

Molecular Structures and Vibrational Spectra of Roesky's Ketone, its Isomers and their Novel Sulfur and Selenium Analogues: An Insight using Density Functional Theory

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ABSTRACT

Roesky's ketone, its isomers and their sulfur and selenium analogues have been studied in the gas phase using B3LYP method with 6-311++G(d,p) as the basis set for all atoms. Molecular parameters, namely bond lengths, bond angles, rotational constants, dipole moments and energies, and vibrational parameters, namely harmonic vibrational frequencies and relative intensities are predicted for these ketones. Relative energies, atomisation energies, HOMO-LUMO gaps and natural charges on the atoms have also been predicted. The molecular parameters and vibrational spectra of Roesky's ketone are in good agreement with some of the available experimental literature data. Therefore, the results from the present theoretical gas phase study are expected to be valid for the molecular structures and vibrational spectra of the novel sulfur and selenium analogues. The findings of this work could be useful for the characterisation of these compounds as and when they are synthesised.

Keywords: DFT, Vibrational frequencies, Infrared spectra, Roesky's ketone

1. INTRODUCTION

5-Oxo-1,3,2,4-dithiadiazole or Roesky's ketone is a five membered ring system containing the $-N=S=N=S-$ fragment. In the last decade, Roesky's ketone has been the target of some investigations¹⁻⁵ and more interestingly, the availability of fast desktop computers and quantum chemical calculation programs such as Gaussian 03W⁶ has led to theoretical investigations^{7,8} being used to support experimental findings. A survey of the literature has been helpful in setting the objectives of the current research.

Droogenbroeck¹ *et al.* studied the molecular and crystal structure of Roesky's ketone experimentally, by re-determining the single crystal structure and, theoretically by computations at the DFT level using an extended basis set. A comprehensive set of properties, consisting of orbital topologies, atomic charges, atomic and molecular dipoles, aromaticity parameters and Fukui functions of Roesky's ketone and a number of its constitutional isomers has been calculated in order to formulate a description of its structure, its aromaticity and reactivity.

Tersago² *et al.* presented a joint experimental-theoretical study of Roesky's ketone. The theoretical results of a vibrational analysis, computed at the B3LYP/6-311+G(d) level of theory, have been compared with experimental data, consisting of Raman and IR frequencies in different phases, and the bands have been assigned to the normal vibrations of the molecule. Additionally, an analysis of the origin of the high intensity of the band assigned to the CO stretching mode was performed based on calculated stockholder charges and atomic dipoles. The results of theoretical computations of the ¹³C and ¹⁴N NMR chemical shifts have been compared to those obtained experimentally.

Droogenbroeck³ *et al.* investigated the molecular structure of Roesky's ketone theoretically using HF, DFT and MP2 methods and the results have been compared to the QCISD geometry. Within DFT, the structure is computed using an elaborate series of functionals. A number of extended basis sets were used to investigate their influence on the computed geometry. Of the nineteen evaluated method/basis set combinations none can reproduce the complete QCISD geometry; methods that reproduce the geometry of the NSNS fragment, overestimate the CS bond length and vice versa. No systematic way to improve the overall geometry of Roesky's ketone is apparent from the data.

Tersago⁴ *et al.* studied the gas-phase geometry of Roesky's ketone using a number of computationally advanced methods. The results of CCSD, QCISD and MP4 (SDQ) computations are compared with the results of different CASSCF and DFT computations. The results obtained with the wave-function-based methods are better than those generated by a large number of different DFT functionals, especially for the description of the carbon-sulfur bond. However, even at the CCSD and QCISD levels no convergence is achieved; upon increasing the level of theory from CCSD to CCSD (T) the quality of the description actually becomes worse.

In 2006, Tersago⁵ *et al.* reported the molecular structure of Roesky's ketone using a large number of computational methods. The results of computations using different DFT functionals are compared with those obtained from HF, MP2, MP4 (SDQ), QCISD and CCSD methods. In addition, the influence of a number of basis sets on the computed geometry was investigated. The results of the post-HF methods show that improving the level of theory from CCSD to CCSD (T) still has a considerable effect on the geometry. Taking the CCSD/cc-pVTZ geometry as a reference the DFT/B1B95/aug-cc-pVTZ combination provides the most valuable description of all the examined functionals.

These studies indicate that Roesky's ketone has been explored and DFT level of computation is a satisfactory method for theoretical investigation of the molecular structures and infrared vibrational spectra. However,

to the best of our knowledge, the sulfur and selenium analogues of Roesky's ketone have not received similar attention although they are all isoivalent and there are increasing possibilities for the synthesis of thio and selenoketones.⁹⁻¹² In 2007, Xu and co-workers¹³ reported the biosynthesis of selenocysteine and its *tRNA* in Euryotes and the selenium-containing amino acid is recognised as the 21st amino acid in the genetic code. More interestingly, they found that the selenium in selenocysteine plays an essential protective role in the body, including preventing cancer, heart disease and delaying aging. In an effort to address the deficiency in the literature of thio and seleno analogues of Roesky's ketone and in continuation with our work dealing with structures and infrared spectra of novel molecules,^{14,15} the present research revisits the four isomers of Roesky's ketone by means of computations at DFT/B3LYP/6-311++G(d,p) level so as to obtain optimised molecular structures and infrared vibrational spectra in the gas phase. The study is then extended to the novel sulfur and selenium analogues of Roesky's ketone and their isomers. The findings of this research are reported herein.

