

Quantum Chemical Studies on Furan and Its Isomers

Emmanuel E. Etim ^{1,*}, Oko Emmanuel, Godwin ¹, ²Sambo, Ifiok Fridy, ³Sulaiman Adeoye Olagboye ²

¹Department of Chemical Sciences, Federal University Wukari, PMB 1020, Wukari, Taraba State, Nigeria

²Department of Chemistry, Akwa Ibom State University, Ikot Akpaden

³Department of Chemistry, Ekiti State University, Ado -Ekiti, Nigeria

* Author to whom correspondence should be addressed; E-Mail: emmaetim@gmail.com

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Abstract: Advances in computational chemistry have greatly increased its effectiveness and attractiveness as an emerging adjunct to experimental chemistry but also as an independent research field. This work studied some basic parameters of the fourteen members of the C₄H₄O isomeric group using the Gaussian 4 (G4) compound model with the Gaussian 09 suit of programs. The results obtained are then compared with experimental data where available. The parameters; enthalpy of formation, rotational constants, IR spectra and frequencies, bond distances and angles, and dipole moment were obtained from the optimized stable geometries of the isomers. From the results, furan was found to be the most stable isomer of the group with enthalpy of formation value of -9.261 kcal/mol. Because of its high stability, it is also found to be the most experimentally investigated isomer of the group. The experimentally reported parameters are found to be in good agreement with the computationally determined ones. The good agreement between the calculated parameters for the isomers and the available experimental value stresses the reliability of the results (at the G4 level) for systems with no experimental data. The importance of the results and other possible applications of the experimentally less studied isomers of the group are discussed.

Keywords: computational; experimental; chemistry; G4; data.

1. Introduction

Computational chemistry is a field/branch of chemistry that overlaps between computer, chemistry and physics. It involves solving chemical problems (phenomena) via the computer based on the fundamental laws of physics (Young, 2001). Computational chemistry have been used in many fields; In modeling stable and unstable (short-lived) intermediate in chemical and biological reactions (Ramachandran *et al.*, 2008), it is used in studying molecular interactions in drugs as applied in the pharmaceutical industry (Alexander *et al.*, 2015), in the studies of bioactivation reactions or toxic metabolic reactions in biology (Anders *et al.*, 1996) and numerous other uses in chemistry such as aiding in finding starting materials for laboratory synthesis, aiding the understanding of data from experiments and in predicting such data accurately for both known and unknown molecules e.g molecules in the Interstellar mediums (ISM), Etim and Arunan (2016), (Etim *et al.*, 2020), elucidation of the position of spectroscopic and vibrational peaks (Dykstra *et al.*, 2008).

Gaussian (G4) compound model is a popular method commonly used in the calculation of electronic energies of the molecular species. The (G4 and G4MP2) analogous have been widely used for thermodynamic property calculations for most systems. G4 level of calculations are mostly used for geometry optimization,

Zero Potential Energy (ZPE), Single Point calculations etc. (Curtiss, 2007)(Heberel, 1999), (Etim *et al.*, 2017)

Furan (1-oxacyclopnta-2,4-diene or 1,4-Epoxybuta-1,3-diene or Oxole, Oxa(5)annulene) as depicted in figure 1 is a five membered aromatic heterocycle consisting of 4 carbon atoms and an oxygen atom with a molecular formula of C_4H_4O (IUPAC, 2014). It is a colorless liquid, soluble in water and other organic solvents like alcohols, actone, chloroform etc. Jakubke and Jeschkeit (1994), (DHHS, 2019) even though toxic to humans but of great economic importance as a starting material in the production of specialties and effect chemicals such as agrochemicals, adhesives, polymers etc (Hoydonckx *et al.*, 2000).

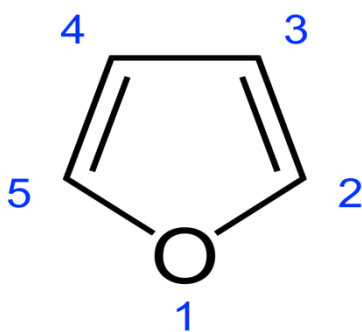


Figure 1. The structure of furan

Furan forms the corresponding isomers when it undergoes rearrangement of its atoms or its chemical bonds connectivity (double bond), (Smith, 2010) thus, Members of this isomeric group include Ethynyloxy ethane, Cyclopropene-1-carbaldehyde, 2-Cyclopropene-1-carbaldehyde, 1-buten-3-yn-2-ol, But-3-ynal, 2-methyl-2-cyclo propenemethanone, Cyclopropylienemethanone, 3-butyne-2-one, 2-butyne, 1, 2-butadiene, 2, 3-butadiene, 2-cyclobutene-1-one, Vinyl ketene and Furan itself.

Owing to the crucial applications of these molecules, only furan has been studied experimentally, there exists wide paucity of information on the rest of the isomeric groups. This therefore necessitate this research with the aim of providing computational data for these molecules which from experience, computational methods have proven to be a substitute for experimental procedures irrespective of the unstable nature of some isomers which makes it impossible for experimental procedure. Etim and Arunan (2016), (Etim *et al.*, 2020a), (Etim *et al.*, 2017a), (Etim *et al.*, 2020b). Also, (Hollis *et al.*, 2005) pointed out that a good pointer to the solution of astronomical issues lies in the demystification of isomerism, Etim and Harunan (2016a) pointed out that the observation of an isomer in space opens up ways for the detection of other isomers yet to be detected, thus this present research also aims at providing candidates for astronomical searches. We have therefore considered 14 isomeric heterocycle; furan and its isomers with the aim of using quantum chemical computational approaches to determine the thermochemistry (standard enthalpy of formation), bond lengths, Vibrational spectroscopy, dipole moments and rotational constants of these molecules which will pave way in closing the gap in literature about these molecules and in providing the needed data for astronomical searches respectively.

