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The Vibrational Spectra and Geometric Configuration of *cis*-1,3,5-Hexatriene[1a,b]

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Spectroscopic data for a second isomer of 1,3,5-hexatriene are reported. They include infrared spectra taken from 2 to 35 microns of the vapor and liquid as well as Raman and polarized Raman spectra of the liquid. These data indicate that the isomer has a *cis* structure. An assignment of the vibrational frequencies to the normal modes of vibration is presented. Minor changes are given for the previously published assignment of the *trans* isomer.

Introduction

A recent[2] paper has reported a separation and purification of two isomers of 1,3,5-hexatriene. One is spectroscopically identical to the previously prepared[3a] and identified[3b] pseudolinear *trans* isomer. The second isomer, with which this paper is concerned, has been tentatively identified[2] as the *cis* form by chemical evidence, notably its non-reactivity as a Diels–Alder adduct.

Experimental

Samples.—The sample of 1,3,5-hexatriene, b.p. 82–83°, n^{25}_D 1.5058 used in these studies was kindly supplied by Drs. Hwa, de Benneville and Sims of Rohm and Haas Company, Philadelphia, Pennsylvania. It was prepared and purified as described elsewhere.[1a] Purity was checked by vapor phase chromatography. A sample of the *trans* isomer for comparison purposes was prepared and purified by standard procedures by Dr. Joseph Xavier and Mr. Mitchell Theil of the University of Maryland.

Raman Spectra.—The Raman spectra of hexatriene were recorded on a photographic instrument assembled at the University of Maryland. Excitation was accomplished using the 4358 Å. line of mercury from a "Toronto" type arc, which operated with about 10 amperes at approximately 100 VDC. Undesired Hg lines were eliminated by the use of filters of potassium nitrite solution and Rhodamine 5 GDN solution. The spectrograph used was a Huet model A-II which employs 2 glass prisms with a dispersion of 45 Å. per. mm. at 5000 Å. with an aperture of $f/8$. Eastman-Kodak 103a-E backed spectroscopic plates were used.

Polarization data were recorded by standard methods by replacing one of the filtering solutions in the condenser with a polarized film jacket. The exposure time ranged from 30 minutes to 25 seconds for the regular Raman and from 60/48 minutes to 2:40/2:00 minutes for the polarized data. The observed Raman frequencies are listed in Table I.

The Infrared Spectra.—The infrared spectrum of liquid hexatriene has been published.[2] A Beckman IR-4 spectrometer equipped with NaCl prisms was used to record the spectra of the liquid and vapor in the infrared region (5,000 to 600 cm.$^{-1}$). CsBr prisms were used to record the spectra in the longer wave length region (900 to 300 cm.$^{-1}$).

All infrared spectra were checked by rerunning the series from 4000 to 500 cm.$^{-1}$ in liquid and vapor cells on a Perkin–Elmer model 421 spectrometer. The observed infrared frequencies are listed in Table I.

Discussion

An earlier paper[3b] proposed various structures for hexatriene. Of the six possible geometric forms, four were ruled out as being highly improbable due to steric requirements. Of the two remaining structures, namely, an extended *cis* and an extended pseudolinear *trans* form, the latter was shown to be the structure of the first isomer.

It has been pointed out[2] that a Courtland model for the *trans* isomer may be oriented properly for a Diels–Alder addition while the *cis* model cannot be so oriented. The two isomers were chemically separated by a Diels–Alder reaction. It has also been pointed out [3b] that it is easier to arrange the *trans* form of the Fischer–Hirschfelder models into a plane structure. Since planarity is a requisite for resonance, it is expected that the *trans* structure should be more stable than the *cis*. Qualitatively speaking it has been noted that the *trans* isomer polymerizes less easily than the other form. Also this form will readily isomerize to the *trans* isomer in the presence of an iodine catalyst.

Since hexatriene has 14 atoms, there are 36 normal vibrational modes for both isomers. However, the different symmetries of the two forms give rise to useful restrictions on the spectral activity. *Trans* hexatriene has a symmetry corresponding to the point group C_{2h}. The *cis* form, on the other hand, is a C_{2v} molecule. Selection rules (summarized in Table II), predict that for the *trans* (C_{2h}) isomer, 18 fundamental modes will be found in the Raman spectrum and the other 18 will be found in the infrared spectrum. However, for the *cis* (C_{2v}) form, all 36 fundamentals are expected to be found in the Raman spectrum and of these, 30 will show also in the infrared spectrum. The *trans* molecule was shown[3b] to have 18 bands in the fundamental region of the Raman and a maximum of 22 which could conceivably be fundamental in the infrared spectrum. The present sample exhibits 24 bands which could be fundamental Raman bands and 24 which are in the fundamental region of the infrared spectrum.

As a corollary to the above arguments, the rule of mutual exclusion may be used. Since the *trans* model has a center of symmetry, no single mode should be active in both Raman and infrared spectra, *i.e.*, no coincidences are required. It was found[3b] that only two, or at most three, such coincidences did occur and these can be explained as accidental degeneracies. The *cis* molecule has no such center and 30 of its modes should show coincidentally in the Raman and infrared spectra. The present studies indicate that the molecule now under consideration has 9 definite cases of coincidence (3097, 1622, 1570, 1448, 1392, 1314, 1182, 947 and 357 cm.$^{-1}$) and if accidental degeneracies are counted, the number is probably closer to 13. This is quite in line with the number of frequencies not observable due to weakness, masking or limited range of the instruments.

(1) (a) Taken in part from a thesis submitted by T. E. K. to the faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for a degree of Master of Science. (b) This work was supported in part by a grant from the National Science Foundation.

(2) J. C. H. Hwa, P. L. de Benneville and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).

