MINDO/3-FORCES Study On Some Monosubstituted Triafulvalenes.
Vibrational Spectra

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الخلاصة:

تم نظريا إيجاد ترددات الأنماط الاهتزاز الأساسية (3N-6) و شدد امتصاص الأشعة تحت الحمراء المقابلة لها إضافة إلى التعيين الكامل لكل نمط من هذه الأنماط في جزيئات الترايافولفيلينات احادية التعويض للمعوضات H , CN , OH, NO$_2$, NH$_2$, CH$_3$ و cyclopropyl وذلك باستخدام طريقة حساب تعتمد على نموذج الميندو 3- فورسيز الشبه التجريبي. كذلك وجدت علاقة بين قيم الترددات لبعض هذه الأنماط الاهتزازية في جزيئات الترايافولفيلينات احادية التعويض المدروسة .

Key words:-MINDO/3-FORCES version 6.00 , 1996 program , mono substituted triafulvalenes

Abstract:-

The (3N-6) fundamental vibration frequencies along with their IR absorption intensities for the X-monosubstituted triafulvalene molecules , where X is H , CN, OH , NO$_2$, NH$_2$, CH$_3$, and cyclopropyl , were evaluated theoretically by calculation based on the Semi- empirical MINDO/3-FORCES MO model. The assignments for each one of all of these vibrations was also, carried out. Also, a correlation of the vibration frequency values of some fundamental vibration modes , in the studied X-mono substituted triafulvalene molecules, was found.

Introduction:-

The fulvalenes are the class of hydrocarbons obtained by formally cross-conjugating two rings through a common exocyclic double bond[1]. The fulvalene and their derivatives have wide industrial, biological and therapeutic conductivity applications[2].In previous paper[3], the MINDO/3-FORCES calculations[4,5] have been done after complete optimization of geometry on X-mono substituted triafulvalene molecules , where X is H, CN, OH , NO$_2$, NH$_2$, CH$_3$, and cyclopropyl., Fig .1. The equilibrium geometries along with some others physical properties of these molecules were reported . However , there is no any available study whether it is experimental and or theoretical one concerning the vibration spectra of these molecules.

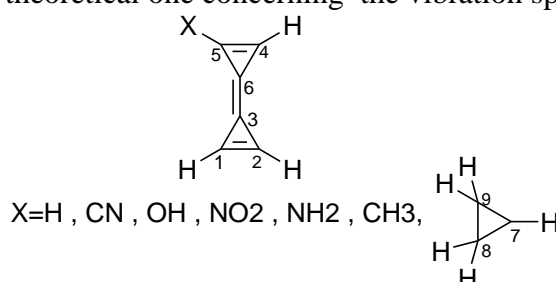X=H , CN , OH , NO2 , NH2 , CH3,

Fig.1-The X-mono substituted triafulvalenes molecules

The aim of present work is the calculations of the 3N-6 fundamental vibration frequencies along with their corresponding IR absorption intensities , for these X-mono substituted triafulvalenes , by the method based on the MINDO/3-FORCES model[4,5].In addition to, give a complete a assignments for each one of the vibration modes of all of these molecules. Finally , to investigate, if any, the correlation of the vibration frequency values of some fundamental vibration modes of the studied X-mono substituted triafulvalene molecules.

The present study is based on MINDO/3-FORCES model which was developed and applied to the treatment of organic molecules [6-12]. Such treatment yields the equilibrium geometry and energy values of the molecules in addition to their fundamental vibration frequencies (3N-6) and IR absorption intensities.

MINDO/3-FORCES model adopts the pulay forces method[13] to evaluate the force constants of molecules which are introduced then into the Wilson Secular equation of the following form[14],

$$\Sigma_j L_j (F_{ij} - M_{ij}\lambda) = 0$$

Solution of this equation yields vibration frequencies ($\lambda = 4\pi^2 \nu^2 C^2$) and vibration mode eigen vector coefficients, L_j. These coefficients are utilized in evaluating the atomic partial participation values (APP) (the partial contribution of each atom to the molecular vibration), the ir absorption intensities and in doing the graphical representation of each of vibrational mode [6-8].