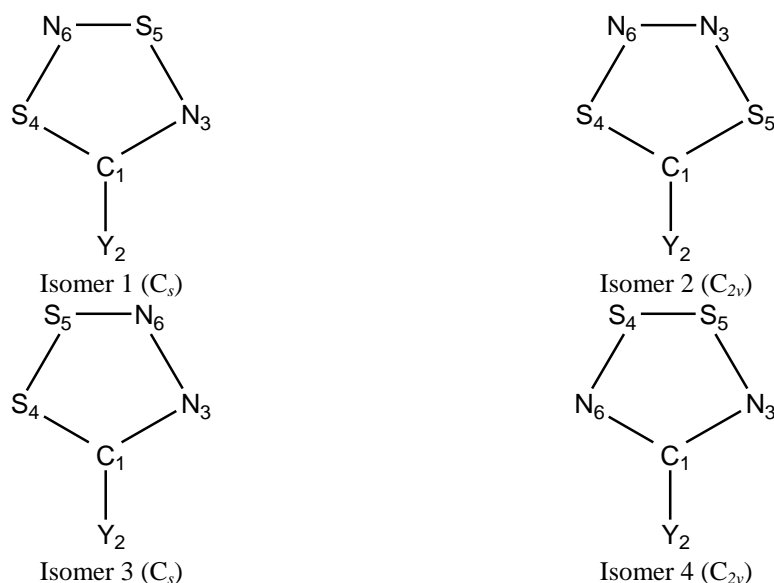


Fig-1: Structures and atoms label of the isomers Roesky's ketone (Y=O), its sulfur (Y=S) and selenium (Y=Se) analogues

Table-1(a): Optimised structural parameters of the isomers 1

(Y=O)	(Y=S)	(Y=Se)	Literature data for Y=O ¹	
Bond length (Å)				
C ₁ -Y ₂	1.1937	1.6422	1.211	1.211
C ₁ -S ₄	1.9416	1.8667	1.8305	1.8293
C ₁ -N ₃	1.3650	1.3555	1.386	1.384
S ₅ -N ₃	1.5958	1.5998	1.5763	1.5750
N ₆ -S ₅	1.6084	1.6045	1.5807	1.5814
N ₆ -S ₄	1.6412	1.6473	1.6395	1.6325
Bond angle (°)				
Y ₂ -C ₁ -N ₃	131.3	129.2	126.5	126.7
Y ₂ -C ₁ -S ₄	120.8	121.7	123.8	123.7
C ₁ -S ₄ -N ₆	96.7	97.7	97.1	97.3
N ₃ -C ₁ -S ₄	107.9	109.0	109.7	109.6
S ₅ -N ₃ -C ₁	116.3	116.0	114.6	114.7
N ₆ -S ₅ -N ₃	106.8	105.8	106.1	106.2
S ₄ -N ₆ -S ₅	112.4	111.4	112.4	112.0
Rotational constant (GHz)				
I _a	4.275	4.307	4.297	
I _b	2.718	1.567	0.888	
I _c	1.661	1.149	0.736	
Dipole moment (Debye)				
μ	3.1047	3.6508	3.8376	
Energy (Hartree)				
	-1019.265628	-1342.219023	-3345.548881	
Atomisation energy (kJ/mol)				
	2234.0	1998.3	1926.5	

Table-1(b): Optimised structural parameters of the isomers 2

	(Y=O)	(Y=S)	(Y=Se)
Bond length (Å)			
C ₁ -Y ₂	1.1941	1.6393	1.7975
C ₁ -S ₄	1.8111	1.7651	1.7498
C ₁ -S ₅	1.8111	1.7651	1.7498
N ₃ -S ₅	1.7417	1.7446	1.7529
N ₆ -N ₃	1.2378	1.2348	1.2326
N ₆ -S ₄	1.7417	1.7446	1.7529
Bond angle (°)			
Y ₂ -C ₁ -S ₅	125.9	125.7	125.3
Y ₂ -C ₁ -S ₄	125.9	125.7	125.3
C ₁ -S ₄ -N ₆	96.7	97.7	97.6
S ₅ -C ₁ -S ₄	108.3	108.7	109.5
N ₃ -S ₅ -C ₁	96.7	97.7	97.6
N ₆ -N ₃ -S ₅	119.2	117.9	117.6
S ₄ -N ₆ -N ₃	119.2	117.9	117.6
Rotational constant (GHz)			
I _a	3.404	3.554	3.579
I _b	3.172	1.773	0.997
I _c	1.642	1.183	0.780
Dipole moment (Debye)			
μ	0.1683	0.3483	0.4262
Energy (Hartree)			
	-1019.269709	-1342.228062	-3345.558788
Atomisation energy (kJ/mol)			
	2244.7	2022.0	1952.4

Table-1(c): Optimised structural parameters of the isomers 3

	(Y=O)	(Y=S)	(Y=Se)
Bond length (Å)			
C ₁ -Y ₂	1.1862	1.6321	1.7894
C ₁ -S ₄	1.8492	1.7941	1.7771
C ₁ -N ₃	1.4553	1.4134	1.3994
N ₃ -N ₆	1.2261	1.2340	1.2380
N ₆ -S ₅	1.7695	1.7592	1.7551
S ₅ -S ₄	2.0622	2.0812	2.0904
Bond angle (°)			
Y ₂ -C ₁ -N ₃	124.8	124.3	123.8
Y ₂ -C ₁ -S ₄	123.4	123.0	122.5
C ₁ -S ₄ -S ₅	92.9	93.3	93.0
N ₃ -C ₁ -S ₄	111.8	112.7	113.7
N ₆ -N ₃ -C ₁	120.8	121.8	121.6
S ₅ -N ₆ -N ₃	118.8	118.0	117.7
S ₄ -S ₅ -N ₆	95.7	94.2	94.0
Rotational constant (GHz)			
I _a	4.543	4.714	4.741
I _b	2.479	1.458	0.844
I _c	1.604	1.114	0.717
Dipole moment (Debye)			
μ	2.8417	2.8057	2.7733
Energy (Hartree)			
	-1019.278196	-1342.231726	-3345.561909
Atomisation energy (kJ/mol)			
	2267.0	2031.6	1960.6