(3) (a) G. F. Woods and L. H. Schwartzman, *ibid.*, **70**, 3394 (1948). (b) E. R. Lippincott, C. E. White and J. P. Sibilia, *ibid.*, **80**, 2926 (1958).

TABLE I

OBSERVED INFRARED AND RAMAN SPECTRA OF *cis*-1,3,5-HEXATRIENE

s = strong, m = medium, w = weak, v = very, P = polarized, b = broad, sh = shoulder.

Raman (liquid)	Infrared (liquid)	Infrared (vapor)
	(4780) vw	
	(4720) vw	
	(4620) vw	
	(4610) vw	
	(4550) vw	
	(4510) vw	
	4430 w	
	(4390) vw	
	(4340) vw	
	4290 vw	
	(4230) vw	
	(4080) vw	
	(4020) vw	
	(3750) vw	
	(3460) vw	
(3254) vw		3190 w (b)
3097 m	3110 vs	3106, 3093 vs
	3080 vs	
3061 vw? P?[5]		3049, 3031, 3020 vs
	3050 vs	
3030 m P		
3015 m P		
		2999 s (sh)
(2961) vw		
(2880) vw		
(2792) vw		
(2704) vw		
	(2600) vw	
2503 w	(2500) vw	
2368 w		
	(2320) vw	
	(2250) vw	
2129 w		
	1980 vw	1985 w (b)
1961 w		
	1930 w	1935 w
1893 w	1895 vw	
(1850) vw		1864, 1854 mw
	1810 vs	1823, 1816 (sh), 1811 vs
		1796 mw (sh)
	1762 s	1769 (sh), 1762, 1757, 1751 (sh) m
1732 w		1740 (sh) vw
	1720 vw	1717, 1714 vw
1705 w		
	1685 vw	1684 vw
	1672 vw	1669 vw
1622 vs P	1612 s	1623, 1618 vs
		1605 s (sh)
1570 s	1560 w	1559 w
		1539 w
1535 w P?	1545 vw	
1519 w		1499, 1497 vw
	1495 vw	
1489 w		1489, 1487 vw
		1457
1448 m	1449 s	(1452) vw
		1447
1392 s P?	1395 w	1325, 1312 m
	1353 w	
1314 vs P	1315 m	1283 mw
		1272 mw
	1250 w	
1236 vs P		1192, 1180 m
1182 s P?	1185 m	
1128–55 w[10]	1148 w	1132 mw[10]
1083 s P		
	1070 w	1090 w[10]
		1050 w[10]
1025 vw		
		998, 990, 978 vs
	990 vs	
978 vw		
947 s	950 s	
		916, 908, 899 vs
	910 vs	
902 m		
883 s	818 m	815 m[10]
	747 w	
709 m		
	680 w	
	650 w	595, 585, 578 vs
	589 vs	
479 w[10]		
393 vs P		
357 w	358 m	
331 m		
264 w		
243 w		
167 s[10]		

TABLE II

SELECTION RULES FOR 1,3,5-HEXATRIENE

cis Isomer—point group C_{2v}

Species	Number of modes	Raman active	Infrared active
A_1	13	Yes	Yes
A_2	6	Yes	No
B_1	12	Yes	Yes
B_2	5	Yes	Yes
		Total = 36	30

trans Isomer—point group C_{2h}

Species	Number of modes	Raman active	Infrared active
A_g	13	Yes	No
A_u	6	No	Yes
B_g	5	Yes	No
B_u	12	No	Yes
		Total = 18	18

The method of Gerhard and Dennison[4a] was applied[3b] to calculate the doublet separation of

(4) (a) S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933). (b) This is a revised figure from new data recently run. Using the old data, the average is 8.9 cm.$^{-1}$ for 7 observed doublets.

both the *trans* and the *cis* models. Although the method is strictly applicable only to symmetric tops (*i.e.* $I_A \neq I_B = I_C$), the moments of inertia show the approximation is not unreasonable, especially for the *trans* structure. The moments, in g. cm.$^2 \times 10^{40}$, are

	cis	*trans*
I_A	72.2	37.5
I_B	486	630
I_C	558	667

For the *trans* structure, the doublet separation was calculated to be 8.8 or 9.1 cm.$^{-1}$ depending upon which larger moment of inertia was used in the Gerhard–Dennison equation. The average experimental value was found[3b] to be 10.5 cm.$^{-1}$ (average for 6 doublets observed[4b]). The doublet separation for the *cis* structure was calculated to be 10.2 or 11.1 cm.$^{-1}$. The experimental values in the present work are 13, 12, 13 and 12 cm.$^{-1}$ for the bands centered at 3100, 1817, 1318 and 1186 cm.$^{-1}$, respectively, giving an average doublet separation of 12.5 cm.$^{-1}$. It should be noted since the *cis* isomer does not approximate a symmetric top as well as the *trans* isomer, that good agreement to the Gerhard–Dennison predictions is not to be expected. Nevertheless, the relative values for the proposed *trans* and *cis* structures agree reasonably well with the calculated values and support the respective structural assignments.

Band envelope shape should also give information concerning the two structures. Qualitatively speaking, the C_{2b} isomer (*trans*) has only two vibrational species active in the infrared region. Therefore, only two types of band envelopes are expected to be found in infrared vapor spectrum. The C_{2v} isomer (*cis*) has three vibrational species active in the infrared region, and three different types of band structure are expected. However, reference to Nielsen's work[5] shows that the B and C type bands (*i.e.*, those whose dipole change is perpendicular to the intermediate and largest moment of inertia, respectively) are nearly indistinguishable for a planar, slightly asymmetric molecule. Moreover, the high number of accidental degeneracies, or near degeneracies, makes observation of band envelope shape exceedingly difficult. Figure 1 shows some typical vapor spectra. The three types of band envelopes shown as examples are bands centered at 908, 1449 and 3100 cm.$^{-1}$.

