

Studying the Polymerization of Aniline on Fullerene

Hanan Elhaes^{1,*}, Afaf Babaier² and Mohamed Abd El-Aal^{3,4}

¹Physics Department, Faculty of Women for Arts, Science, and Education, Ain Shams University, 11757 Cairo, Egypt

²Physics Department, Faculty of Science-Jazan University, 2097 Jazan, Kingdom of Saudi Arabia, KSA

³Spectroscopy Department, National Research Centre, 12311, Dokki, Cairo, Egypt

⁴Physics Department, Faculty of Science, Taif University, Saudi Arabia

Abstract: Polyaniline is among a family of conductive polymers, that exhibits properties similar to some metals. Accordingly quantum mechanical calculations have been performed to study the possible polymerization of aniline on the surface of fullerene. Several model molecules representing the polymerization of aniline are studied; polymerization is tested with fullerene and fulleropyrrolidine surfaces. Total dipole moment, ionization potential, molecular weight, molecular dimension and molecular point group for C₆₀-aniline and C₆₀-pyrrolidine-aniline have been computed with the semiempirical PM3 method. The molecular point group has changed into C₁ point group corresponding to C₆₀-aniline and C₆₀-pyrrolidine-aniline, which reflects a change in the symmetry. Results indicate also that polarization increases the calculated total dipole moment, molecular weight and molecular dimension while ionization potential has slightly decreased. Final heat of formation increases with temperature for both C₆₀-aniline and C₆₀-pyrrolidine aniline. This reflects the thermal stability of the polymerized aniline on both fullerene and fulleropyrrolidine. Calculated HOMO-LUMO energy indicate that polyaniline which polymerizes on fullerene is the most probable.

Keywords: Molecular modeling, Semiempirical calculations. Fullerenes, Fulleropyrrolidine and Polyaniline.

1. INTRODUCTION

Fullerene derivatives were the subject of intensive studies, where a wide variety of those derivatives have been prepared and used in various physical, biological and pharmacological fields [1-4]. Fulleropyrrolidines are among the most studied fullerene derivatives which have been used for numerous biological applications [5, 6]. Polyaniline uniqueness among the class of conducting polymers is based on its wide range of electrical, electrochemical, electroluminescence, optical and anticorrosion applications. It is characterized also by its good stability [7-10]. Polyaniline is typically synthesized by the oxidation of aniline monomer either electrochemically [11]; or chemically [12-14]. Aniline forms complexes with transition metal ions in the clay minerals interlayer by the coordination of free electron like montmorillonite pair of the amino group to the metal ions [15,16]. Car-Parrinello ab initio molecular dynamics MD, was used to investigate polyaniline geometries [17]. Furthermore, the polaron lattice and the mechanism of conduction for doped polyaniline were studied by ab initio MO calculations [18]. A scaled quantum mechanical oligomer force field for oligomers of leucoemeraldine base and for one oligomer of the imine form of polyaniline was established [19]. Both vibra-

tional spectroscopy and ab initio calculations were used to study the adsorption and polymerization of aniline on Cu(II) montmorillonite [20]. Further vibrational assignment for polyaniline emeraldine base was achieved with FTIR; semiempirical; HF and DFT calculations [21]. Recently polyaniline/silica gel composites were prepared by in situ fast polymerization method. The structural characteristics, morphological information of as-prepared polymers were discussed [22]. A study was carried out on the biocompatibility of polyaniline and polyaniline silver coated polyurethane composite. It is stated that, coating polyurethane with polyaniline and polyaniline silver renders the surface conductive [23]. Glucose oxidase (GOx) was self-encapsulated within polyaniline and polypyrrole. Applicability of enzymatically synthesized polyaniline and polypyrrole was evaluated [24]. Recently it is also found that, polyaniline after doping with heavy metals like Cu and Zn furnish as a good surface for adsorption process. Accordingly the adsorption behaviors of Sodium Dodecyl Benzene Sulfonate onto polyaniline were studied [25].

This work has been conducted to study the possible polymerization of aniline on the surface of fullerenes. First the polymerization was tried onto the surface directly; then another attempt was made to perform polymerization through pyrrolidine ring attached with fullerene surface. Semiempirical quantum mechanical calculations were utilized to verify this assumption. For comparison B3LYP/6-31g** as well as experimental results are utilized.

