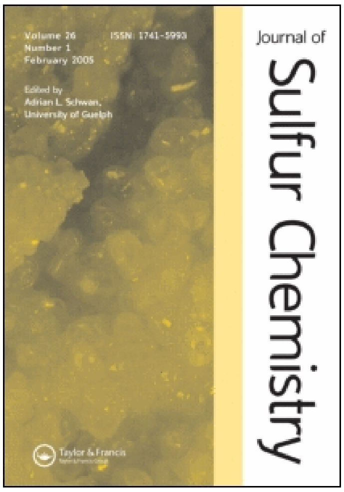

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DFT study of the molecular structures, infrared and Raman spectra of 1,5-dichloropenta-1,4-diyn-3-one, 1,5-dibromopenta-1,4-diyn-3-one, 1,5-diiodopenta-1,4-diyn-3-one, their sulfur, and selenium analogues

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1,5-Dichloropenta-1,4-diyn-3-one, 1,5-dibromopenta-1,4-diyn-3-one, 1,5-diiodopenta-1,4-diyn-3-one, their sulfur, and selenium analogues have been studied, in the gas phase, in C_{2v} symmetry, using density functional theory method. The functional used is B3LYP and the basis sets employed are 6-311++G(d,p) for all atoms except that 6-311G(d,p) has been used for iodine atom only. Molecular parameters, namely bond lengths, bond angles, rotational constants, dipole moments, and energies are predicted for these 1,5-dihalogenoketones. Atomization energies and natural charges on the atoms have also been predicted. Further, vibrational infrared spectra parameters, namely harmonic vibrational frequencies and absolute intensities, Raman activities, and depolarization ratios are also reported. It is generally found that halogens substitution lead to only small steric and geometric perturbations in the 1,5-dihalogenoketones. However, the literature for these 1,5-dihalogenoketones is very limited and therefore data from the present study could be used for their characterization as and when they are synthesized.

Keywords: DFT; infrared frequency; Raman activity; 1,5-dihalogenopenta-1,4-diyne-3-one; 1,5-dihalogenopenta-1,4-diyne-3-thioketone; 1,5-dihalogenopenta-1,4-diyne-3-selenoketone

1. Introduction

Penta-1,4-diyn-3-one was reported for the first time, in 1961, by Wille and Stasser (*1*). Since then, different workers (*2–5*) have studied the ketone and more recently, in 2006, Gupta and Sharma (*6*) reported a detailed analysis of the vibrational spectra of the ketone in harmonic and anharmonic approximations using theoretical methods. A survey of the literature of penta-1,4-diyne-3-one (*2–6*) indicates that it has received good attention but its sulfur and selenium analogues have not been comparably studied, although there have been some attempts to study thiones (*7–10*) and selenoketones (*7, 11–12*). In order to address this deficiency, a previous manuscript (*5*) addressed the effect of substituting oxygen of the carbonyl group by sulfur and selenium. Fluorine, being the most electronegative element, is known to affect the stereoelectronic and polar nature of organic

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compounds (*13*). The effect of fluorine for hydrogen substitution has also been investigated by targeting 1,5-difluoropenta-1,4-diyn-3-one, its sulfur, and selenium analogues (*7*). The results from these studies are expected to be useful for characterizing these ketones when they are synthesized.

Once the 1,5-difluoroketones have been studied, it becomes interesting to explore the 1,5-dihalogenoketones series. In recent years, there have been some papers where the effects of changing the halogen on the structures and vibrational spectra of molecules have been considered (*14–16*) using theoretical methods. Diketones (*17, 18*) have been shown to be useful intermediates in organic synthesis. One of the motivations for this work has been derived from the possible synthesis of 1,5-diketones derivatives (*19–21*). Further, it is now possible to have better predictions for iodine containing compounds with the availability of sufficiently large basis sets (*22*).

In view of the above and in continuation of our previous investigations (*5, 7*), this paper is directed towards the study of the novel 1,5-dichloropenta-1,4-diyn-3-one, 1,5-dibromopenta-1,4-diyn-3-one and 1,5-diiodopenta-1,4-diyn-3-one, their sulfur, and selenium analogues. These ketones have been the targets of this study of this theoretical gas phase study using density functional theory (DFT) method. They have been studied in order to obtain the optimized structural parameters, atomization energies, natural charges and vibrational frequencies. Spectral analysis is a very important component in the identification of molecules and, in this context, DFT method has been shown to be a suitable theoretical method for exploring the structures (*4*) and vibrational spectra (*23, 24*) of molecules. It is important to note that these 1,5-dihalogenoketones have not yet been synthesized and thus experimental data are not yet available for comparison. However, similar computations for penta-1,4-diyn-3-one compare satisfactorily with experimental data and therefore results for the current study should be useful to synthetic organic chemists. The findings of this study are presented herein.

2. Computational methods

The optimized equilibrium structures, atomization energies, uncorrected harmonic frequencies, infrared intensities, Raman activities, depolarization ratios of 1,5-dichloropenta-1,4-diyn-3-one, 1,5-dibromopenta-1,4-diyn-3-one, 1,5-diiodopenta-1,4-diyn-3-one, their sulfur, and selenium analogues are calculated using density functional method. The closed-shell singlets are used in all computations. The functional used is B3LYP and 6-311++G(d,p) is used as the basis sets for all atoms except that 6-311G(d,p) basis sets are used for iodine atom only. The 1,5-dihalogenoketones are studied in C_{2v} symmetry, in the gas phase, and their atoms labels are illustrated in Figures 1(a)–(c). Frequency computations are used to confirm the nature of the stationary points. All computations are performed with the Gaussian 03W (*25*) package. The 1,5-dihalogenketones are subjected to normal coordinate analysis for the assignments of the calculated vibrational frequencies and GaussView 3.0 (*26*) is been used for visualizing the 1,5-dihalogenoketones.

