Comparing Study of The Stability and spectral properties vibrations for some Tellurium (IV) compounds containing cycloctadienyl group by Quantum Mechanical Calculations

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Abstract

Density Functional Theory (DFT) with B3LYP hybrid exchange-correlation functional and 3-21G basis set and semi-empirical methods (PM3) were used to calculate the energies (total energy, binding energy (E_b), molecular orbital energy (E_{HOMO}-E_{LUMO}), heat of formation (ΔH_f)) and vibrational spectra for some Tellurium (IV) compounds containing cycloctadienyl group which can use as ligands with some transition metals or essential metals of periodic table at optimized geometrical structures.

Key words: Tellurium, vibrational spectra, DFT, stability

Introduction

Tellurium is a rare element, which has been regarded as a non-essential, toxic element [1-4]. It is present in the Earth's crust only in 0.001 parts per million. It is obtained commercially from the anode muds produced during the electrolytic refining of copper [5].

Tellurium is used in alloys, mostly with copper and stainless steel, to improve their machinability. When added to lead, it decreases the corrosive action of sulphuric acid on lead and improves its strength and hardness. Tellurium is also used in ceramics. It can be doped with silver, gold, copper or tin in semiconductor applications.

Tellurium is occasionally found native, but is more often found as the telluride of gold (calaverite) or combined with other metals. In the environment, Te exists in its elemental (Te^0), inorganic - telluride ((Te^{2-}), tellurite (TeO_3^{2-}), and tellurate ($TeO_4^{2}-$)), and organic (dimethyl telluride (CH_3TeCH_3) forms [6]. Of these, its oxyanion forms are more common than its non-toxic, elemental state [7]. Tellurium composes both inorganic and organic derivatives. An inorganic tellurium compound differs from an organic derivative because the former has at least one tellurium-carbon bond in its structure. A number of different classes of organotellurium compounds are known. Those classes can be divided in two distinct groups according to the oxidation state of tellurium. The first group contains the divalent derivatives and the second major group is composed by the hypervalent derivatives in which tellurium has the oxidation states of +4 and +6, and the classes of organotelluranes composed by organotellurium trihalides, diorganotellurium dihalides, organotellurium oxides, organotellurates, and organopertelluranes [8].

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the explosive development of Selenium chemistry called attention to the potentiality of Tellurium analogues, resulting in studies on preparation methods for inorganic and organic tellurium compounds and particularly on their applications in Organic Synthesis. In the mid 50's, H. Rheinboldt published the first review (about 50 pages) on selenium and tellurium compounds in organic chemistry [9]. Then in 1990, K. Irgolic dedicated as much as 1000 pages in a review on tellurium compounds. The impressive number of publications on this subject during the last few years shows that Tellurium already plays a new role as a powerful chemical tool [10].

In this paper, the energies and vibrational spectra of some prepared [11] Tellurium (IV) compounds containing cycloctadienyl group, which can be used as ligands with some transition and essential metals of periodic table were calculated to study the stability of these compounds.

Material and method:

Molecular geometry optimization, energies and vibrational spectra calculations were performed with the Gaussian 03W software package [12] by using density functional theory (DFT) method with B3LYP hybrid exchange-correlation functional [13] and 3-21 G basis set. No symmetry restriction was applied during geometry optimization. The vibrational frequencies were computed at the optimized geometry to ensure that no imaginary frequencies were obtained confirming that it corresponds to a local minimum on the potential energy surface.

Results and discussion

The compounds considered here are shown in Table (1). The molecular structures of compounds optimized using PM3 semi-empirical method and the energies (total energy, binding energy, molecular orbital energy (E_{Hom}-E_{Lumo}) and heat of formation for all compounds were calculated and listed in Table (2).