*Address correspondence to this author at the Physics Department, Faculty of Women for Arts, Science, and Education, Ain Shams University, 11757 Cairo, Egypt; Tel: 00201283135136; E-mails: medahmed@yahoo.com, medahmed@hotmail.com

2. MATERIAL AND METHODS

2.1. Polymerization of Aniline

For comparison purpose aniline is prepared by adsorption upon Cu(II)-montmorillonite [20, 21]. Batch adsorption experiments in the presence of oxygen were performed to study the interlayer reactions of aniline on Cu(II)-montmorillonite in aqueous solutions. At concentrations below a critical value of $CC = 2.6 \text{ mmol dm}^{-3}$ only a coloured Cu(II)-aniline complex is formed, characterized by a stability constant of $\log (K_{\text{ass}} / \text{dm}^3 \text{mol}^{-1}) = 1.5$. At concentrations beyond CC aniline polymerizes yielding a dark brown product.

2.2. Calculation Details

In order to build the model molecules aniline monomer is attached to fullerene; fulleropyrrolidine surface respectively. Aniline is further attached with other aniline up to 4 units through hydrogen bonding. Accordingly 8 model molecules are constructed in addition to aniline; fullerene and fulleropyrrolidine.

Calculations were carried out on a personal computer. The geometry of the polymerization of aniline upon the surface of fullerene and fulleropyrrolidine were optimized by performing PM3 semiempirical quantum mechanics calculation using a MOPAC 2002 package which was implemented within the CACHE Program [26]. Some physical parameters like total dipole moment; ionization potential and HOMO-LUMO energies were calculated at the same level of theory. For comparison polyaniline is re-calculated using the Gaus-

sian 03 program system [27]. Geometries were optimized using density functional theory DFT, hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange correlation functional [28-30] with 6-31g** basis set. Vibrational spectrum was calculated at the same level of theory.

3. RESULTS AND DISCUSSION

The polymerization of aniline in aqueous solution was already studied early on 1994 [31]. Tochima *et al.* found that, aniline is oxidized by oxygen and subsequently polymerizes radically. The polymerization process is carried out upon a surface which is tried in this work as fullerene. Aniline monomer is attached to fullerene surface close to carbon atom no 22 (C_{22}), then attached to other aniline units as dimmer, trimer and emeraldine base (4 units). At each step the geometry is optimized then vibrational spectrum is calculated to ensure that the obtained structure is real and not a transition state ones. Another attempt was tried *via* pyrrolidine ring in order to check the possible polymerization of aniline upon fulleropyrrolidine. The change in geometrical; physical and vibrational characteristics will be followed through C_{22} as well as its surrounding atoms. Fig. (1) presents the general formular structure for fullerene; fulleropyrrolidine, and the base form of polyaniline emeraldin base.

Table 1 represents the net charge distribution for C_{60} -aniline and C_{60} -pyrrolidine-aniline in the position of C_{22} and C_{55} . As seen from the table the charge increases by the polymerization of aniline upon the surface of fullerene and fulleropyrrolidine. Table 2 presents some important physical