3. Results and discussion

Tables 1–3 summarize the optimized molecular parameters, namely bond lengths, bond angles, rotational constants, dipole moments, energies, and atomization energies for the 1,5-dihalogenoketones. Analysis of Tables 1–3 allows some conclusions to be drawn. First substitution of oxygen of the carbonyl group by sulfur and selenium systematically increases the C=Y bond length. Secondly, the C=Y becomes slightly longer when the halogen is being substituted. Thirdly,

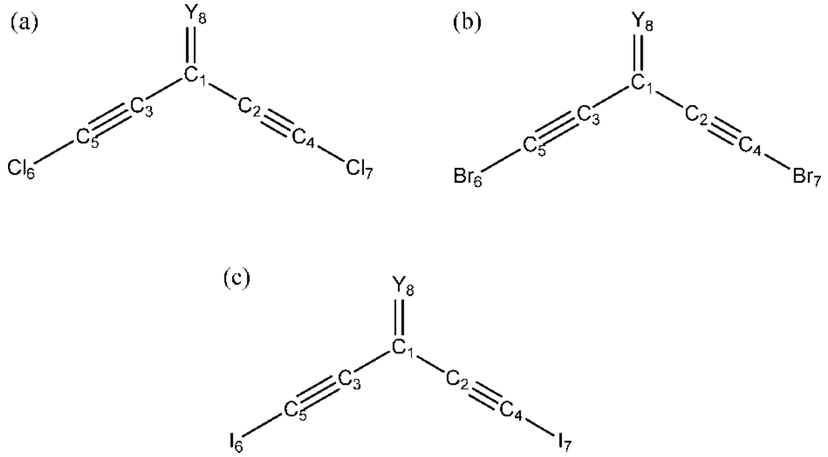


Figure 1. (a) Structures and atoms label of 1,5-dichloropenta-1,4-diyn-3-one (Y=O) or 1,5-dichloropenta-1,4-diyne-3-thioketone (Y=S) or 1,5-dichloropenta-1,4-diyne-3-selenoketone (Y=Se). (b) Structures and atoms label of 1,5-dibromopenta-1,4-diyn-3-one (Y=O) or 1,5-dibromopenta-1,4-diyne-3-thioketone (Y=S) or 1,5-dibromopenta-1,4-diyne-3-selenoketone (Y=Se). (c) Structures and atoms label of 1,5-diiodopenta-1,4-diyn-3-one (Y=O) or 1,5-diiodopenta-1,4-diyne-3-thioketone (Y=S) or 1,5-diiodopenta-1,4-diyne-3-selenoketone (Y=Se).

for a given 1,5-dihalogenoketone, substitution of oxygen decreases the C−C bond length but the lengths of the other bonds (C≡C and C−X) remain almost unaffected. Fourthly, substitution affects mostly $\angle C_3C_1C_2$ bond angle unlike other bond angles. Besides substitution leads to a slight increase in the $\angle C_3C_1C_2$ bond angle but it is not affected by changing the halogens. Fifthly, rotational constants and dipole moments decrease when the oxygen atom is substituted by sulfur or selenium. Further halogens substitution decreases the rotational constants and the

Table 1. Optimized parameters of 1,5-dichloropenta-1,4-diyn-3-one, its sulfur and selenium analogues.

	1,5-Dichloropenta-1,4-diyn-3-one	1,5-Dichloropenta-1,4-diyne-3-thioketone	1,5-Dichloropenta-1,4-diyne-3-selenoketone
Bond length (Å)			
r(C=Y)	1.2172	1.6577	1.8098
r(C≡C)	1.2059	1.2080	1.2091
r(C−C)	1.4461	1.4182	1.4097
r(C-Cl)	1.6381	1.6378	1.6373
Angle (°)			
$\angle(C_3C_1C_2)$	115.0	116.2	117.3
$\angle(C_4C_2C_1)$	179.2	180.0	179.9
$\angle$(CCY)	122.5	121.9	121.3
$\angle(Cl_7C_4C_2)$	180.0	180.0	180.0
Rotational constants (GHz)			
A	2.610	1.455	0.795
B	0.466	0.468	0.464
C	0.395	0.354	0.293
Dipole moment (Debye)			
	3.402	2.059	2.4410
Energy (Hartrees)			
	−1186.097547	−1509.062832	−3512.395648
Atomization energy (kJ/mol)			
	5105.37	4900.83	4836.77

Table 2. Optimized parameters of 1,5-dibromopenta-1,4-diyn-3-one, its sulfur and selenium analogues.

	1,5-Dibromopenta-1,4-diyn-3-one	1,5-Dibromopenta-1,4-diyne-3-thioketone	1,5-Dibromopenta-1,4-diyne-3-selenoketone
Bond length (Å)			
r(C=Y)	1.2174	1.6583	1.8105
r(C≡C)	1.2077	1.2099	1.2111
r(C−C)	1.4462	1.4180	1.4094
r(C-Br)	1.7908	1.7897	1.7892
Angle(°)			
$\angle(C_3C_1C_2)$	115.0	116.2	117.3
$\angle(C_4C_2C_1)$	179.4	180.0	180.0
$\angle(CCY)$	122.5	121.9	121.4
$\angle(Br_7C_4C_2)$	180.0	180.0	180.0
Rotational constants (GHz)			
A	1.947	1.098	0.565
B	0.210	0.211	0.209
C	0.190	0.176	0.153
Dipole moment (Debye)			
	3.672	2.956	2.701
Energy (Hartrees)			
	−5413.942226	−5736.907852	−7740.240789
Atomization energy (kJ/mol)			
	3556.35	3352.70	3288.96

Table 3. Optimized parameters of 1,5-diiodopenta-1,4-diyn-3-one, its sulfur and selenium analogues.

	1,5-Diiodopenta-1,4-diyn-3-one	1,5-Diiodopenta-1,4-diyne-3-thioketone	1,5-Diiodopenta-1,4-diyne-3-selenoketone
Bond length (Å)			
r(C=Y)	1.2179	1.6591	1.8114
r(C≡C)	1.2102	1.2125	1.2138
r(C−C)	1.4461	1.4175	1.4087
r(C−I)	1.9964	1.9939	1.9929
Angle (°)			
$\angle(C_3C_1C_2)$	114.7	115.9	117.0
$\angle(C_4C_2C_1)$	180.0	180.0	180.0
$\angle(CCY)$	122.7	122.1	121.5
$\angle(I_7C_4C_2)$	180.0	180.0	180.0
Rotational constants (GHz)			
A	1.560	0.897	0.451
B	0.125	0.125	0.124
C	0.116	0.110	0.097
Dipole moment (Debye)			
	4.109	3.405	3.149
Energy (Hartrees)			
	-14104.712350	−14427.678518	−16431.011602
Atomization energy (kJ/mol)			
	3481.54	3279.32	3215.97

1,5-dihalogenoketones become more polar. Lastly atomization energies estimated for the 1,5-dihalogenoketones decrease both when oxygen is substituted by sulfur or selenium or when the halogens are varied from chlorine to iodine.