Table-1(d): Optimised structural parameters of the isomers 4

	(Y=O)	(Y=S)*	(Y=Se)
Bond length (Å)			
C ₁ -Y ₂	1.2001	1.6727	1.8130
C ₁ -N ₃	1.4290	1.3680	1.3975
C ₁ -N ₆	1.4290	1.3680	1.3975
N ₃ -S ₅	1.5723	1.5555	1.5804
S ₅ -S ₄	2.1515	2.0051	2.1383
N ₆ -S ₄	1.5723	1.5555	1.5804
Bond angle (°)			
Y ₂ -C ₁ -N ₃	124.1	123.5	123.5
Y ₂ -C ₁ -N ₆	124.1	123.5	123.5
C ₁ -N ₃ -S ₅	120.2	118.5	120.1
N ₆ -C ₁ -N ₃	111.8	112.9	112.9
S ₄ -N ₆ -C ₁	120.2	118.5	120.1
N ₆ -S ₄ -S ₅	93.9	95.1	93.5
S ₄ -S ₅ -N ₃	93.9	95.1	93.5
Rotational constant (GHz)			
I _a	4.464	5.019	4.549
I _b	2.522	1.453	0.804
I _c	1.612	1.127	0.683
Dipole moment (Debye)			
μ	6.4902	9.9178	7.8793
Energy (Hartree)			
	-1019.249030	-1339.192662	-3345.529689
Atomisation energy (kJ/mol)			
	2190.4	1929.05	1876.0

*Optimised parameters at HF level

2. COMPUTATIONAL DETAILS

All computations were performed using the Gaussian 03W package and GaussView 3.0¹⁶ was used for visualising the ketones. The optimised equilibrium structures, atomisation energies, uncorrected harmonic frequencies, infrared intensities of Roesky's ketone, its sulfur and selenium analogues and their structural isomers have been computed using the density functional three-parameter hybrid model (DFT/B3LYP). The ketones have been studied in appropriate symmetries and their atom labels are illustrated in Figure 1. Exceptionally, the Hartree-Fock (HF) model has been used for the optimisation of the sulfur analogue of isomer 4 and then the optimised structure has been used

for single point computation using B3LYP functional. The basis set used for all atoms is 6-311++G(d,p). Frequency computations have also been carried out to confirm the nature of the stationary points. The ketones have been subjected to normal coordinate analysis for the assignments of the computed vibrational frequencies.

3. RESULTS AND DISCUSSION

Tables 1(a)-1(d) summarise the optimised molecular parameters, namely bond lengths, bond angles, rotational constants, dipole moments, energies and atomisation energies for Roesky's ketone, its sulfur and selenium analogues and their isomers. The literature experimental data for Roesky's ketone (isomer 1) are also included in Table 1(a) for comparison. It is worth to note at this stage that there is a good comparison between some of the computed structural parameters and those reported in the literature.¹ Analysis of Tables 1(a)-1(d) allows some conclusions to be drawn. Firstly, substitution systematically increases, as expected, the C_1-Y_2 bond length for the ketones. Secondly, the bond lengths and bond angles are very much dependent on the isomer considered. Thirdly, the ketones for isomer 2 are less polar compared to the other isomers. Fourthly, isomer 3 is more stable for these ketones and this is represented in Figures 2(a)-(c). Fifthly, the calculated atomisation energies are comparable for the four isomers but decrease when the oxygen of the carbonyl group is substituted by sulfur and selenium. Lastly, the optimised parameters for the sulfur analogue of isomer 4 are reported at HF level because computations at B3LYP and even MP2 levels are giving non-planar structures. This behavior is not surprising with theoretical methods.¹⁷