Table (1): The molecular formula and molecular structures of compounds

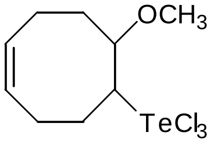
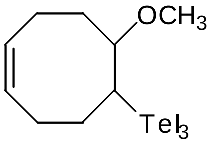
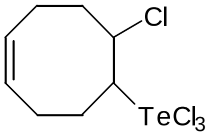
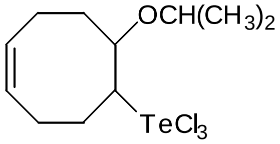
Chemical structure	Molecular structure
$C_9H_{15}Cl_3OTe$	
$C_9H_{15}I_3OTe$	
$C_8H_{12}Cl_4OTe$	
$C_{11}H_{19}Cl_3OTe$	

Table (2): The calculated energies of compounds

Compounds	M.Wt (gm/mol)	ΔH_f (kcal/mol)	Total energy (kcal/mol)	Binding energy kcal/mol	Surface energy (EV)		ΔE_{gab} (EV)
					E_{HOMO}	E_{LUMO}	
$C_9H_{15}Cl_3OTe$	373.176	-102	-62578	-2615	-9.589	-3.577	6.012
$C_9H_{15}I_3OTe$	647.530	-50	-60656	-2552	-8.901	-3.958	4.943
$C_8H_{12}Cl_4OTe$	379.611	-65	-59310	-2595	-9.872	-3.909	5.963
$C_{11}H_{19}Cl_3OTe$	401.230	-119	-69481	-3182	-8.916	-2.365	6.551

As shown in Table (2) the binding energy E_b of the compounds arranged as follow:

$E_b(C_{11}H_{19}Cl_3OTe)<E_b(C_9H_{15}Cl_3OTe)<E_b(C_8H_{12}Cl_4OTe)<E_b(C_9H_{15}I_3OTe)$

The molecular orbital energy (E_{HOMO} and E_{LUMO}) and the HOMO-LUMO gab ΔE_{gab} were calculated. The ΔE_{gab} which represents the energy difference between a molecule's Highest energy Occupied (HOMO) and its Lowest energy Unoccupied (LUMO) figure (1), calculated according to the following equation:

$$\Delta E_{gab} = E_{LUMO} - E_{HOMO}$$

When ΔE_{gab} is large, the molecule will be more stable, so the stability of molecules arranged in the following relationship:

$\Delta E_{gab}(C_{11}H_{19}Cl_3OTe)>\Delta E_{gab}(C_9H_{15}Cl_3OTe) > \Delta E_{gab}(C_8H_{12}Cl_4OTe) >\Delta E_{gab}(C_9H_{15}I_3OTe)$

The relationships above can be explained as follows:

1. The heat of formation for $C_{11}H_{19}Cl_3OTe$ is smaller than it for $C_9H_{15}Cl_3OTe$,thus we expected that the formation of compound with $(CH_3)_2$ is to be thermodynamically more stable than it with (CH_3).
2. The heat of formation of $C_9H_{15}Cl_3OTe$ is smaller than it for $C_8H_{12}Cl_4OTe$, so we expect that the formation of compound with methoxy (OCH_3) group is to be thermodynamically more stable than it with halogen atom (Cl).
3. The heat of formation of $C_9H_{15}Cl_3OTe$ and $C_8H_{12}Cl_4OTe$ are smaller than for $C_9H_{15}I_3OTe$, so we expect that the formation of compound is to be thermodynamically more stable if the polarizability of halogen atom decreased.

