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Spectroscopic analysis of C_{80} doping with group III and group V elements using semiempirical PM3 molecular modelling technique

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Abstract: Semiempirical calculations at the level of PM3 of theory were carried out to study the structural and electronic properties of C_{80} and some of its doped derivatives with the elements of group III and V at the level of PM3 of theory. We have selected these elements to be substituted in the fullerene-C_{80} cage in order to show the effect of such structural change on the electronic properties of the molecules studied. The theoretical IR spectra, some of physical and chemical properties of the molecules studied are obtained and discussed.

Keywords: hetrofullerene; C_{80}; final heat of formation; vibrational spectrum.

Introduction

In recent years there have been continuous studies to investigate the endohedrally [1], exohedrally [2] and substitutionally [3] fullerenes. The great deal of these investigations has been directed toward investigating the photophysical and electrochemical properties of fullerenes [4]. Significant efforts have been directed at the synthesis of functionalized fullerenes in which different atoms are covalently-linked to the fullerene cage [5, 6].

The introduction of heteroatom, such as Fe, Ni, Co, Rh and Ir, into the fullerene cage leads to significant modification in the electronic and structural properties of fullerenes [7, 8].These modified systems exhibit interesting superconducting, optical and electronic properties [9,10].

A variety of heterofullerenes have been reported, where in these systems number of carbon atoms have been substituted by heteroatom such as boron or nitrogen atoms [10-13] . The vast majority of these studies have been done on C_{60} molecule. The electronic properties of such systems have been studied theoretically by performing the semiempirical and DFT calculations to understand the doping influences [13-15].

There are few reports about doped C_{80}. However, heterofullerene such as $C_{79}N$ have been generated [16]. The fact that C_{80}, which in the empty case is an open shell system and therefore very unstable, also efficiently encapsulates rare earth metals, to form stable endohedrals M2@C_{80}, suggests, that the electronic structure of the fullerene shell is dramatically influenced by the central metals [17].

Currently, we are working on the molecular orbital theoretical calculations to predict the structures and behavior of some doped fullerenes. In previous work [18] the structural and vibrational properties of C_{60} doped with Si, Ge and Al. In this paper, we have investigated theoretically the molecular and vibrational structures of C_{80} and some of its doped derivatives with the elements of group III and V by performing the semiempirical calculations at the level of PM3 of theory.

Experimental details

All calculations were carried out on a personal computer, performed using semiempirical quantum mechanics package, MOPAC 2002 which is implemented within the CAChe Program (Full Version 1.33 by Fujitsu). The initial geometry optimizations of both C_{80} and doped C_{80} were performed with the molecular mechanics force field to obtain approximate minimum energy structures. The lowest energy conformations obtained by the molecular mechanics method were further optimized with the semiempirical, PM3 method [19,20].

Results and Discussions

In the present work PM3 is conducted to study the Vibrational spectra of fulleropyrrolidine-1-carbodithioic acid 2; 3 and 4-substituted-benzyl esters. The substituents include: NH_2, OMe, F, Cl, CO_2Me, COMe, CN and NO_2. We have selected these substituents to be in *ortho*, *meta* and *para* positions relative to the methylene group in order to show the effect of such structural change on the structural and electronic properties of the molecules. Vibraional spectra of each structure are obtained.

Calculated optimized geometry

Fig.1. shows the structure of C_{80} which doped with the elements of group III and V.

We have selected the elements of group II and V to be replaced with the carbon atom number 3 in the fullerene-C_{80} cage. The geometry of C_{80} and its derivatives are optimized at semiemprical PM3 method. Some of selected structural parameters (the bond distances, molecular dimensions and molecular point group) of the studied molecules are indicated in table 1 and 2. We have selected the bond lengths (D3-C2, D3-C4 and D3-C16) to show the effect of doping upon the structure of C_{80}. As