Natural charges, of the atoms of the 1,5-dihalogenoketones, calculated using NBO analysis (*28*) are presented in Tables 4–6. The difference in electronegativity (*29*) of these atoms can be

Table 4. Natural charges in *e* of the atoms of 1,5-dichloropenta-1,4-diyn-3-one, its sulfur and selenium analogues.

	1,5-Dichloropenta-1,4-diyn-3-one	1,5-Dichloropenta-1,4-diyne-3-thioketone	1,5-Dichloropenta-1,4-diyne-3-selenoketone
C_1	0.4184	−0.2452	−0.2901
C_2	−0.1349	−0.0837	−0.0929
C_3	−0.1349	−0.0837	−0.0929
C_4	−0.0097	−0.0194	−0.0132
C_5	−0.0097	−0.0194	−0.0132
Cl_6	0.1719	0.1655	0.1746
Cl_7	0.1719	0.1655	0.1746
Y	−0.4730	0.1202	0.1532

Table 5. Natural charges in *e* of the atoms of 1,5-dibromopenta-1,4-diyn-3-one, its sulfur and selenium analogues.

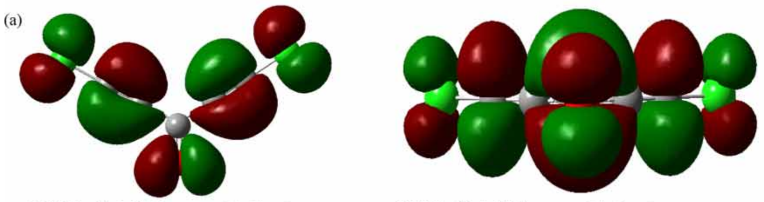
	1,5-Dibromopenta-1,4-diyn-3-one	1,5-Dibromopenta-1,4-diyne-3-thioketone	1,5-Dibromopenta-1,4-diyne-3-selenoketone
C_1	0.4193	−0.2335	−0.2884
C_2	−0.1049	−0.0615	−0.0657
C_3	−0.1049	−0.0615	−0.0657
C_4	−0.1216	−0.1224	−0.1234
C_5	−0.1216	−0.1224	−0.1234
Br_6	0.2531	0.2553	0.2569
Br_7	0.2531	0.2553	0.2569
Y	−0.4726	0.0906	0.1527

Table 6. Natural charges in *e* of the atoms of 1,5-diiodopenta-1,4-diyn-3-one, its sulfur and selenium analogues.

	1,5-Diiodopenta-1,4-diyn-3-one	1,5-Diiodopenta-1,4-diyne-3-thioketone	1,5-Diiodopenta-1,4-diyne-3-selenoketone
C_1	0.4181	−0.2258	−0.2782
C_2	−0.0993	−0.0630	−0.0675
C_3	−0.0993	−0.0630	−0.0675
C_4	−0.2444	−0.2392	−0.2394
C_5	−0.2444	−0.2392	−0.2394
I_6	0.3711	0.3861	0.3890
I_7	0.3711	0.3861	0.3890
Y	−0.4730	0.0581	0.1141

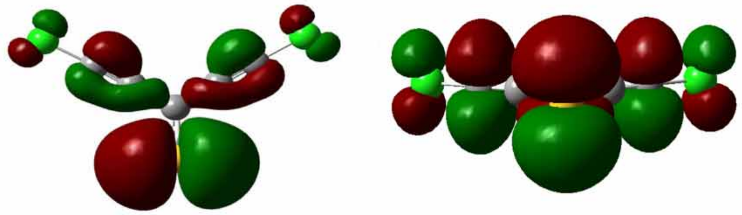
Table 7. Frontier orbital energies (HOMO and LUMO), HOMO–LUMO gap for the 1,5-dihalogenoketones.

	HOMO energy/ Hartrees	LUMO energy/ Hartrees	HOMO–LUMO gap/ kJ/mol
1,5-dichloropenta-1,4-diyn-3-one	−0.2853	−0.1060	470.78
1,5-dichloropenta-1,4-diyne-3-thioketone	−0.2416	−0.1313	289.44
1,5-dichloropenta-1,4-diyne-3-selenoketone	−0.2286	−0.1363	242.36
1,5-dibromopenta-1,4-diyn-3-one	−0.2807	−0.1065	457.47
1,5-dibromopenta-1,4-diyne-3-thioketone	−0.2403	−0.1311	286.55
1,5-dibromopenta-1,4-diyne-3-selenoketone	−0.2274	−0.1360	239.94
1,5-diiodopenta-1,4-diyn-3-one	−0.2711	−0.1065	432.26
1,5-diiodopenta-1,4-diyne-3-thioketone	−0.2381	−0.1306	282.27
1,5-diiodopenta-1,4-diyne-3-selenoketone	−0.2256	−0.1354	236.72



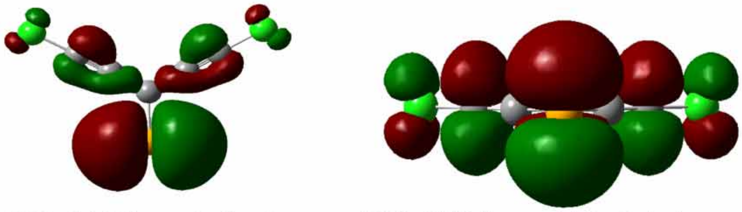
HOMO of 1,5-dichloropenta-1,4-diyn-3-one

LUMO of 1,5-dichloropenta-1,4-diyn-3-one



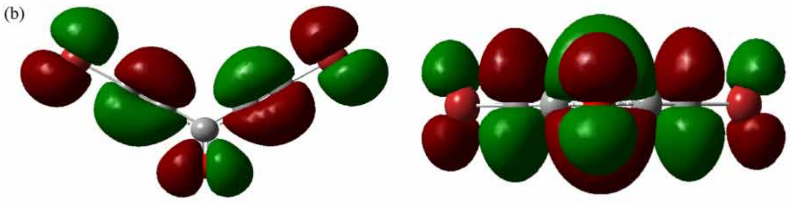
HOMO of 1,5-dichloropenta-1,4-diyne-3-thioketone

