

$$2b_{02} = -v - \frac{q_2^2}{\Sigma_2} + \frac{\beta}{4\Sigma_2} \left( q_2^2 - q_2 \frac{\Sigma_3}{\Sigma_2} \right)^2 \quad (42)$$

Note that  $\beta$ ,  $\Sigma_2$  and  $\Sigma_3$  depend on properties of the equilibrium ions only, species 3, 4, . . . .

In summary: eq. 32 and 34 give the membrane potential; eq. 23, 24 and 40-42 give the activity coefficient ratios for the non-equilibrium species; and eq. 22 and 40-42 give the osmotic pressures.

#### IV. The McMillan-Mayer Method

We consider the same special case as in Sec. III. The basic equations for the osmotic pressure and activity coefficient ratios are eq. 19-21 and 22-24 where, here, the  $b_{ij}$ 's are to be calculated directly from eq. 3 and 4. If we use for  $w_{ij}$  the potential in eq. 54 of reference 4, we find for  $b_{20}$ ,  $b_{11}$  and  $b_{02}$  equations with the same formal appearance as eq. 40-42, but with  $\Sigma_2$ ,  $\Sigma_3$  and  $\beta$  replaced by  $\Sigma_2'$ ,  $\Sigma_3'$  and  $\beta'$ , respectively, where

$$\beta' = \frac{\alpha'}{(1 + \kappa a)^2}$$

$$\alpha' = \epsilon^2 \kappa / D k T'$$

$$\Sigma_n' = \sum_{s \geq 1} \rho_s^* q_s^2$$

and  $\kappa$  has already been defined (following eq. 30). In other words, the "outside electrolyte" here includes the non-equilibrium ions as well as the equilibrium ions.

These results, together with eq. 19-21, represent the best available approximation when  $\rho_1$ ,  $\rho_2$ ,  $\rho_1^*$  and  $\rho_2^*$  are not necessarily small quantities. However, if exact (for this model) expansions in powers of  $\rho_1$ ,  $\rho_2$ ,  $\rho_1^*$  and  $\rho_2^*$  are desired, then eq. 22-24 are appropriate and  $\Sigma_2' \rightarrow \Sigma_2$ ,  $\Sigma_3' \rightarrow \Sigma_3$  and  $\beta' \rightarrow \beta$  (to quadratic terms in the osmotic pressure and linear terms in the activity coefficient ratios). That is, in this case, the McMillan-Mayer method gives the same results as the Donnan method (eq. 40-42).

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF MARYLAND]

## The Vibrational Spectra and Geometrical Configuration of 1,3,5-Hexatriene<sup>1</sup>

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Spectroscopic data for 1,3,5-hexatriene are reported. These include the Raman spectrum of the liquid and the infrared spectrum of the vapor. The spectral data indicate that 1,3,5-hexatriene has the *trans* pseudolinear configuration. An assignment of the vibrational frequencies to the normal modes of vibration is presented.

### Introduction

A synthesis of 1,3,5-hexatriene was first reported by Van Romburgh and Van Dorssen,<sup>2</sup> after which a number of other syntheses have been reported.<sup>3</sup> Alder and Von Brachel<sup>4</sup> have postulated a *trans* configuration based upon a Diels-Alder reaction product.

### Experimental

A sample of 1,3,5-hexatriene was kindly supplied by Professor G. Forrest Woods of the University of Maryland. It was prepared by the dehydration of 1,3-hexadiene-5-ol and purified by fractional crystallization.<sup>3</sup> Its physical properties were: m.p.  $-11.7^\circ$ , b.p.  $80^\circ$ ,  $n_D^{20}$  1.5035.

**The Raman Spectrum.**—The Raman spectrum of 1,3,5-hexatriene was obtained with an automatic recording instrument built at the University of Maryland,<sup>5</sup> using 4358 Å. excitation. The source was a "Toronto-type" arc. This consisted of a 30 mm. diameter helical Pyrex tube of four and one-half turns. Its total arc path is nine feet, of which seven and one-half feet effectively radiate the sample. A saturated potassium nitrite solution was used as a filter for the short wave length radiation. Calibration was accomplished by recording an iron arc spectrum. Figure 1 is a trace of one of the resulting Raman curves of 1,3,5-hexatriene. The observed Raman lines are listed in Table III.

