[Contribution from the Department of Chemistry, the University of Maryland]

The Vibrational Spectra and Geometrical Configuration of 1,3,5,7-Octatetraene

By Ellis R. Lippincott, William R. Feairheller, Jr.,[1] and C. Evans White

Received July 17, 1958

The infrared and Raman spectra of 1,3,5,7-octatetraene are reported. The Raman spectra were obtained using carbon disulfide and cyclohexane as solvents. The infrared spectra in carbon tetrachloride and carbon disulfide solution are reported. The spectral data are best interpreted on the basis of an all-*trans* structure for 1,3,5,7-octatetraene. A tentative assignment of the observed frequencies to the normal modes of vibration is presented.

Introduction

A synthesis of 1,3,5,7-octatetraene has been reported by Woods and Schwartzman.[2] This synthesis consisted of the 1,2-addition of allylmagnesium bromide to 2,4-pentadienal and dehydration of the resulting secondary alcohol to 1,3,5,7-octatetraene. Little additional work has been done on this compound to establish its geometrical configuration.

Experimental

The method of preparation of octatetraene was suggested by Professor G. Forrest Woods of the University of Maryland. A detailed description of this method will be published by Woods and Frank Scotti.[3] Briefly, it consisted of the reaction of vinylmagnesium bromide with 2,4-hexadienal to yield the secondary alcohol. The alcohol was dehydrated over alumina at 230–260°, yielding 1,3,5,7-octatetraene. Recrystallization from Skelly F gave a pale yellow solid. Since the pure solid polymerizes rapidly, it was placed in solution as soon as the crystal crop was dry.

High purity of the product was indicated by the lack of evidence for the characteristic group frequencies associated with expected impurities. No frequencies were found in either the infrared or Raman spectra that could be definitely associated with CH_3, methylene CH_2, OH, C=O, C≡C or unconjugated C=C.

Table I

The Selection Rules of Distribution of Vibrations Among the Species for the Point Group C_{1h} and C_{2h}

Point Group C_{1h}

Species	Symmetry of species		No. of vibrations			Activity
	1	$\sigma(xy)$	C	H	total	
A′	+1	+1	13	20	33	I.R., R.
A″	+1	−1	5	10	15	I.R., R.

Point Group C_{2h}

Species	Symmetry of species				No. of vibrations			Activity
	I	$C_{2(z)}$	$\sigma_{(xy)}$	i	C	H	total	
A_g	+1	+1	+1	+1	7	10	17	R.
A_u	+1	+1	−1	−1	3	5	8	I.R.
B_g	+1	−1	−1	+1	2	5	7	R.
B_u	+1	−1	+1	−1	6	10	16	I.R.

The Raman Spectrum.—The Raman spectrum was obtained using a photographic instrument assembled at the University of Maryland. A photoelectric instrument was not employed because the yellow color of the sample required 5461 Å. Hg excitation. The arc was a "Toronto" type #93-50 manufactured by the Applied Research Laboratory. Saturated neodymium chloride and potassium chromate solutions acted as filters to allow the 5461 Å. line of Hg to be used as the excitation frequency. The spectrograph was a Huet model A-II which employs two glass prisms with a dispersion of 45 Å. per mm. at 5000 Å. with an aperture of f/8. Eastman Kodak 103 a-E backed spectrographic plates were used. Iron arcs were recorded above and below each exposure. Exposures ranged from 5 to 45 minutes at a slit width of 0.25 mm. The observed Raman spectrum is listed in Table II.

