



New organotellurium compounds based on camphor, aniline and p-toluidine: preparation, characterization, and theoretical study

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Abstract

The present study involved the preparation of organomercury and organotellurium compounds derived from camphor and (2-amino-5-methylphenyl) mercury (II) chloride and their derivatives by a condensation reaction. Characterization of the studied compounds was carried out using infrared spectrum (IR), proton nuclear magnetic resonance spectrum (^1H NMR), and elemental analysis (C.H.N). The molecular structure of the organotellurium compounds was investigated using the density functional theory with hybrid functional (B3LYP) and the basis set 3-21G. Geometrical structure, HOMO surfaces, LUMO surfaces, and energy gap have been produced throughout the geometry optimization. The molecular geometry and contours for the organotellurium compounds were investigated throughout the geometrical optimization. The donor and acceptor properties have been studied by comparing the highest occupied molecular orbital energies (HOMO) of organotellurium compounds. The electronegativity, electrophilicity, Ionization potential, electron affinity, Chemical Hardness, and Chemical softness for the organotellurium compounds was calculated for the molecules under the study.

Keywords: organotellurium, camphor, mercury chloride, aniline, HOMO, LUMO, DFT, ^1H NMR and FT – IR.

1. Introduction:

Tellurium, classified in group 16 of the periodic table of the elements, was discovered in 1782 by the Austrian chemist F. J. Müller von Reichenstein [1]. Organic tellurium chemistry is a very broad and exciting field with many opportunities for research and application development [2]. The first organotellurium compound was reported over 181 years ago with the synthesis of diethyl tellurides by Wöhler in 1840 [1]. In recent years, there has been great interest in studying organo-tellurium compounds containing azomethane group due to the high stability and various applications of these compounds [3, 4]. The applications of organotellurium compounds have been reported in several fields [4-8]. Past research reported using organotellurium compounds as antioxidant agents [5, 9, 10], polymerization catalysts [11-13], antitumor and pharmaceutical agents [5, 14, 15], organic superconductors [3, 7], synthetic intermediate [4], and ligands with many transition metal ions [3, 16, 17]. Also, the use of organotellurium compounds has been reported in numerous applications for organic synthetic purposes because of using mild conditions, high yield, and high selectivity of the desired product [2, 18, 19]. Organotellurium compounds have also been used as selective reducing or oxidizing reagents of functional groups [10, 15]. Coupling reaction based

on organotellurium compounds seems to offer an interesting opportunity for synthetic organic chemists. Thus, In recent years, there has been a growing interest in studying the organotellurium compounds which have intramolecular interaction [10, 20]. There are many types of organotellurium compounds containing nitro-amino and azomethane groups that exhibit such reactions [5-7, 9, 11, 13, 21].

Density functional theory (DFT) is used to examine the electronic properties and molecular structure of chemical compounds [22]. The DFT deals with the electron density rather than the wave function [22, 23]. But, the wave function assumes spatial variables and the rotation coordinates are the same, where the positions of the nuclei are constant [24]. The electronic structure and some other properties of atoms, molecules, In several cases the consequences of density functional theory calculations for solid-state molecules agree completely [25-28].

The purpose of this study is to prepare organomercury and organotellurium compounds derived from camphor, (2-amino-5-methylphenyl) mercury (II) chloride and p-aminophenyl mercury (II) chloride and their derivatives by condensation reaction as well as a theoretical study of the prepared organotellurium compounds from By calculating

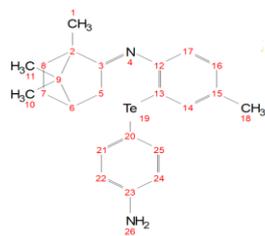
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Receive Date: 05 June 2021, Revise Date: 22 July 2021, Accept Date: 24 August 2021

DOI: 10.21608/EJCHEM.2021.79236.3893

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$^{10}\text{CH}_3$, $^{11}\text{CH}_3$, $^{1}\text{CH}_3$ (9H, t, 2.90); $^5\text{CH}_2$, $^7\text{CH}_2$, $^8\text{CH}_2$ (6H, s, 2.92); ^6CH (1H, s, 4.00); $^{18}\text{CH}_3$ (3H, s, 2.98); Ar-H (7H, m, 6.50 – 7.24); $^{26}\text{NH}_2$ (2H, s, 4.99).