2. Materials and Methods

The quantum chemical studies carried out and reported in this work were performed using the GAUSSIAN 09 suite of programs as described by (Frisch *et al.*, 2009) The G4 method has been found to be very effective in predicting many chemical parameters in many molecules as reported in literatures Etim and Arunan (2015), (NIST, 2017), (Coates, 2000), (Sverdlov *et al.*, 1974), (Maeda, 1995), (Mantele, 1995), (Jacox, 1994), Davis and Orville-Thomas, (1969), (Peccsok *et al.*, 1994), (Villar *et al.*, 2012), Person and Zerbi (1982), as such was duly considered in this work in preference to all the other composite methods known. The molecule was optimized at the G4 level of theory.

Enthalpy of formation

The standard enthalpies of formation of all the molecules in this report were calculated using:

At 0K using equation 1

$$\Delta H_f^0(CD, 0K) = 2\Delta H_f^0(A, 0K) + \Delta H_f^0(B, 0K) - \sum D_0(CD) \dots \dots \dots (1)$$

At 298K using equation 2

$$\Delta H_f^0 (CD, 298K) = \Delta H_f^0 (CD, 0K) + (H_{CD}^0(298K) - H_{CD}^0(0K)) - [2\{H_A^0(298K) - H_A^0(0K)\} + \{H_B^0(298K) - H_B^0(0K)\}] \dots \dots \dots (2)$$

From equation 2, $H_{CD}^0(298K) - H_{CD}^0(0K)$ is defined as $H_{corr} - E_{zpe}$. Where $H_{corr} = E_{tot} + k_B T$ and $E_{tot} = E_t + E_r + E_v + E_e$ [18].

$$\% \text{ Error} = \frac{(\text{Calculated Value} - \text{Experimental Value})}{\text{Calculated Value}} \times 10 \dots \dots \dots (3) \text{ (Bewick and Parrons, 2019)}$$

3. Results and Discussion

The results obtained from the different studies are presented and discussed below.

3.1. Thermochemistry

Figure 2 shows the optimized geometry of the C_4H_4O isomeric group and the calculated standard enthalpies of formation ($\Delta_f H^0$) calculated using equation (1) and (2) and illustrated in table 1 in descending order.

Table 1. Standard enthalpy of formation ($\Delta_f H^0$) of C_4H_4O isomers

Molecule	Enthalpy of formation (kcal/mol)
Ethynyloxy ethane	46.776
Cyclopropene-1-carbaldehyde	39.853
2-Cyclopropene-1-carbaldehyde	38.781
1-buten-3-yn-2-ol	30.702
But-3-ynal	24.553
2-methyl-2-cyclopropenemethanone	21.003
Cyclopropylenemethanone	19.320
3-butyn-2-one	18.218
2-butylnal	17.161
1,2-butadienal	13.283
2,3-butadienal	13.116
2-cyclobutene-1-one	9.180
Vinylketene	3.563
Furan	-9.261