In addition to an essentially reasonable frequency assignment (see below), other observations which support the assignment of a *cis* structure to the molecule under consideration are:

1. Low Frequency Raman Lines.—If the compound under investigation is the *cis* isomer, then, because of its nonplanarity, it should have less resonance energy than the *trans* form as postulated above. Having less resonance energy, the molecular vibrations described as carbon skeletal bending vibrations should occur at lower frequencies than corresponding modes in the *trans* molecule. In addition, examination of the frequency distributions in *cis* and *trans* disubstituted ethylenes

(5) H. H. Nielsen, *Phys. Rev.*, **38**, 1432 (1932).

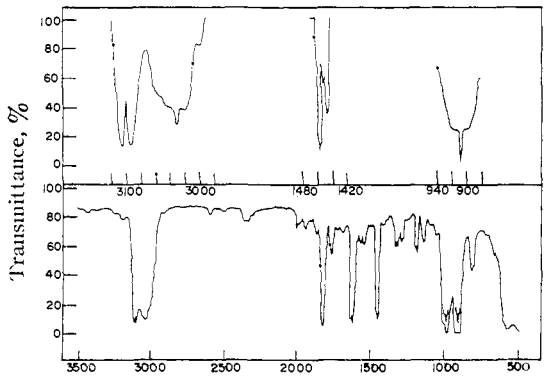


Fig. 1.—Typical vapor infared spectra of hexatriene.

shows that the *cis* isomers have a low bending frequency. The lowest frequencies observed in this work were at 479, 393, 357, 331, 264, 243 and 167 cm.$^{-1}$. Only two frequencies (411 and 347 cm.$^{-1}$) were observed[3b] in the *trans* spectrum below 500 cm.$^{-1}$. However, inspection of the published spectrum in the previous work[3b] (*q.v.*) raises the question as to whether the spectrometer used could actually record a lower frequency. Consequently, a sample of *trans* hexatriene was prepared as described elsewhere[3a] and the Raman spectrum taken under identical conditions as described previously in this paper. The band at 411 cm.$^{-1}$ was resolved into two bands at 444 and 395 cm.$^{-1}$. The second band was observed at 347 cm.$^{-1}$. No other bands were observed.

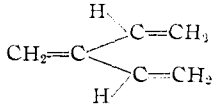
2. Raman Active Modes.—Just as the larger number of fundamental modes and coincidences is an argument for the *cis* structure, so the number of non-coincidences can be used to support this structure. All of the A_2 species of vibration are Raman active only. Discounting the two modes (978 and 902 cm.$^{-1}$) which are accidentally degenerate with B_2 modes and further discounting the two frequencies (331 and 265 cm.$^{-1}$) which are below the range of the instruments used for the infrared work, the Raman spectra exhibit two frequencies (883 and 709 cm.$^{-1}$) which must be assigned as fundamentals because of their strengths and for which there are no corresponding infrared bands. This agrees with the prediction from the selection rules for the Raman activity of the C_{2v} molecule.

3. Similarities to Other *cis* Structures.—If spectra of similar *cis–trans* pairs (for example the 1,3-pentadienes[6]) are compared to the spectra taken in this work, it can be seen that certain similarities exist between the latter and the *cis* forms while no such similarities can be seen to the *trans* isomers. While this is not considered a proof of any structure, it certainly is in line with the expectation that compounds with similar groups should have similar group frequencies.

4. Lack of Other Characteristic Frequencies.—It is conceivable that hexatriene could be a homolog of an unsymmetrical disubstituted ethylene rather than the symmetrical *cis–trans* isomer.

(6) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947); and American Petroleum Institute Research Project 44, Infrared Spectral Data, Spectra 341 and 342.

That is, the form could be



In argument it can be pointed out that, besides being highly sterically strained and therefore improbable, there is no evidence for the very characteristic infrared group frequency expected between 885 and 890 cm.$^{-1}$.

Frequency Assignment.—Assignment of normal modes of vibration to the observed frequencies is best accomplished by considering hexatriene and the compounds to which it is compared as substituted ethylenes. It is to be understood that modes derived in this way are only descriptive and that conjugation will definitely enhance mixing or coupling of various modes. The modes can be divided into mono- and di-substituted ethylene types. In keeping with this approach, the molecules most useful for comparison are: in the first case, vinyl chloride,[7] vinyl bromide[7] and styrene[8] (monochloro-, bromo- and phenyl-ethylene) and in the second case, *cis* dichloro- and *cis* dibromoethylene.[9]