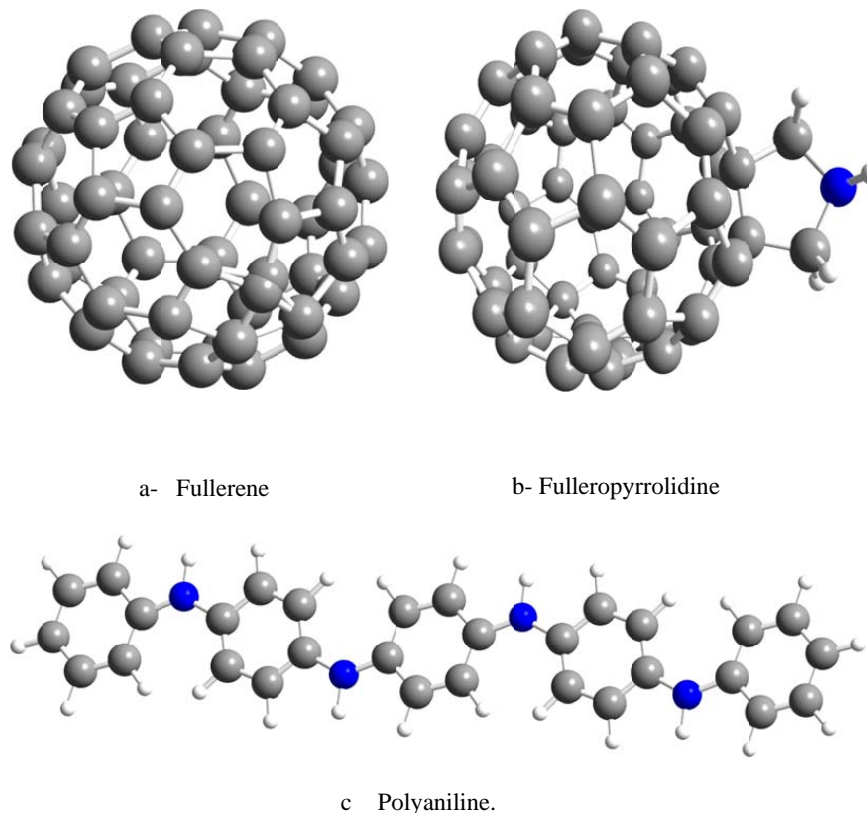


Fig. (1). General formular for a- fullerene; b- fulleropyrrolidine, c- the base form of polyaniline emeraldin base and their calculated structures.

Table 1. Calculated Net Charge Distribution for C₂₂-Anilin, C₂₂-pyraliden –aniline, C₅₅-aniline and C₅₅- pyrrolidine –aniline

	C	N.E	s-Pop	p-Pop
C22	0.000009	4.0000	1.16982	2.83019
C22-monomer	0.123592	3.8764	1.15896	2.71745
C22-dimer	0.155350	3.8447	1.17143	2.67322
C22-trimer	0.189514	3.8105	1.16317	2.64732
C22-poly	0.199133	3.8009	1.15144	2.64943
C22-Pyr	0.063423	4.0634	1.19415	2.86928
C22pyr-monomer	0.060377	3.9396	1.17523	2.76439
C22pyr-dimer	0.060464	3.9395	1.17511	2.76443
C22pyr-trimer	0.059793	3.9402	1.17550	2.76471
C22pyr-poly	0.059574	3.9404	1.17559	2.76484
C55	0.000024	4.0000	1.16983	2.83014
C55-monomer	0.130657	3.8693	1.15888	2.71046
C55-dimer	0.131780	3.8682	1.16411	2.70411
C55-trimer	0.191696	3.8083	1.15557	2.65274
C55-poly	0.140427	3.8596	1.16271	2.69686
C55-Pyr	0.024237	4.0242	1.18659	2.83765
C-55pyr-monomer	0.060717	3.9393	1.17528	2.76400
C-55pyr-dimer	0.061387	3.9386	1.17521	2.76341
C-55pyr-trimer	0.063371	3.9366	1.17503	2.76160
C-55pyr-poly	0.062997	3.9370	1.17495	2.76205

parameters which were calculated with PM3. As seen in Table 2 the molecular weight of optimized C₆₀ is 720.660 increased ongoing from C₆₀-monomer towards C₆₀ – polyaniline. In the case of C₆₀-pyrrolidine–aniline the molecular weight is also increasing from C₆₀ – pyrrolidine - monomer to C₆₀ – pyrrolidine - polyaniline but it is higher than C₆₀ – aniline. The molecular dimension is slightly increasing from 7.09226 Å in case of C₆₀ to 9.89354 Å in case of C₆₀ – pyrrolidine. In both cases, C₆₀ and C₆₀ – pyrrolidine, the molecular dimension has increased by going from aniline monomer to polyaniline and is still higher in the case of C₆₀ – pyrrolidine – aniline.