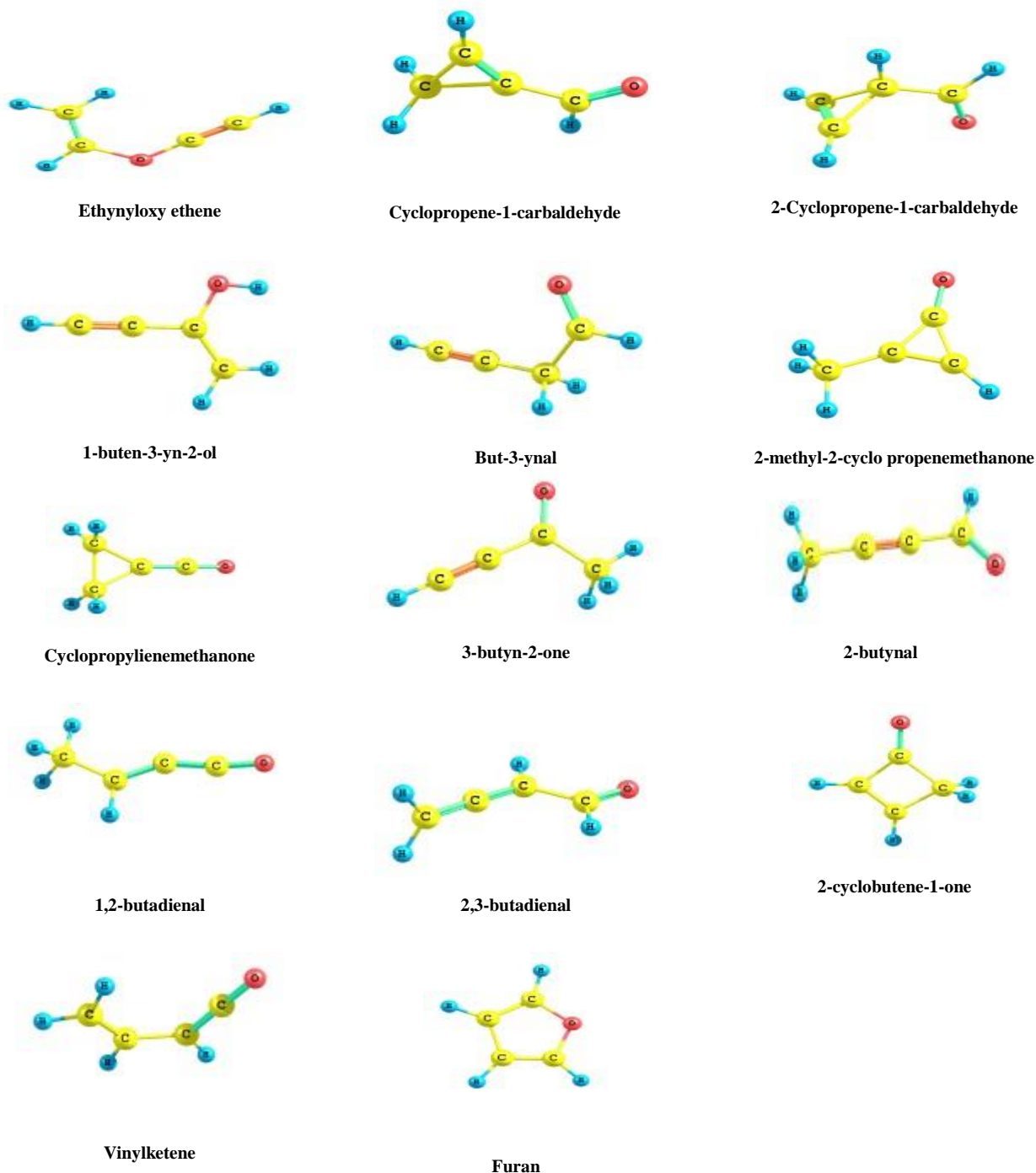


Figure 2. Optimized geometries of furan (C_4H_4O) and its Isomers

From Table 1 it is apparent that the most stable member of the C_4H_4O isomeric group is Furan with a standard enthalpy of formation of -9.261kcal/mol while Ethynyloxy ethane is the least stable isomer of the group with a standard enthalpy of formation of 46.776 kcal/mol . The implication of this is that Furan with a negative enthalpy of formation is exothermic giving rise to a more stable molecule whereas Ethynyloxy ethane with a positive enthalpy of formation absorbs heat during the reaction (endothermic) forming an unstable molecule (Golden *et al.*, 1977) (Papina *et al.*, 2000), thus, Furan is

the most stable amongst all the isomeric species and would serve as a better candidate for astronomical searches compared to its other isomeric groups which are all positive (endothermic).

3.2. Vibrational Spectroscopy

The vibrational frequency or spectroscopy deals with the periodic movement of atoms of a molecule relative to each other and usually range from less than 10^{13} Hz to 10^{14} Hz, or 300 cm^{-1} to 3000 cm^{-1} it is important and necessary because it aids in the elucidation of molecular transition and molecular structure (Howell, 1946). Furan, a non-linear molecule will have 21 modes of vibration (number of vibrational modes for a non-linear molecules = $3N-6$)

Table 2 contains the vibrational frequencies of furan with the percentage error calculated using eqn (3) with that of the isomers indicated by Table A1-A5 presented in the Appendix, figure 3 depicts the corresponding computational spectra of furan with its isomeric groups in appendix labeled figure A1.

Table 2. Vibrational frequencies of furan (cm^{-1})

Experimental Frequency (cm^{-1})	Calculated Frequency (cm^{-1})	% Error (cm^{-1})
3161	3292	4
3140	3285	4
1491	3263	54
1384	3252	57
1140	1598	28
1066	1516	30
995	1414	30
871	1285	32
838	1214	31
728	1169	38
603	1095	45
863	1065	19
745	1018	27
613	890	31
3154	886	-256
3129	861	-263
1556	822	89
1267	766	-65
1180	735	-61
1040	625	-66
873	614	-42

In a related study by (Etim *et al.*,2018b), the G4 composite method has shown great accuracy in the computation of vibrational spectroscopy with an accuracy ranging between 1- 6% but in this case, the percentage error appears quite large, ranging from -263% to 66%, these % errors are too large placing some level of suspicion in the experimentally determined vibrational frequencies of furan meanwhile the large range of vibrational frequencies observed in furan depicts large extent of electronic transition in the molecule giving rise to its planar C_{2v} symmetry structure (Montejo *et al.*, 2004).

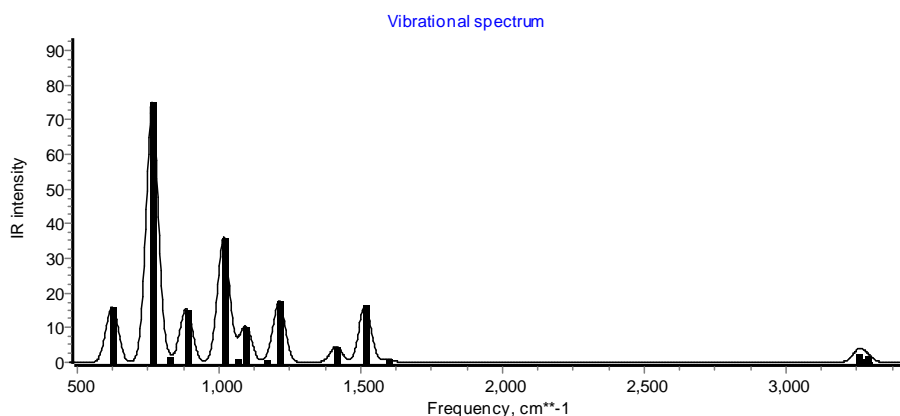


Figure 3: Computational IR spectrum of Furan

3.3. Structural Parameters

Structural parameter like bond distance, length or radius is the average distance between the nuclear of two bonded atoms in a molecule; it has values typically within the range less than 1 to 2 Å. This structural parameter according to (Etim *et al.*, 2017b) influences the force of attraction binding such a molecule. i.e. the smaller the bond length between the bonding atoms, the stronger is the force of attraction between them.

The bond distances and angle for Furan and its other isomeric groups are shown in table 3 and appendix (table B1-B5) respectively, the G4 level of theory was applied in computing the bond distances and angles, the values obtained ranges from 1.077 - 1.434 Å for bond distances and 106 - 134° for bond angles of furan and are all concordant to the experimentally determined values, this finding provides a good background for accepting the values obtained by this method for the bond distances and angles that have not been provided by the experimental procedure for both furan and the other isomeric groups. The bond length range also account for the hydrogen bonding and weak Vander Waal's forces present in the molecule.

Table 3. Bond radius and angles of furan

Description	Calculated Value (Å)	Experimental Value (Å)	Error	Connectivity		
				Atom 1	Atom 2	Atom 3
R(1-2)	1.434	1.431	0.003	1	2	-
R(1-5)	1.357	-	-	1	5	-
R(1-6)	1.079	1.076	0.003	1	6	-
R(2-3)	1.357	-	-	2	3	-
R(2-7)	1.079	-	-	2	7	-
R(3-4)	1.360	1.362	0.002	3	4	-
R(3-8)	1.077	-	-	3	8	-
R(4-5)	1.360	1.361	0.001	4	5	-
R(5-9)	1.077	-	-	5	9	-
A(2-1-5)	106.0	106.6	0.6	4	2	
A(2-1-6)	127.4	-	-	2	1	5
A(1-2-3)	106.0	106.1	0.1	2	1	6
A(1-2-7)	127.4	127.9	0.5	1	2	7
A(5-1-6)	126.5	126.0	0.5	5	1	6
A(1-5-4)	110.6	110.7	0.1	1	5	9
A(1-5-9)	133.8	133.4	0.4	1	5	9
A(3-2-7)	126.5	-	-	3	2	7
A(2-3-4)	110.6	-	-	2	3	4
A(2-3-8)	133.8	-	-	2	3	8
A(4-3-8)	115.6	115.9	0.3	4	3	8
A(3-4-5)	106.8	-	-	3	4	5

