Vibration Frequencies and Normal Coordinates of 3Radialene

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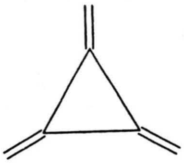
SCF-MO calculations of the vibration frequencies and IR absorption intensities of 3radialene are reported. Complete normal coordinate analysis for the molecule was done. The C=C str. frequencies of 3radialene are found to be intermediate between the values for ethylene and acetylene. The results are explained in terms of a modified Förster-Walsh model for the 3ring in which the central carbon atoms show sp hybridization.

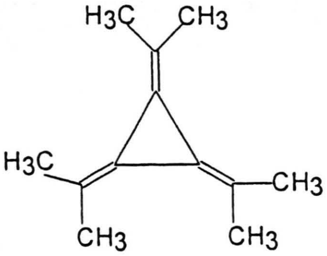
Key words: 3Radialene; Vibration Frequencies; MINDO/3-FORCES.

Introduction

The chemistry of 3radialene started to become known through its synthesis, Köbrich et al. [1]. Its peculiar structure was interesting from both the theoretical and synthetic point of view due to its threefold conjugated cyclopropyl structure (Scheme 1):



In its special type of bonding it formed the first member of a new class of organic compounds. Due to this fact both UV spectroscopic [2] and X-Ray diffraction studies [1] were done for its alkyl substituted derivatives. Hexamethyl-3radialene was found to be coplanar with all six methyl groups falling in the plane of the molecule:



Due to this result the H atoms of the non-substituted 3radialene are expected to fall in the molecular plane too, since less repulsive interaction is expected for them than in the case of the poly-methyl derivatives. The IR-spectrum of the methyl 3radialene showed an absorption band at 1610 cm^{-1}, which was attributed to the C=C bond vibration [1]. Subsequent IR study allowed a detailed discussion of the vibration spectrum for the non-substituted 3radialene [3]. We have decided to study this interesting problem.

Our study is based on applying the MINDO/3-FORCES SCF-MO method, which was described and applied formerly for the IR spectral studies of various molecules [4]. The method allowed good estimations of the forces constants of organic molecules applying the Pulay's Forces method [5]. The solution of Wilson's secular equation [6]

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

provides us with both vibration frequencies ($\lambda = 4 \pi^2 \nu^2$) and vibration mode's eigenvector coefficients (L). These allow a graphical description of the vibration mode of each atom in the molecule when applied to the DRAW.MOL routine developed by Shanshal et al. [7], Figure 1. The same coefficients are used to evaluate the partial contribution of each atom to the molecular vibration in terms of the so-called atomic partial participation (APP) values [8].

Results and Discussion

The evaluation of the vibration frequencies of 3radialene was done for its equilibrium geometry as calculated by minimizing its total energy as function of all its 3N Cartesian coordinates. The resulting geometry corresponds to the following values 1.437 Å (C–C), 1.322 Å

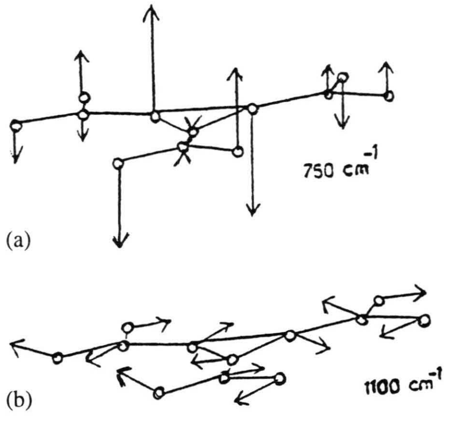
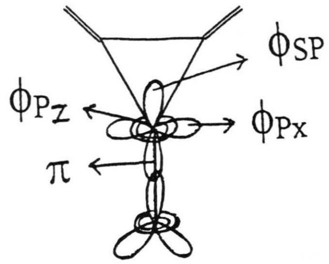


Fig. 1. Graphical representation of two modes of vibration of 3radialene; (a) out of-plane; (b) in-plane, as drawn applying the DROW.MOL routine.

(C=C), 111° (HCH), 124.5° (C–C–H), and 1.100 Å (C–H) (the calculated geometric values are similar to those calculated by Dewar et al. [8]). Interesting is the C=C distance which falls between 1.337 Å for ethylene and 1.21 Å for acetylene. The small HCH bond angles are also remarkable. The ring C–C bond distances are similar to those of the cyclopropyl ring. These results might be explained if one accepts the Förster-Walsh description of bonding in cyclopropane with some modification. Accordingly, the ring C atoms should posses sp hybridization in order to form both cyclopropyl C–C bonds and the external C=C double bond, as the following scheme shows:



This type of bonding explains the short distance, being formed between a C_{sp} atom with small atomic radius and C_{sp2} of an expectedly normal atomic radius. The higher electronegativity of the ring C_{sp} atoms causes an electron shift from the external C_{sp2} atom to the ring atoms. This fact could be partly responsible for the unusual by small HCH bond angles of the external bonds. An impact of this description should be noticed in the frequency values of the molecule.