**The Infrared Spectrum.**—The infrared spectrum of liquid 1,3,5-hexatriene has been reported.<sup>3</sup> However, the

vapor spectrum has not been reported previously. A Perkin-Elmer Model 12-C single-beam, double-pass spectrometer was used. It was equipped with lithium fluoride, calcium fluoride and sodium chloride prisms. The spectra were run in 10-cm. gas cells at 25 and 35°. The absorption bands are listed in Table II and illustrated in Fig. 2. Figure 2 is a trace of the spectrum using a Beckman IR-4 spectrometer.

TABLE I

THE DISTRIBUTION OF VIBRATION AMONG SPECIES AND SELECTION RULES

<i>trans</i> . C <sub>2</sub> h Vibr. species	No. of vibrations			Activity
	C	H	Total	
Ag	5	8	13	Raman
Au	2	4	6	Infrared
Bg	1	4	5	Raman
Bu	4	8	12	Infrared
<i>cis</i> C <sub>2</sub> v				
A <sub>1</sub>	5	8	13	Infrared and Raman
A <sub>2</sub>	2	4	6	Raman
B <sub>1</sub>	4	8	12	Infrared and Raman
B <sub>2</sub>	1	4	5	Infrared and Raman

### Discussion

The comparative stability of 1,3,5-hexatriene may be postulated as due to resonance. In order to have the maximum amount of resonance stabilization, the molecule must be planar. Of the six possible structures, three have *cis* and three have *trans* configurations. Fisher-Hirschfelder models indicate that five of these structures (2,3,4,5,6 of Fig. 3) cannot be made planar because they are sterically hindered. However, structure 4 cannot be en

(1) Taken in part from a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Graduate School of the University of Maryland.

(2) Van Romburgh and Van Dorssen, *Verslag Akad. Wetenschappen Amsterdam*, **8**, 565 (1905).

(3) G. F. Woods and L. H. Schwartzman, *THIS JOURNAL*, **70**, 3394 (1948).

(4) K. Alder and H. Von Brachel, *Ann.*, **608**, 195 (1957).

(5) R. A. Bafford, Master's Thesis, University of Maryland, 1956.

TABLE II  
ASSIGNMENT OF INFRARED FREQUENCIES

Liquid, cm. <sup>-1</sup>	Vapor, cm. <sup>-1</sup>	Band type	Freq. no.	Type of vibration	Predicted band type
3091s	3102				
	3092s	AB	25	CH <sub>2</sub> asym. stretch	AB
3040s	3046				
	3035s	AB	26	Vinyl CH stretch	AB
3012s	3021				
	3012s	AB	27	<i>trans</i> CH stretch	AB
2973s	2953sb	?	28	CH <sub>2</sub> sym. stretch	AB
2943s					
2878ms	2884ms	C	5 + 33	1623 + 1255 = 2878	
2828ms	2839ms	C	7 + 30	1394 + 1429 = 2723 ?	
	2716w	?			
2645w					
2560w					
2435w	2430w	?			
2335m					
2255w					
2165w					
2110w					
2060w					
1990w	2000mw				
	1912w				
1875w					
	1868vw				
	1844vw				
	1834vw				
1810s	1811				
	1802	AB	14 + 21	928 + 899 = 1827	
1750m	1775w		36 + 10	590 + 1187 = 1777	
1675w			11 + 35	1135 + 540 = 1675	
1623s	1632				
	1623s	AB	29	Asym. double bond st.	AB
	1592w	?	22 + 14	672 + 928 = 1600	
1546w					
1502w					
1481w					
	1435				
1429s	1432ms	AB	30	CH <sub>2</sub> bend	AB
1374mw					
1362mw					
1294s	1300				
	1290m	AB	31	Vinyl CH bend	
1255m	1261				
	1251m	AB	33	CH <sub>2</sub> rock	
1242w	1238vw	?			
1218w					
1166m	1178m	AB	32	<i>trans</i> CH bend	AB
	1166				
	1137				
1130s	1130m	AB ?	34	Asym. carbon single bond st.	AB
	1102				
	1018				
1011s	1009vs	C	19	Vinyl CH out-of-plane deformation	C
	1000				
963w	973w	?			
941m	937mw	?	20	<i>trans</i> CH out-of-plane deformation	C
	907				
899s	900vs	C	21	CH <sub>2</sub> out-of-plane deformation	C
	893				
818w	817w	?			
748mw	745w	?			
687s	684				
658s	672s	C	22	CH <sub>2</sub> torsion	C
	659				
590m			36	Skeletal terminal angle bend	AB
560w					
540s			35	Skeletal center angle bend	AB
475m			24	Out-of-plane skeletal deformation	C