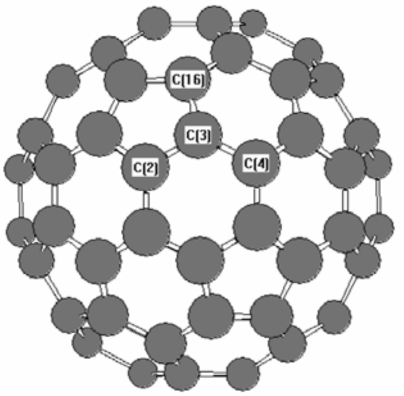
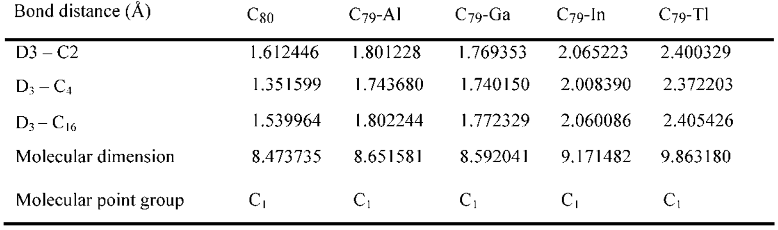


Figure 1. Optimized PM3 structure of C_{80}. Note that the dopant is replaced with carbon atom number 3.

Table 1. Calculated bond lengths, molecular dimensions in angstroms for C80 as well as doped C_{80} which have been optimized at the PM3 semiempirical level of theory. Note: In the table D = C, Al, Ga, In and Tl.



Bond distance (Å)	C_{80}	C_{79}-Al	C_{79}-Ga	C_{79}-In	C_{79}-Tl
D3 – C2	1.612446	1.801228	1.769353	2.065223	2.400329
$D_3 – C_4$	1.351599	1.743680	1.740150	2.008390	2.372203
$D_3 – C_{16}$	1.539964	1.802244	1.772329	2.060086	2.405426
Molecular dimension	8.473735	8.651581	8.592041	9.171482	9.863180
Molecular point group	C_1	C_1	C_1	C_1	C_1

Molecular dimension is the distance from atoms 3-43

Table 2. Calculated bond lengths, molecular dimensions in angstroms for doped C_{80} which have been optimized at the PM3 semiempirical level of theory. *Note*: In the table D = N, P, As, Sb and Bi.

Bond distance (Å)	C_{79}-N	C_{79}-P	C_{79}-As	C_{79}-Sb	C_{79}-Bi
$D_3 - C_2$	1.436360	1.866851	1.960593	2.118798	2.240407
$D_3 - C_4$	1.439764	1.855736	1.948937	2.094853	2.208308
$D_3 - C_{16}$	1.442448	1.867196	1.962403	2.119805	2.243223
Molecular dimension	8.25605	9.08326	9.21818	9.43942	9.64394
Molecular point group	C_1	C_1	C_1	C_1	C_1

Molecular dimension is the distance from atoms 3-43

mentioned in these tables, the molecular point group is not changed as a result of doping and remains corresponding to C1 point group. Furthermore, except C_{79}-N, all the studied structures have shown an enlargement in their bond distances as well as molecular dimension as compared with that of C_{80}. Regarding table 2, Group V doped fullerenes have shown an increase in the calculated bond distances ongoing from C_{79}-N to C_{79}-Bi. Table 1 shows bond lengths which decrease from C79-Al to C79-Ga following an increase from C_{79}-In to C_{79}-Tl. It is worth to mention that the structure C_{79}-B has no optimized geometry at this level of theory so that it is not included in the tables.

