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Investigating the Effect of Fullerene (C_{20}) Substitution on the Structural and Energetic Properties of Tetryl by Density Functional Theory

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ABSTRACT

The substitution reaction of pure, silicon doped and germanium doped fullerenes with tetryl were evaluated computationally at two configurations, in this study. For this purpose, all of the studied structures were optimized geometrically, then IR and NBO calculations were performed on them in the temperature range of 298.15-398.15 K at 10° intervals. The obtained negative values of Gibbs free energy variations (ΔG_f), formation enthalpy alterations (ΔH_f) and great values of the thermodynamic equilibrium constant (K_{th}) prove that the reaction of the doped and also undoped fullerenes with tetryl is exothermic, spontaneous, one-sided and experimentally feasible. The impact of temperature on the thermodynamic parameters of the reaction was also inspected and the results indicate that 298.15 K is the optimum temperature for the synthesis of all of the derived products from the interaction of tetryl and the studied nanostructures. The calculated specific heat capacity values (Cv) show that the sensitivity of tetryl to the shock and heat has decreased significantly after its junction to fullerene nanostructures. Moreover, the increasing of N-O bond lengths after the fullerene substitution shows that the explosive power of tetryl has defused after its binding to the surface of fullerene. The obtained density values demonstrate that germanium doped C_{20} has the best impression on the improvement of the blasting power of tetryl in comparison to ordinary and silicon doped fullerenes.

Keywords: Tetryl; Fullerene; Density functional theory; Explosives; Silicon and Germanium.

1. INTRODUCTION

N-Methyl-N-2, 4, 6-tetraniutroaniline which is mostly known as tetryl is an energetic substance that is usually utilized in the construction of bombs and war weapons [1-3]. Tetryl which its chemical structure is presented in figure 1, was described for the first time by Romburgh at 1883 and it was widely used in the construction of Ammunitions in world war I and II [4-6]. For the synthesis of this substance which is like yellow color powder, dimethylaniline should be dissolved in concentrated sulfuric acid at the outset, in order to form dimethylaniline sulfate. In the next step, a mixture of H_2SO_4 and HNO_3 should be utilized for the nitration reaction and producing tetryl [7-9]. The explosion velocity of this energetic compound is too high and about 7200 to 7300 m/s. It is worth mentioning that the blasting power of tetryl is very high and outstanding so that it was recognized as the

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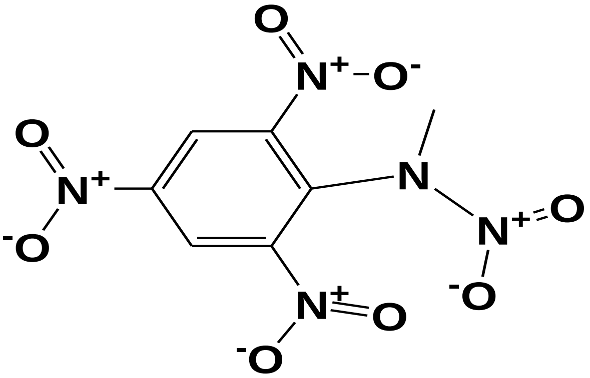
most efficient explosive substance during the first world war [10]. Moreover, prior studies have revealed that tetryl strength is even greater than trinitrotoluene (TNT) which in turn is a very potential explosive material. Despite the mentioned advantages, tetryl has a major downside which has severely constrained its production and usage in military fields in this era so that the united states completely stopped tetryl's production in 1979 and the problem is the tetryl's high sensitivity to heat, shock and friction [11-14]. Indeed, explosive materials sometimes can react to some factors such as Heat, shock and friction and this phenomenon could lead to the explosion before the appropriate time and cause irreparable casualties [15-17].

In this regards, allocating more studies on the energetic compounds and synthesizing substances with more explosive power and less sensitivity to heat and shock is of a great importance [18-20]. But owing to the fact that working with blasting compounds is very dangerous and requires laboratories with advanced and special equipment which are not accessible in many cases due to their high prices, performing experimental research is not economical, safe and intellectual [21-23]. On the other hand, theoretical studies and computational methods provide the privilege for the scholars and scientists to carry out research activities on explosives at a very low cost and without endangering their lives and safety [24-28].