4. Computational Details

HOMO and LUMO energies are electronic states, referring to certain places of existence of the electrons with quantized energies. HOMO energy indicates the high occupied molecular orbital, while LUMO energy refer to the low unoccupied molecular orbital, where the molecular orbitals are the linear combination to the atomic orbitals [40]. The difference between HOMO and LUMO gives energy band gap (E_{gap}) as the relation [41]:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \dots (1)$$

Table 2. The electronic states of the organotellurium compounds

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
B	-4.976	-2.514	2.46
C	-4.224	-2.874	1.35
D	-4.752	-0.778	3.97

In the present study, A comparison of the HOMO energies is presented in Table (2) to find out that HOMO energy of C compound is a greater than D compound and the lowest in HOMO energy was C compound, and the arrangement of energy average [42] in LUMO energy as the following:

$$C > B > D$$

Therefore, energy gap has the highest value at D while the lowest value at C compound [42]. As shown in Table 2, Figure (9 - 11).

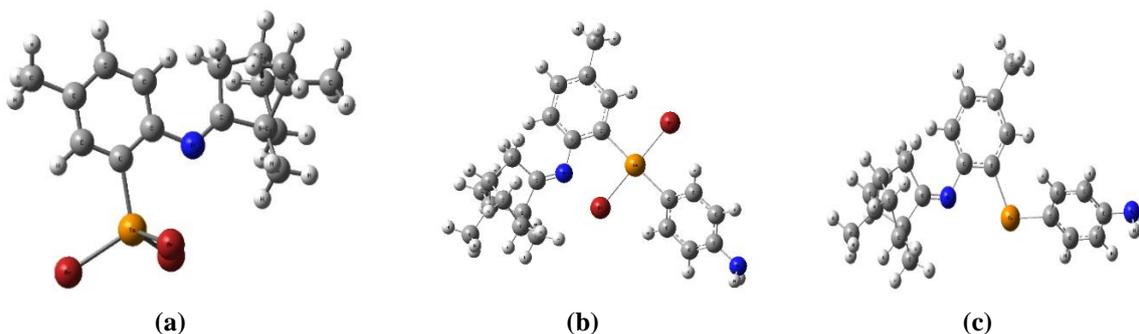


Figure 9. Molecular structure of (a) compound B (b) compound C (c) compound D

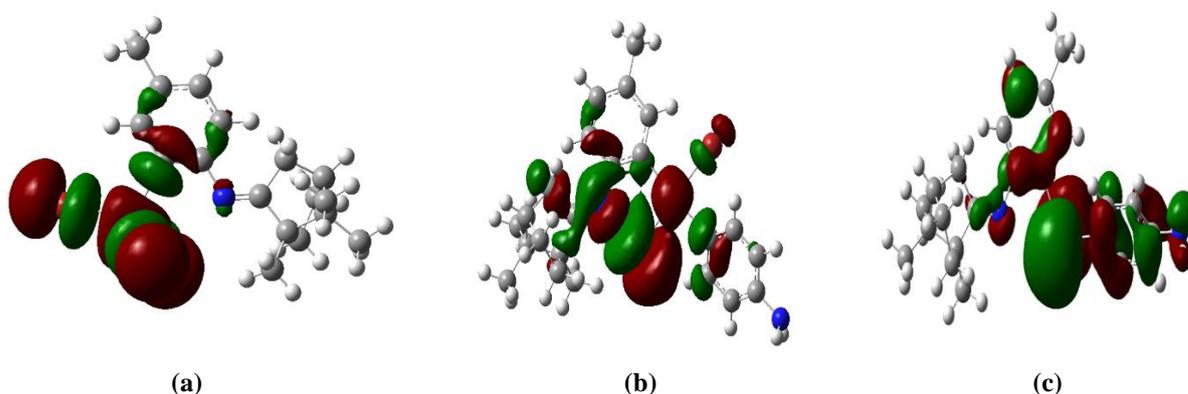


Figure 10. HOMO surfaces of (a) compound B (b) compound C (c) compound D

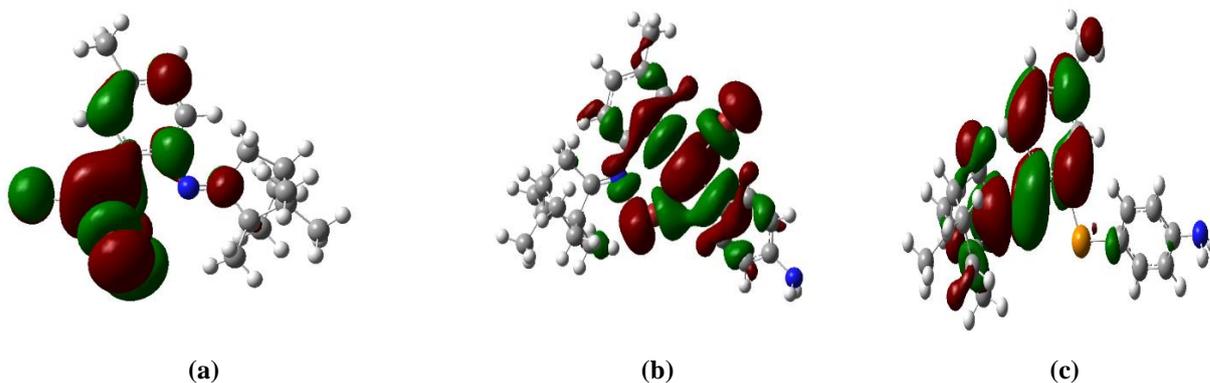


Figure 11. LUMO surfaces of (a) compound B (b) compound C (c) compound D

This principle describes the behavior of molecules or atoms as acids and bases in chemistry. Throughout this principle, one can distinguish the donors and acceptors [43, 44]. It is necessary to show that the soft base and hard base represent donors, whereas the soft acid and hard acid stand for acceptors [43, 44]. The following equations 2 and 3 can express hardness and softness:

$$\eta = \frac{I.P - E.A}{2} \quad \dots (2)$$

$$\sigma = \frac{1}{2\eta} \quad \dots (3)$$

The symbol η refers to hardness, whereas the symbol σ refers to softness.

The comparison between B, C, and D shows that the hardness of D was larger than the hardness of B and C, hence D will behave as a hard base. The softness of C was larger than B and D, indicating that C will behave as a soft base [44, 45]. According to Table (3), the behavior of organotellurium compounds can be classified as donors or acceptors.

Table 3. Chemical hardness and chemical softness of the organotellurium compounds

Comp.	Chemical Hardness	Chemical Softness
	(η)	(σ)
B	1.23	0.41
C	0.68	0.74
D	1.98	0.25

We can define electronegativity as a measure of the tendency of an atom to attract bonding pair of electrons [23, 24, 42, 44], it describes the escaping tendency of the electrons from a balance system such as molecules. Electronegativity and electrophilicity [44] calculated by the relations:

$$\chi = \frac{E_{HOMO} + E_{LUMO}}{2} \quad \dots (4)$$

$$\omega = \frac{\chi^2}{2\eta} \quad \dots (5)$$

Table 4. Electronegativity and electrophilicity of the organotellurium compounds

Compound	Electronegativity (eV)	Electrophilicity (eV)
	(χ)	(ω)
B	-3.74	5.73
C	-3.55	9.32
D	-2.76	1.90

