

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 , NO₂ , NH₂ , CH₃ 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 , NO₂, NH₂, CH₃, 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 , NO₂, NH₂, CH₃, 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.

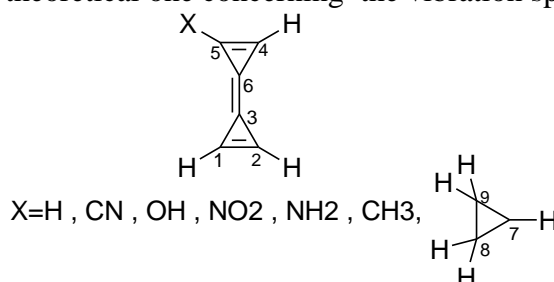


Fig.1-The X-mono substituted triafulvalenes molecules

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⁾,

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

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, NO₂, NH₂, CH₃, and cyclopropyl, with the C_s symmetry, have, respectively, the following irreducible representations,

X=H, $\Gamma_{24} = 5A_g + 2A_u + B_{1g} + 4B_{1u} + 2B_{2g} + 4B_{2u} + 4B_{3g} + 2B_{3u}$

X=CN, $\Gamma_{27} = 19A^- + 8A^+$

X=OH, $\Gamma_{27} = 19A^- + 8A^+$

X=NO₂, $\Gamma_{30} = 21A^- + 9A^+$

X=NH₂, $\Gamma_{30} = 21A^- + 9A^+$

X=CH₃, $\Gamma_{33} = 22A^- + 11A^+$

X=cyclopropyl, $\Gamma_{33} = 30A^- + 15A^+$

where A_g, B_{1u}, B_{2u}, B_{3g}, A⁻ are in plane and A_u, 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 CH₂ groups respectively. Further more B_{1u}, B_{2u}, B_{3u} are IR active only and A_g 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 A_g 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≡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 NO₂ 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 NH₂ stretch ν_1 has the higher value, Table 1. The torsion of the CH₃ 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 CH₂ asymmetric stretch and the analogous symmetric one with the first of the higher frequency value, the in plane bending vibration, ν_8 , localized at 1338 cm⁻¹; the rock vibration, ν_{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 C₄C₆C₅ bending vibrations of the mono substituted triafulvalene with the electron withdrawing groups, NO₂ and CN have the lower frequencies (and the higher, to some extent, frequency of the C₁C₃C₂ in-plane bending vibration modes) than the analogous ones in the remaining mono substituted triafulvalenes. This may be attributed to the inductive effect caused by NO₂ or CN groups. The increment of the vibrations may be attributed to the weakness of this effect due to the far distance of the C₁, C₃, C₂ atoms from the position of the substituent group. The substituents OH, NH₂, CH₃, and cyclopropyl which are electron donating groups, show the contrast effect to that shown by NO₂ and CN group, Table 2.

Table 1: Calculated data of the vibration frequencies (ν 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, NO₂, NH₂, CH₃, and cyclopropyl. See Fig.1 for atoms numbering

1.Triafulvalene

No	MINDO/3-FORCES Freq, cm ⁻¹	IR intensity, km mol ⁻¹	Assignments
A _g			
ν_1	3620	0.32	(C ₁ -C ₂ +C ₄ -C ₅)H st..
ν_2	2183	0.00	ring breath .
ν_3	1724	0.00	(C ₁ -C ₂ +C ₄ -C ₅ +C ₃ -C ₆) st
ν_4	969	0.00	δ (C ₁ -C ₂ +C ₄ -C ₅)H
ν_5	706	0.00	ring elongation
A _u			
ν_6	718	0.00	γ (C ₁ -C ₂ +C ₄ -C ₅)H
ν_7	238	0.00	γ ring
B _{1g}			
ν_8	710	0.00	γ (C ₁ -C ₂ +C ₄ -C ₅)H
B _{1u}			
ν_9	3615	101.51	(C ₁ -C ₂ +C ₄ -C ₅)H st..
ν_{10}	1909	16.84	(C ₁ C ₂ C ₃ + C ₄ C ₅ C ₆) st.
ν_{11}	1337	39.64	δ (C ₁ C ₂ C ₃ + C ₄ C ₅ C ₆)
ν_{12}	914	38.95	δ (C ₁ -C ₂ +C ₄ -C ₅)H
B _{2g}			
ν_{13}	709	0.04	γ ring+ γ (C-H)
ν_{14}	266	0.00	γ ring
B _{2u}			
ν_{15}	3594	30.67	(C ₁ -C ₂)H st.
ν_{16}	1006	5.33	δ C ₁ C ₃ C ₂ + δ C ₄ C ₆ C ₅ + δ CH
ν_{17}	865	0.27	δ (C ₁ -C ₂ +C ₄ -C ₅)H
ν_{18}	170	0.22	δ ring
B _{3g}			