tirely ruled out since the hindrance to planarity is small. The planar *trans* form (structure 1) belongs to the point group C<sub>2h</sub> and the planar *cis* form (structure 4) belongs to the point group C<sub>2v</sub>. Table I lists the distribution of vibrations among

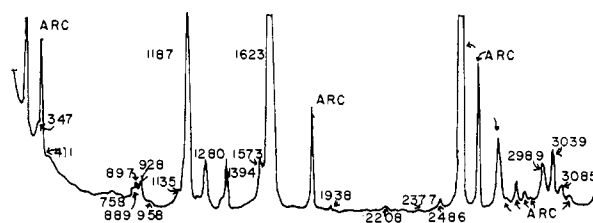


Fig. 1.—The Raman spectrum of 1,3,5-hexatriene using 4358 Å. excitation.

the symmetry species with the selection rules for the C<sub>2v</sub> and C<sub>2h</sub> structures of 1,3,5-hexatriene.<sup>6</sup>

Of the twenty-two lines observed in the Raman spectrum, eighteen are in the fundamental region. This is to be expected if the structure is *trans*. There are twenty-two bands in the infrared spec-

TABLE III  
ASSIGNMENT OF RAMAN FREQUENCIES

Frequency (cm. <sup>-1</sup> )	Freq. no.	Type of vibration
3085mw	1	CH <sub>2</sub> asymmetrical stretch
3039m	2	Vinyl CH stretch
3039	3	<i>trans</i> CH stretch
2989w	4	CH <sub>2</sub> symmetrical stretch
2486w		
2377wb	2 × 17	2 × 1187 = 2374
2208wb		
1938w		
1623vs	5	Double bond stretch
1573s sh	6	Out-of-phase double bond stretch
1394m	7	CH <sub>2</sub> bend
1372vw	2 × 27	2 × 687 = 1374
1280m	8	Vinyl CH bend
1238w	9	<i>trans</i> CH bend
1187vs	10	Carbon single bond stretch
1135w	11	CH <sub>2</sub> rock
958vw		
928	14	<i>trans</i> CH out-of-plane deformation
897m	15	CH <sub>2</sub> out-of-plane wag
889w	16	Vinyl CH out-of-plane deformation
758wb	17	CH <sub>2</sub> torsion
	12 + 18	411 + 347 = 758
411wb	12	Carbon center angle bend
	13	Carbon terminal angle bend
347mw	18	Out-of-plane skeletal deformation

trum which may be considered as fundamentals. This is compared to a predicted value of 17-18 bands in the *trans* form and of 28-30 for the *cis* form. This suggests the presence of a *trans* structure.

If the configuration is *trans*, there should be no coincidence between the infrared and Raman bands. For the *cis* form, all thirty of the infrared bands should appear in the Raman spectrum. Thirty of the thirty-six Raman bands should appear in the infrared spectrum. From Tables II and III it may be seen that there are no corresponding frequencies in the Raman spectrum for the medium to strong bands at 475, 540, 590, 672, 941, 1011, 1166, 1255, 1294 and 1429 cm.<sup>-1</sup>. The infrared bands at 899, 1130 and 1623 cm.<sup>-1</sup> do correspond with the Raman

(6) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. V. Nostrand and Co., Inc., New York, N. Y., 1945, p. 106, 134.