LUMO of 1,5-dichloropenta-1,4-diyne-3-thioketone



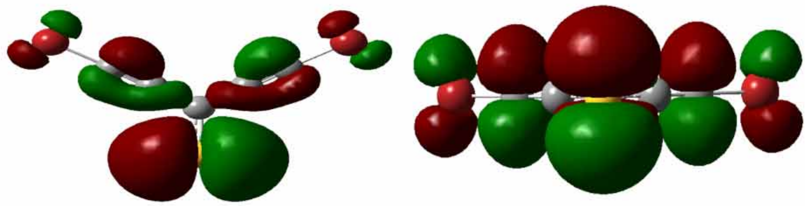
HOMO of 1,5-dichloropenta-1,4-diyne-3-selenoketone

LUMO of 1,5-dichloropenta-1,4-diyne-3-selenoketone



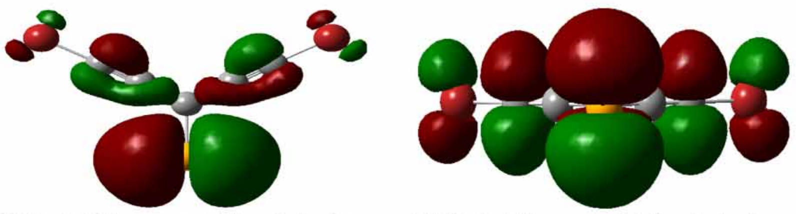
HOMO of 1,5-dibromopenta-1,4-diyn-3-one

LUMO of 1,5-dibromopenta-1,4-diyn-3-one



HOMO of 1,5-dibromopenta-1,4-diyne-3-thioketone

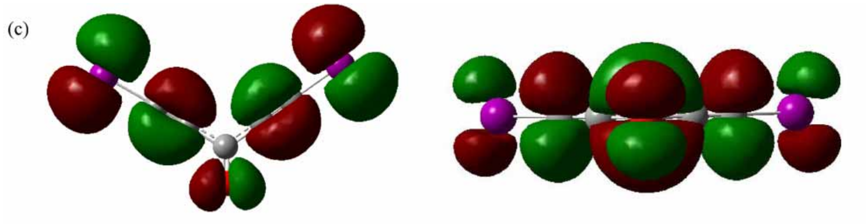
LUMO of 1,5-dibromopenta-1,4-diyne-3-thioketone



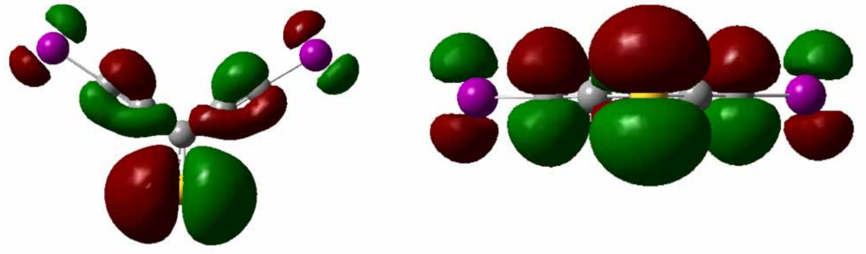
HOMO of 1,5-dibromopenta-1,4-diyne-3-selenoketone

LUMO of 1,5-dibromopenta-1,4-diyne-3-selenoketone

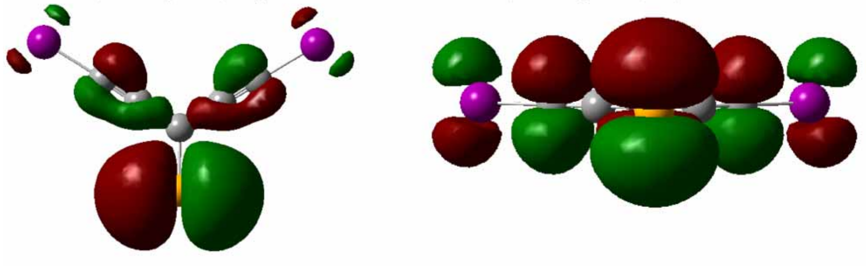
Figure 2. (a) Predicted HOMO and LUMO of 1,5-dichloroketones, (b) predicted HOMO and LUMO of 1,5-dibromoketones, (c) predicted HOMO and LUMO of 1,5-diiodoketones.



HOMO of 1,5-diiodopenta-1,4-diyn-3-one LUMO of 1,5-diiodopenta-1,4-diyn-3-one



HOMO of 1,5-diiodopenta-1,4-diyn-3-one LUMO of 1,5-diiodopenta-1,4-diyn-3-one



HOMO of 1,5-diiodopenta-1,4-diyn-3-one LUMO of 1,5-diiodopenta-1,4-diyn-3-one

Figure 2. Continued.

Table 8. Vibrational parameters of 1,5-dichloropenta-1,4-diyn-3-one.

No.	Frequency (cm^{-1})	Infrared intensity (km mol^{-1})	Raman activity (Å^4 amu^{-1})	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2301.8	146.3	1108.8	0.21	0.34	A_1	C≡C sym stretch
ν_2	1689.9	321.0	224.6	0.13	0.22	A_1	C=O stretch
ν_3	1004.1	1.5	1.5	0.13	0.23	A_1	C-Cl sym stretch
ν_4	625.5	1.8	39.9	0.29	0.45	A_1	C−C−C scissor
ν_5	405.3	3.6	8.1	0.74	0.85	A_1	C−C−C scissor
ν_6	270.7	0.3	1.4	0.58	0.73	A_1	C≡C-Cl bend
ν_7	40.3	0.7	8.1	0.72	0.84	A_1	C≡C−C bend
ν_8	335.2	0	13.0	0.75	0.86	A_2	C≡C-Cl bend
ν_9	152.6	0	1.7	0.75	0.86	A_2	C≡C−C bend
ν_{10}	731.9	12.9	2.0	0.75	0.86	B_1	C≡C−C bend
ν_{11}	320.9	1.4	1.6	0.75	0.86	B_1	C≡C-Cl bend
ν_{12}	101.0	0.5	0.0007	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2293.2	710.6	289.3	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1237.6	261.3	2.0	0.75	0.86	B_2	C−Cl antisym stretch
ν_{15}	767.9	204.5	1.4	0.75	0.86	B_2	C−C stretch
ν_{16}	450.8	2.4	1.3	0.75	0.86	B_2	C=O wag
ν_{17}	311.3	3.6	4.3	0.75	0.86	B_2	C≡C−Cl bend
ν_{18}	135.9	1.6	1.4	0.75	0.86	B_2	C=O wag

Table 9. Vibrational parameters of 1,5-dichloropenta-1,4-diyne-3-thioketone.