3.4 Dipole Moment

Dipole moment is an important molecular property widely used to probe the infra-red spectroscopy of molecule. A molecule is infra-red active only when there is a change in dipole moments. Thus, provided that there is a dipole moment change during a normal molecular rotation, vibration or a combination of the two molecular rotation–vibration, chemical compounds can absorb at the infra-red regions and are said to be IR active. Table 4 shows the dipole moments of C₄H₄O isomers at the G4 method. The highest calculated dipole moment was found to be 3.9984 D for 2, 3-butadienal and the lowest value was observed for Furan 0.7776 D. These computed and experimental dipole moment of 0.660 D are in good agreement. Our results of the calculated dipole moment of furan using the G4 compound method which is in pact with the reported experimental values shows logically that the other calculated parameters and the spectrums of C₄H₄O₂ isomers reported in this work (see appendix) are well predicted since they have no experimentally determined results.

Table 4. Dipole moment of C₄H₄O Isomers

Molecule	Exp. Dipole moment (Debye)	Cal. Dipole moment (Debye)
Ethynyloxy ethane	-	1.3869
Cyclopropene-1-carbaldehyde	-	2.9632
2-Cyclopropene-1-carbaldehyde	-	3.1177
1-buten-3-yn-2-ol	-	1.3041
But-3-ynal	-	2.4937
2-methyl-2-cyclopropenemethanone	-	5.3725
Cyclopropylienemethanone	-	3.1519
3-butyne-2-one	-	2.8510
2-butyne	-	3.7849
1,2-butadienal	-	3.9219
2,3-butadienal	-	3.9984
2-cyclobutene-1-one	-	2.9718
Vinylketene	-	1.2998
Furan	0.660	0.7776

3.5 Rotational Constants

Table 5 depicts the equilibrium rotational constants for C₄H₄O and its isomers calculated using the G4 level of theory. There occurs no significant difference between the experimental and calculated rotational constants data (Etim *et al.*, 2017c), there is consistency of results between the observed and calculated results. The calculated rotational constant values of furan are 9.5032847, 9.2929167, 4.6984617 GHz and the experimental values are 9.4470599, 9.2464987, 4.6707664 GHz at the three coordinates. A similar regularity was also observed by (Etim *et al.*, 2017c) in their studies on rotational constant of pyridine, pyrimidine, pyrazine, imidazole and Pyrazole using the G4 level of theory (Andrew *et al.*, 2018)(Etim *et al.*, 2017d)(Etim *et al.*, 2018).

Table 5. Rotational constant C₄H₄O Isomers

Molecules	Rotation constants (GHz)			
	Calculated	A	B	C
Furan	Calculated			
	Experimental	9.5032847	9.2929167	4.6984617
	% Error	9.4470599	9.2464987	4.6707664
3-butyl-2-one	Calculated	0.000562	0.000464	0.000277
2-butyral	Calculated	10.2188435	4.0431046	2.9497202
but-3-ynal	Calculated	43.0723262	2.1191800	2.0455385
Vinylbetene	Calculated	12.6549946	3.5035786	2.7902650
2-cyclobutene-1-one	Calculated	14.5619464	3.2492230	2.6564797
2,3-butadienal	Calculated	12.5889477	5.2999469	3.8201925
1-buten-3-yn-2-ol	Calculated	35.8446031	2.3990770	2.2838082
1,2-butadienal	Calculated	10.6423669	4.1276979	2.9741560
cyclopropylene methanone	Calculated	52.0516947	2.1401472	2.0818869
2-methyl-2-cyclopropen-1-one	Calculated	21.4585702	3.0889092	2.8011863
2-cyclopropene-1-carbaldehyde	Calculated	13.4751107	3.8464190	3.0484318
ethynyloxy ethane	Calculated	13.2040173	4.1498423	3.8841841
cyclopropene-1-carbaldehyde	Calculated	13.8983024	3.8701225	3.0271750
		19.1829716	3.3768649	2.9272707

4. Conclusions

We have effectively used the G4 level of theory to carry out quantum chemical studies on furan and its isomers (fourteen C₄H₄O isomers). Important quantum chemical parameters like enthalpy of formation, bond length, vibrational spectroscopy, rotational constant and dipole moments have been calculated using the computational chemistry Gaussian 09 suit at the G4 level of theory and compared with measured experimental values where available. The complementary relationship observed between the calculated and the available experimental data for the isomers studied in this work indicates that other C₄H₄O isomers with no experimental values are predicted correctly based on the quantum chemical study using G4 method. The results of the obtained parameters under study can interestingly find applications in the exploration of the chemical composition of astronomical bodies; it has provided candidates for other astronomical searches and have also bridge the dearth of information currently existing in literature about furan and its isomers.

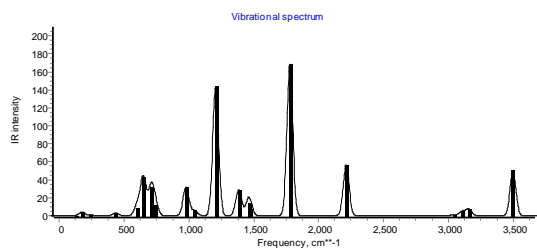
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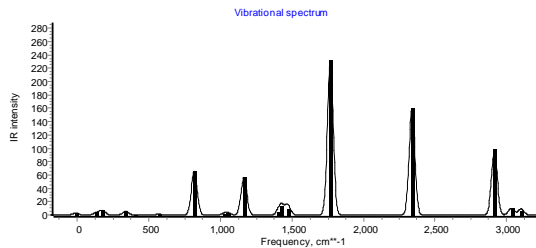
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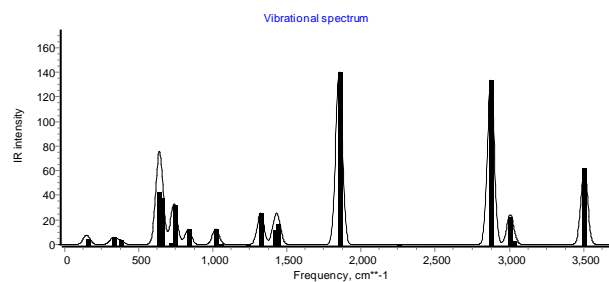
Appendices