ν_{19}	3595	35.20	(C ₄ -C ₅)H st
V_{20}	1001	0.00	δ (C ₁ C ₂ C ₃ + C ₄ C ₅ C ₆ + δ CH
V_{21}	870	0.00	δ CH(clock-anti clock wise)
V_{22}	506	0.00	δ ring
B _{3u}			
V_{23}	705	16.61	γ (C ₁ -C ₂ +C ₄ -C ₅)H+ γ C ₁ C ₂ C 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 ⁻			
ν_1	3621	46.56	(C ₁ -C ₂)H st.
ν_2	3598	30.12	(C ₁ -C ₂)H st. .
ν_3	3596	46.41	(C ₄ -H) st.
ν_4	2378	82.82	(C \equiv N) st.
ν_5	2186	2.57	ring breath
ν_6	1953	23.72	(C ₁ C ₂ C ₃ +C ₄ C ₅ C ₆) st..
ν_7	1745	2.37	(C ₁ -C ₂ +C ₄ -C ₅ +C ₃ -C ₆) st.
ν_8	1339	28.95	δ (C ₁ C ₂ C ₃ +C ₄ C ₅ C ₆)
ν_9	1109	13.25	δ C ₄ C ₅ C ₆
ν_{10}	1009	3.54	δ C ₁ C ₂ C ₃
ν_{11}	968	0.02	δ C ₄ -H+ δ (C ₁ -C ₂)H
ν_{12}	918	34.24	δ C ₄ -H + δ (C ₁ -C ₂)H
ν_{13}	870	0.15	δ (C ₁ -C ₂)H+ δ C ₁ C ₂ C ₃
ν_{14}	784	1.62	ring elongation
ν_{15}	676	1.05	δ ring
ν_{16}	562	1.91	δ ring + δ NCC
ν_{17}	439	0.11	δ NCC + δ ring
ν_{18}	218	0.92	δ ring + δ N \equiv C
ν_{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+ γ (C ₄ -H)
V_{22}	704	5.85	γ (C ₄ -H)+ γ (C ₁ -C ₂)H
V_{23}	538	1.03	γ NCC
V_{24}	287	0.38	γ ring+ γ NC
V_{25}	263	0.66	γ ring+ γ NC
V_{26}	245	0.35	γ ring+ γ NC
V_{27}	137	0.04	γ ring+ γ 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)

ν_{10}	1125	74.88	$\delta C_4C_5C_6$
ν_{11}	1022	6.09	$\delta C_1C_2C_3$
ν_{12}	977	4.07	$\delta C_4-H + \delta (C_1+C_2)H$
ν_{13}	928	21.44	$\delta (C_1+C_2)H + \delta (C_4-H)$
ν_{14}	880	0.10	$\delta (C_1+C_2)H$
ν_{15}	830	19.26	$\delta C_4C_5C_6 + \delta_s NO_2$
ν_{16}	758	14.90	δ ring
ν_{17}	557	1.69	δ ring
ν_{18}	524	15.25	$\delta_s NO_2 + \delta$ ring
ν_{19}	401	2.38	δ ring
ν_{20}	210	0.74	δ ring
ν_{21}	86	0.96	ρNO_2
A^-			
ν_{22}	741	20.00	$\gamma (C_1-C_2)H + \gamma (C_4-H)$
ν_{23}	726	12.08	$\gamma (C_1-C_2)H + \gamma (C_4-H)$
ν_{24}	716	2.21	$\gamma (C_1-C_2)H + \gamma CH$
ν_{25}	697	40.55	$\omega NO_2 + \gamma CH$
ν_{26}	297	0.51	γ ring + ρNO_2
ν_{27}	275	1.86	γ ring
ν_{28}	226	2.94	γ ring
ν_{29}	136	0.26	γ ring + δNO_2
ν_{30}	18	0.36	NO_2 tor.