3radialene is a planar molecule with D_{3h} symmetry. Its total number of vibrations (3N-6) is 30. These are classified into the following irreducible representations:

In plane $4\,A_1' + 3\,A_2' + 7\,E'$,
out of plane $A_1'' + 2\,A_2'' + 3\,E''$,

where A_1', A_2' and E'' are Raman active, E' and A_2' are IR active, A_1'' is Raman and IR inactive.

Our treatment, based on the MINDO/3-FORCES, yielded all these vibration modes correctly. The corresponding scaled frequency values are listed in Table 1 together with the calculated IR absorption intensities. The applied scaling factors were determined for ethylene considering the experimental frequencies of Duncan et al. [9] and are; 0.87 (CH_2 str.); 0.90 (C=C str.); 1.06 (CH_2 sciss.); 1.00 (CH_2 rock.); 1.15 (CH_2 twist.); 1.00 (CH_2 wag.); 1.00 (γCH_2 and γCC); 1.00 (γCCC + γCH_2).

Figure 2 shows graphical pictures for some vibration modes of 3radialene as drawn through DRAW-MOL

Table 1. Vibration frequencies and IR absorption intensities of 3radialene.

Symmetry and description	Frequency cm^{-1} This work scaled	Intensity km/mol	Frequency cm^{-1} [3]
In-plane			
A_1'			
ν_1 CH str.	3068	0.00	3000
ν_2 ring (CC) str. (breathing)	1936	0.00	1800
ν_3 CH_2 (scissoring)	1455	0.00	1422
ν_4 ring str.	946	0.00	779
A_2'			
ν_6 CH_2 str.	3075	0.00	3075
ν_7 =CH_2 (rocking)	917	0.00	917
ν_8 δring (anticlock) + CH_2 (rocking)	458	0.00	495
E'			
ν_{11} CH_2 str.	3077	60.74	3095
ν_{12} CH_2 str.	3063	40.00	2994
ν_{13} C=C str.	1673	3.54	1620
ν_{14} CH_2 (scissoring)	1392	10.78	1398
ν_{15} ring str.	1008	0.45	1108
ν_{16} =CH_2 (rocking) + δCCC	807	4.05	779
ν_{17} =CH_2 (rocking) + δCCC	222	0.30	340
Out of-plane			
A_1''			
ν_5 CH_2 (twisting)	744	0.00	–
A_2''			
ν_9 CH_2 (waging)	846	6.99	885
ν_{10} γring	217	0.00	212
E''			
ν_{18} CH_2 (waging)	851	0.00	873
ν_{19} γring + CH_2 (twisting)	656	0.00	–
ν_{20} γring (γCC) + CH_2 (twisting)	356	0.00	235