No.	Frequency (cm^{-1})	Infrared intensity (km mol^{-1})	Raman activity (Å^4 amu^{-1})	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2291.8	201.7	1526.1	0.15	0.27	A_1	C≡C sym stretch
ν_2	1203.6	94.1	183.3	0.11	0.20	A_1	C=S stretch
ν_3	915.6	67.4	65.1	0.11	0.20	A_1	C-Cl sym stretch
ν_4	547.9	1.1	28.3	0.15	0.26	A_1	C−C−C scissor
ν_5	387.5	3.0	9.1	0.24	0.39	A_1	C−C−C scissor
ν_6	260.1	0.7	2.5	0.74	0.85	A_1	C≡C-Cl bend
ν_7	43.2	0.7	10.0	0.75	0.85	A_1	C≡C−C bend
ν_8	335.8	0	10.3	0.75	0.86	A_2	C≡C-Cl bend
ν_9	166.5	0	0.1	0.75	0.86	A_2	C≡C−C bend
ν_{10}	619.9	0.1	5.6	0.75	0.86	B_1	C≡C−C bend
ν_{11}	307.9	1.0	2.5	0.75	0.86	B_1	C≡C-Cl bend
ν_{12}	91.9	0.1	0.7	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2271.9	648.1	950.2	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1286.5	58.6	25.1	0.75	0.86	B_2	C-Cl antisym stretch
ν_{15}	703.2	123.1	4.1	0.75	0.86	B_2	C−C stretch
ν_{16}	408.0	0.1	8.5	0.75	0.86	B_2	C=S wag
ν_{17}	261.9	1.1	1.6	0.75	0.86	B_2	C≡C-Cl bend
ν_{18}	114.5	0.4	5.1	0.75	0.86	B_2	C=S wag

Table 10. Vibrational parameters of 1,5-dichloropenta-1,4-diyne-3-selenoketone.

No.	Frequency (cm^{-1})	Infrared intensity (km mol^{-1})	Raman activity (Å^4 amu^{-1})	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2284.6	210.5	1673.6	0.14	0.25	A_1	C≡C sym stretch
ν_2	1156.4	35.6	130.8	0.12	0.21	A_1	C=Se stretch
ν_3	846.5	75.3	89.8	0.11	0.20	A_1	C-Cl sym stretch
ν_4	495.1	6.0	21.7	0.18	0.31	A_1	C−C−C scissor
ν_5	332.3	0.7	15.7	0.08	0.14	A_1	C−C−C scissor
ν_6	253.6	1.0	3.5	0.51	0.68	A_1	C≡C-Cl bend
ν_7	40.9	0.5	9.5	0.75	0.86	A_1	C≡C−C bend
ν_8	343.7	0	9.1	0.75	0.86	A_2	C≡C-Cl bend
ν_9	169.7	0	0.1	0.75	0.86	A_2	C≡C−C bend
ν_{10}	586.5	0.3	1.7	0.75	0.86	B_1	C≡C−C bend
ν_{11}	302.8	0.7	4.3	0.75	0.86	B_1	C≡C-Cl bend
ν_{12}	88.1	0.5	0.1	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2260.4	640	1246.8	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1308.0	37.8	38.6	0.75	0.86	B_2	C-Cl antisym stretch
ν_{15}	693.1	110.1	5.3	0.75	0.86	B_2	C−C stretch
ν_{16}	393.8	0.1	11.6	0.75	0.86	B_2	C=Se wag
ν_{17}	241.4	0.5	0.3	0.75	0.86	B_2	C≡C-Cl bend
ν_{18}	91.6	0.1	5.1	0.75	0.86	B_2	C=Se wag

used to account for the natural charges assigned on the atoms. The variation of negative charges on oxygen, sulfur, and selenium explains the charges on the different carbon atoms. The frontier orbital energies of the 1,5-dihalogenoketones are given in Table 7. The data from Table 7 may be interpreted as a molecule to be better electron donor and increasing nucleophilicity when HOMO energy level increases. Additionally, an increase in the LUMO energy level results in decreasing electron accepting ability of a molecule. Further, a decrease in the HOMO–LUMO gap means

Table 11. Vibrational parameters of 1,5-dibromopenta-1,4-diyn-3-one.

No.	Frequency (cm^{-1})	Infrared intensity ($km\ mol^{-1}$)	Raman activity $Å^4\ amu^{-1}$)	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2275.1	126.8	1553.5	0.22	0.37	A_1	C≡C sym stretch
ν_2	1687.2	341.8	295.2	0.13	0.24	A_1	C=O stretch
ν_3	924.4	0.44	6.5	0.19	0.32	A_1	C-Br sym stretch
ν_4	617.0	0.3	48.9	0.32	0.49	A_1	C−C−C scissor
ν_5	333.3	2.2	8.2	0.74	0.85	A_1	C−C−C scissor
ν_6	238.4	0.4	0.1	0.12	0.21	A_1	C≡C-Br bend
ν_7	29.1	0.5	5.7	0.72	0.83	A_1	C≡C−C bend
ν_8	349.2	0	11.6	0.75	0.86	A_2	C≡C- Br bend
ν_9	140.4	0	1.0	0.75	0.86	A_2	C≡C−C bend
ν_{10}	738.2	12.5	2.1	0.75	0.86	B_1	C≡C−C bend
ν_{11}	326.5	2.5	1.0	0.75	0.86	B_1	C≡C-Br bend
ν_{12}	94.3	0.5	0.1	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2268.3	666.0	386.9	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1207.9	414.6	1.9	0.75	0.86	B_2	C-Br antisym stretch
ν_{15}	689.9	105.0	1.4	0.75	0.86	B_2	C−C stretch
ν_{16}	400.0	6.6	3.5	0.75	0.86	B_2	C=O wag
ν_{17}	293.7	3.5	2.5	0.75	0.86	B_2	C≡C-Br bend
ν_{18}	125.2	1.4	1.0	0.75	0.86	B_2	C=O wag

Table 12. Vibrational parameters of 1,5-dibromopenta-1,4-diyne-3-thioketone.