Table II

Assignment of Raman Frequencies

Cm.$^{-1}$	Intensity	Freq. no.	Type of vibration
223	vw,b	27	Out-of-plane C=C skeletal deformation
223		26	In-plane C=C skeletal deformation
288	vw	7	Skeletal center angle bend
470	vvw	5	Skeletal middle angle bend
528	vvw	4	Skeletal terminal angle bend
722	vvw	30	CH_2 torsion
883	w,vb	31	Vinyl out-of-plane bend
905	w	29	CH_2 wag
958	vw	28	Asymmetric *trans* CH out-of-plane bend
1080	vw	32	Central CH symmetric out-of-plane bend
1138	m	14	Symmetric CH_2 rock
1185	s,vb	6	Carbon single-bond stretch
		16	Center CH in-plane bend
		3	Carbon single-bond out-of-phase stretch
1243	w	13	*trans* CH in-plane bend
1304	w	15	Vinyl in-plane bend
1432	m	12	CH_2 bend
1483	vw		
1555	vw		
1608	s,b	1	Double-bond stretch
		2	Out-of-phase double-bond stretch
2657	w		
2693	vw		
2791	w	2 + 3	1608 + 1185 = 2793
3005	m,vb	8	CH_2 in-phase symmetric stretch
		10	*trans* CH in-plane stretch
		11	Vinyl CH in-plane stretch
		17	Center CH stretch
3090	m	9	CH_2 out-of-phase symmetric stretch

The Infrared Spectrum.—The spectral region from 5000 to 675 cm.$^{-1}$ was recorded on a Beckman IR-4 spectrometer using sodium chloride prisms. Solutions of 1,3,5,7-octatetraene in carbon tetrachloride, carbon disulfide and cyclohexane were run in 0.0150 cm. liquid cells. The spectrum from 675 to 300 cm.$^{-1}$ was obtained on a Perkin–Elmer Model 12-C spectrometer equipped with a cesium bromide prism using carbon tetrachloride solutions. An attempt to obtain a vapor spectrum failed due to the low vapor pressure and rapid rate of polymerization of octatetraene. The spectrum in carbon disulfide solution agreed with the previously published spectrum.[2] The observed infrared spectrum is listed in Table III and presented in Fig. 1.

---

(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) G. F. Woods and L. H. Schwartzman, This Journal, 71, 1396 (1949).

(3) Research Fellow, University of Maryland.

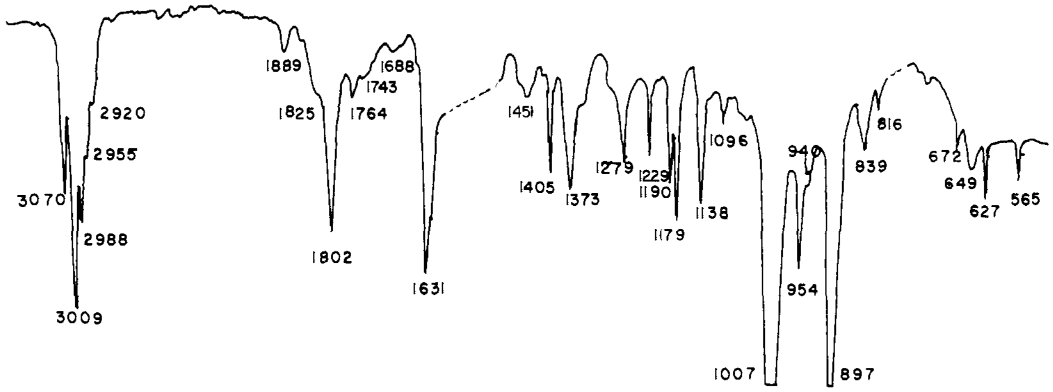

Fig. 1.—Infrared spectrum of 1,3,5,7-octatetraene.

Discussion

1,3,5,7-Octatetraene is relatively reactive, as shown by the fact that the solid polymerizes rapidly in air. In solution, however, this polymerization is reduced to an extent which depends on the nature of the solvent. Stability of this type of molecule depends upon the resonance energy associated with the conjugated bond system. In order that this resonance energy be at a maximum, the molecule must be planar. Octatetraene is relatively much more unstable than 1,3,5-hexatriene.[4]