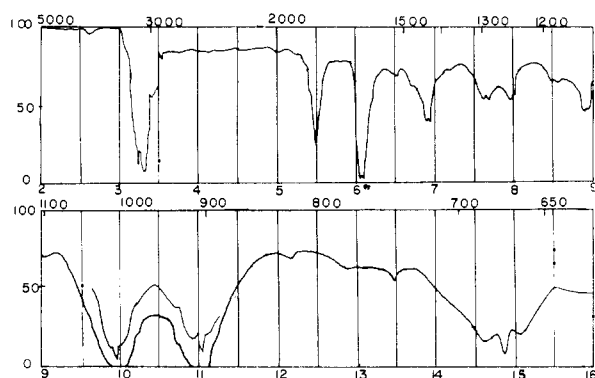


Fig. 2.—The infrared vapor spectrum of 1,3,5-hexatriene using a 10-cm. gas cell.

bands at 897, 1135 and 1623  $\text{cm}^{-1}$ . There are also no corresponding frequencies in the infrared spectrum for the Raman lines at 758, 889, 928, 1187, 1280, 1394 and 1573  $\text{cm}^{-1}$ . The small number of coincidences between the observed infrared and Raman frequencies is interpreted as additional evidence for a *trans* configuration. The few frequencies which are coincidental can be explained as accidental degeneracies. Since Fisher-Hirschfelder models show that the *trans* structure 3 cannot be made planar without considerable strain, the data will be interpreted on the basis of *trans* structure 1.

There are two distinct types of absorption bands in the infrared vapor spectrum—doublet bands (PR bands) and PQR bands. Since band shapes are dependent upon the moments of inertia of the molecule, the principal moments of inertia were calculated thus

	<i>cis</i> (Structure 4)	<i>trans</i> (Structure 1)
$I_x$	$72.2 \times 10^{-40} \text{ g. cm.}^{-2}$	$37.5 \times 10^{-40} \text{ g. cm.}^{-2}$
$I_y$	$486 \times 10^{-40} \text{ g. cm.}^{-2}$	$630 \times 10^{-40} \text{ g. cm.}^{-2}$
$I_z$	$558 \times 10^{-40} \text{ g. cm.}^{-2}$	$667 \times 10^{-40} \text{ g. cm.}^{-2}$

Both the *cis* and *trans* forms are asymmetric top molecules, but they approximate a symmetrical top molecule ( $I_y \cong I_z$ ) because of the pseudolinear configuration. Gerhard and Dennison<sup>7</sup> have derived a formula which gives the doublet separation between the P and R branch maxima for parallel bands of symmetric top molecules. Using both larger moments of inertia for the *cis* and *trans* forms of 1,3,5-hexatriene, the calculated separation at 27° is 8.8 and 9.1  $\text{cm}^{-1}$  for the *trans* form; 10.2 and 11.1  $\text{cm}^{-1}$  for the *cis* form. The experimental doublet separations were 10.7, 12.0, 9.2, 8.4, 3.0, 10.7 and 9.6  $\text{cm}^{-1}$  for the bands 3102, 3046, 3021, 1632, 1435, 1300 and 1261  $\text{cm}^{-1}$ , respectively. Although no definite conclusions could be made of the configuration of the molecule, these calculations do indicate that the assumption of a symmetrical top molecule was reasonable and that any reasonable structure is pseudolinear. The *trans* structure 1 gives a better approximation to a linear molecule than does the *cis* form. For  $C_{2h}$  linear molecules parallel bands are doublets. Perpendicular bands are PQR bands. The observation of only two types of band envelopes furnishes additional evidence for the *trans* structure since these bands readily may be assigned to the two infrared active species,  $A_u$

(7) S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933).

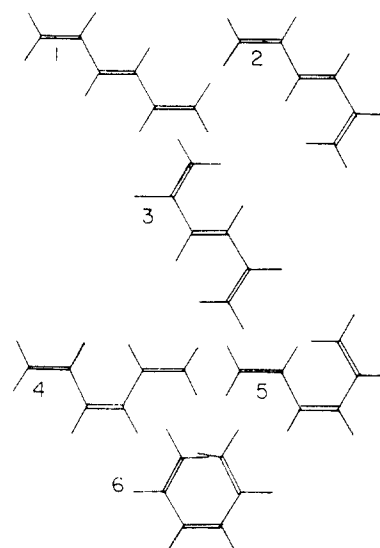


Fig. 3.—Six possible structures for 1,3,5-hexatriene.