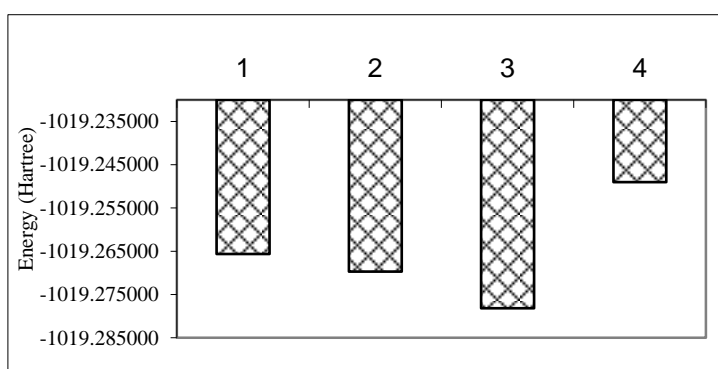


Fig-2(a): Energy (Hartree) of the four isomers for Y=O

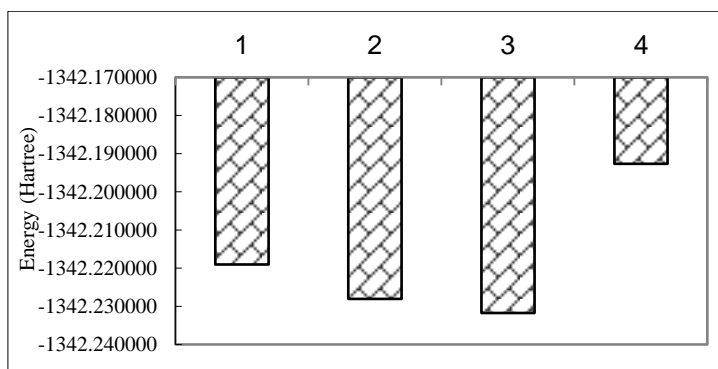


Fig-2(b): Energy (Hartree) of the four isomers for Y=S

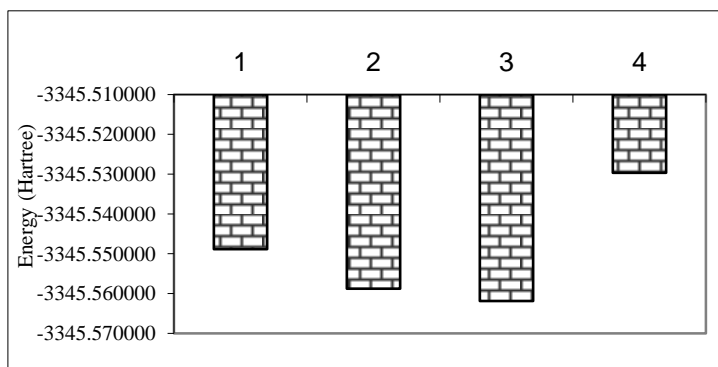


Fig-2(c): Energy (Hartree) of the four isomers for Y=Se

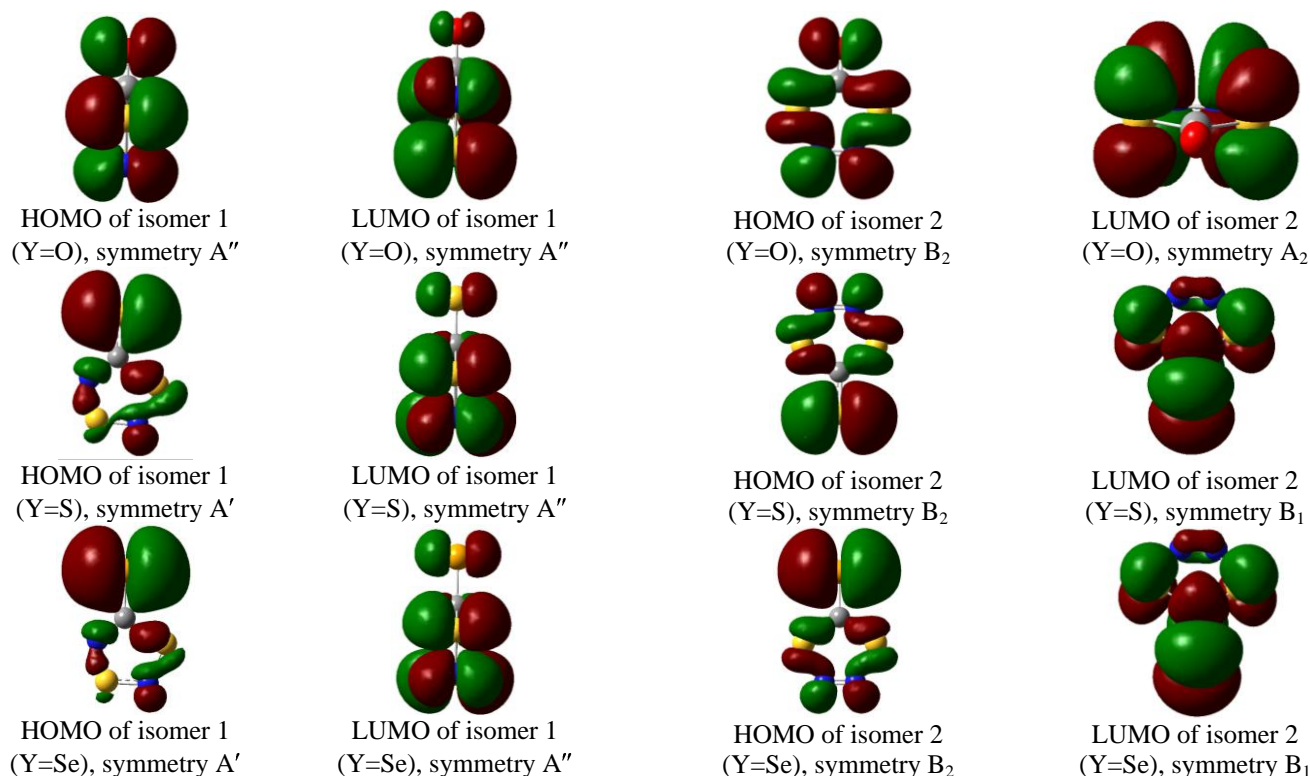


Fig-3(a): Predicted HOMO and LUMO of the ketones for isomer 1

Fig-3(b): Predicted HOMO and LUMO of the ketones for isomer 2

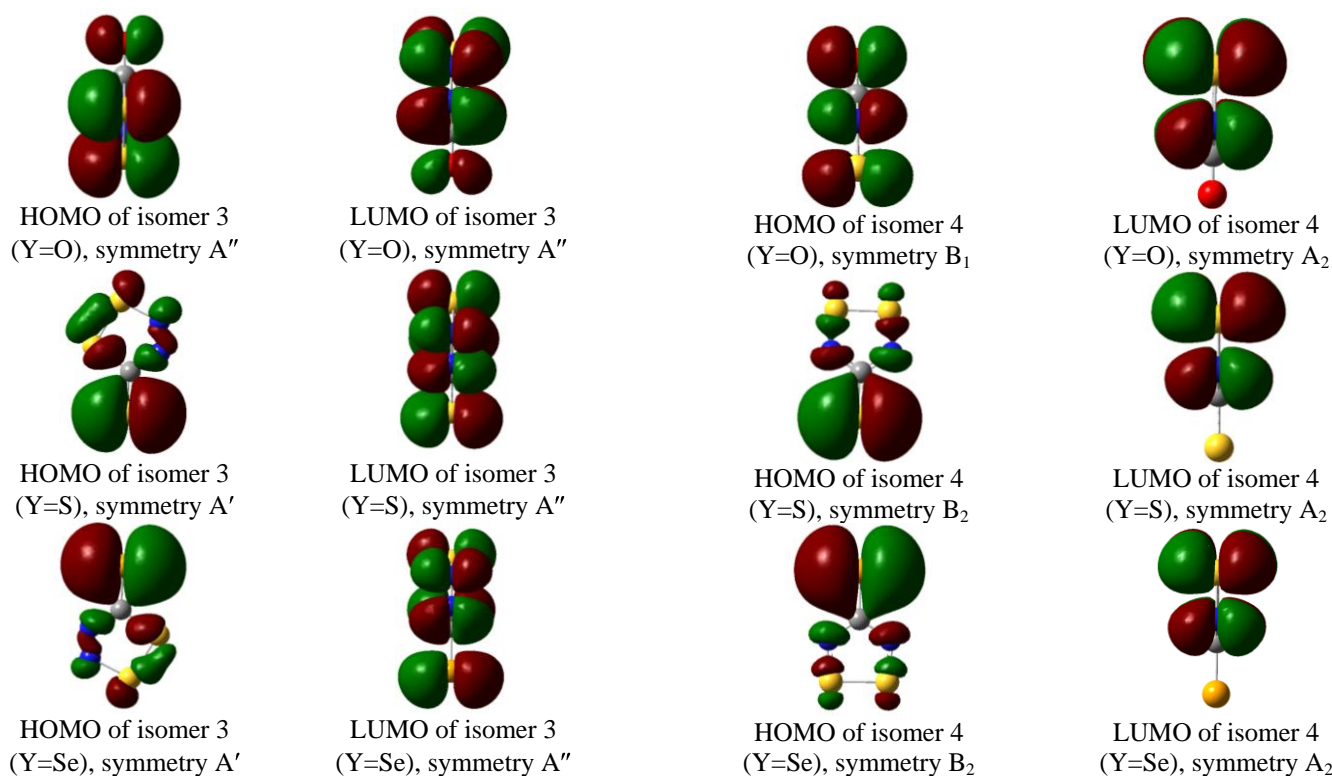


Fig-3(c): Predicted HOMO and LUMO of the ketones for isomer 3

Fig 3(d): Predicted HOMO and LUMO of the ketones for isomer 4

Natural charges for the ketones and their isomers computed using NBO analysis¹⁸ are presented in Table 2. These charges may be interpreted using the electronegativity of the atoms.¹⁹ Table 3 summarises the computed ^{13}C NMR, ^{14}N NMR and ^{17}O NMR (ppm) of ketones and their isomers. Literature data are also included for isomer 1 of Roesky's ketone and again it is interesting to note that there is a good correlation. The Kohn-Sham HOMO and LUMO surfaces for the ketones and their isomers are illustrated in Figures 3(a)-3(d). In DFT framework²⁰, two parameters namely μ and η can be calculated using Kohn-Sham HOMO and LUMO energies as:

$$\mu \cong \frac{1}{2} (E_{LUMO} + E_{HOMO}) \quad \text{Equation (1)}$$

$$\eta \cong \frac{1}{2} (E_{LUMO} - E_{HOMO}) \quad \text{Equation (2)}$$