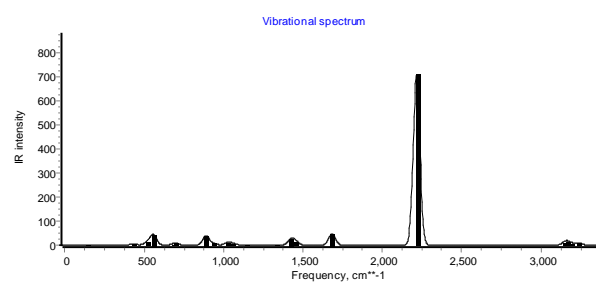
3-butyl-2-one



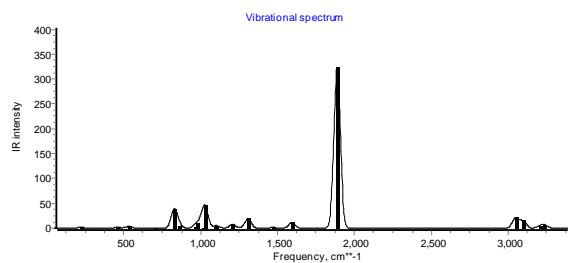
2-butylnal



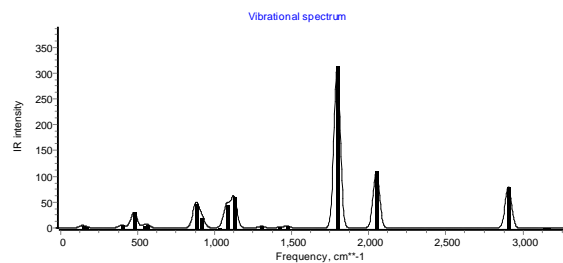
but-3-yn-1-ol



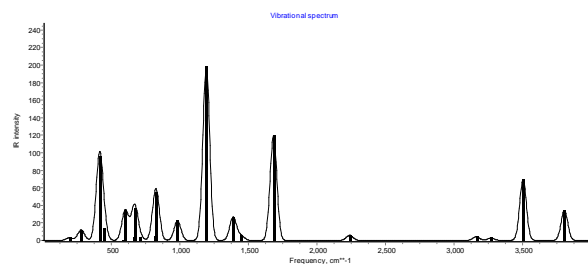
Vinylbetene



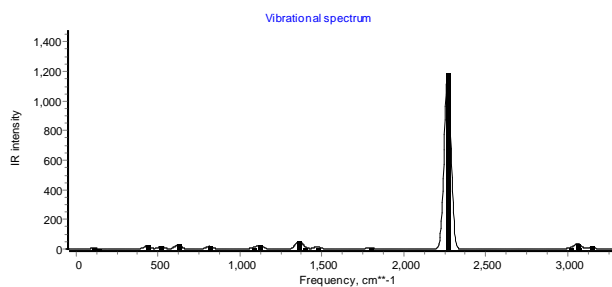
2-cyclobutene-1-one



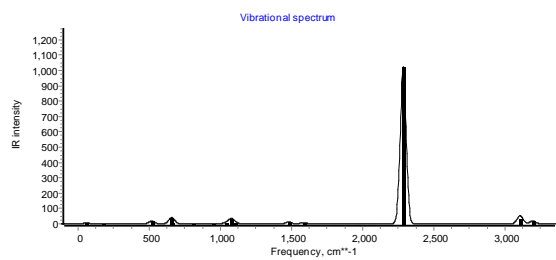
2,3-butadienal



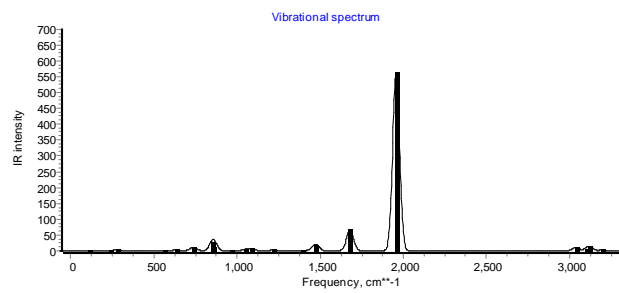
1-buten-3-yn-2-ol



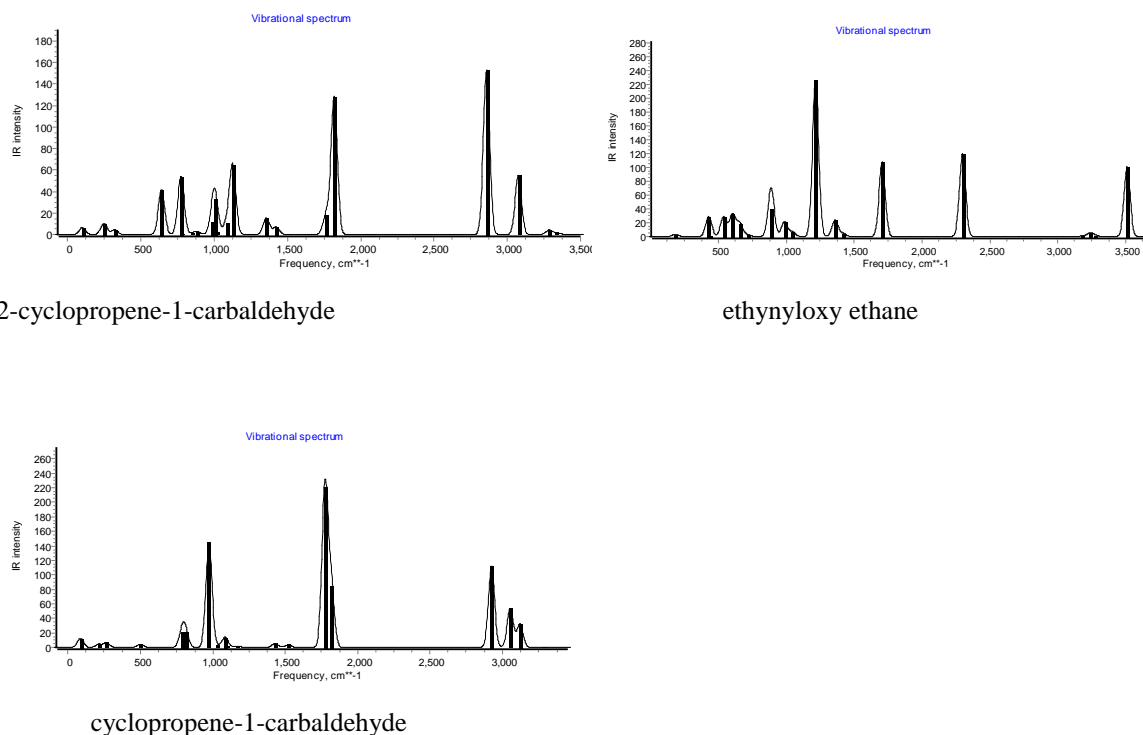
1,2-butadienal



cyclopropylene methanone



2-methyl-2-cyclopropen-1-one

**Figure A1:** Calculated IR Spectra of C₄H₄O Isomers**Table A1:** Vibrational Frequency and Intensity of C₄H₄O Isomers

3-butyl-2-one		2-butylnal		but-3-ynal	
Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities
128.506	0.022	-10.2262	2.9273	146.66	3.5953
176.3539	3.7381	133.8515	3.7032	147.689	4.1826
240.5959	0.8813	176.7045	7.0389	325.2479	5.5199
435.6162	3.0672	337.9733	5.3477	373.9987	3.4653
601.1008	2.841	404.2085	0.1688	630.6616	42.7643
602.4391	8.8839	568.0378	1.004	646.7586	37.8776
648.8413	42.6359	817.7946	65.8232	713.6252	0.7036
710.7122	32.013	1023.0724	0.9774	736.723	32.4287
742.8334	11.9276	1043.0997	2.7208	832.4168	12.0459
977.9072	31.8792	1053.3163	1.418	1018.2314	12.4335
1043.9962	5.9554	1164.3054	55.9973	1051.8264	0.0915
1206.7728	143.4826	1409.0908	3.4985	1229.9718	0.2629
1383.5226	29.0459	1424.7915	13.7698	1321.4951	25.2986
1459.9989	13.6183	1468.1286	7.7249	1417.8974	11.483
1468.0585	7.328	1472.4734	7.2678	1436.8594	16.236
1777.4585	168.0417	1768.2003	230.7667	1850.7418	139.6442
2211.1924	56.69	2338.8752	159.0976	2251.1906	0.121
3039.8838	1.0248	2914.1967	97.2909	2875.0497	133.6687

3103.9431	4.6492	3033.314	10.1677	3004.3705	22.3968
3153.9273	7.3471	3097.0042	3.6385	3027.8572	2.8148
3494.9806	50.199	3102.2083	5.4026	3505.897	61.8158

Table A2: Vibrational Frequency and Intensity of C₄H₄O Isomers

Vinylbetene		2-cyclobutene-1-one		2,3-butadienal	
Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities
83.125	0.063	217.5125	1.541	137.549	4.2175
140.2527	1.1936	456.2121	1.4441	163.5138	1.262
432.8656	5.2851	531.002	3.1577	395.7157	5.6411