TABLE III

ASSIGNMENT OF INFRARED FREQUENCIES

Cm.$^{-1}$	Intensity	Freq. no.	Type of vibration
. .		18	C—C out-of-plane deformation
. .		19	C=C out-of-plane deformation
. .		20	Complete skeletal deformation
565	w	38	Skeletal center angle bend
627	m	36	Skeletal middle angle bend
649	w,b	37	Skeletal terminal angle bend
672	vw		
816	w	24	CH_2 torsion
839	m	25	Central CH out-of-plane bend
897	s	23	CH_2 out-of-plane wag
940	vw		
954	m	22	*trans* CH out-of-plane bend
1007	s	21	Vinyl CH out-of-plane bend
1096	w	46	Central CH in-plane bend
1138	m	34	Asymmetric carbon single-bond stretch
1179	m	45	*trans* CH in-plane bend
1190	w		
1229	m	39	CH_2 rock
1279	m	47	Vinyl CH in-plane bend
1373	w,b		
1405	m	42	CH_2 bend
1451	w,b		
1631	s	33	Asymmetric in-phrase double-bond stretch
		35	Asymmetric out-of-phase double-bond stretch
1688	w		
1743	vw		
1764	w	14 + 36	1138 + 627 = 1765
1802	s	23 + 29	897 + 905 = 1802
1825	vw		
1889	w	21 + 31	1007 + 883 = 1890
2878	vw		
2920	vw		
2955	m	40	CH_2 in-phase asymmetric stretch
2988	s	43	*trans* asymmetric CH stretch
		48	Central asymmetric CH stretch
3009	s	44	Vinyl asymmetric CH stretch
3070	m,s	41	CH_2 out-of-phase asymmetric stretch

At least eighteen possible rotational geometrical isomers can be postulated for the structure of octatetraene, of which six are all-*trans* forms, six are all-*cis* forms and six are *cis–trans* forms. Fischer–Hirschfelder models indicate that only one of each type can be planar because of steric hindrance (see Fig. 2). Of these only the all-*trans* form is completely free of hindrance. However, the all-*cis* and *cis–trans* forms are not nearly as hindered as the other forms.

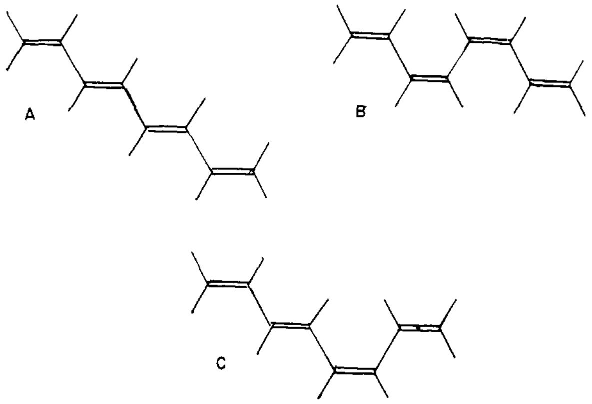

Fig. 2.—The possible planar structures of 1,3,5,7-octatetraene: A, the *trans–trans* form; B, the *cis–cis form;* C, the *trans–cis* form.

The planar *trans* and planar *cis* forms belong to the C_{2h} point group. The planar *cis–trans* form belongs to the C_{1h} point group. Table I lists the distribution of vibrations among the symmetry species with the selection rules for the C_{1h} and C_{2h} structures. If the molecule was the all-*trans* or the all-*cis* structure, 24 of the 48 fundamental vibrations would be active in the Raman and 24 in the infrared spectrum. The *cis-trans* structure would have 48 vibrations active in both the infrared and Raman spectra.

---

(4) E. R. Lippincott, C. E. White and J. P. Sibilia, THIS JOURNAL, **80**, 2926 (1958).

Twenty-two Raman bands were observed, of which 19 are in the regions expected for fundamental frequencies. The infrared spectrum showed 32 bands, at least eight of which could be assigned as non-fundamental frequencies. Only four of the observed Raman bands were coincident with bands in the infrared spectrum, within the experimental error of ± 5 cm.$^{-1}$. These are the bands at 958, 1138, 1185 and 3065 cm.$^{-1}$. This was sufficient evidence to eliminate the planar *cis–trans* form, as well as any non-planar structure.

In order to distinguish between the planar all-*cis* and planar all-*trans* forms, it was necessary to rely on group frequencies. Differences between the two structures can be expected to be observed in three general regions. These regions contain frequencies due to the C=C stretching vibrations, C=C—C bending vibrations and the C–H bending vibrations. The last was found to be the most useful in this structure determination.

A vapor spectrum would have been very helpful in the assignment of the vibrations to observed frequencies. The type of band obtained would indicate whether the vibration was an in-plane or out-of-plane type. Both the planar *cis* and *trans* forms would approximate a symmetric top molecule.