(type C) and  $B_u$  (type AB) of the  $C_{2h}$  point group. A *cis* structure should show three types of infrared band envelopes. These correspond to A, B and C type bands which would be assigned to the three infrared active species of the  $C_{2v}$  point group.

**Frequency Assignment.**—The assignment was based on the characteristic group frequencies of similar molecules such as ethylene,<sup>8</sup> propylene,<sup>9</sup> 1,3-butadiene<sup>10</sup> and 1,3-pentadiene<sup>11</sup> and the group frequencies listed in Bellamy.<sup>12</sup>

**Infrared Frequency Assignment.**—There are four carbon hydrogen stretching modes for *trans*-1,3,5-hexatriene which are of the type AB. The anti-symmetric  $\text{CH}_2$  stretching mode occurs at 3089.7  $\text{cm}^{-1}$  for propylene; 3105.5  $\text{cm}^{-1}$  for ethylene; and 3100  $\text{cm}^{-1}$  for 1,3-butadiene. Bellamy lists this frequency at 3095–3075  $\text{cm}^{-1}$ . The corresponding frequency in hexatriene is assigned to the doublet at 3102, 3092  $\text{cm}^{-1}$ . Symmetric  $\text{CH}_2$  stretching in ethylene is at 2989.5  $\text{cm}^{-1}$ ; in propylene at 2991.5  $\text{cm}^{-1}$ ; and in butadiene at 3000  $\text{cm}^{-1}$ . The broad band at 2953  $\text{cm}^{-1}$  is assigned to this mode. Vinyl CH stretching occurs at 3060  $\text{cm}^{-1}$  in butadiene and 3013  $\text{cm}^{-1}$  in propylene. Bellamy lists this range at 3040–3010  $\text{cm}^{-1}$ . It should also be expected that the *trans* CH stretching should occur in this region and Bellamy gives this frequency range as 3040–3010  $\text{cm}^{-1}$ . Since butadiene corresponds more closely to hexatriene than does propylene, the vinyl CH stretching is assigned to the doublet at 3046–3035  $\text{cm}^{-1}$ . These last two assignments may possibly be reversed. Three of these four vibrations were doublets, as expected by the analogy with an approximately linear molecule.

(8) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 326; R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.*, **18**, 118 (1950).

(9) R. C. Lord and P. Venkateswarlu, *J. Opt. Soc. Am.*, **40**, 1079 (1953).

(10) C. M. Richards and J. R. Nielsen, *ibid.*, **40**, 438 (1950).

(11) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947).

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

The non-conjugated double bond carbon stretching frequency occurs between 1680–1620  $\text{cm}^{-1}$  and for conjugated double bonds near 1600  $\text{cm}^{-1}$  with enhanced intensity. The *trans* form should have only one infrared active double bond stretching mode, the antisymmetric stretching of type AB. This mode is assigned to the strong doublet at 1632, 1623  $\text{cm}^{-1}$ . Conjugation decreases the double bond character of the bond, resulting in a lowered frequency. Aromatic carbon double bond frequencies occur near 1600  $\text{cm}^{-1}$ .

For the *cis* structure, there should be three double bond frequencies. Three carbon double bond frequencies are present in the infrared spectrum of 2,4,6-octatriene at 1601, 1646 and 1685  $\text{cm}^{-1}$ . Hexatriene does show two very weak bands in the double bond region in addition to the band at 1623, 1632  $\text{cm}^{-1}$ . One at 1592  $\text{cm}^{-1}$  is not present in the liquid. This band may be explained as a combination band of the Raman line at 928  $\text{cm}^{-1}$  and the strong infrared band at 672  $\text{cm}^{-1}$ . The other weak band at 1675  $\text{cm}^{-1}$ , found only in the liquid spectrum, may be explained as a combination of the 1135  $\text{cm}^{-1}$  Raman band and the 540  $\text{cm}^{-1}$  infrared band.