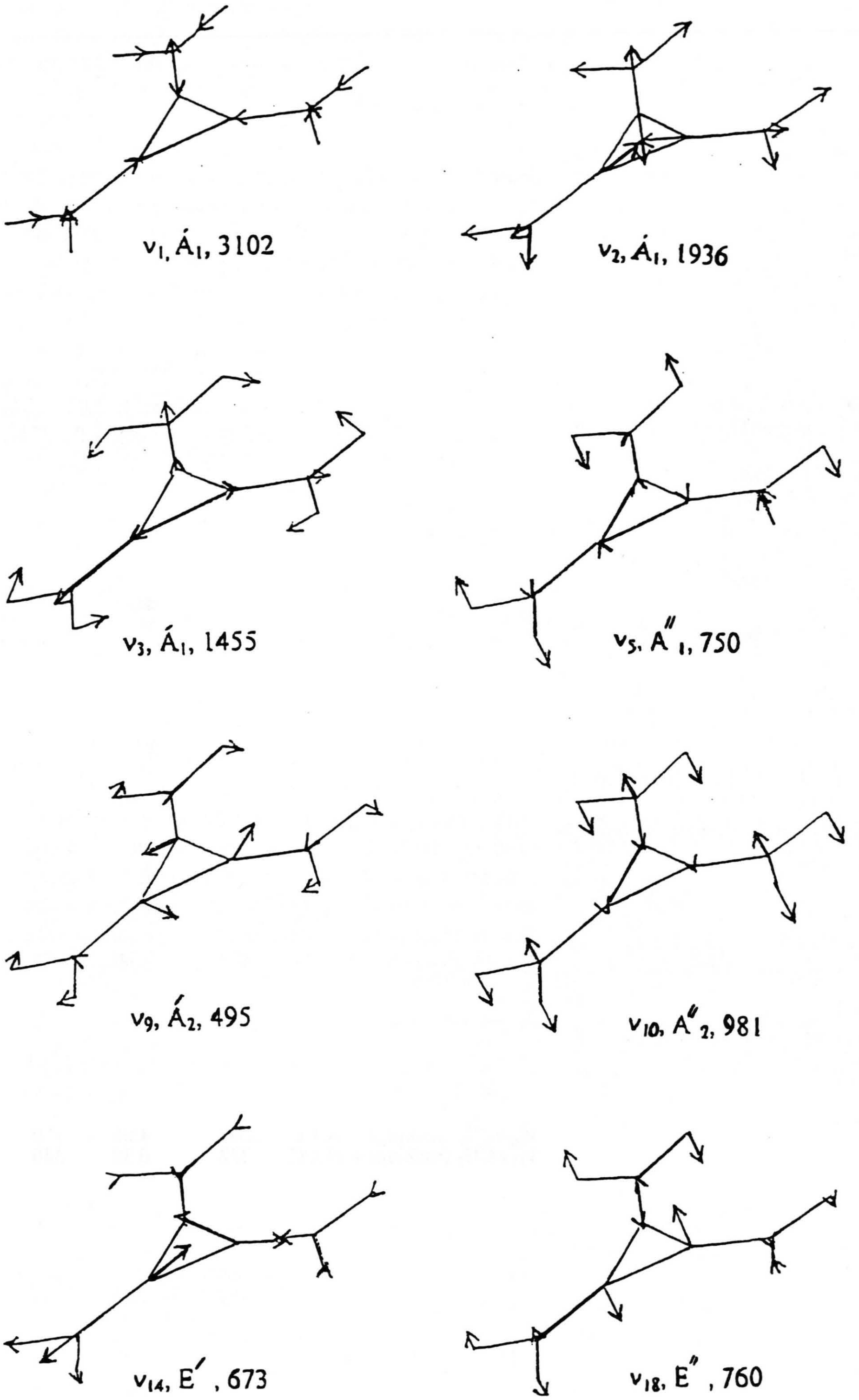


Fig. 2. Graphical representation of some modes of vibration of 3radialene.

Table 2. Scaled MINDO/3-FORCES calculated vibration frequencies for ethylene compared with the experimental frequencies.

Symmetry and description	Frequency cm^{-1}		
	This work scaled	Exp. [9] harmonic	Exp. [9] unharmonic
In-plane			
A_g			
ν_1 CH sym. str.	3081	3153	3026
ν_2 C=C str.	1656	1655	1630
ν_3 δCH_2 (scissoring)	1371	1370	1342
B_{1g}			
ν_5 CH_2 str.	3084	3232	3103
ν_6 CH_2 (rocking)	1029	1245	1220
B_{2u}			
ν_9 CH_2 str.	3102	3234	3104
ν_{10} CH_2 (rocking)	705	843	697
B_{3u}			
ν_{11} CH_2 str.	3067	3147	3021
ν_{10} δCH_2 (scissoring)	1378	1473	1444
Out of-plane			
A_u			
ν_4 CH_2 (twisting)	1021	1044	1023
B_{1u}			
ν_7 CH_2 (waging)	973	969	949
B_{2g}			
ν_8 CH_2 (waging)	937	959	940

routine. Such pictures were used for the assignment of the vibration frequencies.

Inspection of the frequency values in Table 1 reveals the following interesting results;

νCH_2 asym.str. > νCH_2 sym.str.,
νC=C sym.str. > νC=C asym.str.,
νCH_2 (rock.) > νCH_2 (sciss.),
νCH_2 (wag.) > νCH_2 (twist.).

The most apparent difference is that νC=C str. in ethylene (1656 cm^{-1}) [10] is lower than both νC=C sym.str. and νC=C asym.str. in 3radialene. The obvious reason is the different hybridization of the C atom of the ring in 3radialene, C_{sp}, as explained in a former paragraph causing a shift of the frequency towards that of the C≡C bond ($\Delta\nu$ = 17 cm^{-1}). Also, the calculated νCH sym.str. in ethylene (3116 cm^{-1}) is higher than νCH sym.str. in 3radialene (3068 cm^{-1}). The reason seems to be the diminishing of electron density at the external C atoms of 3radialene caused by the higher electronegativity of the (C_{sp}) ring atom. The smaller number of electrons does cause a decrease in the C–H force constant and the vibration frequencies. The electron transfer from $C_{sp2} \rightarrow C_{sp}$ carbon atom seems to be responsible for the following comparative relations too;

scaled ethylene scaled 3radialene
νCH_2 sym. (sciss.) > νCH_2 sym. (sciss.)
(1371 cm^{-1}) (1455 cm^{-1}),
νCH_2 asym. (rock.) > νCH_2 sym. (rock.)
(1029 cm^{-1}) (917 cm^{-1}),
νCH_2 (twist.) (1021 cm^{-1}) > νCH_2 (twist.) (744 cm^{-1}),
νCH_2 (wag.) (973 cm^{-1}) > νCH_2 (wag.) (851 cm^{-1}).

Other interesting results are viewed on comparing the 3radialene frequencies with the frequencies of similar nature of ethylene, Table 2.

Conclusion

The calculated vibration frequencies of 3radialene as well as its geometric values show some peculiar properties when compared with those of ethylene. A thorough discussion of the results suggests their explanation through the C_{sp} hybridization form of the ring C atom. The type of C–C bonding conforms to a description which might be viewed as an extension of the Förster-Walsh bond description of cyclopropane.

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