Vinyl Type Carbon–Hydrogen Stretching Modes.—A CH_2 asymmetric, a vinyl CH and a CH_2 symmetric stretch, each in the A_1 and B_1 modes is expected to appear in both the Raman and infrared spectra of hexatriene. The infrared spectrum shows three frequencies and the Raman spectrum shows three or possibly four[10] frequencies. These vibrations, in the order mentioned above, appear in the spectra of vinyl chloride at 3130 cm.$^{-1}$ (infrared), 3112 cm.$^{-1}$ (Raman); 3030 cm.$^{-1}$ (infrared), 3070 cm.$^{-1}$ (Raman); and 3030 cm.$^{-1}$ (infrared), 3027 cm.$^{-1}$ (Raman). In vinyl bromide (vapor infrared only being reported), these modes are at 3100, 3076 and 3014 cm.$^{-1}$, respectively. The CH stretching vibrations of propylene[11] show, respectively, at 3090 cm.$^{-1}$ (infrared), 3087 cm.$^{-1}$ (Raman); 3013 cm.$^{-1}$ (infrared), 3010 cm.$^{-1}$ (Raman); and 2991 cm.$^{-1}$ (infrared), 2990 cm.$^{-1}$ (Raman). Therefore, both the A_1 and B_1 CH_2 asymmetric vibrations in *cis*-hexatriene are assigned to the frequencies 3097 cm.$^{-1}$ (Raman) and 3110 cm.$^{-1}$ (infrared). The A_1 CH_2 symmetric stretch is assigned to the lowest frequency in this region, namely 3015 cm.$^{-1}$ in the Raman spectrum, and the B_1 CH_2 symmetric stretch is assigned to the lowest infrared frequency in the same region namely at 3050 cm.$^{-1}$. The corresponding infrared and Raman frequencies respectively are assumed to be masked or too weak to be observed. The vinyl CH modes, both A_1 and B_1, are assigned to the 3050 cm.$^{-1}$ (infrared) and 3030 cm.$^{-1}$ (Raman) frequencies.

Vinyl Type Carbon–Hydrogen In-plane Deformation Modes.—The CH_2 vibrations are divisible into two types, the scissoring and the rocking motions. The scissoring vibration is found in vinyl chloride at 1342 cm.$^{-1}$ (Raman) and 1370 cm.$^{-1}$ (infrared); in styrene at 1415 cm.$^{-1}$; in propylene at 1415 cm.$^{-1}$; in butadiene the A_g mode at 1442 cm.$^{-1}$ (Raman) and the B_u at 1484 cm.$^{-1}$ infrared; and finally for *trans*-hexatriene, the A_g mode appears at 1394 cm.$^{-1}$ (Raman) and the B_u appears at 1429 cm.$^{-1}$ (infrared). For the *cis* hexatriene, the intense polarized line at 1392 cm.$^{-1}$ (Raman) and the weak 1395 cm.$^{-1}$ (infrared) line is assigned to the A_1 bending mode. The B_1 bending mode is assigned to the intense 1449 cm.$^{-1}$ infrared line and the medium 1448 cm.$^{-1}$ (Raman) line.

Vinyl chloride has the rocking modes at 1026 cm.$^{-1}$ (Raman) and 1030 cm.$^{-1}$ (infrared), respectively, for the symmetric and asymmetric motions. The frequency calculated for styrene is 1172 cm.$^{-1}$ while propylene exhibits an infrared frequency at 1229 cm.$^{-1}$ for this vibration. Butadiene has an A_g mode at 1279 cm.$^{-1}$ and a B_u mode at 1290 cm.$^{-1}$ (infrared). *trans*-Hexatriene has the A_g mode assigned[12] at 1128 cm.$^{-1}$ (Raman) and a B_u mode at 1255 cm.$^{-1}$ (infrared). Therefore, in the *cis* spectra, the intense polarized line at 1236 cm.$^{-1}$ (Raman) is assigned to the A_1 mode while the B_1 mode may be assigned at 1148 cm.$^{-1}$ (infrared), with the Raman band hidden in the diffuse area near 1128–1155 cm.$^{-1}$.

The vinyl CH group frequency is 1290–1300 cm.$^{-1}$. This mode is observed at 1274 cm.$^{-1}$ (Raman) and 1280 cm.$^{-1}$ (infrared) in vinyl chloride, and 1301 cm.$^{-1}$ (Raman) in styrene. The A_g mode is at 1302 cm.$^{-1}$ (Raman) with the B_u at 1379 cm.$^{-1}$ (infrared) for butadiene. The A_g mode is at 1280 cm.$^{-1}$ (Raman) with the B_u at 1294 cm.$^{-1}$ (infrared) for *trans*-hexatriene. The very intense line at 1314 cm.$^{-1}$ (Raman) and the medium line at 1315 cm.$^{-1}$ (infrared) is therefore assigned to the A_1 mode. The medium line at 1280 cm.$^{-1}$ (infrared) is assigned to the B_u mode with the corresponding Raman line being masked by the very intense lines immediately above and below it.

Vinyl Type Carbon–Hydrogen Out-of-plane Deformation Modes.—A recent paper[13] has summarized a large amount of data on factors affecting out-of-plane bending modes for hydrogens attached to doubly bonded carbon atoms. The names of the modes are: "CH_2 twist," "CH_2 wag" and "vinyl CH torsion." The associated frequencies are 990 cm.$^{-1}$, 910 cm.$^{-1}$; and approximately 589 cm.$^{-1}$, with the intermediate frequency giving rise to a first overtone at slightly *more* than double the frequency, *i.e.*, >1820 cm.$^{-1}$. Vinyl chloride has these frequencies at 940, 900 and 622 cm.$^{-1}$ (infrared). Styrene has them at 990 cm.$^{-1}$ (infrared), 908 cm.$^{-1}$ (infrared) and 560 cm.$^{-1}$ (Raman). The more complicated molecule of

(7) J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, **33**, 1792 (1955); and H. W. Thompson and P. Torkington, *Proc. Roy. Soc.* (London), **A184**, 21 (1945).

(8) K. S. Pitzer, L. Guttman and E. F. Westrum, Jr., *J. Am. Chem. Soc.*, **68**, 2211 (1946).

(9) G. Herzberg, "Molecular Spectra and Molecular Structure II, Infrared Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945.

(10) The apparently very weak Raman line at 3061 cm.$^{-1}$ seems to shift downward and increase in intensity by a factor of about 10 in the polarized Raman. For this reason, it is of doubtful value to assign a fundamental mode to the line at 3061 cm.$^{-1}$. However, it may be that this is a real line.