Other skeletal vibrations are quite sensitive to structural changes in the molecule and, therefore, the frequency range is quite broad. The carbon single bond stretching mode occurs in the infrared at 870  $\text{cm}^{-1}$  in propane; at 920.4  $\text{cm}^{-1}$  in propylene; and at 1205  $\text{cm}^{-1}$  in the Raman spectrum of 1,3-butadiene. Conjugation increases the single bond frequency. The band at 1130  $\text{cm}^{-1}$  which is considered a doublet with P and R branches at 1137, 1130  $\text{cm}^{-1}$ , is assigned to the asymmetric single bond carbon stretching mode. There is considerable difficulty in the assignment of the two out-of-plane skeletal deformation modes. For propylene, the skeletal deformation frequency is at 427.5  $\text{cm}^{-1}$ , and for butadiene at 513  $\text{cm}^{-1}$  in the Raman spectrum. The infrared frequency for the out-of-plane mode of 1,3-butadiene was calculated to be 170  $\text{cm}^{-1}$  and the in-plane skeletal mode appeared in the Raman at 320  $\text{cm}^{-1}$  because of a breakdown in selection rules. The infrared spectrum reveals three bands in the region between 650 and 430  $\text{cm}^{-1}$ . As a general rule, the out-of-plane deformations are of lower frequency than the in-plane deformations. Therefore, the bands at 590 and 540  $\text{cm}^{-1}$  were assigned to the in-plane skeletal deformations and the 475  $\text{cm}^{-1}$  to one of the out-of-plane skeletal deformation modes. The other out-of-plane skeletal deformation is out of the range of the infrared prism instrument.

Of the four carbon hydrogen out-of-plane modes of species  $B_u$ , the most important one is the *trans* CH out-of-plane deformation. Bellamy assigns this mode at 970–960  $\text{cm}^{-1}$ . This strong band has been observed in many *trans* compounds and is considered to be an excellent means for the determination of *cis* and *trans* isomers. However, the infrared spectrum of 1,3,5-hexatriene showed only a very weak band at 973  $\text{cm}^{-1}$  in the vapor and at 963  $\text{cm}^{-1}$  in the liquid, which would indicate a *cis* structure. Examination of the spectrum of the *cis* and *trans* isomers of 1,3-pentadienes and of the three geometrical isomers of 1,4-diacetyl-1,3-buta-

diene<sup>13</sup> revealed that the strong 970  $\text{cm}^{-1}$  *trans* band is shifted to lower frequencies with lowered intensity. *trans*-1,3-Pentadiene has a medium band at 949  $\text{cm}^{-1}$ , which may be assigned to the *trans* hydrogen out-of-plane bending. The *cis-cis*-1,4-diacetyl-1,3-butadiene spectrum showed no band in the region of 980–930  $\text{cm}^{-1}$ , but the *trans-trans* and *cis-trans* spectrum revealed a band of medium to weak intensity at 940–945  $\text{cm}^{-1}$ . It is assumed that conjugation lowers the *trans* CH band and also lowers its intensity. Because of this effect, the medium weak band at 937  $\text{cm}^{-1}$  has been assigned to the *trans* CH out-of-plane bending mode. Another interesting difference observed in these two compounds was that in the spectra of the *cis* structures there was a strong band at 760–770  $\text{cm}^{-1}$  which is absent in the *trans* forms. Hexatriene has no strong band in this region.

Vinyl CH out-of-plane deformation has a characteristic frequency at 995–985  $\text{cm}^{-1}$  of strong intensity. The type C band (PQR branches) at 1009  $\text{cm}^{-1}$  has been assigned to this mode. The  $\text{CH}_2$  out-of-plane deformation is assigned to the type C band at 900  $\text{cm}^{-1}$  which is close to the range of 915–905  $\text{cm}^{-1}$ . The corresponding frequencies are 1014 and 909  $\text{cm}^{-1}$  for 1,3-butadiene.