Ionization potential measures the binding force between an electron and atom and equivalent to the required energy to remove one electron from a neutral atom in the gas state. In hydrogen atom, there is one ionization energy in the outer shell. The atoms

Where χ and ω refer to the electronegativity and electrophilicity respectively, as explain in Table 4

In Table (4), the electronegativity of D was larger than the electronegativity of C and B. C compound was the larger electrophilic molecule, whereas D has the least electrophilicity among all prepared compounds [24, 44].

which have over one electron in the outer shell will have one ionization energy for every electron [45, 46].

Electron affinity may be defined as the energy released when an atom gains an electron. Sometimes electron affinity is named zero ionization energy. The atoms that have seven electrons in the outer shell have high electron affinity, whereas the

atoms that have closed shells have small electron affinity [45]. According to Koopman's theory [36, 44-46]:

$$I.P = -E_{HOMO} \quad \dots (6)$$

$$E.A = -E_{LUMO} \quad \dots (7)$$

Table (7) showed the values of ionization potential and electron affinity in (eV) for B, C and D compounds. Ionization potential and electron affinity results depends on the energies in the valence band and conduction band according to Koopman's theorem.

Table 5. Ionization potential and electron affinity of the organotellurium compounds

Comp.	Ionization potential (eV) (I.P)	Electron affinity (eV) (E.A)
B	4.97	2.51
C	4.22	2.87
D	4.75	0.77

Conclusions:

The present work described the efficient routes of synthesizing some novel organomercury and organotellurium compounds by a simple and convenient method. Compounds A, B, C and D were obtained at a 33 – 83% yield.

All the obtained results (i.e., CHN, FT-IR, and ¹H NMR) concurred with previous findings and confirmed the correctness of the proposed structures for all the prepared compounds. As for the theoretical study, the density functional theory used in this study is a powerful method and B3LYP functional is a suitable and efficient function for studying the electronic properties of these structures. 6-31G (d, p) gives good agreement results for geometrical parameters with experimental data. The density functional theory method has been used in this work to study the geometry optimization and the electronic properties of organometallic by using B3LYP functional.

The total energies donor-acceptor system showed that the proposed structures are more stable. The donor-acceptor system has large average polarizability comparing with donor and acceptor and this system has high reactivity than others. The results got in this work help us select a type of bridge to interact with the donor and acceptor to calculate the physical properties of the donor-bridge-acceptor.

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One can see from the table the arrangement of the prepared compounds according to the increase of the ionization potential:

$$B > D > C$$

This means that the electrons will need less energy to escape from the surfaces, which is very advantageous. On the other hand, the electron affinity increased as follows:

$$C > B > D$$

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