(11) R. C. Lord and P. V. Venkateswarlu, *J. Opt. Soc. Am.*, **43**, 1079 (1953).

(12) This is a remeasured value. See below.

(13) W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, **15**, 679 (1959).

butadiene exhibits A_u bending modes at 1014, 909 and 520 cm.$^{-1}$ (infrared) with the B_g bending modes appearing at 911, 890 and 686 cm.$^{-1}$ (Raman). The A_u bending vibrations of *trans*-hexatriene appear at 1011, 899 and 658 cm.$^{-1}$ (infrared); the B_g modes are exhibited at 990,[14] 897 and 758 cm.$^{-1}$ (Raman). A C_{2v} molecule with two vinyl groups will give rise to axially symmetric (A_2-Raman active only) and axially anti-symmetric (B_2-infrared and Raman active) modes for each of the three vibrations. The B_2 twisting and wagging modes can be assigned the 990 cm.$^{-1}$ (infrared), 978 cm.$^{-1}$ (Raman) bands and 910 cm.$^{-1}$ (infrared), 902 cm.$^{-1}$ (Raman) bands respectively. The lower Raman frequencies can be explained as being due to accidental degeneracies with the corresponding A_2 modes. The B_2 vinyl CH torsion is assigned at 589 cm.$^{-1}$ (infrared), a corresponding Raman band not being observed. The A_2 vinyl CH torsion is observed in the Raman as the medium strength band at 709 cm.$^{-1}$. A different assignment of this line is discussed below (*cf.* "Alternate Assignments").

cis–trans **Type Carbon–Hydrogen Stretching Modes.**—The characteristic group frequency for the carbon–hydrogen stretching modes due to *cis* or *trans* hydrogen atoms lies between the frequencies of vibration of CH_2 asymmetric and CH_2 symmetric stretching motions. In *trans*-hexatriene, the A_g mode was assigned the 3054[15] cm.$^{-1}$ (Raman) band and the B_u mode was assigned the 3012 cm.$^{-1}$ (infrared) band. In the *cis* spectra, the band at 3015 cm.$^{-1}$ (Raman) is assigned to the A_1 stretching mode. The B_1 mode is assigned the 3080 cm.$^{-1}$ (infrared) band. The corresponding infrared and Raman bands, respectively, were not observed.

cis–trans **Type Carbon–Hydrogen In-plane Deformation Modes.**—Characteristic frequencies due to deformation vibrations of hydrogen atoms attached to double bonds have been discussed.[16] The observed group frequencies for in-plane bending modes are: *trans* A_g 1295–1310 cm.$^{-1}$ (Raman), *trans* B_u 1298–1310 cm.$^{-1}$; *cis* A_1 1250–1270 cm.$^{-1}$ (strong in the Raman), *cis* B_1 uncharacterized. For butene-2, the corresponding values are: *trans* 1309 cm.$^{-1}$ (Raman) and 1302 cm.$^{-1}$ (infrared); and *cis* 1261 cm.$^{-1}$ (Raman) and 1408 cm.$^{-1}$ (infrared), respectively. In *trans*-hexatriene, the A_g mode had been assigned to 1238 cm.$^{-1}$ (Raman). Since this band was remeasured and reassigned to the single bond stretch (*cf.* below), a new assignment is needed. The intense band at 1187 cm.$^{-1}$ (Raman) is in agreement with the trends noted above. Furthermore, inspection of the Raman spectra of other molecules with conjugated double bonds (see, for example, the 1,3-pentadienes) consistently reveals an intense line in the region 1180–1200 cm.$^{-1}$. Since the type of double bonds seems to be the constant factor rather than the type of single bond, it is not unreasonable to assign the Raman band in question to the *cis* or *trans* in-plane bend rather than the single bond stretch. In hexatriene, the A_g *trans* CH bending vibration assignment is therefore changed to the frequency 1187 cm.$^{-1}$ (Raman). The B_u assignment at 1166 cm.$^{-1}$ (infrared) is unchanged. For the *cis* molecule, the same arguments hold, so that the A_1 mode is assigned to the intense bands at 1182 cm.$^{-1}$ (Raman) and 1185 cm.$^{-1}$ (infrared). The B_1 mode is assigned to the 1140 cm.$^{-1}$ band in the infrared with the corresponding Raman frequency being hidden in the diffuse 1128–1155 cm.$^{-1}$ area.

cis–trans **Type Carbon–Hydrogen Out-of-plane Deformation Modes.**—Sheppard and Sutherland[16] give the *trans* CH out-of-plane frequency at 965–980 cm.$^{-1}$ (infrared) for the A_u with the Raman B_g mode unassigned. The *cis* B_2 frequency is given as 690 cm.$^{-1}$ (infrared), with the Raman A_2 frequency unassigned. *Trans* and *cis* butene fall in nicely with these assignments, the two assigned modes being at 964 cm.$^{-1}$ (infrared) and 673 cm.$^{-1}$ (infrared), respectively. The situation with the hexatrienes is not so definite. The *trans* isomer has an A_u mode at 941 cm.$^{-1}$ (infrared) as may be expected, and the B_g mode has been assigned to 928 cm.$^{-1}$ (Raman). The *cis*-hexatriene has only weak bands around 690 cm.$^{-1}$, but the strong 818 cm.$^{-1}$ (infrared) band seems to be very characteristic (*i.e.*, completely absent in the *trans* spectrum) and is therefore assigned to the B_2 *cis* CH out-of-plane vibration. Further support of this assignment comes from a study of the isomers of 1,3-pentadienes and of 1,4-diacetyl-1,3-butadienes,[17] in that the *cis* forms show a very strong band at about 760–770 cm.$^{-1}$ which is completely missing in the *trans* spectra. The A_2 *cis* CH out-of-plane mode is assigned to the strong line at 883 cm.$^{-1}$ (Raman).