The molecular point group has changed from Ih to C1 point group corresponding to C₆₀-aniline. A decrease in ionization potential goes from C₆₀ –aniline monomer toward C₆₀ –polyaniline. The same behavior has been observed in the case of C₆₀ – pyrrolidine -aniline. The total dipole moment has increased from 0.000 to 2.710 debeye corresponding to C₆₀ –pyrrolidine. The possible change in the partial charge distribution leads to an increase in the total dipole moment of C₆₀ –aniline and C₆₀ – pyrrolidine -aniline by going from C₆₀ –aniline monomer towards C₆₀ –polyaniline and from C₆₀ – pyrrolidine –aniline monomer towards C₆₀ – pyrrolidine – polyaniline.

Table 3 represents the calculated, final heat of formation (HF), enthalpy (En), heat capacity (HC), entropy (Et), free energy (FE) and band gap energy (ΔE) at 298 k using PM3 method. Band gap energy (ΔE) is calculated as the difference between highest occupied molecular orbital HOMO; and lowest unoccupied molecular orbital LUMO. From the table it is clear that ΔE decreases by increasing the polymerization of C₆₀-aniline and C₆₀ - pyrrolidine - aniline. Adding the pyrrolidine to C₆₀ decreases the value of the band gap energy. Final heat of formation of C₆₀ has changed from 12434.0 to 799.62 Kcal/mol by adding the pyrrolidine. Final heat of formation decreases from 12434.0 Kcal/mol corresponding to C₆₀ to 835.150 Kcal/mol which corresponds to C₆₀-monomer. Heat of formation increases by going from C₆₀-monomer to C₆₀- polyaniline in both cases of C₆₀ – aniline and of C₆₀ – pyr- aniline. Enthalpy increases from 104.8 cal/mol corresponding to C₆₀ to 14440.811 cal/mol corresponding to C₆₀- pyr. Enthalpy increases by going from C₆₀-monomer to C₆₀-polyaniline but it has higher value in the case of C₆₀ – pyr- aniline compared to C₆₀ – aniline. Heat capacity decreases from 124.7 cal/mol/Kelvin in case of C₆₀ to 118.485 cal/mol/k for C₆₀ – pyr. Heat capacity increases by going from C₆₀-monomer to C₆₀-polyaniline in both cases of C₆₀ – aniline and of C₆₀ – pyr- aniline and it has higher value in the case of C₆₀ – pyr- aniline than C₆₀ – aniline. En-

Table 2. Calculated, Total Dipole Moment (TDM) as Debye; Ionization Potential (IP) as eV; Molecular Weight (MW) Molecular Dimensional (MD) as Å and Molecular Point Group (MPG) for C₆₀-aniline and C₆₀-pyrrolidine -aniline

	TDM	IP	MW	MD	MPG
C ₆₀	0.00	9.48189	720.660	7.09226	Ih
C ₆₀ -monomer	2.315	8.76369	787.750	10.93786	C1
C ₆₀ -dimer	5.151	8.03331	878.862	11.60551	C1
C ₆₀ -trimer	13.990	7.18361	969.975	14.27213	C1
C ₆₀ -poly	12.058	6.97516	1061.087	14.65865	C1
C ₆₀ -Pyr	2.710	8.91921	763.728	9.89354	C1
C ₆₀ -pyr-monomer	1.764	8.79927	839.826	14.83739	C1
C ₆₀ -pyr-dimer	1.813	8.32169	930.938	19.22302	C1
C ₆₀ -pyr-trimer	2.332	8.21727	1022.050	21.20113	C1
C ₆₀ pyr-poly	3.211	8.00945	1113.162	20.47864	C1

Table 3. Calculated, Heat of Formation (HF) as Kcal/mol, Enthalpy (En) as (cal/mol). Heat Capacity (HC) as (cal/mol/Kelvin), Entropy (Et) as (cal/mol/Kelvin), Free Energy (FE) as (Kcal/mol) and HOMO-LUMO Band Gap Energy (ΔE) as (eV) at 298 k Using PM3 Method at 298 k, for C₆₀-aniline and C₆₀-pyrrolidine -aniline

