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AB INITIO QUANTUM CHEMICAL STUDIES IN CTAB

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ABSTRACT

Quaternary ammonium compounds (QACS) are employed both as disinfectants for manual processing lines and surfaces in the food industry, and in human medicine area. QACS also cause cell death by protein denaturation . One of the QAC is cetyl trimethyl ammonium bromide (CTAB) that appears to rupture the cell membrane. The primary site of action of CTAB has been suggested to be the lipid components of the membrane, causing cell lysis as secondary effect.

For these important roles of CTAB as a cationic surfactant, CTA (cetyl trimethyl ammonium) was studied as the main active site of CTAB. After optimization the values of thermodynamic functions, chemical shifts and Mulliken charges were obtained by calculation in Gaussian 98 program

Keywords: Surfactant;CTAB;Freq; Chemical shift

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INTRODUCTION

Surfactants are amphiphilic molecules containing a hydrophilic head group that can be charged and a hydrophobic tail. In aqueous solution surfactants assemble in various structures. CTAB, Hexadecyl trimethyl ammonium bromide is a cationic surfactant with a sixteen carbon hydrophobic tail that can assemble into rod-like micelles. CTAB appears to rupture the cell membrane. The primary site of action of CTAB has been suggested to be the lipid components of the membrane, causing cell lysis as secondary effect [2]

Aqueous solution of cetyl trimethyl ammonium bromide (CTAB) form an isotropic phase in different concentration between 0-0.7 mol L⁻¹, above its kraft point (25°C) solutions from the critical micellar concentration, 0.9 mM -0.3 M, contain small spherical micelles with 2 – 6 nm radii. The micelles start to grow after this concentration and become thread-like in shape. Above 0.7 M, a hexagonal liquid crystalline phase is formed consisting of very long rods or threads of CTAB packed in hexagonal array [3].

We know CTAB as a surfactant. The cationic surfactant CTAB is used for control biofilms formed by *Pseudomonas fluorescens* [2].

Because of the strong association of DNA to CTAB containing vesicles, CTAB is widely used in model systems [4]. CTAB as a single-chain surfactant can be incorporated in a triple-chain phosphatidylcholine (TPHPC) monolayer because of its complementary molecule shape and reduces the tilt angle of TPHPC. So the phase and miscibility behaviour of the TPHPC and CTAB were investigated in aqueous dispersions and in monolayers at the air/water interface. Pokhriyal and co-workers studied Rheological behaviour of CTAB/sodium salicylate/oil/water system [3]. So because of the importance of CTAB as a cationic surfactant, we studied CTA (cetyl trimethyl ammonium) as the main active +site of CTAB (see Fig. 1). The frequency and NMR studies were investigated by Gaussian 98 software. The values of chemical shift tensors (isotropic and

anisotropic) were studied theoretically. Some of CTA's thermodynamic values are reported.

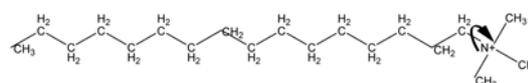


Fig1. Cetyl trimethyl ammonium ion

Computer calculations have come of age, in that they are now regularly able to complement experimental data on fundamental processes that underlie biology, and have been a major complement to modern structural biology. This has partly come about from advances in hardware, software and theory on the one hand and partly from experimental advances on the other.

Computational methods

System has been optimized at the HF level. In all cases the steady-state nature (minimum of the potential energy surface) of the optimized complexes have been confirmed by calculating the corresponding frequencies at the same computational level. For the optimized geometries, the correlations described in this paper were performed with G98 program using the standard 6-31 G basis set. The interaction energies, enthalpies and free energies in cetyl trimethyl ammonium ion were carried out in gas phase. Chemical shift calculations were performed with G98 suit of program using the HF/6-31G approach [4]. This method makes use of an efficient implementation of the gauge including atomic orbitals (GIAO) method [5-10]. The calculated ¹⁵N and ¹³C chemical shielding tensors are reported in present paper. Also Mulliken atomic charges and C—N bond lengths in each NMR calculations are available in this work.

RESULTS AND DISCUSSION

The values of energy differences and C—N bond length in rotations are summarized in table 1. We rotated this ion around C—N bond 10° to 10° (from 0° - 180°). Fig 2a shows ΔE values versus angle of rotation. Fig 2b shows ΔE values versus C—N bond length in every rotation. As you see, ΔE has a linear correspondence with bond length.