Carbon–Carbon Double Bond Stretching Modes.—Two A_1 double bond stretching vibrations (an "in-phase" and "out-of-phase" mode) and one B_1 double bond stretching vibration are expected to appear in the Raman and infrared spectra. The ordinary range for such vibrations is in the region 1600 to 1650 cm.$^{-1}$. A comparison may be made to butadiene,[18] which has an "in-phase" A_g mode active in the Raman at 1623 cm.$^{-1}$ and an "out-of-phase" B_u mode active in the infrared at 1559 cm.$^{-1}$. The assignments for *trans*-hexatriene in the order listed above are 1623 cm.$^{-1}$ (Raman), 1573 cm.$^{-1}$ (Raman) and 1623 cm.$^{-1}$ (infrared). Therefore the assignments for the *cis* are, respectively: "in-phase" 1622 (Raman), (the corresponding infrared frequency is masked by the intense 1612 cm.$^{-1}$ band); "out-of-phase" 1570 cm.$^{-1}$ (Raman), 1560 cm.$^{-1}$ (infrared) and the asymmetric B_1 at 1612 cm.$^{-1}$ (infrared), (the corresponding Raman frequency is masked by the intense 1622 cm.$^{-1}$ band). It is interesting to note here that the Raman lines are so strong that with the apparatus described, it was necessary to use an exposure of only 25 seconds to avoid blackening the region of 1622 cm.$^{-1}$ beyond the point where the line could be read accurately.

(14) This is a change from the previously published work. See below.

(15) This is a remeasured value. See below.

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TABLE III

THE COMPLETE ASSIGNMENT FOR *cis*-1,3,5-HEXATRIENE

Mode	Symmetry to the axis of the molecule			
	A (symmetric)		B (anti-symmetric)	
	Raman	Infrared	Raman	Infrared
Stretchings	A_1		B_1	
CH_2 antisymmetric	3097	3110	3097	3110
cis CH	3015			3080
Vinyl CH	3030	3050	3030	3050
CH_2 sym.	3015			3050
Double bond	1622 (in phase)	(1612 masks)	(1622 masks)	1612
	1570 (out of phase)	1560		
Single bond	1083		947	950
In-plane deformations	A_1		B_1	
CH_2 scissors	1392	1395	1448	1449
Vinyl CH	1314	1315		1280
cis CH	1182	1185	1128–55	1148
CH_2 rock	1136		1128–55	1148
Skeletal (term. angle)	393		479	
Skeletal (center angle)	167	Below range	243	Below range
Our-of-plane deformations	A_2		B_2	
CH_2 twist[a]	978	X	978	990
CH_2 wag[b]	902	X	902	910
cis CH	883	X		818
Vinyl CH torsion[c]	709	X		589
Skeletal	331 (term. angle)	X	357	358
	264 (center angle)	X		

[a] $H\diagdown C{=}C\begin{smallmatrix}H^{\oplus}\\H^{\ominus}\end{smallmatrix}$. Formerly called "vinyl CH out of plane deformation." [b] $H^{-1/2}\ C{=}C\begin{smallmatrix}H^{\oplus}\\H^{\ominus}\end{smallmatrix}$. [c] $H^{\oplus}\ C{=}C\ H^{\oplus}$ ($H^{\ominus}$). Formerly called "CH_2 torsion." This new nomenclature is in accord with Potts and Nyquist.[13]

Carbon–Carbon Single Bond Stretching Modes.—The remaining stretching modes are due to the single bonds between adjacent carbon atoms. The spectrum of propylene exhibits a carbon–carbon single bond stretching frequency at 920 cm.$^{-1}$. *trans*-Butene-2 has a band at 866 cm.$^{-1}$ (Raman) for the symmetric stretching mode and one at 1065 cm.$^{-1}$ for the asymmetric stretching mode, while these bands in the spectra of *cis*-butene-2 appear at 873 cm.$^{-1}$ and 970 cm.$^{-1}$, respectively. The effect of the *cis–trans* isomerization in the butenes is a splitting of frequencies with the differences between the symmetric and asymmetric modes being about 200 wave numbers in the *trans* isomer, but only about 100 wave numbers in the *cis* isomer. Before attempting to find any trend in the hexatrienes, it should be noted that a change has been made in the assignment of the *trans* isomer. As discussed above, the intense band at about 1180–1200 cm.$^{-1}$ seems to be characteristic of an in-plane CH bending mode rather than a single bond stretching mode. In this regard, the A_g single bond stretching mode of *trans*-hexatriene is now assigned to the 1245 cm.$^{-1}$ band. (All changes will be summarized below along the supporting arguments.) The B_u stretching mode is not changed from its assignment at 1130 cm.$^{-1}$ (infrared). Here the trend seems to be splitting of about 115 wave numbers. The actual values are in line with the single bond stretching mode of butadiene at 1205 cm.$^{-1}$. If *cis*-hexatriene possesses less conjugation, then its single bonds have less double bond character, or specifically, their stretching modes should be lower in frequency than those of the *trans* isomer. The strong polarized line at 1083 cm.$^{-1}$ (Raman) is assigned to the A_1 single bond stretching mode, while the 947 cm.$^{-1}$ (Raman) and 950 cm.$^{-1}$ (infrared) bands are assigned to the B_1 stretching vibration. Here again, a splitting of about 135 wave numbers can be seen.

At this point, a word is in order concerning the certainty of assignment of various bands. Mixing, coupling, conjugation and other factors may radically shift the frequencies of certain modes. The single bond stretching vibrations are among the most susceptible to these changes. For this reason, these assignments are, at best, doubtful and therefore alternate assignments are given below.