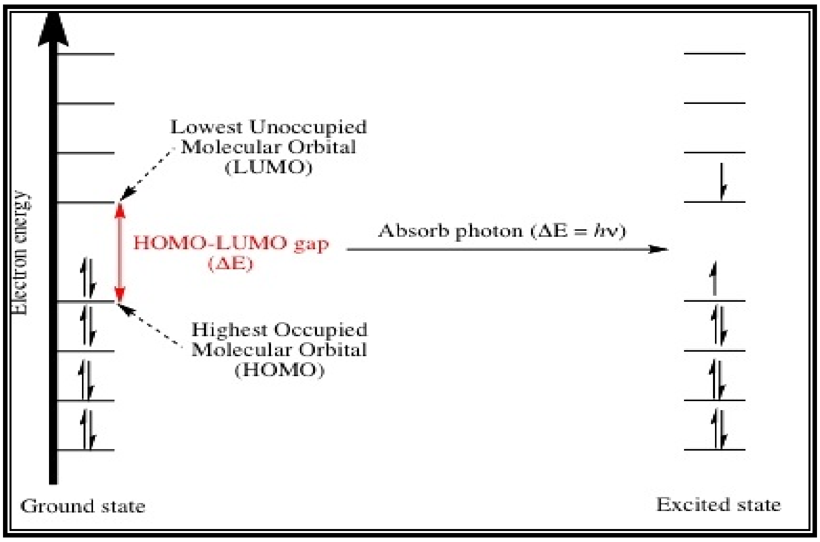


Fig.(1): HOMO-LUMO gab

For a proper understanding of the vibrational spectra, a reliable assignment of all vibrational bands is essential. For this purpose, DFT methods, particularly B3LYP hybrid functional methods and 3-21 G basis set have evolved, the geometries of the compounds were optimized, for all compounds C_1 symmetry are obtained. The vibration frequencies and IR absorbance intensities of the compounds were calculated and listed in Tables (3, 4, 5 and 6).

Table (3): vibration frequencies and IR intensities of $C_9H_{15}Cl_3OTe$

No.	Frequency cm^{-1}	Intensity km/mol	Exp. [11]	No.	Frequency cm^{-1}	Exp. [11]	Intensity km/mol
1	40	0.3885		42	1134		2.9215
2	57	1.1498		43	1158		4.7696
3	78	1.4705		44	1195		3.3602
4	87	0.9380		45	1196		2.7469
5	95	4.0671		46	1210		1.5435
6	112	5.3053		47	1263		5.2863
7	120	6.2964		48	1296		2.5641
8	130	6.6998		49	1303		3.5610
9	155	0.7070		50	1317		2.1929
10	164	4.6802		51	1333		4.2786
11	187	5.3399		52	1355		3.1525
12	196	5.8157		53	1373		0.1604
13	209	0.5599		54	1396		1.8680
14	238	8.2274		55	1405		2.8568
15	254	15.6215		56	1411		6.7785
16	272	85.9957		57	1420		3.0544
17	282	24.7138	300	58	1458	1440	0.5087
18	293	61.1107		59	1485	1470	2.2593
19	308	2.3985		60	1540		0.1037
20	343	5.6382		61	1544		1.4867
21	364	9.9208		62	1549		21.8313
22	457	1.5693		63	1558		4.2990
23	474	26.3223		64	1560		9.7901
24	490	6.7298		65	1562		34.2620
25	562	1.0492		66	1716		0.1773
26	603	2.6403	540	67	3057	3010	12.4437
27	698	18.0972		68	3059		11.4147
28	757	45.5407		69	3066		27.2813
29	801	7.7073		70	3071		18.1149
30	835	1.2518		71	3080		1.1738
31	860	16.1250		72	3099		15.8934
32	906	12.2033		73	3105		4.9945
33	918	15.6809		74	3116		8.5962
34	976	2.9968		75	3117		1.4231
35	999	3.9296		76	3135		0.4147
36	1021	1.8556		77	3143		1.9902
37	1026	122.6005		78	3151		3.9701
38	1031	15.9021		79	3152		6.3918
39	1035	0.9197		80	3166		3.7456
40	1071	2.2078		81	3176		27.6899
41	1096	5.5375					