No.	Frequency (cm^{-1})	Infrared intensity ($km\ mol^{-1}$)	Raman activity $Å^4\ amu^{-1}$)	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2264.6	170.9	2098.5	0.17	0.29	A_1	C≡C sym stretch
ν_2	1184.9	137.2	243.0	0.11	0.20	A_1	C=S stretch
ν_3	842.8	28.1	70.3	0.12	0.21	A_1	C-Br sym stretch
ν_4	554.0	1.7	36.7	0.16	0.28	A_1	C−C−C scissor
ν_5	306.6	2.0	8.9	0.43	0.60	A_1	C−C−C scissor
ν_6	231.9	0.6	0.1	0.71	0.83	A_1	C≡C-Br bend
ν_7	30.8	0.5	7.3	0.74	0.85	A_1	C≡C−C bend
ν_8	357.6	0	8.0	0.75	0.86	A_2	C≡C-Br bend
ν_9	151.0	0	0.0004	0.75	0.86	A_2	C≡C−C bend
ν_{10}	628.2	0.04	5.9	0.75	0.86	B_1	C≡C−C bend
ν_{11}	311.2	1.2	1.3	0.75	0.86	B_1	C≡C-Br bend
ν_{12}	81.6	0.2	1.4	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2245.8	600.8	1248.0	0.75	0.86	B_2	C≡C antisym
ν_{14}	1258.1	128.6	28.1	0.75	0.86	B_2	C-Br antisym
ν_{15}	598.2	62.5	3.1	0.75	0.86	B_2	C−C stretch
ν_{16}	392.7	1.3	12.6	0.75	0.86	B_2	C=S wag
ν_{17}	237.1	1.1	0.4	0.75	0.86	B_2	C≡C-Br bend
ν_{18}	102.8	0.4	4.1	0.75	0.86	B_2	C=S wag

a decrease in the kinetic stability of the molecule. Figures 2(a)–(c) illustrates the HOMO and LUMO surfaces of the title compounds.

Raw harmonic vibrational frequencies, their intensities, Raman activities, and symmetries for the 1,5-dihalogenoketones are reported in Tables 8–16. The predicted infrared and Raman spectra of the 1,5-dihalogenoketones are illustrated in Figures 3(a)–(c) and 4(a)–4(c), respectively. The 18 modes of vibrations account for the irreducible representations $\Gamma_v = 7A_1 + 2A_2 + 3B_1 + 6B_2$ of the C_{2v} point group. These vibrations have been assigned on the basis of different motions namely C≡C stretching, C−X stretching, C−C stretching, C=Y stretching, X−C≡C bending,

Table 13. Vibrational parameters of 1,5-dibromopenta-1,4-diyne-3-selenoketone.

No.	Frequency (cm^{-1})	Infrared intensity (km mol^{-1})	Raman activity Å^4 amu^{-1})	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2257.1	175.5	2280.5	0.16	0.27	A_1	C≡C sym stretch
ν_2	1125.4	72.8	179.3	0.11	0.20	A_1	C=Se stretch
ν_3	782.5	35.0	91.0	0.11	0.20	A_1	C-Br sym stretch
ν_4	494.1	6.4	39.6	0.16	0.27	A_1	C−C−C scissor
ν_5	257.6	1.4	10.6	0.17	0.29	A_1	C−C−C scissor
ν_6	228.3	0.4	0.3	0.18	0.31	A_1	C≡C-Br bend
ν_7	29.1	0.4	6.9	0.75	0.86	A_1	C≡C−C bend
ν_8	364.9	0	7.0	0.75	0.86	A_2	C≡C-Br bend
ν_9	152.4	0	0.1	0.75	0.86	A_2	C≡C−C bend
ν_{10}	599.1	0.4	1.8	0.75	0.86	B_1	C≡C−C bend
ν_{11}	308.2	0.9	2.5	0.75	0.86	B_1	C≡C-Br bend
ν_{12}	78.0	0.1	3.8	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2233.8	590.9	1641.0	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1280.4	94.0	43.3	0.75	0.86	B_2	C-Br antisym stretch
ν_{15}	580.5	54.6	4.1	0.75	0.86	B_2	C−C stretch
ν_{16}	388.4	0.4	16.6	0.75	0.86	B_2	C=Se wag
ν_{17}	216.7	0.6	0.01	0.75	0.86	B_2	C≡C-Br bend
ν_{18}	78.0	0.1	3.8	0.75	0.86	B_2	C=Se wag

Table 14. Vibrational parameters of 1,5-diiodopenta-1,4-diyn-3-one.

No.	Frequency (cm^{-1})	Infrared intensity (km mol^{-1})	Raman activity Å^4 amu^{-1})	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2251.2	118.8	2352.3	0.24	0.38	A_1	C≡C sym stretch
ν_2	1684.0	372.5	456.4	0.14	0.25	A_1	C=O stretch
ν_3	887.0	4.6	16.4	0.20	0.34	A_1	C−I sym stretch
ν_4	615.0	0.2	68.0	0.34	0.50	A_1	C−C−C scissor
ν_5	300.0	1.7	8.8	0.75	0.86	A_1	C−C−C scissor
ν_6	212.8	1.5	1.2	0.75	0.86	A_1	C≡C−I bend
ν_7	26.6	0.5	5.0	0.70	0.83	A_1	C≡C−C bend
ν_8	350.6	0	11.4	0.75	0.86	A_2	C≡C−I bend
ν_9	136.6	0	0.7	0.75	0.86	A_2	C≡C−C bend
ν_{10}	743.5	10.3	2.1	0.75	0.86	B_1	C≡C−C bend
ν_{11}	316.3	6.8	0.8	0.75	0.86	B_1	C≡C−I bend
ν_{12}	95.5	0.3	0.1	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2246.1	632.2	570.1	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1189.9	573.6	3.2	0.75	0.86	B_2	C−I antisym stretch
ν_{15}	659.9	50.7	2.0	0.75	0.86	B_2	C−C stretch
ν_{16}	368.8	6.5	5.8	0.75	0.86	B_2	C=O wag
ν_{17}	272.2	7.0	1.5	0.75	0.86	B_2	C≡C−I bend
ν_{18}	119.1	0.9	0.7	0.75	0.86	B_2	C=O wag