In addition, C_{20} molecule is the smallest member of the fullerene family with a dodecahedral cage structure (figure 2). This fullerene consists of only pentagonal rings and has extreme curvature. Due to the fact that former reports have proved that fullerenes from C_{20} to C_{58} have narrow HOMO- LUMO gaps and prominent reactivity. It seems these small fullerenes can have a good impression on the energetic features of explosives. Hence, the effect of C_{20} cage substitution on the structural properties and blasting power of tetryl was evaluated by Ab initio calculations in this study, for the first time.



N-methyl-N-2,4,6-tetranitroaniline

Fig. 1. Chemical structure and IUPAC name of tetryl.

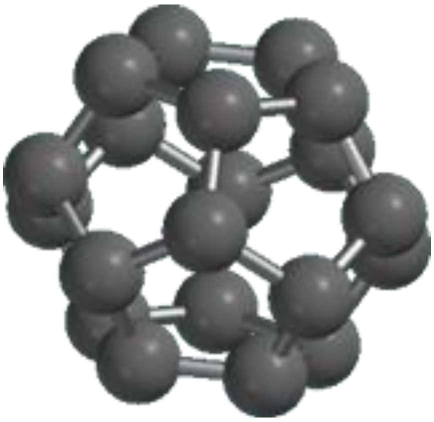
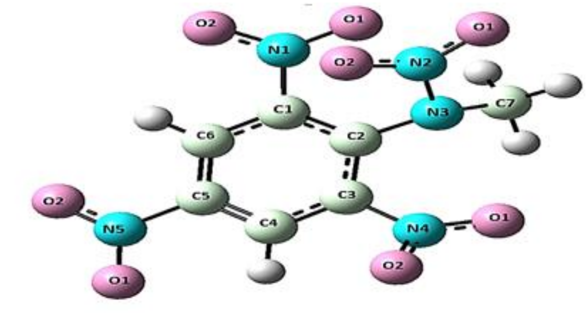


Fig. 2: Fullerene C_{20} cage structure.

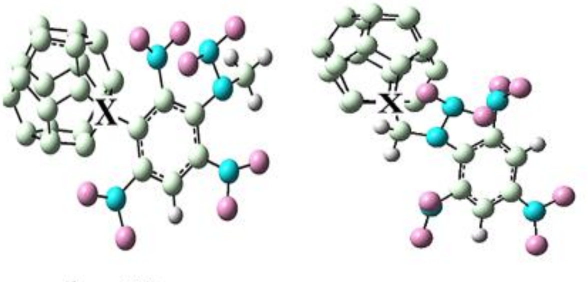
2. COMPUTATIONAL METHODS

In the beginning, the structures of the pure, silicon doped and germanium doped C_{20} cages, tetryl and the derived products of the reaction between tetryl and nanostructures at two different configurations were designed primarily by nanotube modeler 1.3.0.3 and Gauss View Softwares. Then, the designed structures were optimized geometrically and in the next step, IR and NBO calculations were implemented on them in the temperature range of 298.15-398.15 K at 10° intervals by spartan software. All of the calculations were performed by density functional theory in the B3LYP/6-31G (d) basis set. The reactions were assumed in the gaseous phase and one atmosphere pressure. The studied reaction is as follows:

$$\text{Tetryl} + C_{20} \rightarrow \text{Tetryl-}C_{20} \qquad (1)$$



a **Tetryl**



b **I-Isomer** c **II-Isomer**

X=C, Ge, Si

Fig. 3. The structures of tetryl and its derived products with C_{20} at two configurations.

3. RESULTS AND DISCUSSIONS

3.1. Evaluating the Structural Properties

As it can be seen from figure 3, the reaction of tetryl with pure, silicon doped and germanium doped C_{20} was investigated from two sites: C_6 and C_7. In order to realize the carried out studies in this project more easily, an abbreviated name is considered for each derived product of the reaction. The naming method is explained in the following:

The derived product that is created from the junction of C_6 of tetryl to the surface of the C_{20} cage (fig. 3a) is called I-Isomer. In this derivative fullerene is connected directly to the benzene ring of tetryl. As it is obvious from the figure, the effect of doping fullerene with silicon and germanium is also inspected at both configurations. And two derivatives that are produced from the interaction at this site with silicon doped and germanium doped fullerenes are called Si-I-Isomer and Ge-I-Isomer respectively.