These parameters and the Kohn-Sham HOMO-LUMO gaps are reported in Table 4. The significances of μ and η are that μ is related to charge transfer processes and η is related to chemical hardness. In this case, the values of μ indicate that charge transfer processes are more predominant in the selenoketones and this may favour stabilisation through hyperconjugative interactions. The values of η indicate that hardness decreases from ketones (Y=O) to selenoketones (Y=Se).

Table-2: Natural charges in e for the isomers of the ketones

Isomer 1			
	1(Y=O)	1(Y=S)	1(Y=Se)
Y ₂	-0.5423	-0.0332	-0.0007
C ₁	0.5012	-0.1948	-0.2545
N ₃	-0.7392	-0.6789	-0.6721
S ₅	1.0606	1.0662	1.0656
N ₆	-0.8057	-0.8083	-0.8087
S ₄	0.5255	0.6491	0.6704
Isomer 2			
Y ₂	-0.5187	0.0469	0.0869
C ₁	0.1493	-0.6487	-0.7339
S ₅ =S ₄	0.4505	0.5649	0.5826
N ₃ =N ₆	-0.2657	-0.2640	-0.2591
Isomer 3			
Y ₂	-0.4908	0.0874	0.1472
C ₁	0.4660	-0.2524	-0.3228
N ₃	-0.1978	-0.1789	-0.1843
N ₆	-0.2093	-0.2164	-0.2193
S ₅	0.3228	0.3290	0.3311
S ₄	0.1091	0.2313	0.2481
Isomer 4			
Y ₂	-0.5713	-0.1129	-0.0998
C ₁	0.6968	0.1147	0.0806
N ₃ =N ₆	-0.6462	-0.5966	-0.5888
S ₅ =S ₄	-0.5834	0.5956	0.5984

Table-3: ¹³C NMR, ¹⁴N NMR and ¹⁷O NMR (ppm) of the ketones*

Isomer 1			
	(Y=O)	(Y=S)	(Y=Se)
Y ₂	426.86		
C ₁	190.49 (189.91)**	222.48	237.28
N ₃	283.97 (269.05)**	355.08	374.55
N ₆	503.61 (375.30)**	508.35	506.98
Isomer 2			
Y ₂	463.43		
C ₁	202.35	229.87	243.30
N ₃ =N ₆	538.38	546.28	546.40
Isomer 3			
Y ₂	464.79		
C ₁	197.20	227.18	240.63
N ₃	441.99	497.91	481.76
N ₆	514.67	522.57	511.71
Isomer 4			
Y ₂	295.30		
C ₁	180.43	217.79	194.98
N ₃ =N ₆	429.57	867.27	406.76