Final heat of formation

Figures 2 and 3 present the final heat of formation (FHF) as a function of temperature in the temperature range 200k to 500k for C80 as well as C80 doped with the elements of groups III and V respectively. FHF is treated in our previous work [18, 21].It is relative to the elements in their standard state at 298 K. As shown in Fig.2, C_{80} indicates an increase in its FHF values as the temperature increases. Other doped fullerenes obey the same behavior. Comparing doped fullerenes with C_{80} revealed that, doped fullerenes have lower FHF as compared with that of C80. Moreover the FHF of the group III could be arranged according to the following order:

$C_{80} > C_{79}$-Tl $> C_{79}$-In $> C_{79}$-Al$> C_{79}$-Ga

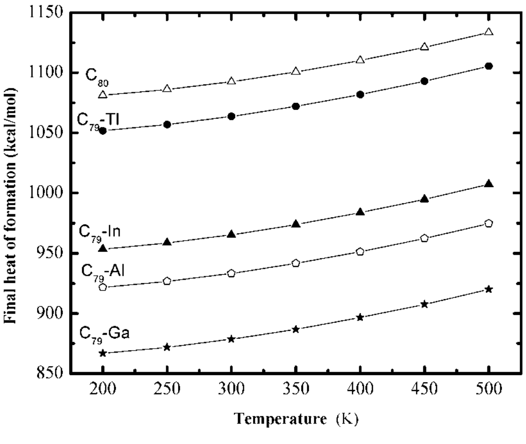


Figure 2. Final heats of formation (kcal/mol) as a function of temperature for C_{80} as well as C_{80} doped with the studied III elements.

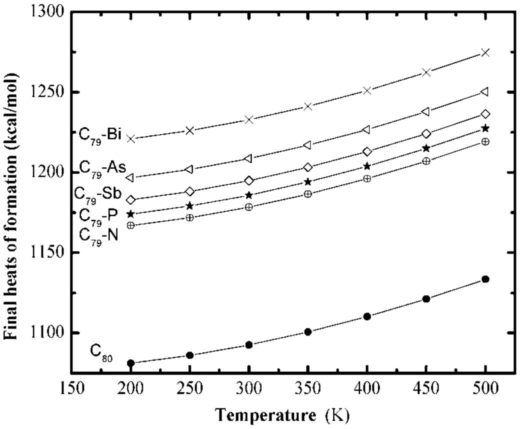


Figure 3. Final heats of formation (kcal/mol) as a function of temperature for C_{80} as well as C_{80} doped with the studied V elements.

Calculated FHF at Fig. 3 shows that fullerenes which doped with group V have higher FHF as compared with that of C_{80}. FHF is increased from C_{79}-N to C_{79}-As then decrease from C_{79}-Sb to C_{79}-Bi. Finally the FHF of the group V could be arranged according to the following order:

C_{79}-Bi > C_{79}-As > C_{79}-Sb > C_{79}-P > C_{79}-N > C_{80}

Charge and Dipole moment

As listed in tables 3 to 7; the charge, number of electrons, number of electrons in s-state

Table 3. PM3 computed net atomic charge and dipole moment contributions in the X, Y and Z directions for both C_{80} and C_{79}-Al.

	C_{80}				C_{79}-Al			
	C_2	C_3	C_4	C_{16}	C_2	Al_3	C_4	C_{16}
C	-0.020785	0.058173	0.008965	-0.069571	-0.250178	0.596944	-0.174032	-0.263521
N. E.	4.020800	3.941800	3.991000	4.069600	4.250200	2.403100	4.174000	4.263500
s-Pop	1.166230	1.202980	1.149330	1.2090100	1.246760	0.603470	1.228040	1.246760
p-Pop	2.854550	2.738840	2.841710	2.860560	3.003420	1.799590	2.945990	3.016760
DPC	X	Y	Z		X	Y	Z	
	-1.400	2.350	1.475		-0.393	3.065	5.210	
Total dipole moment			3.107		6.057			

C: Charge, NE: Number of electrons, s-Pop: no of electrons in s-state, p-Pop: no of electrons in p- state and DPC: Dipole moment contribution.

Table 4. PM3 computed net atomic charge and dipole moment contributions in the X, Y and Z directions for both C_{79}-Ga and C_{79}-In.