The other derived product which is originated from the binding of C_7 of the methyl group of tetryl to the surface of C_{20} (fig. 3b) is called II-Isomer. The influence of doping fullerene with silicon and germanium in this situation was also checked out. Therefore, the Si-II-Isomer and Ge-II-Isomer, abbreviated names are heeded for the derivatives that are created from the tetryl reaction with silicon doped fullerene and germanium doped fullerene at this position respectively.

Due to the fact that the nitrogen-oxygen bonds play a key role in the explosive and destroying power of energetic compounds that have NO_2 functional groups in their chemical structure, the length of the bonds between nitrogen and oxygen atoms were measured Afterward, the structures of the studied compounds were designed by the software, and the geometrical optimization was performed on them. As the provided data in table1 demonstrate clearly the N-O bond lengths have increased remarkably in the C_{20} derivatives in comparison to pure tetryl. This phenomenon indicates that the bonds between nitrogen and oxygen atoms in fullerene derivatives have become weaker and can become disconnected more easily. In other words, C_{20}-tetryl derivatives can undergo combustion and explosion reaction more conveniently and their blasting power has improved substantially.

By a closer look at the table, it will be realized there is not a meaningful discrepancy between I-Isomers and II-Isomers in terms of bond lengths and this fact applies for both of the pure fullerene and doped fullerene derivatives. Because there is not a tangible difference between the N-O bond lengths of pure C_{20}-tetryl derivatives and the doped ones. Hence, on the basis of bond lengths, it can be deduced that there is not a tangible discrepancy between the I-Isomers and II-Isomers and doping fullerene with silicon and germanium does not have any influence on this parameter. It should be noted that the IR calculations show that all of the structures do not have any negative frequency and the positive frequency values that are presented in the table have also confirmed this fact. The next matter that can be understood from the table is that the total energy of fullerene derivatives is lower than ordinary tetryl and doping C_{20} with silicon and germanium leads to more decreasing of total energy so that germanium doped fullerene derivatives have the lowest energy among the other ones. Given the fact that by decreasing the total energy the stability of the evaluated compound has ameliorated. So; it can be inferred that the stability of tetryl has improved after the junction to the surface of fullerene and doping with silicon and germanium has also eventuated to the enhancing of stability.

Table 1. Total energy, the lowest frequency, and bond lengths of tetryl and its derivatives with fullerene

	Tetryl	**I-Isomer**	**Si-I - Isomer**	**Ge-I-Isomer**	**II-Isomer**	**Si-II - Isomer**	**Ge-II-Isomer**
Total energy (a.u)	-1123.575	-1870.876	-2119.291	-3885.474	-1871.057	-2119.326	-3885.477
Lowest frequency (cm-1)	31.169	16.154	15.988	14.675	16.680	10.221	10.831
N1-O1 (Å)	1.279	1.372	1.363	1.365	1.369	1.380	1.382
N1-O2 (Å)	1.275	1.360	1.374	1.368	1.375	1.381	1.382
N2-O1 (Å)	1.268	1.389	1.400	1.376	1.386	1.388	1.387
N2-O2 (Å)	1.276	1.386	1.403	1.384	1.391	1.390	1.388
N4-O1 (Å)	1.278	1.373	1.362	1.347	1.370	1.369	1.366
N4-O2 (Å)	1.276	1.363	1.374	1.361	1.365	1.364	1.378
N5-O1 (Å)	1.277	1.379	1.361	1.375	1.354	1.368	1.369
N5-O2 (Å)	1.278	1.368	1.369	1.363	1.369	1.354	1.355
C6-C (Å)	---	1.544	---	---	---	---	---
C7-C (Å)	---	---	---	---	1.556	---	---
C6-Si (Å)	---	---	1.863	---	---	---	---
C7-Si (Å)	---	---	---	---	---	1.883	---
C6-Ge (Å)	---	---	---	1.893	---	---	---
C7-Ge (Å)	---	---	---	---	---	---	1.926

3.2. Calculation and verifying the formation enthalpy changes values (ΔH_f)

In order to achieve formation enthalpy alterations values, the subsequent equation would be applied. In this formula, ΔE° is the symbol of variations in the total energy of the system which can be calculated by subtracting the total energy of the products from the total energy of the reactants. H_{th} also represents the thermal enthalpy values that were computed by the software for raw materials and products of the desired process.