520.388	11.2496	701.2973	0.2764	473.9422	29.5748
557.7656	42.4558	828.4837	38.9288	542.3524	3.5642
685.8181	0.5016	860.6081	3.6057	559.9276	4.7357
697.4975	8.3566	967.1183	1.2219	876.6655	46.732
890.4073	37.8236	976.7407	9.3405	914.6035	19.0993
937.0249	6.2712	1012.884	0.5112	999.6643	0.0008
1026.4762	9.758	1024.9179	45.9408	1028.7448	0.8029
1060.3357	6.1188	1091.9367	1.3237	1075.8051	43.8339
1146.8725	0.4792	1102.1188	3.785	1122.8014	58.7839
1336.1303	1.1342	1205.426	7.3966	1302.2857	3.104
1427.513	24.4605	1307.0645	18.8036	1419.2505	1.2768
1455.3549	11.8531	1467.1686	1.2476	1465.7803	3.4289
1684.2939	45.7698	1592.4895	10.851	1793.6869	311.6658
2217.1008	707.4594	1886.6555	322.3856	2048.4595	109.5439
3149.4459	6.3747	3047.42	20.9439	2905.7759	79.9133
3164.4697	11.872	3096.8468	14.3732	3136.5024	0.4519
3193.807	5.6657	3206.0066	4.1161	3166.1531	0.247
3239.5762	9.1555	3235.5948	5.398	3211.1919	0.0051

Table A3: Vibrational Frequency and Intensity of C₄H₄O Isomers

1-buten-3-yn-2-ol		1,2-butadienal		cyclopropylene methanone	
Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities
194.5066	3.0024	108.5098	5.0861	57.3112	5.6444
279.3279	11.9457	140.7418	0.3326	174.8068	0.4754
413.0812	95.7334	202.789	0.1127	514.3739	16.9476
444.9507	13.8726	432.7891	19.3646	654.4554	34.3444
582.5723	0.0455	519.275	14.2386	658.6394	6.2121
600.8194	34.2502	622.1241	26.4854	801.0771	0.1166
662.3586	3.9638	814.1194	16.5555	932.209	0
670.2668	36.364	815.2526	1.0213	948.9752	2.0909
708.724	2.7821	1064.0608	0.0005	1035.1956	5.2022
817.9983	4.6921	1085.7926	9.1287	1070.2846	1.1251
825.2516	54.7927	1123.484	21.0619	1071.8562	30.3671
982.5585	22.4681	1358.6533	50.1664	1099.7339	7.5282
1192.3519	198.5517	1392.6447	8.4141	1168.0107	0
1387.8761	26.5179	1472.1334	8.3471	1472.5817	0.0159
1446.2036	5.1965	1473.8462	6.6122	1476.4377	11.5293
1682.6364	119.6271	1792.6101	9.1343	1580.3888	7.1285
2238.3987	5.812	2268.6611	1183.6999	2281.9901	1021.135
3162.6903	4.3372	3018.7504	6.5904	3102.3431	30.5413
3269.7238	2.7814	3061.846	26.8364	3102.8131	22.5133
3503.2848	69.0103	3065.6747	9.1691	3177.0117	0.0002
3804.8299	33.8951	3146.1037	11.435	3190.859	19.4555