Table (4): vibration frequencies and IR intensities of $C_9H_{15}I_3OTe$

No.	Frequency cm^{-1}	Intensity km/mol	Exp. [11]	No.	Frequency cm^{-1}	Exp. [11]	Intensity km/mol
1	28	0.4135		42	1128		1.9875
2	32	0.2555		43	1161		6.7381
3	42	0.0634		44	1193		3.1534
4	47	1.6699		45	1196		6.1778
5	69	0.2204		46	1209		1.1152
6	75	2.8404		47	1264		6.1789
7	94	3.0191		48	1294		3.9863
8	99	0.8121		49	1305		2.7194
9	112	1.3324		50	1319		1.7660
10	132	1.4809		51	1330		4.5557
11	142	14.3966		52	1359		4.4236
12	168	35.0296		53	1373		0.4296
13	171	27.8621		54	1398		1.8929
14	184	6.2878		55	1405		4.6055
15	195	14.0347		56	1414		6.7558
16	208	9.4735		57	1425	1440	3.7335
17	256	1.0230		58	1458	1470	0.8887
18	285	8.8434		59	1492		2.5859
19	310	7.4832		60	1542		0.2423
20	335	1.1792		61	1547		1.2814
21	348	5.6059		62	1552		12.0515
22	456	2.2059		63	1553		18.2860
23	470	28.8560		64	1560		8.6593
24	488	4.2101		65	1569		24.5674
25	562	0.6441	540	66	1717		0.1467
26	602	1.7128		67	3055	3010	1.3646
27	683	26.1343		68	3058		45.4855
28	759	46.8374		69	3060		11.0030
29	797	7.1888		70	3070		16.9321
30	837	2.2222		71	3074		4.4401
31	862	18.3532		72	3099		14.8475
32	906	21.3205		73	3101		2.7399
33	919	15.0444		74	3109		6.0990
34	978	1.8346		75	3115		3.9531
35	998	5.0741		76	3123		2.6219
36	1021	1.0206		77	3135		3.3167
37	1029	20.7342		78	3136		4.6802
38	1032	1.4541		79	3151		5.2708
39	1037	100.7956		80	3163		4.3639
40	1067	3.6743		81	3176		27.5270
41	1090	5.2695					

Table (5) vibration frequencies and IR intensities of $C_8H_{12}Cl_4Ote$

No.	Frequency cm^{-1}	Intensity km/mol	No.	Frequency cm^{-1}	Intensity km/mol
1	36	0.1467	36	1073	4.4226
2	52	0.3952	37	1109	7.6760
3	76	3.6710	38	1121	5.6924
4	89	0.0598	39	1172	5.8232
5	99	0.0687	40	1220	4.6516
6	118	0.0968	41	1242	1.5595
7	126	2.1424	42	1285	12.0461
8	137	16.1355	43	1302	12.9037
9	159	1.4192	44	1320	3.3055
10	166	4.2956	45	1341	1.6963
11	207	1.0824	46	1361	1.6078
12	238	9.3433	47	1394	4.8483
13	249	0.8300	48	1405	3.3573
14	258	4.1516	49	1407	2.0090
15	278	114.4819	50	1436	10.9091
16	294	7.3046	51	1441	3.3549
17	303	30.8708	52	1470	0.2794
18	316	0.4512	53	1533	11.0360
19	360	5.6091	54	1546	9.8005
20	382	3.2567	55	1552	16.9469
21	480	2.2057	56	1590	20.4340
22	511	1.4076	57	1725	0.6450
23	627	28.0778	58	3024	13.8301
24	686	66.8770	59	3057	9.3274
25	706	6.7332	60	3084	6.6423
26	741	9.0464	61	3091	3.9425
27	780	2.1400	62	3093	12.5277
28	813	7.6009	63	3103	2.3336
29	874	2.8630	64	3135	3.4533
30	910	7.7918	65	3143	6.6681
31	915	3.2885	66	3156	1.3724
32	996	4.5220	67	3166	30.6708
33	1012	0.3339	68	3173	7.3468
34	1033	2.0252	69	3181	3.0442
35	1036	1.7451			