C−C−C scissoring, C≡C−C bending, and C=Y wagging. Analysis of Tables 8–16 indicates that substitution of oxygen of the carbonyl by sulfur or selenium affects mainly those vibrational modes involving C_3, C_1, and C_2. This is reflected by the close similarities of the spectra in Figures 3(a)–3(c) and 4(a)–4(c) and it is important the shift in the C=Y stretching frequencies. The decreasing force constant and increasing reduced mass of the C=Y bond account for this decrease in wave

Table 15. Vibrational parameters of 1,5-diiodopenta-1,4-diyne-3-thioketone.

No.	Frequency (cm^{-1})	Infrared intensity ($km\ mol^{-1}$)	Raman activity $Å^4\ amu^{-1}$)	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2239.6	155.8	3112.5	0.19	0.31	A_1	C≡C sym stretch
ν_2	1177.2	174.1	344.4	0.11	0.20	A_1	C=S stretch
ν_3	805.6	10.8	104.2	0.13	0.22	A_1	C−I sym stretch
ν_4	557.4	3.1	61.4	0.18	0.30	A_1	C−C−C scissor
ν_5	271.9	1.5	9.1	0.57	0.73	A_1	C−C−C scissor
ν_6	205.2	1.6	0.5	0.75	0.86	A_1	C≡C−I bend
ν_7	26.3	0.4	6.7	0.74	0.85	A_1	C≡C−C bend
ν_8	360.6	0	8.1	0.75	0.86	A_2	C≡C−I bend
ν_9	140.6	0	0.04	0.75	0.86	A_2	C≡C−C bend
ν_{10}	645.8	0.0002	6.1	0.75	0.86	B_1	C≡C−C bend
ν_{11}	302.2	3.8	0.7	0.75	0.86	B_1	C≡C−I bend
ν_{12}	81.4	0.4	1.8	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2221.7	575.4	1773.9	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1240.8	215.9	37.6	0.75	0.86	B_2	C−I antisym stretch
ν_{15}	558.2	26.3	3.6	0.75	0.86	B_2	C−C stretch
ν_{16}	375.7	2.4	18.4	0.75	0.86	B_2	C=S wag
ν_{17}	213.3	3.0	0.1	0.75	0.86	B_2	C≡C−I bend
ν_{18}	96.3	0.2	3.4	0.75	0.86	B_2	C=S wag

Table 16. Vibrational parameters of 1,5-diiodopenta-1,4-diyne-3-selenoketone.

No.	Frequency (cm^{-1})	Infrared intensity ($km\ mol^{-1}$)	Raman activity $Å^4\ amu^{-1}$)	Depolarization ratio (P)	Depolarization ratio (U)	Symmetry	Assignment
ν_1	2231.5	158.0	3350.8	0.17	0.29	A_1	C≡C sym stretch
ν_2	1112.8	106.6	245.4	0.11	0.19	A_1	C=Se stretch
ν_3	749.5	14.4	119.5	0.12	0.21	A_1	C−I sym stretch
ν_4	494.9	7.5	76.1	0.16	0.28	A_1	C−C−C scissor
ν_5	231.4	2.2	7.5	0.22	0.36	A_1	C−C−C scissor
ν_6	194.1	0.8	1.3	0.29	0.45	A_1	C≡C−I bend
ν_7	23.8	0.4	6.5	0.74	0.85	A_1	C≡C−C bend
ν_8	374.2	0	6.6	0.75	0.86	A_2	C≡C−I bend
ν_9	141.1	0	0.3	0.75	0.86	A_2	C≡C−C bend
ν_{10}	613.2	1.1	1.9	0.75	0.86	B_1	C≡C−C bend
ν_{11}	297.8	3.1	1.7	0.75	0.86	B_1	C≡C−I bend
ν_{12}	76.4	1.0	0.6	0.75	0.86	B_1	C≡C−C bend
ν_{13}	2208.8	568.5	2318.7	0.75	0.86	B_2	C≡C antisym stretch
ν_{14}	1263.7	169.5	56.6	0.75	0.86	B_2	C−I c stretch
ν_{15}	535.0	21.8	4.6	0.75	0.86	B_2	C−C stretch
ν_{16}	376.2	1.1	23.7	0.75	0.86	B_2	C=Se wag
ν_{17}	191.2	1.9	0.1	0.75	0.86	B_2	C≡C−I bend
ν_{18}	70.8	0.1	3.2	0.75	0.86	B_2	C=Se wag

number. The spectra of the title compounds are generally highly dominated by C=Y stretching vibrational mode.

It is interesting at this stage to compare the calculated parameters of the 1,5-dihalogenoketones with their parent ketones (*4, 5*). This is because selective substitution of hydrogen by halogen is of considerable importance in organic chemistry (*29*). Analysis of the data from this work indicates that halogen for hydrogen substitution leads to only small steric and geometric perturbations with major differences being in the charge distributions on the different atoms.

