$), the enthalpy finally becomes the function of log K. From the fact of the stabilization energy, ΔE is closely related to the reaction enthalpy ΔH ($\Delta E = \Delta H - P\Delta V$), the stabilization energy can be written as the function of $-\Delta E = 2.303RT \log K - T\Delta S$. At the constant temperature, if no change of ΔS is occurred, the plot between the stabilization energies of the ligand L's protonated species and their corresponding log K must be linear. A tendency towards such a linear correlation between the computed stabilization energies and their corresponding log K values⁵ of this system cannot be recognized as shown in Figure 2. Small differences in DS and probably also in solvation on the protonated species are important cofactor determining the equilibrium constants. The log K values of reference 5 ($\log K_1 = 11.50$, $\log K_2 = 9.38$, $\log K_3 = 3.22$), represent the equilibria of the L and its related species in the methanol. Although, the stabilization energies of the protonation process from *ab initio* calculations are quite high, the correlation between them and their log K values should be, more or less, closed to the Figure 2. We concluded, therefore, that the solvation by methanol solvent has slightly affected on the protonation process.⁵ Nevertheless, the

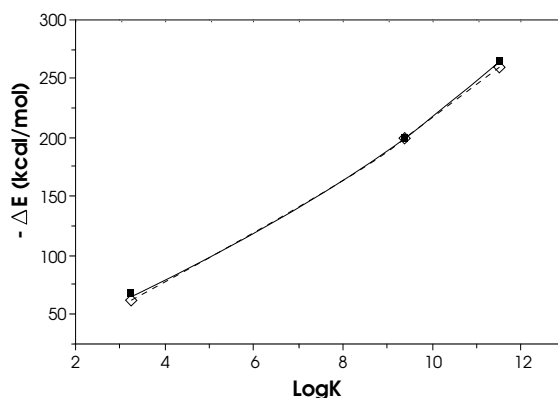


Fig 2. The correlation between the stabilization energies, derived from the *ab initio* calculations using 6-31G basis set with (—) and without (-----) the counterpoise correction, of the protonated species of the 25,27-[2,2'-(2,2'-(2,5,8-triazanonyl)diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene and their corresponding log K.

stabilization energies of the protonation of the ligand L, in Table 1, were not included the methanol molecules as the environmental solvent in the model of calculations. Since, the methanol molecules were included as the solvation of the ligand L in the quantum-chemical calculations, the linear relationship between the stabilization energies of their protonated species and their log K values may not be expected

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