$$\Delta H_f = \Delta E^{\circ} + (H_{th\ (Tetryl\text{-}C20)} - (H_{th\ (Tetryl)} + H_{th\ (C20)})) \qquad (2)$$

As the provided data in table 2, exhibit clearly the obtained ΔH_f values for all of the evaluated derivatives are negative. And this fact proves that the synthesis procedure is exothermic for all of the derived products from the reaction between tetryl and fullerene. Indeed, the heat is transferred from the system to the environment in this process. As it can be witnessed from the table, the ΔH_f values for II-Isomers are more negative than the formation enthalpy changes values of I-isomers. Hence, it seems the reaction of tetryl and C_{20} nanostructures from the C_7 situation is more exothermic and experimentally feasible. The next point that can be realized from the table is that doping of fullerene with silicon and germanium has different effects on each configuration. Because in I-Isomer by using silicon and germanium impurities in the C_{20} structure, the synthesis process has become more exothermic because ΔH_f value has decreased remarkably. On the other hand, in II-Isomer this parameter has become more positive after superseding the carbon atom of fullerene by silicon and germanium in the junction position of tetryl and C_{20} which shows that by doping phenomenon the synthesis of II-isomer has become less exothermic. Owing to the fact that temperature is one of the most important variables that can influence the synthesis mechanism and efficiency sharply. The effect of this factor on thermodynamic parameters was also inspected. As it is obvious from the table, temperature does not have a remarkable effect on the formation enthalpy changes values of all derivatives and it seems 298.15 K is the best temperature for the synthesis procedure of all derived products.

Table 2. The formation enthalpy changes values for the synthesis of the tetryl-fullerene derivatives in the temperature range of 298.15-398.15 K

	ΔH_f (KJ/mol)					
Temperature (K)	**I-Isomer**	**II-Isomer**	**Si-I -Isomer**	**Si-II –Isomer**	**Ge-I-Isomer**	**Ge -II-Isomer**
298.15	-326.648	-800.363	-629.810	-720.761	-671.659	-680.022
308.15	-326.541	-800.292	-629.758	-720.689	-671.575	-679.910
318.15	-326.425	-800.210	-629.728	-720.640	-671.511	-679.824
328.15	-326.301	-800.148	-629.697	-720.615	-671.454	-679.747
338.15	-326.185	-800.075	-629.663	-720.590	-671.395	-679.682
348.15	-326.054	-799.970	-629.604	-720.538	-671.325	-679.598
358.15	-325.922	-799.888	-629.536	-720.497	-671.264	-679.523
368.15	-325.804	-799.819	-629.497	-720.471	-671.179	-679.453
378.15	-325.681	-799.750	-629.458	-720.463	-671.085	-679.375
388.15	-325.561	-799.692	-629.439	-720.447	-670.991	-679.287
398.15	-325.438	-799.586	-629.398	-720.417	-670.889	-679.173

3.3. *Calculation and Verifying the Values of Gibbs Free Energy Changes (ΔG_f) and Thermodynamic Constant (K_{th})*

For calculating Gibbs free energy variations, the following equation was utilized. In this formula, G_{th} is the thermal Gibbs Free energy that was computed by the software for each material in the synthesis procedure and ΔE° represents the total energy changes of the system.

$$\Delta G_f = \Delta E^{\circ} + (G_{th\,(Tetryl\text{-}\,C24)} - (G_{th\,(Tetryl)} + G_{th\,(C24)})) \qquad (3)$$

As the calculated ΔG_f in table 3 demonstrate clearly, the synthesis process of all of the studied derivatives is spontaneous because this variable is negative for all of the derived products. By a more precise glance at the table, it could be understood that the formation reaction of II-Isomers is more spontaneous than I-Isomers since the values of Gibbs free energy changes for II-Isomers are more negative than I-Isomers and this matter can be observed in both pure and doped fullerene derivatives. The next point that can be witnessed in the table is that in I-Isomer doping C_{20} with silicon and germanium eventuates to a substantial decrease in ΔG_f values. Thus, replacing carbon with the dopant atoms eventuates to the more spontaneous formation reactions. However, in the II-Isomers the ΔG_f values of the doped fullerene derivatives are more positive than the undoped C_{20} derived product. Indeed, by using impurities in this configuration, the synthesis process has become less spontaneous. The influence of temperature on this variable has also been checked out and the results indicate that the 298.15 K is the optimum temperature for the formation reaction of all of the evaluated derivatives. Because the values of Gibbs free energy alterations have increased by incrementing of temperature. This phenomenon can be attributed to the fact that tetryl is unstable at high temperature since it is sensitive to heat and takes part in combustion and explosion reactions.