Skeletal Deformation Modes.—The seven remaining modes of vibration are not so easily related to modes in more simple molecules. However, they should be easily recognizable. Two (A_1) are polarized in the Raman. Two more (A_2) are Raman active only. The remaining three are non-polarized and coincident in Raman and infrared spectra. They are treated in order.

A_1. Only one polarized Raman line (at 393 cm.$^{-1}$) appears in the skeletal deformation region; however, because of its strength, the line at 167 cm.$^{-1}$ is also assigned to an A_1 mode. The schematic descriptions of the vibrations are, respectively, terminal angle bending and center angle bending motions.

A_2. Because of the limited range of the infrared instruments, only one clear cut case of coincidence is observable and thus, only the band at 357 cm.$^{-1}$ can definitely be eliminated from the A_2 species. However, since out-of-plane deformations usually occur at lower frequencies than corresponding in-plane motions, the line (331 cm.$^{-1}$)

just below the A_1 terminal angle bending mode (at 393 cm.$^{-1}$) is assigned to the A_2 terminal angle bending mode. The band at 264 cm.$^{-1}$ is assigned to the center angle bending motion.

B_1. In keeping with the previous argument, the B_1 terminal angle bending and center angle bending modes are assigned to the lines at 479 and 243 cm.$^{-1}$. It is recognized that, in the latter assignment, an equally strong case could be made to assign the 243 cm.$^{-1}$ line to the A_2 mode and 264 cm.$^{-1}$ line to the B_1 mode.

B_2. The remaining frequency (coincident at 357 cm.$^{-1}$ in the Raman spectrum with 358 cm.$^{-1}$ in the infrared spectrum) is assigned to the B_2 mode. Since this mode is primarily due to neither terminal nor center angle bending motions, it is best assigned to a frequency in the middle of the other pairs.

A complete assignment of observed frequencies to schematic modes of vibration is listed in Table III.

TABLE IV

THE COMPLETE ASSIGNMENT FOR *trans*-1,3,5-HEXATRIENE UTILIZING NEW DATA

w = weak, m = medium, s = strong, v = very, b = broad, sh = shoulder, P = polarized.

Mode	Symmetry	
Stretchings	A_g(Raman)	B_u(infrared)
CH_2 antisymmetric	3085 m	3091 s
Vinyl CH	3054 mw	3040 s
trans-CH	3054 mw	3012 s
CH_2 symmetric	2989 s	2953 s
Double bond, in phase	1623 vs	
Double bond, out of phase	1573s sh	1623 vs
Single bond	1245 w	1130 s
In plane bend		
CH_2 scissors	1394 m	1429 s
Vinyl CH	1280 m	1294 s
trans CH	1187 vs	1166 m
CH_2 rock	1128 m	1255 m
Center angle bend	347 m P	540 s
Terminal angle bend	444 mw	590 m
Out of plane bend	A_u(infrared)	B_g(Raman)
CH_2 twist[a]	1011 s	990 mw
trans CH	941 m	928 m
CH_2 wag	899 s	897 m
Vinyl CH torsion[a]	658 s	758 w,b
Skeletal	...	395 w
	475 m	

[a] Nomenclature in accord with Potts and Nyquist.[13]

Alternate Assignments. Carbon–Carbon Single Bond Stretching Modes.—Assuming that the strong band at about 1180–1200 cm.$^{-1}$ is not characteristic of a CH in-plane mode, then the assignment for the stretching vibrations in the *trans* structure should remain unchanged (*i.e.*, the *trans* A_g single bond stretching mode would be assigned to 1187 cm.$^{-1}$ in the Raman spectrum). In this case, the bands at 1182 cm.$^{-1}$ (Raman) and 1185 cm.$^{-1}$ (infrared) in the *cis* spectra should be assigned to the A_1 single bond stretching mode. The assignment of the bands at about 950 cm.$^{-1}$ to the B_1 mode gives the 200 wave number splitting as was noticed in the 2-butenes.

Carbon–Hydrogen In-plane Deformation Modes.—The former *trans* assignment listed the 1245 cm.$^{-1}$ Raman band as assigned to the A_g *trans* CH in-plane bending mode. If this were unchanged, then the *cis* A_1 mode should be assigned to the 1236 cm.$^{-1}$ Raman band. This alternate assignment now allows the polarized intense 1083 cm.$^{-1}$ Raman band to be assigned to the CH_2 rocking motion. This value is closer to the assigned value for the similar vibration in the *trans* molecule, namely, 1128 cm.$^{-1}$ (Raman). However, the intensities seem to be anomalous.

Carbon–Hydrogen Out-of-plane Deformation Modes.—It was noted above that the group frequencies for the *cis* CH out-of-plane bending and the vinyl CH torsional modes are about 690 cm.$^{-1}$ and 580 cm.$^{-1}$, respectively. The present assignments in the same order are 883 cm.$^{-1}$ and 709 cm.$^{-1}$. One could argue that the assignments should be switched so that the *cis* CH bending vibration would be nearer to its characteristic group frequency. The resulting difficulty with the assignment of the vinyl CH torsional mode is apparent.

Conclusion

The vibrational spectrum of the 1,3,5-hexatriene isomer investigated indicates a *cis* molecule with somewhat less resonance energy than the previously identified *trans* isomer. Although the interpretation was made for the extended *cis* model, the folded structures are not to be ruled out by the spectroscopic evidence alone.