	H.F	En	HC	Et	FE	ΔE
C ₆₀	12434.0	104.8	124.7	811.1	773.9	6.593
C ₆₀ -monomer	835.150	15647.817	125.645	151.545	789.990	5.768
C ₆₀ -dimer	1004.34	19136.9	150.500	172.986	952.793	4.838
C ₆₀ -trimer	1017.93	21627.6	170.572	187.737	961.992	4.462
C ₆₀ -poly	1191.052	24878.9	194.664	206.501	1129.515	4.173
C ₆₀ -Pyr	799.062	14440.811	118.485	143.348	756.344	5.868
C ₆₀ pyr-monomer	828.860	17569.736	137.873	169.267	778.418	5.744
C ₆₀ pyr-dimer	856.217	21251.998	161.002	200.427	796.490	5.276
C ₆₀ pyr-trimer	883.786	24934.656	184.339	231.390	814.832	5.145
C ₆₀ pyr-poly	910.653	28512.3	207.402	260.911	832.902	4.945

entropy decreases from 811.1cal/mol/Kelvin for C₆₀ to 143.348 cal/mol/Kelvin for C₆₀-pyr. Entropy increases by going from C₆₀-monomer to C₆₀-poly in both cases of C₆₀-aniline and C₆₀-pyr-aniline. However it has higher value in the case of C₆₀-pyr-aniline than C₆₀-aniline. Free energy increases by going from C₆₀-monomer to C₆₀-poly in both cases of C₆₀-aniline and C₆₀-pyr-aniline but it has lower value in the case of C₆₀-pyr-aniline than C₆₀-aniline. Table 4 represents the calculated, heat of formation (HF) entropy (Et), enthalpy (En), heat capacity (HC) and free energy (FE) using PM3 method at different temperatures for C₆₀-pyr-polyaniline. From the table we notice that all these parameters increase with increasing temperature except for free energy which decreases with increasing temperature. Still the values of heat of formation, entropy, enthalpy, and heat capacity of C₆₀-pyr-aniline are higher than C₆₀-aniline but the opposite side saw for free energy. The same

behaviour observed in the case of C₆₀-aniline as shown in Table 5.

The calculated vibrational spectra provide clear verification for the structural parameters. The calculated spectra of C₆₀-aniline as compared with C₆₀ are shown in Fig. (2). The characteristic spectrum of C₆₀ has been discussed in our previous work [32, 33]. The spectrum of C₆₀ shows sharp spectral bands as a result of the highly symmetric structure of C₆₀. As a result of polymerization fullerenes showed the four characteristic bands remaining unchanged but broadened as a result of changing the molecular symmetry. The same behaviour is observed in the calculated spectra of C₆₀-pyr-aniline as compared with C₆₀ as seen in Fig. (3). In fact, the assignment of such structure needs higher level of theory. Polyaniline is calculated at B3LYP/6-31g (d,p). Table 6 presents the experimental vibrational spectrum of aniline in liquid phase. The spectrum of aniline can be assigned as: NH₂ bending or scissors mode which is attributed to 1626 cm⁻¹,

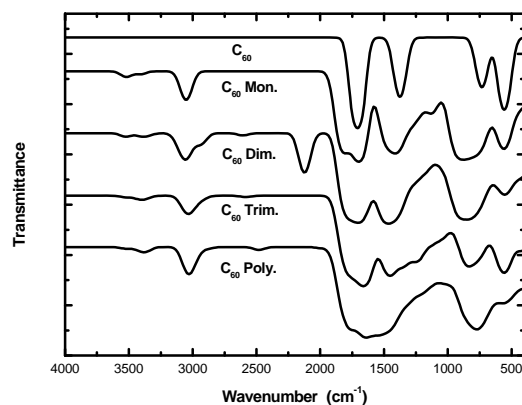


Fig. (2). PM3 calculated vibrational spectra for fullerene; fullerene– aniline monomer (C_{60} -Mon); fullerene– aniline dimer (C_{60} -Dim); fullerene– aniline trimmer (C_{60} -Trim) and fullerene– polyaniline (C_{60} -Poly).