Table 3. The values of Gibbs free energy changes for the synthesis of tetryl-C_{20} derivatives in the temperature range of 298.15-398.15 K

ΔG_f (KJ/mol)						
Temperature (K)	**I-Isomer**	**II-Isomer**	**Si-I -Isomer**	**Si-II –Isomer**	**Ge-I-Isomer**	**Ge -II-Isomer**
298.15	-253.930	-723.840	-561.610	-649.837	-603.164	-608.438
308.15	-251.449	-721.230	-559.168	-647.306	-600.630	-605.885
318.15	-248.912	-718.574	-556.747	-644.801	-598.114	-603.362
328.15	-246.323	-715.948	-554.302	-642.323	-595.546	-600.853
338.15	-243.723	-713.283	-551.798	-639.840	-592.950	-598.361
348.15	-241.112	-710.555	-549.265	-637.263	-590.337	-595.844
358.15	-238.535	-707.916	-546.716	-634.754	-587.785	-593.331
368.15	-236.100	-705.470	-544.193	-632.283	-585.226	-590.844
378.15	-233.668	-703.038	-541.592	-629.782	-582.621	-588.298
388.15	-231.247	-700.587	-539.006	-627.221	-579.968	-585.722
398.15	-228.830	-698.065	-536.391	-624.593	-577.300	-583.050

The thermodynamic equilibrium constants of the desired reaction were also calculated by inserting the values of Gibbs free energy changes that were obtained in the last step at the following equation. In this formula, R and T denote the ideal gas constant and temperature respectively.

$$K = \exp(-\Delta G_f / RT) \tag{4}$$

As the reported data in Table 4 reveal clearly, the synthesis procedure for all of the derivatives is one-sided and non-equilibrium because the achieved thermodynamic constants are great values for all of the derived products of the reaction between tetryl and fullerene nanostructures. As it can be expected from the previous results of ΔH_f and ΔG_f values, the formation reaction of II-Isomers is more one-sided than the synthesis process of I-Isomers. In other words, the interaction of tetryl and C_{20} is more experimentally possible from the C atom of the tetryl's methyl group. One of the main advantages of the thermodynamic equilibrium constant is that it can depict the influence of temperature more clearly in comparison to other parameters. As it can be seen from the table, the highest K_{th} values are obtained at the ambient temperature and by enhancing of temperature this variable has declined significantly. So, it can be deduced that 298.15 K is the best temperature for all of the derivatives. By a closer look at the table, it can be perceived that the synthesis of II-Isomers is more one-sided than I-isomers because the K_{th} values of II-Isomers are higher than I-Isomers and this fact is applied in both undoped and doped fullerene derivatives. At I-Isomers doping fullerene with silicon and germanium leads to a remarkable surge in the thermodynamic equilibrium constant values and this fact implies that the formation reaction of I-Isomer has become more one-sided by using silicon and germanium impurities. But in II-Isomer replacing the carbon atom with the dopant atom eventuates to a tangible decline in the thermodynamic constants. Indeed, the synthesis of this derivative has become less experimentally possible by doping fullerene with silicon and germanium.

Table 4. The values of the thermodynamic equilibrium constant for the synthesis of tetryl-C_{20} derivatives in the temperature range of 298.15-398.15 K