Frequency Assignment.—The tentative frequency assignment is based on the characteristic group frequencies of similar molecules such as ethylene,[5] 1,3-butadiene,[6] propylene,[7] 1,3,5-hexatriene[8] and the group frequencies listed in Herzberg[9] and Bellamy.[10]

The fundamental vibrations of octatetraene can be classified into five general groups. The region around 3000 cm.$^{-1}$ contains the C–H stretching frequencies. The C=C frequencies occur around 1600 cm.$^{-1}$. The C–C stretching frequencies occurs between 1100-1200 cm.$^{-1}$. C–H bending modes occur above and below 1000 cm.$^{-1}$. The last group, consisting of the skeletal bending or deformation vibrations, lies near and below 600 cm.$^{-1}$.

The selection rules for the all-*cis* and all-*trans* 1,3,5,7-octatetraene indicate that there should be ten C–H stretching modes, five of which should be infrared active and five, Raman active. There are four observed infrared bands and two observed Raman bands, so it is concluded either that there is accidental degeneracy or that the bands were not resolved by the instrument. The Raman spectrum contains a very broad band, centered about 3005 cm.$^{-1}$, which probably contains more than one frequency.

In ethylene, the asymmetric stretching vibration occurs at 3105.5 cm.$^{-1}$ in the infrared spectrum and 3075 cm.$^{-1}$ in the Raman spectrum. The corresponding symmetric stretching modes are at 2989.5 and 3019.3 cm.$^{-1}$, respectively. In propylene, these modes are assigned at 3090 and 3087 cm.$^{-1}$ for the asymmetric and 2991 and 2990 cm.$^{-1}$ for the symmetric vibrations. Two CH_2 asymmetric stretching frequencies of ocatatetraene are infrared active. These were assigned to 3070 cm.$^{-1}$ for the out-of-phase stretching vibration (ν_{41}) and 2955 cm.$^{-1}$ for the in-phase stretching vibration (ν_{40}). The corresponding symmetric frequencies, which are Raman active (ν_9 and ν_8), are assigned at 3090 and 3005 cm.$^{-1}$.

Bellamy lists the range of 3040–3010 cm.$^{-1}$ for the *trans* and vinyl C–H stretching vibration, with the vinyl being somewhat higher. In the infrared spectrum the vinyl mode (ν_{44}) was assigned to 3009 cm.$^{-1}$ and the *trans* mode (ν_{43}) at 2988 cm.$^{-1}$. Both the vinyl (ν_{11}) and *trans* (ν_{10}) stretching vibrations were assigned to 3005 cm.$^{-1}$ in the Raman spectrum. In hexatriene, the vinyl vibrations were assigned at 3040 cm.$^{-1}$ infrared and 3039 cm.$^{-1}$ Raman and the *trans* vibrations at 3012 and 3039 cm.$^{-1}$, respectively. These differences may be explained by the effect of conjugation in octatetraene. Also, in the infrared spectrum, an instrumental error of ± 15 cm.$^{-1}$ in the region above 2000 cm.$^{-1}$ is possible. The *trans* central C–H stretching modes were assigned at 2988 cm.$^{-1}$ in the infrared spectrum (ν_{48}) and 3005 cm.$^{-1}$ in the Raman spectrum (ν_{17}).

The next group to be assigned is the C=C stretching vibrations, which are usually assigned in the narrow range of 1640-1670 cm.$^{-1}$ for a non-conjugated system. For a conjugated system the frequency is lowered toward 1600 cm.$^{-1}$ with an increase of intensity. The selection rules associated with the all *trans* octatetraene indicate that there should be two infrared and two Raman active frequencies in this region. There are only two observed bands with suitable intensity for this assignment. The Raman active frequencies must be symmetric to the center of symmetry corresponding to in-phase (ν_1) and out-of-phase (ν_2) modes. The infrared active frequencies are the asymmetric in-phase (ν_{33}) and out-of-phase (ν_{35}) modes. (ν_1) and (ν_2) were assigned to the Raman band at 1608 cm.$^{-1}$. These low values definitely indicate the conjugated nature of the bond system in octatetraene. It is interesting that there is such a small interaction of (ν_1) with (ν_2) and also (ν_{33}) with (ν_{36}).