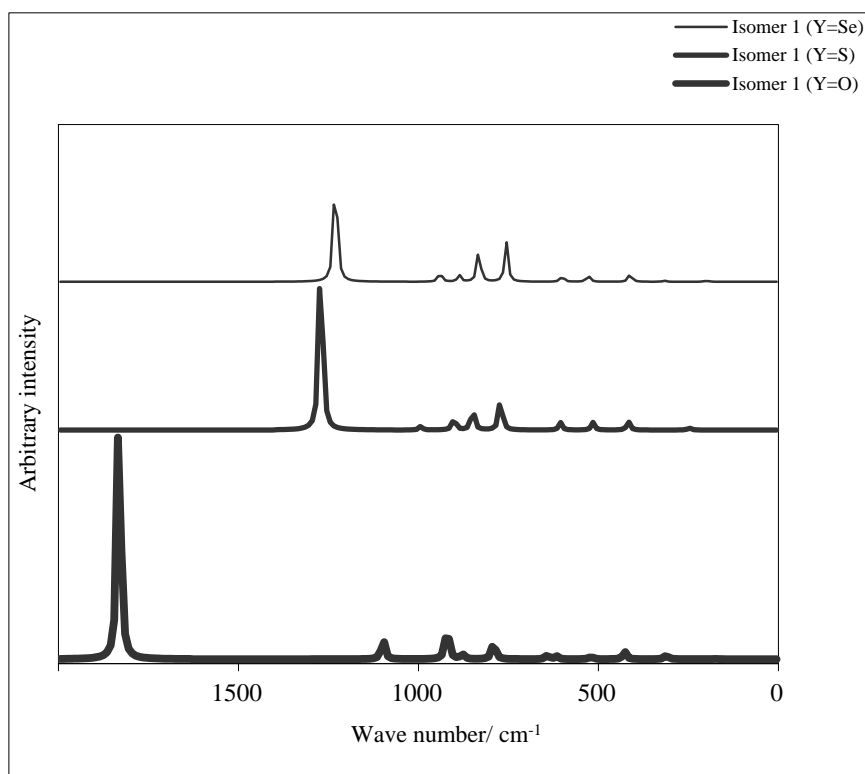
* References are TMS (6-311+G(2d,p)), NH₃ (6-311+G(2d,p)) and H₂O (6-311+G(2d,p)) for ¹³C NMR, ¹⁴N NMR and ¹⁷O NMR, respectively.

** Values in brackets are the literature experimental values in CHCl₃ [ref 2]

Table-4: Parameters μ and η and Kohn-Sham HOMO-LUMO gap (kJ/mol) of the ketones

	Y=O	Y=S	Y=Se
Isomer 1			
μ	-561.21	-517.72	-499.90
η	174.82	114.29	89.16
Kohn-Sham HOMO-LUMO gap	349.64	228.58	178.32
Isomer 2			
μ	-498.83	-467.55	-457.27
η	251.61	193.53	168.54
Kohn-Sham HOMO-LUMO gap	503.23	387.05	337.09
Isomer 3			
μ	-536.72	-530.30	-512.38
η	198.26	156.66	129.06
Kohn-Sham HOMO-LUMO gap	396.53	313.33	258.11
Isomer 4			
μ	-563.81	-501.34	-500.38
η	121.68	45.16	21.88
Kohn-Sham HOMO-LUMO gap	243.35	90.32	43.76

Raw harmonic vibrational frequencies, their intensities and symmetries computed for the ketones and their isomers are reported in Tables 5(a)-5(d). The simulated infrared spectra are illustrated in Figures 4(a)-4(d). The 12 modes of vibrations account for the irreducible representations $\Gamma_v = 3A'' + 9A'$ of the C_s point group and $\Gamma_v = 5A_1 + A_2 + B_1 + 4B_2$ the C_{2v} point group. These vibrations have been assigned on the basis of different motions namely stretching and bending modes. Since the vibrations for these ketones are mostly similar, assignments are done for the ketones (Y=O). Analysis of Tables 5(a)-5(d) indicates that substitution of the oxygen atom of the carbonyl by sulfur or selenium affects mainly those vibrational modes involving atoms attached to the carbon atom of C=Y. This is reflected by the close similarities of the spectra in each of the Figures 4(a)-4(d). At this stage, it is worth noting the decrease in the C=O stretching frequencies and this decrease in wave number can be accounted in terms of the decreasing force constant and increasing reduced mass of the C=Y bond. The C=Y frequencies are relatively high and these are well depicted in Figures 4(a)-4(d).