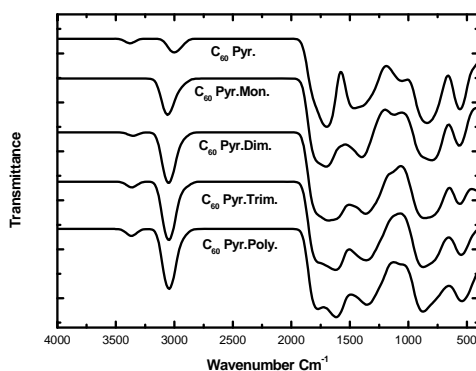


Fig. (3). PM3 calculated vibrational spectra for fulleropyrrolidine; fulleropyrrolidine – aniline monomer (C_{60} -Pyr.Mon); fulleropyrrolidine – aniline dimer (C_{60} -Pyr.Dim); fulleropyrrolidine – aniline trimmer (C_{60} -Pyr.Trim) and fulleropyrrolidine – polyaniline (C_{60} -Pyr.Poly).

Table 4. Calculated, Heat of Formation (HF) as Kcal/mol, Enthalpy (En) as (cal/mol), Heat Capacity (HC) as (cal/mol/Kelvin), Entropy (Et) as (cal/mol/Kelvin), Free Energy (FE) as (Kcal/mol) and HOMO-LUMO Band Gap Energy (ΔE) as (eV) Using PM3 Method at Different Temperature for C_{60} - pyrrolidine - polyaniline

Temperature	HF	En	HC	Et	FE
298.000	910.653	28512.390	207.402	260.911	832.902
200.00	894.313	12172.963	126.210	195.500	855.213
250.00	901.652	19511.466	167.531	228.079	844.632
300.00	911.069	28928.845	209.045	262.304	832.378
350.000	922.533	40392.395	249.164	297.567	818.385
400.000	935.945	53804.735	286.866	333.330	802.613
450.000	951.170	69029.113	321.585	369.153	785.051
500.000	968.050	85909.881	353.111	404.695	765.702

and a ring stretching with a contribution of the NH_2 scissoring band at 1604 cm^{-1} . A band at 1497 cm^{-1} is characterized as typical ring stretching. The mode at 1264 cm^{-1} is assigned as partly to C-N stretching and partly to the ring stretching vibration. Comparing between both calculated and experimental frequencies indicates that results of B3LYP/6-31G(d,p) are in good agreement with the experimental one. The optimized calculated polyaniline at this level of theory is indicated in Fig. (1-c). PM3 vibrations are not as accurate as

B3LYP/6-31G(d,p) however but it gives satisfactory vibrational frequencies of the studied polyaniline.

4. CONCLUSION

It is worth to mention that fullerene can exist in both gaseous as well as solid phases. Fulleropyrrolidine could be found only in the liquid phase. Accordingly we try to test the polymerization of aniline in solid phase through fullerene and in liquid phase through fulleropyrrolidine. Fullerene as

Table 5. Calculated, Heat of Formation (HF) as Kcal/mol, Enthalpy (En) as (cal/mol), Heat Capacity (HC) as (cal/mol/Kelvin), Entropy (Et) as (cal/mol/Kelvin), Free Energy (FE) as (Kcal/mol) and HOMO-LUMO Band Gap Energy (ΔE) as (eV) Using PM3 Method at Different Temperature for C₆₀- polyaniline

Temperature	HF	En	HC	Et	FE
298.00	1191.052	24878.917	194.664	206.501	1129.515
200.00	1175.845	9671.417	115.366	145.670	1146.711
250.00	1182.630	16456.358	156.081	175.782	1138.685
300.00	1191.440	25269.824	196.242	207.808	1129.101
350.000	1202.224	36049.9	234.582	240.968	1117.885
400.000	1214.858	48684.518	270.323	274.657	1104.995
450.000	1229.206	63032.027	303.059	308.417	1090.418
500.000	1245.112	78938.201	332.670	341.907	1074.159

Table 6. Comparison Between PM3 and B3LYP/6-31G(d,p) as Well as Experimental Vibrational Frequencies (cm⁻¹) of Polyaniline