Table A4: Vibrational Frequency and Intensity of C₄H₄O Isomers

2-methyl-2-cyclopropen-1-one		2-cyclopropene-1-carbaldehyde		ethynyloxy ethane	
Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities	Frequency (cm ⁻¹)	IR Intensities
107.728	1.5209	99.6366	6.1805	175.9323	0.46
235.0395	0.6556	246.1499	10.1017	182.4097	2.7478
279.9394	3.1823	319.572	4.3941	426.2891	28.1419
562.4936	0.386	639.704	41.6445	436.5458	0.8104
630.4426	2.4468	772.8817	53.5172	535.8367	28.2934
737.5385	10.5766	780.0794	0.3888	601.5827	32.3066
857.0333	26.1496	848.0134	0.7211	654.3779	19.1587
858.4429	10.0162	880.4381	2.7604	713.2949	2.6133

968.3506	0.9947	986.5695	11.4485	885.478	39.359
1050.2718	3.7217	1004.4443	33.5375	887.3515	31.2662
1087.2505	7.1424	1022.1432	1.4511	984.7407	21.2936
1220.4752	2.7815	1083.3743	10.5853	1043.0416	6.7596
1397.4356	1.5734	1125.5779	64.9001	1214.689	226.1775
1471.6793	14.9431	1355.212	15.1098	1357.9014	23.7934
1473.7158	6.6112	1421.9049	7.0022	1415.8568	4.4333
1680.0248	67.257	1763.9233	18.362	1705.1959	107.4323
1957.8703	562.2047	1819.2634	127.7062	2297.2623	119.5114
3037.9501	10.0929	2858.7994	152.589	3179.9502	0.8585
3102.3179	3.2798	3075.9716	54.9071	3238.4616	5.145
3120.8509	12.1697	3285.9369	4.0771	3274.3764	1.5669
3200.0906	2.4451	3339.0082	1.6888	3510.4578	100.9889

Table A5: Vibrational Frequency and Intensity of C₄H₄O Isomers

cyclopropene-1-carbaldehyde	
Frequency (cm ⁻¹)	IR Intensities
85.9694	12.2413
211.7983	4.3259
265.8312	6.2572
499.7028	4.3781
787.4167	20.3619
810.4045	20.3211
972.9936	143.9725
1011.8627	0.0058
1026.5895	2.0513
1028.5844	0.0039
1082.7338	13.0883
1100.9915	1.3012
1168.9986	1.7715
1429.7906	5.2135
1520.6785	3.2826
1774.1662	220.9074
1817.5084	84.1956
2924.2842	111.4937
3053.6867	53.8162
3121.4178	31.9596
3290.6313	0.5674

Table B1: Bond radius and angles of C₄H₄O Isomers

3-butyn-2-one		2-butynal		But-3-ynal	
Description	Cal. Value	Description	Cal. Value	Description	Cal. Value
R(1-2)	1.211	R(1-2)	1.210	R(1-2)	1.199
R(1-3)	1.513	R(2-3)	1.439	R(2-3)	1.526
R(1-4)	1.456	R(2-4)	1.109	R(2-4)	1.114
R(3-5)	1.091	R(3-5)	1.208	R(3-5)	1.452
R(3-6)	1.095	R(5-6)	1.452	R(3-8)	1.101
R(3-7)	1.095	R(6-7)	1.096	R(3-9)	1.100
R(4-8)	1.204	R(6-8)	1.095	R(5-6)	1.200
R(8-9)	1.063	R(6-9)	1.095	R(6-7)	1.062
A(2-1-3)	123.4	A(1-2-3)	124.7	A(1-2-3)	125.7
A(2-1-4)	121.3	A(1-2-4)	121.3	A(1-2-4)	121.7
A(3-1-4)	115.3	A(3-2-4)	114.1	A(3-2-4)	112.6
A(1-3-5)	109.6	A(2-3-5)	178.2	A(2-3-5)	115.4
A(1-3-6)	110.0	A(3-5-6)	179.1	A(2-3-8)	106.8
A(1-3-7)	110.0	A(5-6-7)	110.5	A(2-3-9)	106.8
A(1-4-8)	179.5	A(5-6-8)	111.5	A(5-3-8)	111.3
A(5-3-6)	110.1	A(5-6-9)	110.9	A(5-3-9)	111.3
A(5-3-7)	110.1	A(7-6-8)	108.0	A(3-5-6)	180.0
A(6-3-7)	106.9	A(7-6-9)	107.6	A(8-3-9)	104.7
A(4-8-9)	179.1	A(8-6-9)	108.3	A(5-6-7)	179.7
R(1-2)	1.211	R(1-2)	1.210	R(1-2)	1.199