	C_{79}-Ga				C_{79}-In			
	C_2	Ga_3	C_4	C_{16}	C_2	In_3	C_4	C_{16}
C	-0.390395	0.958739	-0.286245	-0.392136	-0.084775	-0.065822	0.011005	-0.122946
N. E.	4.390400	2.041300	4.286200	4.392100	4.08480	3.065800	3.98900	4.122900
s-Pop	1.282640	1.116840	1.262640	1.282540	1.202670	1.090540	1.179450	1.203630
p-Pop	3.107750	0.924420	3.023600	3.109600	2.882110	1.975290	2.809540	2.919320
DPC	X	Y	Z		X	Y	Z	
	-0.468	3.154	5.350		-0.135	3.342	5.039	
Total dipole moment			6.228		6.048			

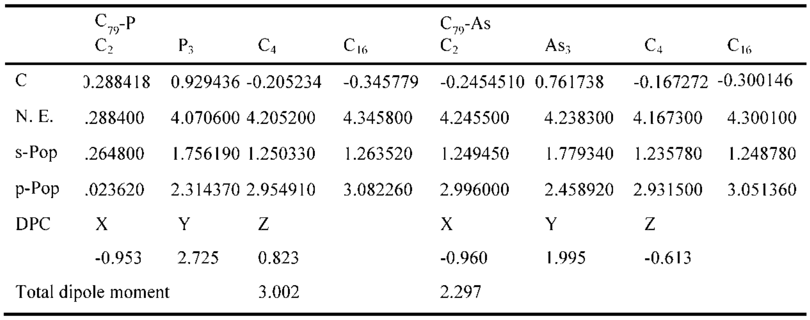
C: Charge, NE: Number of electrons, s-Pop: no of electrons in s-state, p-Pop: no of electrons in p-state and DPC: Dipole moment contribution.

Table 5. PM3 computed net atomic charge and dipole moment contributions in the X, Y and Z directions for both C_{79}-Tl and C_{79}-N.

	C_{79}-Tl				C_{79}-N			
	C_2	Tl_3	C_4	C_{16}	C_2	N_3	C_4	C_{16}
C	-0.173758	0.552648	-0.107440	-0.176676	-0.121529	0.413449	0.017006	-0.167632
N. E.	4.1738	2.447400	4.107400	4.176700	4.121500	4.586600	3.983000	4.1676
s-Pop	1.24991	0.003700	1.231780	1.248120	1.202800	1.288460	1.183770	1.20200
p-Pop	2.92385	2.443650	2.875660	2.928560	2.918720	3.298090	2.799230	2.96563
DPC	X	Y	Z		X	Y	Z	
	0.509	7.603	12.499		-0.955	1.545	-0.612	
Total dipole moment			14.639		1.917			

C: Charge, NE: Number of electrons, s-Pop: no of electrons in s-state, p-Pop: no of electrons in p- state and DPC: Dipole moment contribution.

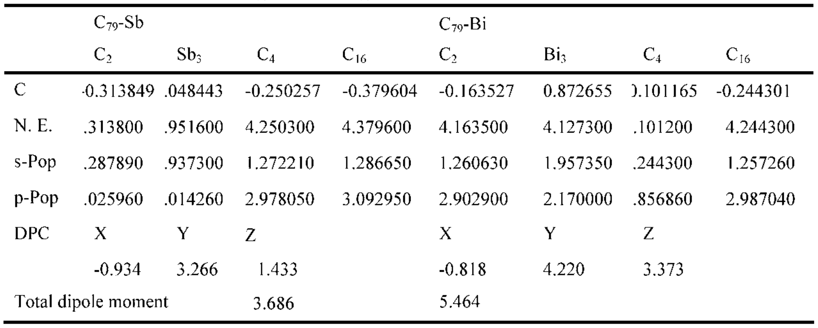
Table 6. PM3 computed net atomic charge and dipole moment contributions in the X, Y and Z directions for both C_{79}-P and C_{79}-As.