Vibration spectra:-

According to the character tables, the X-mono substituted triafulvalene , where X=H , belongs to the D_2h symmetry point group and the others X-mono substituted triafulvalenes , where X is CN, OH , NO_2, NH_2, CH_3, and cyclopropyl ,with the Cs symmetry , have , respectively, the following irreducible representations,

X=H, Γ_{24} =5Ag+2Au+B_1g+4B_1u+2B_2g+4B_2u+4B_3g+2B_3u

X=CN, Γ_{27}=19A$^-$+8A$^=$

X=OH, Γ_{27}=19A$^-$+8A$^=$

X= NO_2 , Γ_{30}=21A$^-$+9A$^=$

X=NH_2 , Γ_{30}=21A$^-$+9A$^=$

X=CH_3 , Γ_{33}=22A$^-$+11A$^=$

X=cyclopropyl, Γ_{33}=30A$^-$+15A$^=$

where Ag , B_1u, B_2u, B_3g , A$^-$ are in plane and Au, B_1g, B_2g , 2B_3u , A$^=$ are out of plane .In all of these molecules , the symmetry plane is its self the molecular plane, in except of the methyl and cyclopropyl triafulvalenes , where the symmetry plane includes also, one hydrogen atom from the three hydrogen atoms of methyl group and the one hydrogen from each one of the two CH_2 groups respectively. Further more B_1u, B_2u, B_3u are IR active only and Ag is Raman active only. The B_1g , B_2g, B_3g, A$^-$ and A$^=$ are IR and Raman active simultaneously.

The 3N-6 fundamental vibration frequencies along with their assignments and their corresponding IR absorption intensities , for the triafulvalene and each one of the X-mono substituted triafulvalene molecules, were listed in Table.1 .From this Table , it was shown that , for the triafulvalene ring only, the CH stretch. vibrations , localized at the C-H bonds , have the higher frequencies values. The next higher ones are those of CC stretch. vibration modes which are concentrated on the C=C bonds. The stretch vibrations are strongly affected by the anharmonicity . So , we expect that these vibrations frequencies show a large deviation from the observed ones. In order to reduce these differences , a scaling factors [15] may be used. The in plane and out of plane bending vibrations are also, included .Further more, it is obvious that the normal modes vibrations with the Ag symmetry have the zero IR absorption intensities , Table.1. This Table, also, shows the fundamental vibrations associated with the substituents X . In cyano triafulvalene, the ν_4, C$\equiv$N st., has the higher IR intensity value; 82.82 km mol^{-1}, Table 1. This may be attributed to the big change in the dipole moment with respect to coordinates during this vibration motion. The O-H stretch vibration, ν_1 , localized at O-H bond, has the highest frequency value;3921 cm^{-1}, Table 1 .The NO_2 asymmetric stretch, ν_6, has higher frequency than the corresponding symmetric stretch one, ν_8;1900 against 1506 cm^{-1}, Table 1 .However, the situation is opposite to that with the amino substituent; the symmetric NH_2 stretch ν_1 has the higher value, Table 1. The torsion of the CH_3 substituent has the lowest values for both frequency and intensity. Also, the symmetric bending vibrations , of this substituent , ν_9 and ν_{24} have the higher frequency values than the asymmetric one, ν_{11}, Table 1 . Further more , the normal vibrations modes associated with the each one of the methylene

groups, in the cyclopropyl substituent, are the CH_2 asymmetric stretch and the analogous symmetric one with the first of the higher frequency value , the in plane bending vibration , v_s , localized at 1338 cm^{-1} ; the rock vibration , v_{25} , is centered at 712 cm^{-1} and , the last modes are the out of plane wagging and twisting fundamental vibrations , Table 1.

Table 2 shows the correlation of the vibration frequency values of some fundamental vibration modes. of the studied X-mono substituted triafulvalene molecules. From this Table , it is obvious that the normal modes include C=C stretch and the in-plane $C_4C_6C_5$ bending vibrations of the mono substituted triafulvalene with the electron with drawing groups , NO_2 and CN have the lower frequencies (and the higher , to some extent, frequency of the $C_1C_3C_2$ in-plane bending vibration modes) than the analogous ones in the remaining mono substituted triafulvalenes .This may be attributed to the inductive effect causes by NO_2 or CN groups. The increment of the vibrations may be attributed to the weakness of this effect due to the far distance of the C_1 , C_3 , C_2 atoms from the position of the substituent group. The substituents OH , NH_2, CH_3, and cyclopropyl which are electron donating group, show the contrast effect to that shown by NO_2 and CN group, Table 2 .