PM3	B3LYP/6-31G(d,p)	Exp.	Assignment
1776	1627	1626	NH ₂ sciss, ring str
1678	1608	1604	ring str., NH ₂ sciss,
1580	1503	1497	C-H bend, ring str
1369	1271	1264	C-N str., ring str
1239	1176	1175	C-H bend
1170	1156	1153	C-H bend,
1049	1020	1030	ring def,
971	994		Ring breathing
643	800	792	C-N str., ring str.,

well as fulleropyrrolidine could be a good surface for the process of polymerization of aniline. The polymerized aniline is thermally stable in terms of the PM3 calculated parameters. The band gap energy based upon HOMO/LUMO indicate that lower energy was achieved in case of fullerene (4.173 eV) while it was slightly higher for fulleropyrrolidine. (4.945eV). Supporting the assumption that fullerene in the solid phase is more likely to be used as a surface for polymerization of aniline.

Another confirmation obtained from the calculated total dipole moment points to the fact that; the higher dipole moment (12.059 debye) of fullerene-polyaniline indicates that the fullerene surface became more reactive for further polymerization of aniline. Lower total dipole moment value (3.211 debye) corresponds to fulleropyrrolidine-polyaniline, indicating that fulleropyrrolidine is becoming slightly more stable after polymerization of aniline and no further polymerization took place on its surface.

PM3 semiempirical calculation is not in a good agreement with experimental results due to the effect of electron correlation which is not included in the semiempirical method. But the calculations are considered satisfactory as it

takes relatively short time. The calculated physical parameters and HOMO/LUMO energy are considered good indicator for a given interaction. Accordingly, from this study one can conclude that precise spectroscopic data could be achieved with DFT, while satisfactory physical parameters could be achieved with semiempirical calculations.

ACKNOWLEDGEMENT

Authors would like to express their thanks to Prof. Dr. M.A. Kamel, Physics Department, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt. For his assistance during carrying out the calculations.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

REFERENCES

- [1] Martin N. New challenges in fullerene chemistry. Chem Commun 2006; 20: 2093-104.