The carbon hydrogen twisting mode of ethylene occurs at 1027  $\text{cm}^{-1}$ . For propylene a band at 577.6  $\text{cm}^{-1}$  has been assigned to this mode. For 1,3-butadiene the CH torsional mode is assigned at 686  $\text{cm}^{-1}$  in the Raman spectrum and at 520  $\text{cm}^{-1}$  in the infrared spectrum. The strong type C band at 672  $\text{cm}^{-1}$  of hexatriene has been assigned to the  $\text{CH}_2$  torsional frequency. This frequency is too high to be a skeletal deformation and too low for other assignments. The band shape also corresponds to that predicted by analogy to a linear molecule.

Four in-plane hydrogen deformation modes are present in the *trans* form. The terminal  $\text{CH}_2$  bending mode has been assigned to the doublet band 1435, 1432  $\text{cm}^{-1}$  which corresponds to the same vibrational mode of 1,3-butadiene at 1484  $\text{cm}^{-1}$  and of propylene at 1419.2  $\text{cm}^{-1}$ . The  $\text{CH}_2$  rocking mode is assigned to the doublet at 1261, 1251  $\text{cm}^{-1}$ . For butadiene the corresponding frequency is at 1290  $\text{cm}^{-1}$  and in propylene at 1229  $\text{cm}^{-1}$ . According to Bellamy, both the vinyl and *trans* CH in-plane deformation should occur between 1310–1290  $\text{cm}^{-1}$  with the vinyl range lower. The band at 1294  $\text{cm}^{-1}$  in the liquid appears as either a doublet or as two bands in the vapor. Since this mode is a type AB band, it should be a doublet and was assigned to the vinyl CH bend. The *trans* CH bending mode is then assigned to the medium weak doublet at 1178, 1166  $\text{cm}^{-1}$ . Since the *trans* hydrogen out-of-plane bending frequency was lowered and its intensity was quite low, it is concluded that the in-plane bending mode is also affected by the conjugation.

Table II summarizes the infrared assignment.

**The Raman Assignment.**—For propylene the  $\text{CH}_2$  asymmetric stretching is assigned at 3087  $\text{cm}^{-1}$  in the Raman spectrum; the  $\text{CH}_2$  symmetrical stretching at 2990  $\text{cm}^{-1}$ ; and the CH stretch-

(13) H. H. Inhoffen, J. Heimann-Trosien, H. Muxfeldt and H. D. Kramer, *Chem. Ber.*, **90**, 187 (1957).

ing at 3010  $\text{cm}^{-1}$ . These frequencies fall within the range given in Bellamy for infrared frequencies. *trans* CH stretching and vinyl CH stretching fall in the same range, 3040–3010  $\text{cm}^{-1}$ . The Raman band at 3039  $\text{cm}^{-1}$  which is stronger than the other two lines in the CH region, was assigned to both the vinyl and the *trans* CH stretch. The asymmetric  $\text{CH}_2$  stretch was assigned at 3085  $\text{cm}^{-1}$  and the symmetrical  $\text{CH}_2$  stretch assigned at 2989  $\text{cm}^{-1}$ . The last two assignments are quite similar to propylene. The symmetrical  $\text{CH}_2$  bend was assigned to the 1394  $\text{cm}^{-1}$  frequency. For propylene, the corresponding frequency is 1415  $\text{cm}^{-1}$  and for butadiene it is 1442  $\text{cm}^{-1}$ . Bellamy lists this frequency as 1420–1410  $\text{cm}^{-1}$  in the infrared as a general range. Vinyl CH and *trans* CH in-plane deformation frequencies should occur in the 1200–1300  $\text{cm}^{-1}$  region of the spectrum. It is therefore reasonable to assign the CH *trans* and CH vinyl bending modes at 1238 and 1280  $\text{cm}^{-1}$ , respectively. The higher frequency was assigned to the vinyl CH bend since it compares favorably with the assigned CH vinyl bend of 1309  $\text{cm}^{-1}$  in butadiene. The  $\text{CH}_2$  rocking mode was assigned to the 1135  $\text{cm}^{-1}$  band which is the remaining unassigned band in this region.