5.Amino triafulvalene

No	MINDO/3-FORCES Freq, cm^{-1}	IR intensity, $km\ mol^{-1}$	Assignments
A^-			
ν_1	3744	14.45	NH_2 s. st.
ν_2	3705	35.89	NH_2 as. st.
ν_3	3624	9.67	(C_4-H) st.
ν_4	3616	68.13	$(C_1+C_2)H$ st
ν_5	3592	34.04	$(C_1+C_2)H$ st
ν_6	2196	19.15	ring breath..
ν_7	1977	53.88	$(C_1-C_2+C_4-C_5)$ st.
ν_8	1754	45.91	$(C_1-C_2+C_4-C_5+C_3-C_6)$ st
ν_9	1476	3.33	$\delta_s NH_2$
ν_{10}	1331	105.87	$N-C$ st + $(C_1-C_2+C_4-C_5)$ st.
ν_{11}	1289	4.97	$\delta C_4C_5C_6$
ν_{12}	995	2.11	$\delta C_1C_2C_3$
ν_{13}	970	7.04	$\delta (C_4-H) + \delta (C_1+C_2)H$
ν_{14}	963	0.05	$\rho NH_2 + \delta (C_1-C_2+C_4)H$
ν_{15}	914	24.99	$\delta (C_1+C_2)H + \delta (C_4-H) + \rho NH_2$
ν_{16}	867	0.10	$\delta (C_1+C_2)H + \delta C_1C_3C_2$
ν_{17}	850	0.17	$\delta C_4C_5C_6$
ν_{18}	682	0.18	ring elongation
ν_{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	$(\text{C}_1+\text{C}_2)\text{H}$ st.
v_2	3597	46.54	$(\text{C}_4\text{-H})\text{st.}$
v_3	3593	32.56	$(\text{C}_1+\text{C}_2)\text{H}$ 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	$\text{C}_7\text{-H}$ st..
v_9	2193	1.32	$(\text{C}_1\text{-C}_2+\text{C}_4\text{-C}_5+\text{C}_3\text{-C}_6)$ st
v_{10}	1965	14.37	$(\text{C}_1\text{C}_2\text{C}_3+\text{C}_4\text{C}_5\text{C}_6)$ st+ $(\text{C}_5\text{-C}_7)$ st
v_{11}	1757	1.12	$(\text{C}_1\text{-C}_2+\text{C}_4\text{-C}_5+\text{C}_3\text{-C}_6)$ st+ $\text{C}_7\text{C}_8\text{C}_9$ st
v_{12}	1647	0.15	Cyclopropyl(ring breath)+ $(\text{C}_1\text{-C}_2 + \text{C}_4 - \text{C}_5)$ st.
v_{13}	1355	11.18	$(\text{C}_5\text{-C}_7+\text{C}_1\text{-C}_2+\text{C}_8\text{-C}_9)\text{st.}+\delta_s \text{CH}_2$
v_{14}	1338	20.24	$\delta_s \text{CH}_2$.
v_{15}	1322	33.23	$\delta_s \text{CH}_2+(\text{C}_1\text{-C}_2+\text{C}_4\text{-C}_5)\text{st}$
v_{16}	1238	4.75	$(\text{C}_8\text{-C}_9)\text{st}+\delta_s \text{CH}_2+\delta (\text{C}_7\text{-H})$
v_{17}	1185	19.99	$\delta (\text{C}_4\text{-C}_6)+\delta (\text{C}_5\text{-C}_7)$
v_{18}	1074	23.04	$\delta \text{C}_7\text{C}_8\text{C}_9+\delta \text{C}_4\text{C}_6\text{C}_5+\text{CH}_2$ wag.
v_{19}	1003	0.42	$\delta \text{C}_1\text{C}_3\text{C}_2$
V_{20}	976	2.09	$\delta (\text{C}_1+\text{C}_2)\text{H}+\delta (\text{C}_4\text{-H})+\text{CH}_2$ rock
V_{21}	931	29.30	$\delta (\text{C}_1+\text{C}_2)\text{H}+\delta \text{C}_4\text{C}_6\text{C}_5+\text{CH}_2$ twist
V_{22}	906	11.32	$\delta (\text{C}_4\text{-H})+\delta (\text{C}_4\text{C}_6\text{C}_5)$
V_{23}	866	0.13	$\delta (\text{C}_1+\text{C}_2)\text{H}+\delta \text{C}_1\text{C}_2\text{C}_3$
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	$\delta (\text{C}_3\text{-C}_6)$
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	$\gamma (\text{C}_7\text{-H})+\text{CH}_2$ wag.+ $\gamma (\text{C}_7\text{C}_8\text{C}_9)$
v_{32}	1030	0.42	CH_2 twist+ $\gamma (\text{C}_7\text{C}_8\text{C}_9)$
v_{33}	997	0.25	$\gamma (\text{C}_7\text{-H})+\gamma (\text{C}_7\text{C}_8\text{C}_9)+\text{CH}_2$ rock.
v_{34}	990	3.55	CH_2 wag + $\delta (\text{C}_4\text{-H})$
v_{35}	951	0.23	CH_2 twist + $\gamma (\text{C}_7\text{C}_8\text{C}_9)$

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}

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