- [2] Hirsch A, Brettreich M. Fullerenes: chemistry and reactions. Weinheim: Wiley-VCH 2005.
- [3] Kanwal A, Paul S, Chhowalla M. Organic memory devices using C₆₀ and insulating polymer. *Mater Res Soc Symp Proc* 2005; 830: D7.2.1.
- [4] Hameed AJ. Computational note on substitution effects on the structural and electronic properties of 1-(para-substituted phenyl diazenyl)pyrrolidinofullerenes. *J Mol Struct* 2006; 766: 73-5.
- [5] Da Ros T, Spalluto G, Prato M. Biological applications of fullerene derivatives: a brief overview. *Croat Chem Acta* 2001; 74: 743-55.
- [6] Tagmatarchis N, Prato M. The addition of azomethine ylides to [60] fullerene leading to fulleropyrrolidines. *Synlett* 2003; 34: 768-79.
- [7] Liu G, Freund MS. New approach for the controlled cross-linking of polyaniline: synthesis and characterization. *Macromolecules* 1997; 30: 5660-5.
- [8] Nalwa HS. Handbook of organic conductive molecules and polymers. Vol. 1-4. New York: Wiley 1997.
- [9] Novak P, Muller K, Santhanam KSV, Haas O. Electrochemically active polymers for rechargeable batteries. *Chem Rev* 1997; 97: 207-81.
- [10] Angelopoulos M, Dipietro R, Zheng WG, MacDiarmid AG, Epstein AJ. Effect of selected processing parameters on solution properties and morphology of Polyaniline and impact on conductivity. *Synth Met* 1997; 84: 35-9.
- [11] Liu G, Freund MS. Nucleophilic substitution reactions of polyaniline with substituted benzenediazonium ions: a facile method for controlling the surface chemistry of conducting polymers. *Chem Mater* 1996; 8: 1164-6.
- [12] Yang J, Zhu W, Hou J, Xu M, Wan M. Substituted polyaniline-polypropylene film composites: preparation and properties. *Synth Met* 1996; 80: 283-9.
- [13] Chen CH. Thermal and morphological studies of chemically prepared EB form polyaniline powder. *J Appl Polym Sci* 2003; 89: 2142-8.
- [14] Vecino M, Gonzalez I, Munoz ME, Santamaria A, Ochoteco EM, Pomposo JA. Synthesis of polyaniline and application in the design of formulations of conductive paintspolymer. *Polym Adv Technol* 2004; 15: 560-3.
- [15] Edward B, Roman P, Semion S, *et al.* Infrared optics applications of thin polyaniline emeraldine base films. *Polym Synth Met* 2004; 140: 49-52.
- [16] Heller L, Yariv S. Sorption of some anilines by Mn-, Co-, Ni-, Cu-, Zn-, and Cd-montmorillonite. In: Heller L, Ed. *Proc Int Clay Conf Tokyo*, Vol. 1. Jerusalem: Israel Univ Press 1969; pp. 741-55.
- [17] Brocks G, Kelly PJ. Structure and properties of polymers calculated by ab-initio molecular dynamics. *Synth Met* 1993; 55-57: 4243-8.
- [18] Baird NC, Huizhong W. The polaron lattice and the mechanism of conduction for doped polyaniline. *Chem Phys Lett* 1993; 202: 501-5.
- [19] Kertsz M, Choi CH, Hong SY. Conformational information from vibrational spectra of polyaniline. *Synth Met* 1997; 85: 1073-6.
- [20] Ilic M, Koglin E, Pohlmeier A, Narres HD, Schwuger MJ. Adsorption and polymerization of aniline on Cu(II)-montmorillonite: Vibrational spectroscopy and ab initio calculation. *Langmuir* 2000; 16: 8946-51.
- [21] Ibrahim M, Koglin E. Spectroscopic study of polyaniline emeraldine base: Modelling approach. *Acta Chim Slov* 2005; 52(2): 159-63.
- [22] Pan J, Yao H, Guan W, *et al.* Selective adsorption of 2, 6-dichlorophenol by surface imprinted polymers using polyaniline/silica gel composites as functional support: Equilibrium, kinetics, thermodynamics modeling. *Chem Eng J* 2011; 172(2-3): 847-55.
- [23] Prabhakar PK, Raj S, Anuradha PR, Sawant SN, Doble M. Biocompatibility studies on polyaniline and polyaniline-silver nanoparticle coated polyurethane composite. *Colloid Surf B Biointerface* 2011; 86(1): 146-53.
- [24] Kausaite-Minkstimiene A, Mazeiko V, Ramanaviciene A, Ramanavicius A. Evaluation of amperometric glucose biosensors based on glucose oxidase encapsulated within enzymatically synthesized polyaniline and polypyrrole. *Sens Actuators B Chem* 2011; 158(1): 278-85.
- [25] Özdemir U, Özbay B, Veli S, Zor S. Modeling adsorption of Sodium Dodecyl Benzene Sulfonate (Sdbs) Onto Polyaniline (Pani) by using multi linear regression and artificial neural networks. *Chem Eng J* 2010, [Epub ahead of print].
- [26] MOPAC. Version 2.5.3, J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan 2002.
- [27] Frisch J, Trucks GW, Schlegel HB, *et al.* Gaussian 3, Revision c. 02. Wallingford CT: Gaussian Inc. 2004.
- [28] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 1993; 98: 5648-52.
- [29] Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 1988; 37(2): 785-9.
- [30] Miehlich B, Savin A, Stoll H, Preuss H. Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr. *Chem Phys Lett* 1989; 157(3): 200-6.
- [31] Toshima N, Yan H, Ishiwatari M. Catalytic polymerization of Aniline and its derivatives by using Copper(II) salts and oxygen. New type of polyaniline with branched structure. *Bull Chem Soc Jpn* 1994; 67: 1947-53.
- [32] Ibrahim M, El-Haes H. Spectroscopic study of C₆₀ and C₈₀ and their epoxides. *Chin J Phys* 2005; 43: 915-23.
- [33] Ibrahim M, El-Haes H, Jalbout AF. Semiempirical molecular modelling study of C₆₀ doped with Silicon, Germanium and Aluminium. *Chin J Phys* 2006; 44: 432-9.

Received: October 01, 2011

Revised: December 09, 2011

Accepted: December 11, 2011

© Elhaes *et al.*; Licensee *Bentham Open*.This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.