K_{th}						
Temperature (K)	**I-Isomer**	**II-Isomer**	**Si-I -Isomer**	**Si-II –Isomer**	**Ge-I-Isomer**	**Ge -II-Isomer**
298.15	$3.084\times10^{+44}$	$6.583\times10^{+126}$	$2.485\times10^{+98}$	$7.126\times10^{+113}$	$4.738\times10^{+105}$	$3.978\times10^{+106}$
308.15	$4.214\times10^{+42}$	$1.821\times10^{+122}$	$6.141\times10^{+94}$	$5.358\times10^{+109}$	$6.556\times10^{+101}$	$5.100\times10^{+102}$
318.15	$7.388\times10^{+40}$	$9.582\times10^{+117}$	$2.579\times10^{+91}$	$7.393\times10^{+105}$	$1.597\times10^{+98}$	$1.162\times10^{+99}$
328.15	$1.625\times10^{+39}$	$9.291\times10^{+113}$	$1.724\times10^{+88}$	$1.770\times10^{+102}$	$6.337\times10^{+94}$	$4.434\times10^{+95}$
338.15	$4.463\times10^{+37}$	$1.535\times10^{+110}$	$1.739\times10^{+85}$	$6.932\times10^{+98}$	$3.957\times10^{+91}$	$2.712\times10^{+92}$
348.15	$1.501\times10^{+36}$	$4.091\times10^{+106}$	$2.581\times10^{+82}$	$4.122\times10^{+95}$	$3.753\times10^{+88}$	$2.516\times10^{+89}$
358.15	$6.174\times10^{+34}$	$1.779\times10^{+103}$	$5.483\times10^{+79}$	$3.798\times10^{+92}$	$5.358\times10^{+85}$	$3.450\times10^{+86}$
368.15	$3.162\times10^{+33}$	$1.255\times10^{+100}$	$1.641\times10^{+77}$	$5.178\times10^{+89}$	$1.090\times10^{+83}$	$6.831\times10^{+83}$
378.15	$1.897\times10^{+32}$	$1.305\times10^{+97}$	$6.516\times10^{+74}$	$9.914\times10^{+86}$	$3.031\times10^{+80}$	$1.844\times10^{+81}$
388.15	$1.321\times10^{+31}$	$1.922\times10^{+94}$	$3.455\times10^{+72}$	$2.572\times10^{+84}$	$1.125\times10^{+78}$	$6.689\times10^{+78}$
398.15	$1.052\times10^{+30}$	$3.844\times10^{+91}$	$2.363\times10^{+70}$	$8.820\times10^{+81}$	$5.504\times10^{+75}$	$3.126\times10^{+76}$

3.4. Calculation and inquiring the specific heat capacity values (Cv)

Specific heat capacity is defined as the amount of heat which is needed for incrementing the temperature of a certain amount of material to one degree. In this regards, this variable can be an appropriate parameter for estimating the sensitivity of an explosive compound to heat and shock. For this reason, the specific heat capacity values of all of the studied structures were computed in the temperature range of 298.15-398.15 K at 10° intervals and the obtained results were tabulated in table 5. The tabulated results in the table clearly demonstrate that the specific heat capacity values of the fullerene derivatives are considerably higher than the pure tetryl ones. This subject indicates that for raising the temperature of C_{20} derived products with tetryl, more heat and energy is required in comparison to single tetryl. Therefore, it can be concluded that the sensitivity of tetryl has abated noticeably after its junction to the C_{20} surface. The next matter that could be seen in the table is that the Cv values of I-Isomers are higher than II-Isomers. So, the safety of I-Isomers is more than the other ones. In addition, the Cv values of germanium doped fullerene derivative are greater than the Cv values of silicon doped fullerene derivatives. And pure C_{20} derived products have a lower specific heat capacity in comparison to the doped fullerene derivatives. Hence, supplanting carbon with silicon and germanium in the connection situation between fullerene and tetryl can play a decisive role in demolishing the sensitivity of this energetic compound to heat and shock. It seems this parameter has a direct linear relationship with temperature since by enhancing the temperature specific heat capacity has also increased linearly in all of the evaluated structures.

Table 5. The values of specific heat capacity (Cv) for tetryl and its fullerene derivatives in the temperature range of 298.15-398.15 K

				Cv (J/mol. K)			
Temperature (K)	**Tetryl**	**I-Isomer**	**II-Isomer**	**Si-I -Isomer**	**Si-II –Isomer**	**Ge-I-Isomer**	**Ge -II-Isomer**
298.15	252.9529	428.144	418.060	435.563	430.306	443.172	438.371
308.15	258.555	440.579	430.711	448.152	443.133	455.595	451.156
318.15	264.0864	452.884	443.245	460.599	455.815	467.873	463.785
328.15	269.5475	465.048	455.648	472.891	468.341	479.995	476.249
338.15	274.9382	477.062	467.909	485.020	480.700	491.954	488.537
348.15	280.2581	488.917	480.015	496.976	492.882	503.740	500.640
358.15	285.5067	500.604	491.956	508.751	504.876	515.346	512.550
368.15	290.6832	512.117	503.723	520.337	516.675	526.765	524.259
378.15	295.7867	523.447	515.307	531.729	528.273	537.991	535.762
388.15	300.8163	534.590	526.702	542.920	539.663	549.019	547.052
398.15	305.7712	545.539	537.900	553.906	550.839	559.845	558.126