Table 1: Calculated data of the vibration frequencies (v in cm^{-1}) and the infrared absorption intensities (IR intensities in km mol^{-1}) for the triafulvalene and X-mono substituted triafulvalene molecules , where X is H, CN, OH , NO_2, NH_2, CH_3, and cyclopropyl .See Fig.1 for atoms numbering

1.Triafulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, km mol^{-1}	Assignments
	Ag		
v_1	3620	0.32	$(C_1-C_2+C_4-C_5)H$ st..
v_2	2183	0.00	ring breath .
v_3	1724	0.00	$(C_1-C_2+C_4-C_5+C_3-C_6)$ st
v_4	969	0.00	$\delta (C_1-C_2+C_4-C_5)H$
v_5	706	0.00	ring elongation
	Au		
v_6	718	0.00	$\gamma (C_1-C_2+C_4-C_5)H$
v_7	238	0.00	γ ring
	B_1g		
v_8	710	0.00	$\gamma (C_1-C_2+C_4-C_5)H$
	B_1u		
v_9	3615	101.51	$(C_1-C_2+C_4-C_5)H$ st..
v_{10}	1909	16.84	$(C_1C_2C_3+ C_4C_5C_6)$ st.
v_{11}	1337	39.64	$\delta (C_1C_2C_3+ C_4C_5C_6)$
v_{12}	914	38.95	$\delta (C_1-C_2+C_4-C_5)H$
	B_2g		
v_{13}	709	0.04	γ ring+ γ (C-H)
v_{14}	266	0.00	γ ring
	B_2u		
v_{15}	3594	30.67	$(C_1-C_2)H$ st.
v_{16}	1006	5.33	$\delta C_1C_3C_2 +\delta C_4C_6C_5+\delta$ CH
v_{17}	865	0.27	$\delta (C_1-C_2+C_4-C_5)H$
v_{18}	170	0.22	δ ring
	B_3g		

v_{19}	3595	35.20	$(C_4-C_5)H$ st
V_{20}	1001	0.00	δ $(C_1C_2C_3+ C_4C_5C_6+ \delta$ CH
V_{21}	870	0.00	δ CH(clock-anti clock wise)
V_{22}	506	0.00	δ ring
B$_3$u			
V_{23}	705	16.61	γ $(C_1-C_2+C_4-C_5)H+ \gamma$ $C_1C_2C_3$
V_{24}	253	0.91	γ ring

2.Cyano triafulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, km mol^{-1}	Assignments
A$^-$			
v_1	3621	46.56	$(C_1-C_2)H$ st.
v_2	3598	30.12	$(C_1-C_2)H$ st. .
v_3	3596	46.41	(C_4-H) st.
v_4	2378	82.82	$(C\equiv N)$ st.
v_5	2186	2.57	ring breath
v_6	1953	23.72	$(C_1C_2C_3+C_4C_5C_6)$ st..
v_7	1745	2.37	$(C_1-C_2+C_4-C_5+C_3-C_6)$ st.
v_8	1339	28.95	δ $(C_1C_2C_3+C_4C_5C_6)$
v_9	1109	13.25	δ $C_4C_5C_6$
v_{10}	1009	3.54	δ $C_1C_2C_3$
v_{11}	968	0.02	δ $C_4-H+ \delta$ $(C_1-C_2)H$
v_{12}	918	34.24	δ $C_4-H + \delta$ $(C_1-C_2)H$
v_{13}	870	0.15	δ $(C_1-C_2)H+ \delta$ $C_1C_2C_3$
v_{14}	784	1.62	ring elongation
v_{15}	676	1.05	δ ring
v_{16}	562	1.91	δ ring $+ \delta$ NCC
v_{17}	439	0.11	δ NCC $+ \delta$ ring
v_{18}	218	0.92	δ ring $+ \delta$ N$\equiv$C
v_{19}	89	0.36	δ ring
A$^=$			
V_{20}	717	0.08	γ $(C_1-C_2)H$
V_{21}	711	6.24	γ $(C_1-C_2)H+ \gamma$ (C_4-H)
V_{22}	704	5.85	γ $(C_4-H)+ \gamma$ $(C_1-C_2)H$
V_{23}	538	1.03	γ NCC
V_{24}	287	0.38	γ ring$+ \gamma$ NC
V_{25}	263	0.66	γ ring$+ \gamma$ NC
V_{26}	245	0.35	γ ring$+ \gamma$ NC
V_{27}	137	0.04	γ ring$+ \gamma$ NC