	C_{79}-P				C_{79}-As			
	C_2	P_3	C_4	C_{16}	C_2	As_3	C_4	C_{16}
C	).288418	0.929436	-0.205234	-0.345779	-0.2454510	0.761738	-0.167272	-0.300146
N. E.	.288400	4.070600	4.205200	4.345800	4.245500	4.238300	4.167300	4.300100
s-Pop	.264800	1.756190	1.250330	1.263520	1.249450	1.779340	1.235780	1.248780
p-Pop	.023620	2.314370	2.954910	3.082260	2.996000	2.458920	2.931500	3.051360
DPC	X	Y	Z		X	Y	Z	
	-0.953	2.725	0.823		-0.960	1.995	-0.613	
Total dipole moment			3.002		2.297			

C: Charge, NE: Number of electrons, s-Pop: no of electrons in s-state, p-Pop: no of electrons in p- state and DPC Dipole moment contribution

Table 7. PM3 computed net atomic charge and dipole moment contributions in the X, Y and Z directions for both C_{79}-Sb and C_{79}-Bi.



	C_{79}-Sb				C_{79}-Bi			
	C_2	Sb_3	C_4	C_{16}	C_2	Bi_3	C_4	C_{16}
C	-0.313849	.048443	-0.250257	-0.379604	-0.163527	0.872655	).101165	-0.244301
N. E.	.313800	.951600	4.250300	4.379600	4.163500	4.127300	.101200	4.244300
s-Pop	.287890	.937300	1.272210	1.286650	1.260630	1.957350	.244300	1.257260
p-Pop	.025960	.014260	2.978050	3.092950	2.902900	2.170000	.856860	2.987040
DPC	X	Y	Z		X	Y	Z	
	-0.934	3.266	1.433		-0.818	4.220	3.373	
Total dipole moment			3.686		5.464			

C: Charge, NE: Number of electrons, s-Pop: no of electrons in s-state, p-Pop: no of electrons in p- state and DPC: Dipole moment contribution.

and p-state as well as the dipole moment are calculated. Regarding C_{80} the charge is nearly tend to zero with nearly 4 electrons distributed as 1.2 electron at s-state and 2.8 electron at p-state. The total dipole moment is 3.1017 debye distributed as -1.400, 2.350 and 1.475 in the x, y and z directions respectively. As the effect of doping the change in the carbon atom number 3 will be discussed. Al shows an increase in its charge to be 0.596 with a net number of electrons 2.4 distributed as 0.6 and 1.79 in s-state and p-state respectively. The value of dipole moment is twice as compared with that of C_{80}. Ga and Tl has nearly the same charge as Al while a negative charge of -0.065 is regarded in case of In. Al, Ga and In showed dipole moment value around 6.0 debye while it increases as 14.639 debye corresponding to Tl. Regarding the calculated values of group V the charge is 0.413, 0.929, 0.761, 1.048 and 0.872 respectively. Although the net number of electrons is around four there a difference in the electron distribution such that; at s-state 1.2 corresponding to N, 1.7 corresponding to P and As finally 1.9 corresponding to Sb and Bi. The remaining electrons are distributed in p-state. The calculated dipole moment was 1.917, 3.002, 2.297, 3.686 and 5.464 debye respectively. This indicates that, both C_{79}-N and C_{79}-As are lower than C_{80}. While both C_{79}-P has the same dipole moment value as C_{80}, C_{79}-Sb is slightly higher than C80. Finally C_{79}-Bi is higher than C_{80}.

Vibrational spectra

Fig. 4 and Fig.5 shown the active vibrational modes for C_{80} as well as C_{80} doped with the elements of groups III and V respectively. There

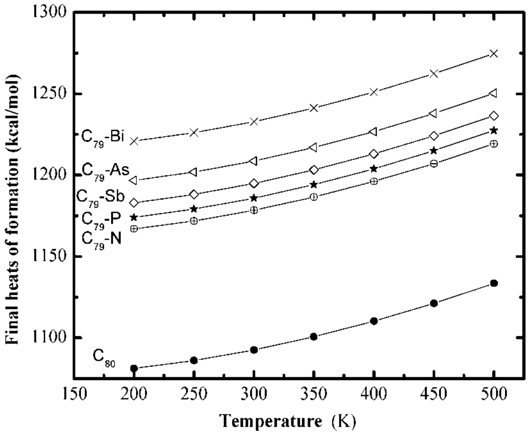


Figure 4. Active vibrational modes for C_{80} as well as C_{80} doped with the studied III elements.