3.5. NBO Analysis

Some of the structural and energetic properties including the energy of HOMO and LUMO molecular orbital (E_H and E_L), the energy gap between HOMO and LUMO orbitals (HLG), electrophilicity (ω), maximum transferred charge (ΔN_{max}), chemical hardness (η), dipole moment, chemical potential (μ), density, zero point energy, weight and volume were calculated and reported at table 6. HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital in chemistry and the energy difference between them is known as energy gap which is shown usually by HLG abbreviation. This parameter can be calculated by using equation 5. As it is obvious from table 6, the amount of energy gap has increased after tetryl's junction to the surface of C_{20} in all of the evaluated derivatives. And owing to the fact that the compounds with high energy gap need more energy for transferring the electron to the excited situation. It can be inferred that the conductivity of tetryl has reduced after its binding to the fullerene. In addition, it is worth mentioning that the HLG values of II-Isomers are higher than I-Isomers. Hence, I-Isomers are less conductive than II-Isomers. Doping fullerene with silicon and germanium leads to a modest rise in the HLG values of at I-Isomers but in the other configuration, there is not a clear relationship between the HLG value and doping effect.

The next inspected variable was chemical hardness which was calculated by equation 6. Chemical hardness is an ideal standard for estimating the softness of a molecule. Indeed, if a structure has a high chemical hardness value it will be chemically harder. As it can be observed from the table, the chemical hardness of tetryl-fullerene derivatives is higher than pure tetryl ones and given the fact that soft molecules can change their electron density more easily, this type of compounds could undergo chemical reactions more conveniently because the electron transmission, which is essential for the implementation of chemical reaction will be done comfortably in soft materials. Thus, it can be concluded that the reactivity of the fullerene derived products with tetryl is lower than the reactivity of pure tetryl. In other words, C_{20}-tetryl derivatives are more stable than single tetryl in terms of energetic aspects. The next matter which is obvious from the table is that doping fullerene with silicon and germanium leads to a little increase in the amount of chemical hardness at I-Isomer but at II-Isomer replacing carbon with the two other dopant atoms does not have a clear effect on this parameter. The chemical potential values that are necessary for obtaining electrophilicity and maximum transferred charge values were also calculated by means of equation 7. This parameter has also incremented after the connection of tetryl to the surface of fullerene.

$$HLG=E_{LUMO} - E_{HOMO} \tag{5}$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \tag{6}$$

$$\mu = (E_{LUMO} + E_{HOMO})/2 \tag{7}$$

$$\omega = \mu^2/2\eta \tag{8}$$

$$\Delta N_{max}=- \mu/ \eta \tag{9}$$

Table 6. The values of Calculated E_H and E_L, HLG, chemical hardness (η), electrophilicity index (ω), chemical potential (μ), the maximum amount of electronic charge index (ΔN_{max}), volume, weight, density, zero point energy and dipole moment

	Tetryl	**I-Isomer**	**II-Isomer**	**Si-I -Isomer**	**Si-II -Isomer**	**Ge-I-Isomer**	**Ge-II-Isomer**
E_H (eV)	-8.220	-7.420	-7.460	-7.600	-7.020	-7.110	-7.060
E_L (eV)	2.680	4.800	5.960	5.540	6.290	6.190	6.360
HLG (eV)	10.900	12.220	13.420	13.140	13.310	13.300	13.420
η (eV)	5.450	6.110	6.710	6.570	6.655	6.650	6.710
μ (eV)	-2.770	-1.310	-0.750	-1.030	-0.365	-0.460	-0.350
ω (eV)	0.704	0.140	0.042	0.081	0.010	0.016	0.009
ΔN_{max}(eV)	0.508	0.214	0.112	0.157	0.055	0.069	0.052
Dipole moment (deby)	3.170	1.720	1.500	1.880	2.200	2.570	2.550
Volume (Å^3)	220.210	439.880	436.490	448.600	448.750	448.830	449.580
Weight (amu)	287.144	526.356	526.356	542.431	542.431	586.955	586.955
Density=m/v (amu/Å^3)	1.304	1.197	1.206	1.209	1.209	1.308	1.306
Zero point energy (KJ/mol)	444.080	718.430	723.960	706.940	708.100	700.480	699.990