3.Hdroxy triafulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, km mol^{-1}	Assignments
	A$^-$		
v_1	3921	1.15	(O-H) st.
v_2	3621	31.66	(C$_1$-C$_2$)H st.+ (C$_4$-H) st .
v_3	3616	36.55	(C$_4$-H) st.+ (C$_1$-C$_2$)H st
v_4	3597	29.89	(C$_1$-C$_2$)H st.
v_5	2203	28.19	ring breath
v_6	2003	60.51	(C$_4$-C$_5$)st+ δ C$_1$C$_2$C$_3$+O-C st..
v_7	1762	38.32	(C$_1$-C$_2$+C$_4$-C$_5$+C$_3$-C$_6$) st.
v_8	1337	52.71	δ (C$_1$C$_2$C$_3$+C$_4$C$_5$C$_6$)
v_9	1294	55.11	δ C$_4$C$_5$C$_6$+ δ C$_1$C$_2$C$_3$
v_{10}	1083	35.37	δ (O-H)+ δ C$_4$C$_5$C$_6$+ δ (C$_1$-C$_2$)H
v_{11}	1003	2.30	δ C$_1$C$_2$C$_3$
v_{12}	958	11.36	δ C$_4$-H + δ (C$_1$-C$_2$)H + δ (O-H)
v_{13}	921	11.92	δ (C$_1$-C$_2$)H+ δ C$_4$-H
v_{14}	871	0.10	δ (C$_1$-C$_2$)H+ δ C$_1$C$_2$C$_3$
v_{15}	840	4.17	δ C$_4$C$_5$C$_6$
v_{16}	698	1.35	ring elongation
v_{17}	530	5.43	δ ring
v_{18}	324	4.22	δ ring + δ O-H
v_{19}	127	0.88	δ ring
	A$^=$		
V_{20}	713	0.28	γ (C$_1$-C$_2$)H
V_{21}	712	7.99	γ (C$_1$-C$_2$)H+ γ C$_1$C$_2$C$_3$
V_{22}	579	8.41	γ (C$_4$-H)+ γ (O-H)
V_{23}	416	7.66	γ C$_4$C$_5$C$_6$
V_{24}	328	50.63	γ O-H + γ ring
V_{25}	257	0.80	γ ring+ γ (O-H)
V_{26}	234	10.73	γ ring+ γ (O-H)
V_{27}	169	0.34	γ ring

4.Nitrofulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, km mol^{-1}	Assignments
	A$^-$		
v_1	3637	26.88	(C$_1$+C$_2$)H st.
v_2	3614	17.47	(C$_1$+C$_2$)H st. .
v_3	3588	44.77	(C$_4$-H) st.
v_4	2182	5.29	ring breath
v_5	1946	61.71	(C$_1$C$_2$C$_3$+C$_4$C$_5$C$_6$) st
v_6	1900	288.46	NO$_2$ as st..
v_7	1722	61.71	(C$_1$-C$_2$+C$_4$-C$_5$+C$_3$-C$_6$) st.
v_8	1506	272.17	NO$_2$ s st..
v_9	1338	24.01	δ (C$_1$C$_2$C$_3$+C$_4$C$_5$C$_6$)

v_{10}	1125	74.88	$\delta\ C_4C_5C_6$
v_{11}	1022	6.09	$\delta\ C_1C_2C_3$
v_{12}	977	4.07	$\delta\ C_4\text{-}H + \delta\ (C_1+C_2)H$
v_{13}	928	21.44	$\delta\ (C_1+C_2)H + \delta\ (C_4\text{-}H)$
v_{14}	880	0.10	$\delta\ (C_1+C_2)H$
v_{15}	830	19.26	$\delta\ C_4C_5C_6 + \delta\ _sNO_2$
v_{16}	758	14.90	δ ring
v_{17}	557	1.69	δ ring
v_{18}	524	15.25	$\delta\ _sNO_2 + \delta$ ring
v_{19}	401	2.38	δ ring
V_{20}	210	0.74	δ ring
V_{21}	86	0.96	$\rho\ NO_2$
	$A^=$		
V_{22}	741	20.00	$\gamma\ (C_1\text{-}C_2)H + \gamma\ (C_4\text{-}H)$
V_{23}	726	12.08	$\gamma\ (C_1\text{-}C_2)H + \gamma\ (C_4\text{-}H)$
V_{24}	716	2.21	$\gamma\ (C_1\text{-}C_2)H + \gamma\ CH$
V_{25}	697	40.55	$\omega\ NO_2 + \gamma\ CH$
V_{26}	297	0.51	γ ring $+ \rho\ NO_2$
V_{27}	275	1.86	γ ring
V_{28}	226	2.94	γ ring
V_{29}	136	0.26	γ ring $+ \delta\ NO_2$
V_{30}	18	0.36	NO_2 tor.