Gaussian can compute the vibrational spectra of molecules in their ground and excited states

. In addition to predicting the frequencies and intensities of spectral lines, the program can also describe the displacements a system undergoes in its normal modes. Molecular frequencies depend on the second derivation of the energy with respect to the nuclear positions .

Table1. Energy differences and C—N Bond length for different rotations

Rotation (°)	$\Delta E \times 10^{24}$ (kcal/particle)	C—N Length(Å)
0	0	1.53262
10	0.28	1.53339
20	1.35	1.53628
30	3.29	1.54168
40	5.57	1.54846
50	7.67	1.55408
60	8.37	1.55620
70	7.57	1.55382
80	5.59	1.54810
90	3.18	1.54145
100	1.22	1.53609
110	0.22	1.53329
120	0	1.53267
130	0.35	1.53367
140	1.58	1.53701
150	3.69	1.54279
160	6.08	1.54948
170	8.27	1.55466
180	8.34	1.55612

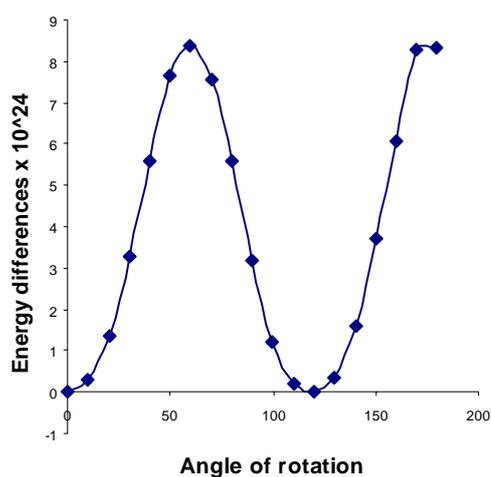


Fig. 2a . Energy differences in kcal mol⁻¹ versus angles of rotation.

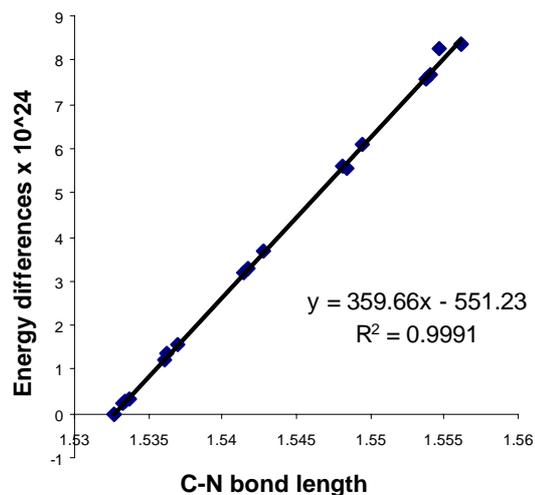


Fig.2b. Energy differences in kcal mol⁻¹ versus C—N bond length.

Because of the nature of the computations involved, frequency calculations are valid only at stationary points on the potential energy surface .

We summarize zero-point energy differences and thermal energy, enthalpy and free Gibbs energy differences by freq calculations in table 2 and the relations between these energy differences versus angle of rotation can be seen in figures from 3 to 6, respectively.

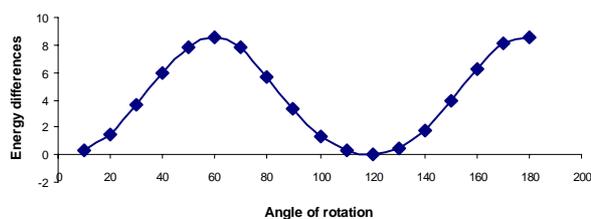


Fig.3. Electronic & zero-point energy differences in kcal mol⁻¹ versus angles of rotation.

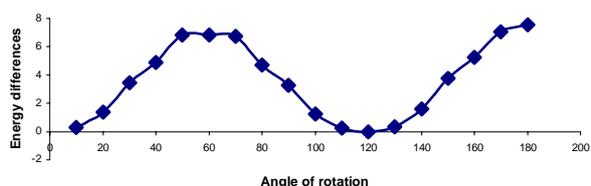


Fig.4. Electronic & thermal energy differences in kcal mol⁻¹ versus angles of rotation.