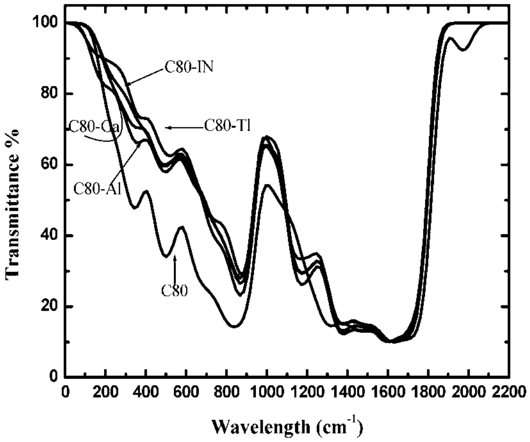


Figure 5. Active vibrational modes for C_{80} as well as C_{80} doped with the studied V elements.

are 174 genuine vibrations for C_{80}. As a result of the extremely high symmetry of C_{80} there are only 4 strong vibrational bands; two weak bands in addition to two shoulders. The assignment of C_{80} spectrum is aided by the program; by comparing the coordinates of each vibrational mode with that of the coordinates corresponding to the energy minimum. C_{80} showed comparable vibrational characteristic to that of C_{60}. On these bases the spectrum of C_{80} could be assigned. A C_{80} line at 406.38 cm^{-1} is assigned as the lowest frequency H_g "squashing" mode of Buckminsterfullerene. The A_g (1) mode was obtained around 581.67 cm^{-1}. The two strongest C_{80} lines, found at 1011.95 cm^{-1} and 1904.38 cm^{-1}, can consistently be assigned to the two totally symmetric A_g (2) modes. Two weak bands at 1537.85 cm^{-1} and 1370.48 cm^{-1} are assigned also as symmetric A_g (2) modes. The two shoulders were obtained at 693.22 cm^{-1} and 1123.51 cm^{-1}. The first shoulder is asymmetric A_g (1) mode so that it's too small. The second shoulder is assigned as asymmetric A_g (2) mode. The effect off doping on the vibrational catachrestic is varied from an element to another as in the following.

Regarding group III, an increase in transmittance of the doped fullerenes is regarded as compared with C_{80}. The four strong bands are not shifted; while the two shoulders are shifted toward higher frequencies. Furthermore the two shoulders became more obvious as a result of doping. The increase in the transmittance of the four strong bands -as a symmetric bands - and the increase in the transmittance of the shoulders -as asymmetric bands- match each other and keep the symmetry of the doped molecules unchanged.

Regarding group V, we could distinguish between two areas. The first up to 900.00 cm^{-1} and the second beyond 900.00 cm^{-1}.

The transmittances of the C_{79}-P and C_{79}-As bands are lower than C_{80}; while the others are higher. In the second region all the bands have higher transmittance as compared with C_{80}. As the effect of doping the weak bands became stronger with a shift toward higher frequencies. The symmetric A_g (2) band is shifted toward higher frequencies while the other strong bands remain unshifted. The shift in the asymmetric A_g (1) shoulder became more obvious toward higher frequencies. Which is also notices for the second shoulder.

Conclusions

In this work we have studied the structural and electronic properties of C80 and some of its doped derivatives with the elements of group III and V by performing the semiempirical molecular orbital theory at the level of PM3 of theory. We have seen that no change in the symmetry of the doped fullerenes, while the molecular dimensions as well as bond distance were changed. Dipole moments of the doped C_{80} with group III element are increased while that of group V is decreased except C_{79}-Sb and C_{79}-Bi. An increase in the total charge is recorded with net electrons in group III doped fullerenes. Although the number of electrons was around 4 the distribution of electrons in both S and p states are changed in group V doped fullerenes.

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