Table (6) vibration frequencies and IR intensities of $C_{11}H_{19}Cl_3OTe$

No.	Frequency cm^{-1}	Intensity km/mol	No.	Frequency cm^{-1}	Intensity km/mol
1	18	1.0915	43	1006	1.2766
2	24	5.0346	44	1018	43.4319
3	30	1.7370	45	1030	42.0305
4	39	0.7255	46	1041	7.9648
5	45	0.7147	47	1048	48.3305
6	63	0.7618	48	1082	3.7264
7	81	0.3625	49	1106	10.3320
8	110	3.3135	50	1129	4.2395
9	118	0.7660	51	1147	17.4525
10	120	0.6739	52	1171	22.4379
11	136	5.7235	53	1208	10.1939
12	147	1.2674	54	1221	7.4507
13	173	1.0485	55	1231	14.4436
14	188	2.7132	56	1278	7.1474
15	220	0.2931	57	1292	15.7269
16	233	0.0597	58	1307	23.8761
17	237	0.0473	59	1311	20.4747
18	265	0.2480	60	1343	1.6101
19	290	2.3350	61	1359	2.2503
20	292	0.8843	62	1384	35.1142
21	307	11.8726	63	1392	4.9405
22	321	164.6992	64	1398	7.8584
23	345	0.4310	65	1401	4.0081
24	359	1.6959	66	1404	15.7901
25	369	0.7031	67	1427	21.7236
26	427	8.5535	68	1433	0.8562
27	436	1.0180	69	1450	15.8703
28	482	5.5515	70	1468	18.1018
29	523	2.7855	71	1471	0.7872
30	576	2.5945	72	1534	11.9187
31	623	17.3200	73	1546	12.2562
32	706	3.0631	74	1547	1.0951
33	728	39.1292	75	1553	2.6567
34	785	8.9426	76	1560	11.6932
35	805	8.1262	77	1564	3.6645
36	815	5.7845	78	1578	4.0520
37	865	7.1835	79	1595	15.2224
38	899	6.5972	80	1727	0.9743
39	910	5.6534	81	3017	15.1312
40	942	3.7519	82	3027	11.9911
41	960	0.9572	83	3040	9.7270
42	985	0.8176	84	3045	4.2740
85	3054	7.5650	93	3129	2.1895
86	3055	16.9104	94	3131	10.8659
87	3060	5.4101	95	3138	22.1492
88	3069	10.1362	96	3150	0.9169
89	3075	15.5812	97	3159	34.3454
90	3083	21.1890	98	3160	5.3223
91	3116	25.3840	99	3171	15.1666
92	3124	8.3157			

Conclusion:

The geometry of compounds is optimized, for all compounds C_1 symmetry is obtained. Binding energy $\mathbf{E_b}$ and ΔEgab of compounds were calculated and the following relationship is found:

$\mathbf{E_b\ (C_{11}H_{19}Cl_3OTe) < E_b\ (C_9H_{15}Cl_3OTe) < E_b\ (C_8H_{12}Cl_4OTe) < E_b\ (C_9H_{15}I_3OTe)}$

$\mathbf{\Delta E_{\mathit{gab}}\ (C_{11}H_{19}Cl_3OTe) > \Delta E_{\mathit{gab}}\ (C_9H_{15}Cl_3OTe) > \Delta E_{\mathit{gab}}\ (C_8H_{12}Cl_4OTe) > \Delta E_{gab}\ (C_9H_{15}I_3OTe)}$

The relationships above indicated the following:

1. When the methoxy group (OCH_3) replaced with ($OCH(CH_3)_2$), the formed of compound become more stable. In other words, increasing the alkyly groups increased the stability of compounds.
2. When the methoxy group (OCH_3) is replaced with halogen atom (Cl), the formed compound becomes less stable.
3. When dichloride (Cl_3) is replaced with tri-iodide (I_3), the formed compound becomes less stable. In other words, increasing the polarizability of halide decreased the stability of compounds.

Finally, the IR frequencies were calculated, and the results showed a suitable agreement between the calculated values with those measured experimentally.

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دراسة مقارنه لاستقراريه الطيف في المواصفات الاهتزازيه لبعض مركبات التلوريوم (17) المحتويه على مجموعه السايكلواوكتاداينيل بوساطه حسابات كيمياء الكم

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الخلاصة:

تم استخدام نظرية دوال الكثافة Density Functional Theory (DFT) بالاقتران مع المستوى B3LYP وعند عناصر القاعدة 3-21G والطرائق شبه التجريبية (PM3) لحساب الطاقات (الطاقة الكلية total energy، طاقة الترابط binding energy (ΔE_b)، طاقة المدارات الجزيئية (طاقة اعلى مدار جزيئي محجوز بالالكترونات E_{HOMO} وطاقة اوطأ مدار جزيئي غير محجوز بالالكترونات E_{LUMO})، حرارة التكوين (ΔH_f)، واطياف الاهتزاز vibrational spectra لبعض مركبات التلوريوم الرباعي التكافؤ الحاوية على مجموعة السايكلواوكتاداينيل التي يمكن ان تستخدم كمعقدات مع بعض العناصر الانتقالية او العناصر الاساسية في الجدول الدوري عند اشكالها الهندسية الفراغية التوازنية.