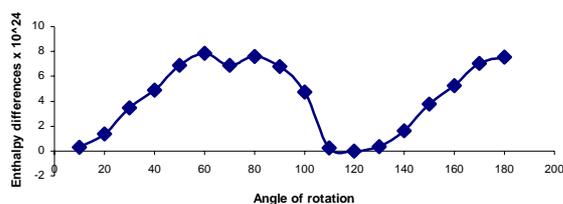


Fig.5. Electronic & thermal enthalpy differences in kcal mol⁻¹ versus angles of rotation.

provides a highly diagnostic probe of the electronic environment of the nucleus of interest and it allows to correlate the orientation of particular shielding or deshielding influences with the molecular structure.

The last work that we did, was NMR calculations which gave us energy differences, chemical shifts in two part (isotropy and anisotropy) and Mulliken partial charges for N and C atoms. These values are presented in table 3.

Table 3. NMR values for different rotations at HF/6-31G level

rotation (°)	$\Delta E \times 10^{24}$ (kcal/particle)	N			C		
		isotropy	anisotropy	charge	isotropy	anisotropy	charge
10	0.26	246.7235	12.3098	-0.784260	143.9651	78.9427	-0.100447
20	1.36	247.4824	13.3338	-0.785510	143.8758	81.2160	-0.099490
30	3.36	248.3145	15.3615	-0.788315	143.2502	85.3192	-0.096542
40	5.75	249.0277	17.9360	-0.792037	142.3090	90.3062	-0.092410
50	7.66	249.5194	20.1768	-0.795326	141.5077	94.3920	-0.089018
60	8.37	249.6934	21.2844	-0.796667	141.2177	95.9178	-0.087822
70	7.57	249.4926	20.8484	-0.795376	141.6374	94.1427	-0.089384
80	5.59	248.9854	19.0485	-0.792043	142.5537	89.8789	-0.092991
90	3.19	248.2668	16.5009	-0.788208	143.4823	84.9288	-0.096992
100	1.23	247.4390	13.9895	-0.785370	144.0329	80.8985	-0.099711
110	0.23	246.6824	12.4947	-0.784204	143.9976	78.8086	-0.100436
120	0	246.4070	12.1127	-0.784038	143.8355	78.3724	-0.100357
130	0.35	246.8209	12.7029	-0.784337	144.0415	79.0888	-0.100426
140	1.58	247.6180	14.4847	-0.785867	143.9741	81.6165	-0.099278
150	3.69	248.4379	17.0780	-0.788997	143.3167	85.9556	-0.096195
160	6.08	249.1174	19.5247	-0.792880	142.3507	90.9071	-0.092127
170	7.86	249.5708	21.0602	-0.795865	141.5035	94.7644	-0.088853
180	8.34	249.6889	21.1773	-0.796592	141.2175	95.8741	-0.087835

Zero point energy is a correction to the electronic energy of the molecule to account for the effects of molecular vibrations which persist even at 0 K.

When comparing calculated results to thermodynamic quantities extrapolated to zero Kelvin, the zero point energy needs to be added to the total energy. As with the frequencies themselves, this predicted quantity is scaled to eliminate known systematic errors in frequency calculations. NMR shielding tensors are some kinds of properties that can be computed in the context of a every calculation. The output gives the predicted value for each atom in the molecule in turn.

Characterization of the anisotropy or three – dimensional nature of the chemical shielding

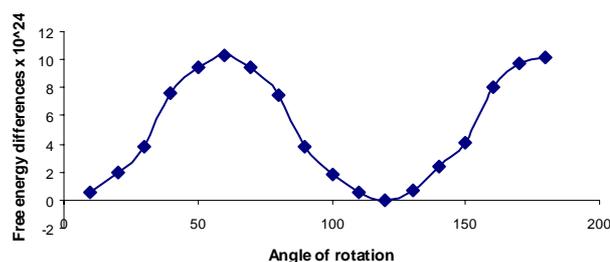


Fig.6. Electronic & thermal free energy differences in kcal mol⁻¹ versus angles of rotation.

Figures 7,8,9,10,11,12,13 show relations between energy differences, isotropic chemical shifts, anisotropic chemical shift and Mulliken charges versus angles of rotation for N and C atoms, respectively.