5.Amino triafulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, km mol^{-1}	Assignments
	A^-		
v_1	3744	14.45	NH_2 s. st.
v_2	3705	35.89	NH_2 as. st.
v_3	3624	9.67	$(C_4\text{-}H)$ st.
v_4	3616	68.13	$(C_1+C_2)H$ st
v_5	3592	34.04	$(C_1+C_2)H$ st
v_6	2196	19.15	ring breath..
v_7	1977	53.88	$(C_1\text{-}C_2+C_4\text{-}C_5)$ st.
v_8	1754	45.91	$(C_1\text{-}C_2+C_4\text{-}C_5+C_3\text{-}C_6)$ st
v_9	1476	3.33	$\delta\ _s NH_2$
v_{10}	1331	105.87	N-C st + $(C_1\text{-}C_2+C_4\text{-}C_5)$ st.
v_{11}	1289	4.97	$\delta\ C_4C_5C_6$
v_{12}	995	2.11	$\delta\ C_1C_2C_3$
v_{13}	970	7.04	$\delta\ (C_4\text{-}H) + \delta\ (C_1+C_2)H$
v_{14}	963	0.05	$\rho\ NH_2 + \delta\ (C_1\text{-}C_2+C_4)H$
v_{15}	914	24.99	$\delta\ (C_1+C_2)H + \delta\ (C_4\text{-}H) + \rho\ NH_2$
v_{16}	867	0.10	$\delta\ (C_1+C_2)H + \delta\ C_1C_3C_2$
v_{17}	850	0.17	$\delta\ C_4C_5C_6$
v_{18}	682	0.18	ring elongation
v_{19}	522	1.12	δ ring

V_{20}	311	0.40	δ ring
V_{21}	125	0.36	δ ring
$A^=$			
V_{22}	708	0.86	γ (C$_1$+C$_2$)H
V_{23}	704	26.57	γ (C$_1$+C$_2$)H+ γ C$_1$C$_2$C$_3$
V_{24}	542	14.62	γ (C$_4$-H)+ τ NH$_2$
V_{25}	415	0.55	γ ring
V_{26}	330	7.01	γ ring+ τ NH$_2$
V_{27}	241	0.40	γ ring
V_{28}	229	0.25	γ ring+ τ NH$_2$
V_{29}	180	10.65	γ ring
V_{30}	34	37.63	NH$_2$ tor.

6.Methyl triafulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, km mol^{-1}	Assignments
A^-			
v_1	3616	48.92	(C$_1$+C$_2$)H st.
v_2	3594	50.65	(C$_4$-H) st.
v_3	3593	31.93	(C$_1$ +C$_2$) H st.
v_4	3449	44.57	CH$_3$ as st.
v_5	3448	50.68	CH$_3$ as. st.
v_6	3447	100.76	CH$_3$ s. st.
v_7	2197	0.04	ring breath.
v_8	1758	0.38	(C$_1$-C$_2$+C$_4$-C$_5$+C$_3$-C$_6$) st
v_9	1381	16.08	δ $_s$ CH$_3$
v_{10}	1330	63.80	δ (C$_1$C$_2$C$_3$+ C$_4$C$_5$C$_6$)+ δ $_s$ CH$_3$
v_{11}	1300	2.71	δ $_{as}$ CH$_3$
v_{12}	1170	0.5.47	δ C$_4$C$_5$C$_6$
v_{13}	1005	2.73	δ C$_1$C$_3$C$_2$
v_{14}	974	0.40	δ (C$_4$-H)+ δ (C$_1$-C$_2$)
v_{15}	950	7.72	τ CH$_3$+ δ (C$_1$+C$_2$)H+ δ (C$_4$-H)
v_{16}	912	29.75	δ (C$_1$+C$_2$)H+ δ (C$_4$-H)+ δ $_{as}$ CH$_3$
v_{17}	866	0.15	δ (C$_1$+C$_2$)H + δ C$_1$C$_3$C$_2$
v_{18}	834	0.26	δ ring+ δ s CH$_3$
v_{19}	677	0.14	δ ring+ δ s CH$_3$
V_{20}	520	0.78	δ ring
V_{21}	300	0.58	δ ring
V_{22}	120	0.09	δ ring
$A^=$			
V_{23}	1975	20.78	C1C2C3 st.+(C4-C5) st
V_{24}	1304	4.70	δ s CH$_3$
V_{25}	916	4.38	ω CH$_3$
V_{26}	716	0.03	γ (C$_1$+C$_2$)H
V_{27}	707	6.69	γ (C$_1$+C$_2$)H+ γ (C$_4$-H)
V_{28}	695	7,17	γ (C$_4$-H)+ γ (C$_1$-H)+ γ (C $_4$C$_5$C$_6$)
V_{29}	385	0.10	γ ring+ δ CH$_3$