Table B2: Bond radius and angles of C₄H₄O Isomers

Vinylbetene		2-cyclobutene-1-one		2,3-butadienal	
Description	Cal. Value	Description	Cal. Value	Description	Cal. Vaue
R(1-2)	1.162	R(1-2)	1.347	R(1-2)	1.311
R(2-3)	1.319	R(1-4)	1.495	R(1-3)	1.087
R(3-4)	1.463	R(1-5)	1.083	R(1-7)	1.479
R(3-7)	1.084	R(2-3)	1.525	R(2-4)	1.298
R(4-5)	1.336	R(2-6)	1.083	R(4-5)	1.086
R(4-9)	1.087	R(3-4)	1.571	R(4-6)	1.086
R(5-6)	1.083	R(3-7)	1.095	R(7-8)	1.111
R(5-8)	1.086	R(3-8)	1.095	R(7-9)	1.208
A(1-2-3)	179.8	R(4-9)	1.196	A(2-1-3)	121.9
A(2-3-4)	125.2	A(2-1-4)	91.7	A(2-1-7)	121.1
A(2-3-7)	114.8	A(2-1-5)	134.3	A(1-2-4)	178.1
A(4-3-7)	120.1	A(1-2-3)	96.8	A(3-1-7)	117.0
A(3-4-5)	128.1	A(1-2-6)	132.4	A(1-7-8)	114.3
A(3-4-9)	113.0	A(4-1-5)	134.0	A(1-7-9)	123.7
A(5-4-9)	118.9	A(1-4-3)	89.0	A(2-4-5)	121.4
A(4-5-6)	120.8	A(1-4-9)	136.8	A(2-4-6)	121.4
A(4-5-8)	122.6	A(3-2-6)	130.8	A(5-4-6)	117.2
A(6-5-8)	116.6	A(2-3-4)	82.5	A(8-7-9)	122.0
R(1-2)	1.162	A(2-3-7)	116.5	R(1-2)	1.311
R(2-3)	1.319	A(2-3-8)	116.5	R(1-3)	1.087

Table B3: Bond radius and angles of C₄H₄O Isomers

1-buten-3-yn-2-ol		1,2-butadienal		Cyclopropylene methanone	
Description	Cal. Value	Description	Cal. Value	Description	Cal. Value
R(1-2)	1.427	R(1-2)	1.326	R(1-2)	1.481
R(1-5)	1.339	R(1-8)	1.286	R(1-3)	1.510
R(1-8)	1.366	R(2-3)	1.095	R(1-4)	1.087
R(2-3)	1.203	R(2-4)	1.496	R(1-5)	1.087
R(3-4)	1.062	R(4-5)	1.098	R(2-3)	1.481
R(5-6)	1.080	R(4-6)	1.091	R(2-8)	1.283
R(5-7)	1.085	R(4-7)	1.098	R(3-6)	1.087
R(8-9)	0.964	R(8-9)	1.172	R(3-7)	1.087

A(2-1-5)	122.6	A(2-1-8)	151.3	R(8-9)	1.171
A(2-1-8)	112.4	A(1-2-3)	120.2	A(2-1-3)	59.4
A(1-2-3)	180.0	A(1-2-4)	125.0	A(2-1-4)	117.8
A(5-1-8)	125.0	A(1-8-9)	171.2	A(2-1-5)	117.8
A(1-5-6)	120.4	A(3-2-4)	114.7	A(1-2-3)	61.3
A(1-5-7)	121.6	A(2-4-5)	110.1	A(1-2-8)	149.4
A(1-8-9)	108.4	A(2-4-6)	111.7	A(3-1-4)	118.2
A(2-3-4)	179.8	A(2-4-7)	110.1	A(3-1-5)	118.2
A(6-5-7)	118.0	A(5-4-6)	109.4	A(1-3-2)	59.4
R(1-2)	1.427	A(5-4-7)	106.0	A(1-3-6)	118.2
R(1-5)	1.339	A(6-4-7)	109.3	A(1-3-7)	118.2
R(1-8)	1.366	R(1-2)	1.326	A(4-1-5)	114.5

Table B4: Bond radius and angles of C₄H₄O Isomers

2-methyl-2-cyclopropen-1-one		2-cyclopropene-1-cabaldehyde		Ethynyloxy ethane	
Description	Cal. Value	Description	Cal. Value	Description	Cal. Vaue
R(1-2)	1.428	R(1-2)	1.517	R(1-2)	1.082
R(1-3)	1.347	R(1-3)	1.282	R(1-3)	1.083
R(1-9)	1.083	R(1-4)	1.075	R(1-7)	1.322
R(2-5)	1.203	R(2-5)	1.092	R(4-5)	1.060
R(3-6)	1.479	R(2-7)	1.495	R(4-6)	1.199
R(4-6)	1.095	R(3-6)	1.075	R(6-9)	1.302
R(6-7)	1.095	R(7-8)	1.207	R(7-8)	1.082
R(6-8)	1.093	R(7-9)	1.115	R(7-9)	1.391
A(2-1-3)	62.3	A(2-1-3)	65.0	A(2-1-3)	118.7
A(2-1-9)	153.7	A(2-1-4)	142.8	A(2-1-7)	119.1
A(1-2-5)	152.1	A(1-2-5)	119.7	A(3-1-7)	122.2
A(3-1-9)	144.0	A(1-2-7)	119.2	A(1-7-8)	125.5
A(1-3-6)	145.9	A(3-1-4)	152.2	A(1-7-9)	126.1
A(3-6-4)	109.9	A(1-3-6)	152.2	A(5-4-6)	179.6
A(3-6-7)	109.9	A(5-2-7)	114.3	A(4-6-9)	176.9
A(3-6-8)	112.0	A(2-7-8)	124.6	A(6-9-7)	118.9
A(4-6-7)	106.7	A(2-7-9)	114.4	A(8-7-9)	108.4
A(4-6-8)	109.0	A(8-7-9)	121.0	R(1-2)	1.082
A(7-6-8)	109.2	R(1-2)	1.517	R(1-3)	1.083
R(1-2)	1.428	R(1-3)	1.282	R(1-7)	1.322

Table B5: Bond radius and angles of C₄H₄O Isomers

Cyclopropene-1-carbaldehyde	
Description	Cal. Value
R(1-2)	1.299
R(1-3)	1.504
R(1-4)	1.076
R(2-7)	1.462
R(3-5)	1.091
R(3-6)	1.091
R(7-8)	1.209
R(7-9)	1.109
A(2-1-3)	64.7
A(2-1-4)	149.4
A(1-2-7)	148.9
A(3-1-4)	145.9
A(1-3-5)	119.3
A(1-3-6)	119.3
A(2-7-8)	123.7
A(2-7-9)	114.7
A(5-3-6)	113.5
A(8-7-9)	121.6
R(1-2)	1.299
R(1-3)	1.504