Electrophilicity index which can be calculated by equation 8, is an excellent criterion for estimating the tendency of a substance towards electron. When two molecules take part in a reaction, one of them behaves as a nucleophile while the other one acts as an electrophile. And if a compound has a high electrophilicity value, it will have a high affinity for absorbing the electron. The maximum transferred charge index (ΔN_{max}) that was calculated by equation 9, demonstrates the charge capacity of a system. In fact, if a material has a positive value of ΔN_{max} it will act as an electron acceptor, but if a substance has a negative value of ΔN_{max} it will play the role of an electron donor. As it is clear from the table, both of the electrophilicity and maximum transferred charge values have decreased after the attachment of tetryl to the surface of fullerene. This evidence proves that tetryl has a greater tendency for absorbing the electron in comparison to its fullerene derivatives. Moreover, II-Isomers have lower ω and ΔN_{max} values than I-Isomers so, II-Isomers have less affinity to the electron in comparison to I-Isomers. The next matter that can be realized from the table is that germanium doped and silicon doped fullerene derivatives at both configurations have lower ω and ΔN_{max} indices than pure C_{20} derived products. Hence, doping procedure eventuates to a significant decline in the electrophilicity of the system.

The dipole moment is a key factor which has a direct relationship with the solubility of a compound in polar solvents. Indeed, a structure with high dipole moment has a good solubility in polar solvents like water and a substance with a low dipole moment has a poor solubility in polar solvents. The obtained results from the calculations have revealed that the solubility of tetryl has reduced after its reaction with C_{20} due to the lowering of dipole moment values in the fullerene derivatives. By a closer look, it will be perceived that replacing carbon with silicon and germanium has defused the solubility in water considerably.

The next important studied parameter is the density of tetryl and its derived products with fullerene. Density has an obvious relationship with the destructive and explosive power of an energetic substance. An explosive with higher density has stronger destructive and blasting power, whereas an explosive with lower density has weaker destructive and blasting power. The provided data in table 6 show that by binding of tetryl to the surface of pure fullerene the density has decreased substantially. Therefore, the explosive power of pure C_{20}-tetryl derivatives can be lower than single tetryl. But doping fullerene with silicon and germanium impurities has led to a surge in the densities of the evaluated structures so that Ge-I-Isomer and Ge-II-Isomer have higher density values than pure tetryl. Hence, it can be expected that these two compounds will be stronger explosives than tetryl because the nitrogen-oxygen bond lengths have also increased in these derivatives. In addition, the amount of specific heat capacity values of Ge-I-Isomer and Ge-II-Isomer have experienced a remarkable rise which proves that the sensitivity of these structures has reduced dramatically. Therefore, Ge-I-Isomer and Ge-II-Isomer were the best-evaluated explosives in this study.

CONCLUSIONS

Performing research and development activities on energetic compounds in order to find an explosive with higher blasting power and lower sensitivity to heat and shock is of a great importance. And computational methods provide the opportunity for chemists to study this field with low cost and without endangering their health. Hence, the effect of pure, silicon doped and germanium doped C_{20} substitution on the energetic and structural features of tetryl was evaluated in this study. The obtained thermodynamic parameters have shown that the reaction between tetryl with pure and doped fullerenes are exothermic, spontaneous, one-sided and experimentally feasible and the best temperature for the synthesis of tetryl-C_{20} derivatives is 298.15 K. The calculated specific heat capacity values have revealed that the sensitivity of tetryl to heat and shock has declined drastically after its junction to the fullerene surface. Moreover, the achieved results from the density values and also nitrogen-oxygen bond lengths have exhibited that the explosive and destructive power of germanium doped fullerene derivatives is better than pure tetryl. Due to the fact that the theoretical results proved that germanium doped tetryl-C20 derivatives are more powerful and safe explosives than pure tetryl, the experimental synthesis of these compounds and checking their energetic properties is recommended to be evaluated in the future to the experts of this field.

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