V_{30}	264	0.07	γ ring
v_{31}	249	0.63	γ ring
v_{32}	165	0.19	γ ring
v_{33}	50	0.03	CH_3 tor.

7.Cyclopropyl triafulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, km mol^{-1}	Assignments
	A$^-$		
v_1	3616	51.47	(C_1+C_2)H st.
v_2	3597	46. 54	$(C_4$-H)st.
v_3	3593	32.56	(C_1+C_2)H st.
v_4	3502	73.99	CH_2 as st.
v_5	3488	31.57	CH_2 s. st.
v_6	3486	45.10	CH_2 s. st.
v_7	3483	7.98	CH_2 as. st.
v_8	3371	64.10	C_7-H st..
v_9	2193	1.32	$(C_1$-C_2+C_4-C_5+C_3-$C_6)$ st
v_{10}	1965	14.37	$(C_1C_2C_3+ C_4C_5C_6)$ st+$(C_5$-$C_7)$ st
v_{11}	1757	1.12	$(C_1$-C_2+C_4-C_5+C_3-$C_6)$ st+ $C_7C_8C_9$ st
v_{12}	1647	0.15	Cyclopropyl(ring breath)+(C_1-C_2 + C_4 - C_5) st.
v_{13}	1355	11.18	$(C_5$-C_7+C_1-C_2+C_8-$C_9)$st.+δ_s CH_2
v_{14}	1338	20.24	δ_s CH_2.
v_{15}	1322	33.23	δ_s CH_2+$(C_1$-C_2+C_4-$C_5)$st
v_{16}	1238	4.75	$(C_8$-$C_9)$st+δ_s CH_2+.δ $(C_7$-H)
v_{17}	1185	19.99	δ $(C_4$-$C_6)$+δ $(C_5$-$C_7)$
v_{18}	1074	23.04	δ $C_7C_8C_9$+δ $C_4C_6C_5$+CH_2 wag.
v_{19}	1003	0.42	δ $C_1C_3C_2$
V_{20}	976	2.09	δ (C_1+C_2)H+δ $(C_4$-H)+CH_2 rock
V_{21}	931	29.30	δ (C_1+C_2)H+δ $C_4C_6C_5$+ CH_2 twist
V_{22}	906	11.32	δ $(C_4$-H)+δ $(C_4C_6C_5)$
V_{23}	866	0.13	δ (C_1+C_2)H+δ $C_1C_2C_3$
V_{24}	772	0.04	triafulvalene (ring elongation)+ δ cyclopropyl ring
V_{25}	712	2.23	CH_2 rock
V_{26}	641	0.03	Triafulvalene (ring elongation)
V_{27}	524	0.49	δ $(C_3$-$C_6)$
V_{28}	430	0.03	δ ring (triafulvalene + cyclopropyl)
V_{29}	209	0.28	δ ring (triafulvalene + cyclopropyl)
V_{30}	82	0.04	ring(triafulvalene+cyclopropyl) def.
	A$^=$		
v_{31}	1052	3.07	γ $(C_7$-H)+ CH_2 wag.+γ $(C_7C_8C_9)$
v_{32}	1030	0.42	CH_2 twist+γ $(C_7C_8C_9)$
v_{33}	997	0.25	γ $(C_7$-H)+ γ $(C_7C_8C_9)$+ CH_2 rock.
v_{34}	990	3.55	CH_2 wag +δ $(C_4$-H)
v_{35}	951	0.23	CH_2 twist + γ $(C_7C_8C_9)$