**Fig 4(a):** Simulated infrared spectra of the ketones for isomer 1

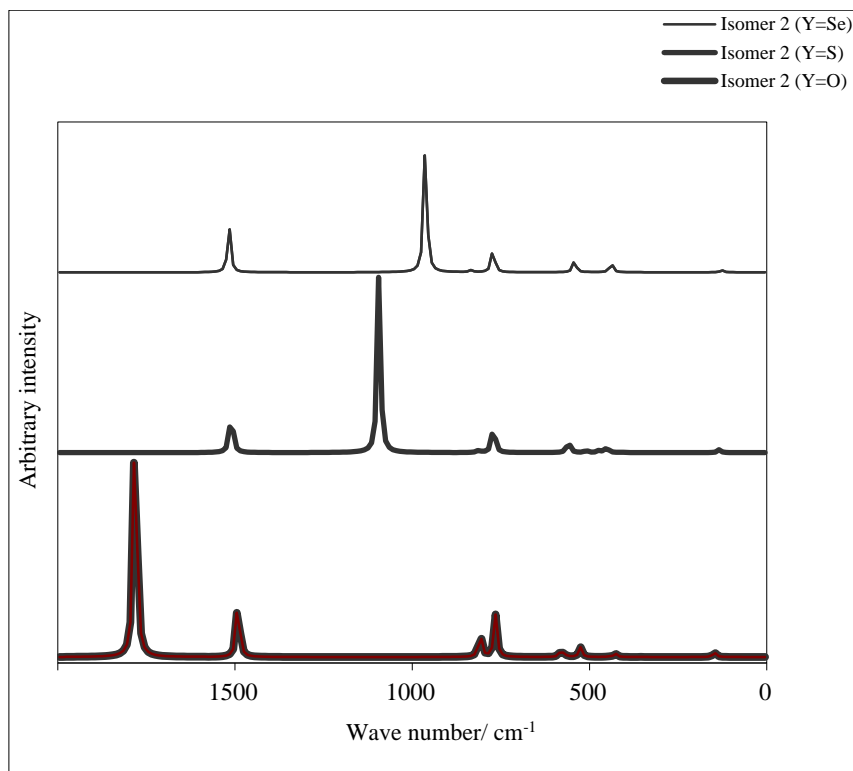


Fig 4(b): Simulated infrared spectra of the ketones for isomer 2

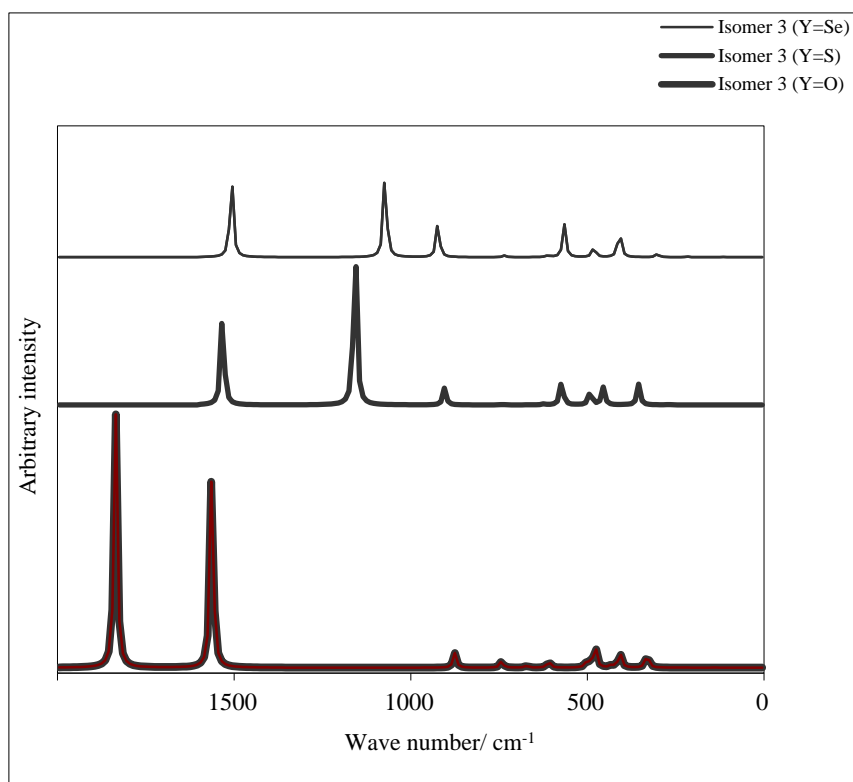


Fig 4(c): Simulated infrared spectra of the ketones for isomer 3

4. CONCLUDING REMARKS

To summarise, this theoretical gas phase study has investigated the optimised molecular structures and vibrational harmonic frequencies of Roesky's ketone, its sulfur and selenium analogues and their isomers. The optimised structural parameters and infrared vibrational spectra of Roesky's ketone (isomer 1) are in good agreement with some of the available experimental literature data. Therefore, data from the present theoretical gas phase study are expected to be valid for the molecular structures and vibrational spectra of the novel sulfur and selenium analogues. The results of this work could be useful for the characterisation of these ketones and interpretation of future experiments. A major consequence of this study is that these thio and seleno ketones are rational potential candidates for experimental chemists as new areas of research.