A frequency assignment based on the extended *cis* model (point group C_{2v}) was made to the observed frequencies. In its main points, the assignment is in accord with symmetry properties, line strengths, envelope shape, doublet separation and polarization data. However, it should be reemphasized that conjugation gives rise to coupling effects which make the concept of group frequencies a difficult one to apply. This coupling between the various modes can shift frequencies appreciably from their expected values. In particular, with respect to the models used (*i.e.* the substituted ethylenes), the bonds which link these models, (*viz.*, the carbon–carbon single bonds), have the least certain assignments. Therefore, alternate assignments for these modes and the carbon-hydrogen in-plane bending motions are presented.

The revised assignment (see below) of observed frequencies to schematic modes of vibration for the *trans*-hexatriene is likewise consistent with the C_{2h} model, band strength and shapes, doublet separation and other symmetry properties and polarization data.

Revision to the Spectra and Assignments of *trans*-Hexatriene.—During the course of the present work, it was found necessary to re-examine the Raman spectrum of *trans*-hexatriene on an instrument capable of detecting low frequency lines. In addition, polarization runs were made to check the assignments of the A_g modes. These experiments necessitated the following changes and interpretations:

1. The reported very weak line at 958 cm.$^{-1}$ is not observable, but two other medium weak lines in

that region can be seen, namely 990 cm.$^{-1}$ and 1083 cm.$^{-1}$. The 958 cm.$^{-1}$ line had been unassigned. The 990 cm.$^{-1}$ band is assigned to the out-of-plane twisting motion.

2. The weak line at 889 cm.$^{-1}$ which had been assigned to the out-of-plane twisting motion seems actually to be slightly lower, about 863 cm.$^{-1}$. It is now unassigned.

3. The weak broad line at 411 cm.$^{-1}$ was resolved into two lines at 395 cm.$^{-1}$ and 444 cm.$^{-1}$. It had been assigned to the A_g center and terminal angle bending modes. The 444 cm.$^{-1}$ line is assigned to the terminal angle bending mode, and the 395 cm.$^{-1}$ line is reassigned to the B_g skeletal bending mode.

4. The line at 347 cm.$^{-1}$ is polarized and cannot be the B_g mode as previously assigned. It therefore is assigned to the A_g center angle bending vibration.

5. The assignments of the lines at 1187 cm.$^{-1}$ and 1238 cm.$^{-1}$ were switched as noted in the text.

At the same time the infrared spectra of the liquid and vapor were taken on a Perkin–Elmer Model 421 spectrometer. No essential differences from the previously reported work[3b] were noted. Table IV gives the complete assignment of *trans*-hexatriene utilizing the remeasured infrared and Raman spectra and the changed Raman assignments.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Ionic and Free Radical Processes in the Radiolysis and Sensitized Photolysis of Benzene Solutions[1]

BY WILLIAM VAN DUSEN, JR., AND WILLIAM H. HAMILL

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The gamma radiolysis of various binary liquid mixtures, mostly with benzene as one component, has been observed over the complete range of composition, for the primary purpose of correlating chemical effects with dissociative electron attachment and also to obtain evidence for positive charge exchange. Parallel measurements of benzene photosensitized decomposition at 2537 Å. were also performed to establish the quantum efficiency of energy transfer. Systems included various alkyl chlorides, bromides and iodides as well as chloroform, carbon tetrachloride, phenylacetyl chloride and benzyl acetate, all with benzene, as well as chlorobenzene–chloroform and methyl iodide–carbon tetrachloride. In conjunction with other evidence (P. S. Rao, *et al.*, *J. Am. Chem. Soc.*, **84**, 500 (1962)) the results support the hypothesis that dissociative electron attachment is an important primary process in the radiation chemistry of liquid systems with components which can readily attach slow electrons in the low pressure gas. Attachment can produce a large sensitized radiolysis of a minor component of the system. Positive charge transfer is indicated by a marked depression of G(product) from carbon tetrachloride, chloroform or benzyl acetate for small additions of benzene. It is concluded that evidence from luminescence of solutes demonstrates the very minor role in radiation chemistry of energy transfer from singlet states.

Introduction

The work reported here extends previous studies[2–4] which are concerned with distinguishing between ionic and other processes. It also attempts to assess the contributions of excited states and the corresponding energy transfer, exclusive of ionic processes.

These studies are concerned, in particular, with chemical consequences of dissociative electron attachment. Organic halides are expected to be suitable for this purpose, if the results of mass spectrometry may be used as a tentative guide. If chemical effects attributable to electron attachment can be demonstrated, it would also be desirable to measure their relative reactivities with various solutes and the approximate number of molecules they encounter before recapture.

Chemical evidence alone cannot ordinarily furnish conclusive evidence for dissociative electron attachment since similar dissociative processes presumably occur concurrently by other routes. The ultimate stable products of ionic reactions are largely those which arise subsequent to charge neutralization, *i.e.*, they are products of atom and free radical reactions. It is also particularly important to distinguish between the reactions of electrons and of H-atoms. By examining a sufficient number of solutions in benzene as a common component and by choosing for solutes, as far as possible, molecular species of characterizable reactivity toward electrons, we hope to accumulate sufficient evidence to demonstrate our working hypothesis, *viz.*, that ionic processes play an important role in radiation chemistry.

It appeared desirable to maintain one common hydrocarbon component throughout this work. Because of the considerable G(H) for cyclohexane and other alkanes, the use of benzene was indicated because of its reported relative stability under gamma radiation.[5,6] Some of the systems studied in this work have been investigated previously by Magat, Bouby and Chapiro,[7–9] using diphenylpicryl-

(1) This article is based on a thesis submitted by W. Van Dusen, Jr., in partial fulfillment of the requirements for the Ph.D. degree in the University of Notre Dame, June, 1961. The Radiation Laboratory is operated under Atomic Energy Commission contract AT (11-1)-38.

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