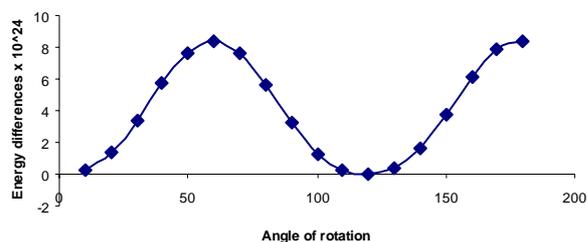


Fig.7. Energy differences in kcal mol⁻¹ versus angles of rotation calculated by NMR investigation.

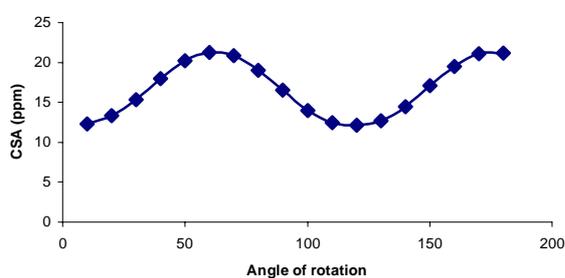


Fig.8. Chemical shift isotropy in ppm versus angles of rotation for nitrogen atom

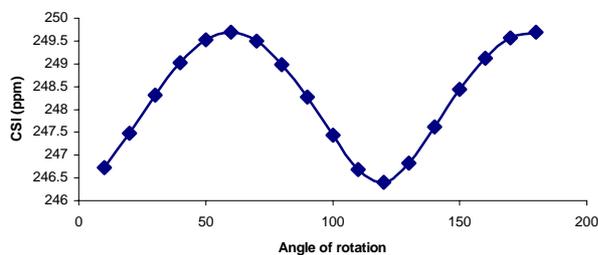


Fig.9. Chemical shift anisotropy in ppm versus angles of rotation for nitrogen atom.

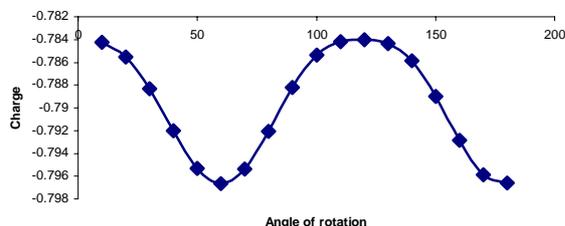


Fig.10. Mulliken partial charges versus angles of rotation for Nitrogen atom

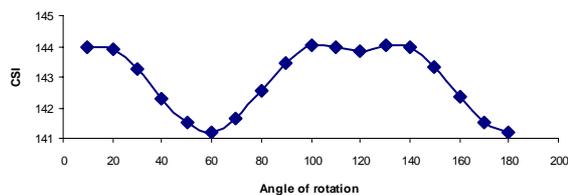


Fig.11. Chemical shift isotropy in ppm versus angles of rotation for carbon atom.

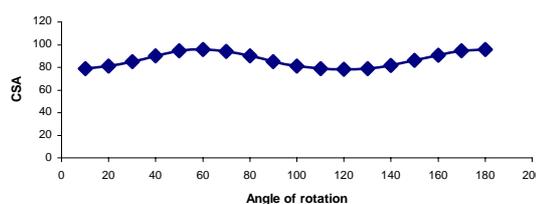


Fig.12. Chemical shift anisotropy in ppm versus angles of rotation for carbon atom.

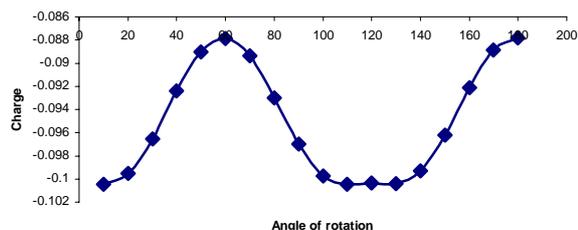


Fig.13. Mulliken partial charges versus angles of rotation for carbon atom

As you can see, values of energy in 0° rotation are equal by 120° rotation which has minimum value. Also it can be seen, there is a regular sinuous curve in all figures, except one (ΔE versus C—N bond length).

4. CONCLUSION

We summarize zero-point energy differences and thermal energy, enthalpy and free Gibbs energy differences by freq calculations in table 2 and the relations between these energy differences versus angle of rotation can be seen in figures above. NMR calculations which gave us energy differences, chemical shifts in two part (isotropy and anisotropy) and Mulliken partial charges for N and C atoms.

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