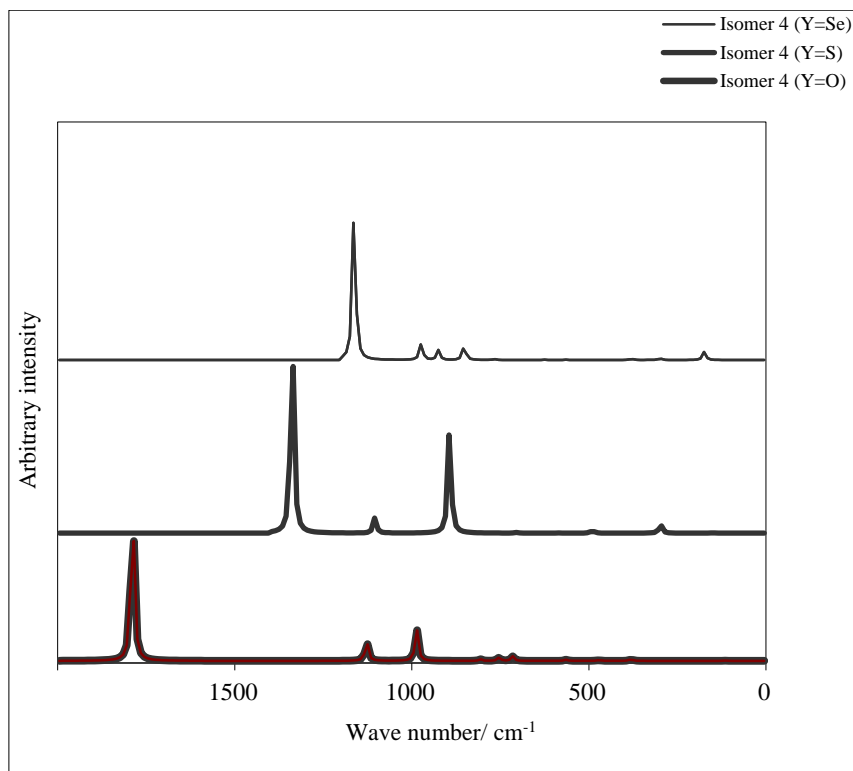


Fig 4(d): Simulated infrared spectra of the ketones for isomer 4

Table-5(a): Infrared vibrational parameters of the isomers 1

No.	Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)			Assignment for Y=O	Infrared intensity (km mol ⁻¹)			Symmetry	
		O	S	Se		O	S	Se		
v ₁	636.5 (637)*	10.5			Out of plane mode CO	558.7	0.03	535.5	0.04	A''
v ₂	422.2 (422)	18.7			Ring out of plane mode	411.7	19.4	406.6	20.1	A''
v ₃	173.7 (173)	0.8			Ring out of plane mode	136.8	0.07	117.8	0.0009	A''
v ₄	1826.8 (1826)	693.2			CO stretching	1266.2	496.7	1225.5	313.4	A'
v ₅	1093.3 (1094)	53.9			CN ₃ stretching	988.2	8.6	935.0	24.7	A'
v ₆	915.1 (916)	91.2			S ₅ N ₃ stretching	895.7	30.8	881.6	15.2	A'
v ₇	873.1 (874)	12.7			S ₅ N ₆ stretching	844.1	55.8	827.0	81.4	A'
v ₈	785.8 (786)	47.1			S ₄ N ₆ stretching	766.6	81.7	750.8	89.3	A'
v ₉	611.6 (612)	7.1			Ring bending mode	600.4	16.6	595.4	14.4	A'
v ₁₀	521.3 (522)	1.7			Ring bending mode	510.4	17.1	523.4	16.2	A'
v ₁₁	513.9 (515)	5.1			Bending mode CO	419.9	0.3	312.7	2.8	A'
v ₁₂	305.9 (307)	11.1			CS stretching	242.8	5.0	194.9	2.9	A'

*Values in bracket are literature values obtained using B3LYP/6-311+G(d) [ref 2]

Table-5(b): Infrared vibrational parameters of the isomers 2

No.	Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	Assignment for Y=O	O		S		Symmetry
				Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	
v ₁	1776.6	473.5	CO stretching	1505.5	77.7	1511.7	79.1	A ₁
v ₂	1486.6	108.1	NN stretching	1089.0	302.7	958.1	222.7	A ₁
v ₃	575.0	13.6	SN stretching	554.3	21.3	537.1	21.7	A ₁
v ₄	520.4	16.2	Ring bending mode	504.5	4.0	495.4	0.3	A ₁
v ₅	442.2	0.8	Ring bending mode	404.7	0.5	301.9	0.01	A ₁
v ₆	518.1	0	Ring out of plane mode	516.6	0	516.5	0	A ₂
v ₇	558.2	1.6	Out of plane CO	467.1	4.1	434.1	7.4	B ₁
v ₈	142.8	8.4	Ring out of plane mode	129.7	4.7	122.0	3.2	B ₁
v ₉	803.5	43.8	Ring bending mode	806.9	4.1	828.3	3.5	B ₂
v ₁₀	760.2	70.3	Ring bending mode	765.8	52.3	766.7	44.2	B ₂
v ₁₁	422.2	6.1	CS stretching	446.0	9.8	433.4	10.1	B ₂
v ₁₂	351.9	0.2	Bending mode CO	218.6	0.0011	165.9	0.008	B ₂

Table-5(c): Infrared vibrational parameters of the isomers 3

No.	Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	Assignment for Y=O	O		S		Symmetry
				Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	
v ₁	666.1	4.2	Out of plane mode (CO)	618.4	1.8	606.1	3.4	A''
v ₂	426.1	5.3	Ring bending mode	388.5	0.4	372.3	0.06	A''
v ₃	135.4	0.1	Ring out of plane mode	114.6	0.1	107.2	0.3	A''
v ₄	1830.7	471.7	CO stretching	1527.6	183.3	1502.5	162.1	A'
v ₅	1558.2	382.7	NN stretching	1152.8	329.4	1067.5	168.4	A'
v ₆	870.3	26.8	Ring bending mode	899.3	31.3	917.9	67.3	A'
v ₇	737.7	12.6	CN stretching	735.5	1.0	730.4	3.0	A'
v ₈	604.2	13.5	CS stretching	567.5	47.1	560.6	60.9	A'
v ₉	495.0	15.7	SS stretching	486.4	28.6	476.2	21.1	A'
v ₁₀	473.2	49.9	Ring bending mode	449.9	32.0	404.2	57.6	A'
v ₁₁	402.9	30.5	Bending mode CO	350.0	37.8	296.8	6.5	A'
v ₁₂	325.4	28.7	SN stretching	265.4	0.7	212.1	1.0	A'

Table-5(d): Infrared vibrational parameters of the isomers 4

No.	Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	Assignment	O		S		Symmetry
				Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	Frequency (cm ⁻¹)	Infrared intensity (km mol ⁻¹)	
v ₁	1783.6	846.7	CO stretching	1332.8	1012.0	1157.9	743.2	A ₁
v ₂	1122.5	96.2	Ring bending mode	1099.3	70.9	968.2	80.4	A ₁
v ₃	748.5	15.5	Ring bending mode	913.8	0.02	762.2	4.5	A ₁
v ₄	602.5	0.1	Ring bending mode	577.4	1.5	374.7	7.2	A ₁
v ₅	375.7	8.4	SS stretching	485.2	14.0	326.3	1.3	A ₁
v ₆	354.8	0	Ring out of plane mode	394.9	0	328.1	0	A ₂
v ₇	709.9	20.8	Ring out of plane mode	697.9	3.4	621.1	1.9	B ₁
v ₈	108.4	1.2	Ring out of plane mode	146.5	1.7	294.2	8.6	B ₁
v ₉	981.3	150.6	SN stretching	1060.4	0.8	919.7	45.9	B ₂
v ₁₀	801.7	7.7	CN stretching	888.4	500.5	846.8	73.7	B ₂
v ₁₁	558.6	5.5	Ring bending mode	623.4	0.002	559.0	1.4	B ₂
v ₁₂	465.8	4.4	Out of plane mode CO	292.8	43.8	169.1	38.4	B ₂

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