v_{36}	795	0.04	γ (C$_7$-H)+CH$_2$ twist
v_{37}	715	0.00	γ (C$_1$+C$_2$)H
v_{38}	706	7.32	γ (C$_1$+C$_2$)H
v_{39}	684	6.37	γ (C$_4$-H)
V_{40}	499	0.49	γ (C$_4$-C$_5$)+ γ (C$_5$-C$_7$)
V_{41}	273	0.00	γ (C$_3$-C$_6$)
V_{42}	253	0.65	γ (C$_1$C$_3$C$_2$)+ γ (C$_4$C$_6$C$_5$)
V_{43}	232	0.00	γ Triafulvalene ring
V_{44}	133	0.10	γ (C$_1$-C$_2$)+ γ (C$_4$-C$_5$)
V_{45}	25	0.00	γ ring (Triafulvalene+ cycloprpyl)

st: stretching, δ : in plane bending, s: symmetric, as: anti symmetric,γ : out of plane bending ,
ω :wag., τ :twist, tor: torsion ; def. deformation

Table 2: the correlation of the vibration frequencies values of some fundamental vibration   modes of the studied X-mono substituted triafulvalene molecules.

X	(C$_1$-C$_2$+C$_4$-C$_5$+C$_3$-C$_6$) as. st	δ C$_4$C$_6$C$_5$	δ C$_1$C$_3$C$_2$	ring breath
H	1724 , v_3	1001, v_{20}	1006 , v_{16}	2183 , v_2
CN	1745, v_7	1109, v_{11}	1008 , v_{10}	2186 , v_5
OH	1762 , v_7	1294, v_9	1003, v_{11}	2203, v_5
NO$_2$	1722 , v_7	1124, v_{10}	1021, v_{11}	2182, v_4
NH$_2$	1753, v_8	1288, v_{11}	994, v_{12}	2196 ,v_6
CH$_3$	1758, v_8	1170, v_{12}	1005, v_{13}	2197, v_7
Cyclopropyl	1757, v_{11}	1184, v_{17}	1003, v_{21}	2192, v_{10}

References
1-Brian Halton, European Journal of Organic Chemistry, Volume 2005 issue 16, 3391 ,2005.
2- Salem E. Zayed ; M. Ezel-Dean Hassan ; Rawia Ragab, Phosphorous, Sulfur, and Silicon and related Elements,V.182,Issue 9,P.1945,2007.
3- J.H. Ali, Journal of Kerbla University, 7, 2, 166, 2009.
4- S. M. Khalil and M. Shanshal**.** Theor. Chem. Acta. 46, 23, 1977 : Z. Naturforsch, 33a, 722, 1978.
5-J. H. Ali and M. Shanshal, Z. Naturforsch. 58a, 1, 2003.
6-D. H, Abed and M. Shanshal, Arbeitsherich Des institüts Für theoretische chemie, Stüttgart, 27, 389, 1990.
7-D. H. Abed, S. f. Al- Saidi and M. Shanshal, Chim. Acta Turc, 23, 7, 1995.
8- R. M. Kubba, S. H. Rida and A. H. Hanoon, National Journal of chemistry , 17, 60, 2005.
9-J.H.Ali, A.M. Bashi and S.M. Haddawal , Journal of Kerbala University, 5,1, 90, 2007.
10-J.H. Ali , S.M. Haddawi, A.Bashi, and R. T. Haiwal, National Journal of Chemistry, 31, 439,2008.
11-J.H .Ali, A.M. Bashi and S.M. Haddawal, National Journal of Chemistry, 33, 60, 2009.
12- J.H. Ali , CSASC En.,Vol.4, College of Science [4th]Scientific Conference, 193 , 2009.
13-P. Pulay , Molec Phys**., 17**, 197, 1969.
14-E. B, Wilson, Jr. J. C. Decius, P. C, Cross, "Molecular Vibration", McGraw- Hill, New York , 1955.
15- M. J. S. Dewar and G. P. Ford, J. Am. Chem.. Soc, 99, 6, 1685, 1977.