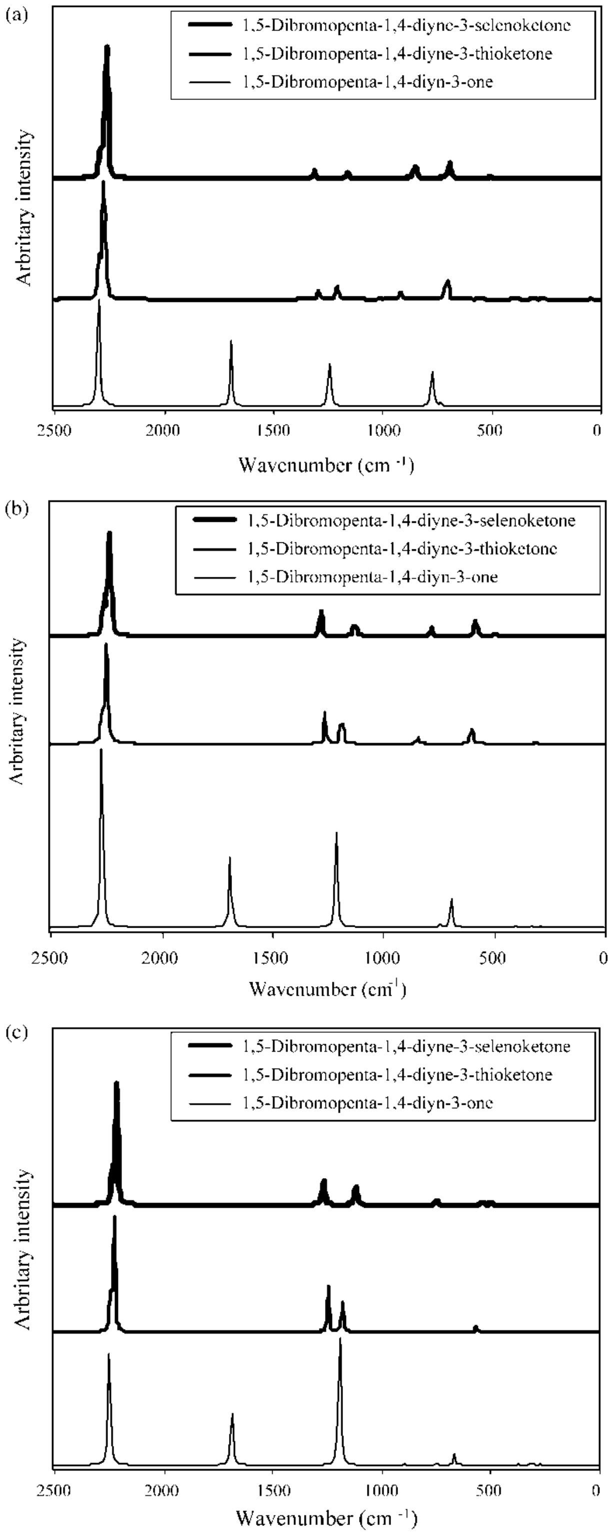


Figure 3. (a) Infrared spectra of the 1,5-dichloroketones, (b) Infrared spectra of the 1,5-dibromoketones, (c) Infrared spectra of the 1,5-diodoketones.

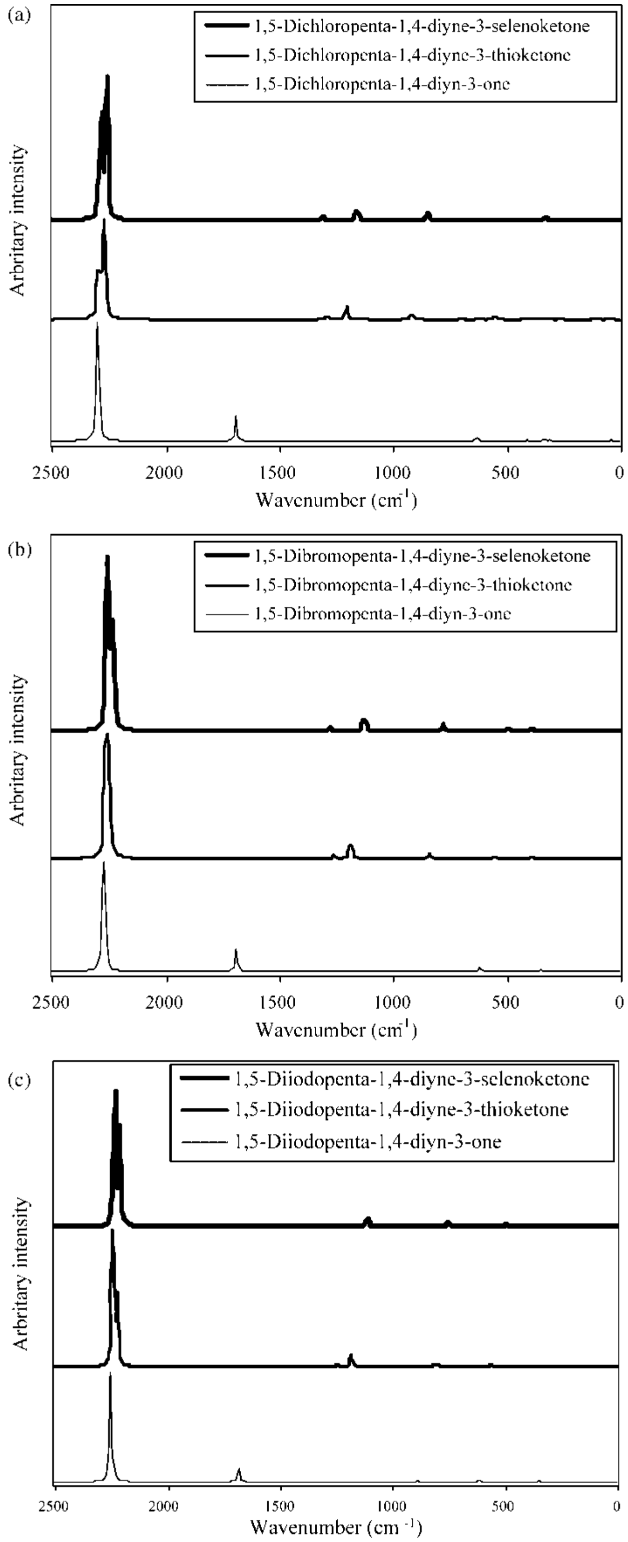


Figure 4. (a) Raman spectra of the 1,5-dichloroketones, (b) Raman spectra of the 1,5-dibromoketones, (c) Raman spectra of the 1,5-diiodoketones.

4. Concluding remarks

This theoretical gas phase study has investigated the molecular structures, vibrational harmonic frequencies and Raman activities of 1,5-dichloropenta-1,4-diyn-3-one, 1,5-dibromopenta-1,4-diyn-3-one, 1,5-diiodopenta-1,4-diyn-3-one, their sulfur, and selenium analogues, in C_{2v} symmetry, using density functional theory method. A major consequence of this study is that these 1,5-dihalogenoketones are rational potential candidates for experimental organic chemists as new areas of research. One of the motivations for this study is the non-available literature of these compounds. The results from this gas phase study should be useful in the characterization of these compounds as and when they are synthesized.

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