The  $\text{CH}_2$  out-of-plane wagging frequency was assigned at 897  $\text{cm}^{-1}$ . This frequency for butadiene is at 911  $\text{cm}^{-1}$  and is easily identified in the infrared band spectrum at 899  $\text{cm}^{-1}$ . Vinyl  $\text{CH}_2$  twist or torsion was assigned at 758  $\text{cm}^{-1}$ . This frequency in propylene is at 580  $\text{cm}^{-1}$  and in butadiene at 686  $\text{cm}^{-1}$ . Since this mode of vibration twists the carbon double bond, it is reasonable to assume that more energy must be used in twisting bonds of this conjugated molecule than in an unconjugated one, and an increase in frequency is expected.

Vinyl CH out-of-plane deformation has been assigned to the weak line at 889  $\text{cm}^{-1}$ . In butadiene it is assigned at 890  $\text{cm}^{-1}$ , which is also recorded as weak. The *trans* out-of-plane deformation is assigned at 928  $\text{cm}^{-1}$ . It is possible that the two frequencies might be interchanged.

The very strong band at 1623  $\text{cm}^{-1}$  was assigned to the carbon double bond stretching mode. As expected the frequency is lower than the normal double bond stretch because of conjugation. Conjugation also increases the intensity of the band. It is interesting that this frequency is lower than the double bond stretching mode in 1,3-butadiene at 1643  $\text{cm}^{-1}$ . In propylene it is at 1648  $\text{cm}^{-1}$ . The out-of-phase symmetrical double bond stretch is assigned at 1573  $\text{cm}^{-1}$ . This type of vibration in butadiene is active in the infrared and occurs at 1599  $\text{cm}^{-1}$ . Again the frequency is lowered because of the greater resonance energy of hexatriene.

Carbon single bond frequencies are usually quite sensitive to changes in the environment of the vibrating group. Hence, there is a considerable frequency range for this vibration as well as for the other skeletal vibrations. For 1,3-butadiene, the 1205  $\text{cm}^{-1}$  line, and the 920  $\text{cm}^{-1}$  line for propylene are assigned to carbon single bond stretching. Based on this, the very strong line at 1187  $\text{cm}^{-1}$  was assigned to the single bond stretching vibration.

Skeletal angle bending modes are also quite sensitive to neighboring groups. Therefore, their characteristic frequencies fall into a wide range. A weak broad line at 411  $\text{cm}^{-1}$  has been assigned tentatively to both skeletal angle bending modes. The corresponding frequency in propylene is 432  $\text{cm}^{-1}$ .

The 347  $\text{cm}^{-1}$  band has been assigned to the out-of-plane skeletal deformation. Out-of-plane vibrational modes are lower than in-plane modes. This was the lowest Raman line observed.

Table III lists all the Raman frequencies and their assignments.

### Conclusions

The vibrational spectra of 1,3,5-hexatriene indicate that the molecule has a *trans* configuration which is in agreement with Alder's structure.<sup>4</sup> The *trans* form is consistent with the lack of coincidences between the infrared and Raman spectra. Because of steric hindrance to planarity structure 1 appears to be the more likely configuration of hexatriene than does structure 3. However, the latter cannot be definitely ruled out by the spectroscopic data. Fair agreement between the parallel band doublet separation and the calculated values indicates that the molecule approximates a symmetric top molecule. By assuming a pseudo-linear molecule the predicted infrared band shapes were similar to the experimental types for most of the bands. Although the infrared assignment accounted for all the stronger bands, there are some weak bands which could not be explained as combinations or overtones. These bands are too weak to be considered as fundamentals of the *cis* form. It is possible that these unexplained bands are due to impurities formed as reaction products of 1,3,5-hexatriene. All but one very weak band in the fundamental region of the Raman spectrum was assigned to the predicted vibrational modes of the *trans* form.

The *trans* group frequency band which is very strong and located at  $965 \pm 5 \text{ cm}^{-1}$  for isolated double bonds is shifted to lower  $\text{cm}^{-1}$  values with a considerable drop in intensity for *trans* conjugated double bonds.

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