The infrared active asymmetric C–C stretching mode (ν_{33}) is assigned at 1138 cm.$^{-1}$. Two bands should occur in the Raman spectrum, the symmetric C–C in-phase stretching mode (ν_6) and the corresponding out-of-phase stretching mode (ν_3). This type of symmetric mode occurred in hexatriene at 1187 cm.$^{-1}$. Both (ν_3) and (ν_6) were assigned to the band at 1185 cm.$^{-1}$.

Carbon–hydrogen bending vibrations occur over a rather wide range and usually give highly characteristic absorption, independent of the nature of surrounding structure, in the region 1000-800 cm.$^{-1}$. The structure of octatetraene is such that there are some types of possible deformations or bendings which would not appear in simple related compounds.

There are four CH_2 bending modes for octatetraene. These are: the CH_2 in-plane bending mode

---

(5) 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).

(6) C. M. Richards and J. R. Nielsen, *J. Opt. Soc. Am.*, **40**, 438 (1950).

(7) R. C. Lord and P. Venkateswarlu, *ibid.*, **43**, 1079 (1953).

(8) Lippincott, White and Sibila, ref. 4.

(9) Herzberg, ref. 5.

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

the CH_2 rocking mode, which is also an in-plane motion; the CH_2 wagging mode, an out-of plane motion; and the CH_2 torsional mode. A rocking type of motion requires less energy than a bending type of motion for a corresponding displacement, so the rocking vibration would be expected at a lower frequency. Similarly, an out-of plane bending vibration would be observed at a lower frequency than an in-plane vibration.

For ethylene, the infrared active CH_2 vibration is an asymmetric in-plane bending mode and is assigned at 1444 cm.$^{-1}$. The Raman band at 1342 cm.$^{-1}$ is assigned to the symmetric in-plane bending mode. The same vibrations in propylene are assigned at 1419 cm.$^{-1}$ in the infrared spectrum and at 1415 cm.$^{-1}$ in the Raman spectrum. Similar vibrations for 1,3-butadiene are assigned at 1484 and 1442 cm.$^{-1}$, respectively. For hexatriene these bands occur at 1429 and 1394 cm.$^{-1}$. It is noted that the bands in hexatriene are somewhat lower than those of simpler molecules. Octatetraene has an infrared band at 1405 cm.$^{-1}$, and a Raman band at 1432 cm.$^{-1}$. The infrared active CH_2 in-plane asymmetric bending (ν_{42}) was assigned to the band at 1405 cm.$^{-1}$. The band at 1432 cm.$^{-1}$ in the Raman spectrum was assigned to the CH_2 in-plane symmetric bending mode (ν_{12}).

Another fairly well defined CH_2 mode is the wag or out-of-plane deformation, which occurs in the 915-905 cm.$^{-1}$ frequency range. For ethylene the symmetric out-of-plane CH_2 wag is assigned at 943 cm.$^{-1}$ in the Raman spectrum. The similar asymmetric vibration is assigned to the band at 949 cm.$^{-1}$. The corresponding bands in 1,3-butadiene occur at 911 cm.$^{-1}$ and 909 cm.$^{-1}$. Similarly in 1,3,5-hexatriene the bands occur at 897 cm.$^{-1}$ in the Raman spectrum and 899 cm.$^{-1}$ in the infrared spectrum. With the exception of butadiene, these are close to, but not in the accepted range. Therefore, some variation could be expected in the observed frequencies of octatetraene. An infrared band was observed at 897 cm.$^{-1}$, which was assigned to the CH_2 asymmetric wagging vibration (ν_{23}). A Raman active band at 905 cm.$^{-1}$ was assigned as the corresponding symmetric mode (ν_{29}).

Rocking motions of the CH_2 group are not as well defined as are the previous type of deformations. A band at 1229 cm.$^{-1}$ in the infrared spectrum of propylene was assigned to this mode, as is the band at 1290 cm.$^{-1}$ in 1,3-butadiene. The assignment of 1,3,5-hexatriene indicates two possible CH_2 rocking vibrations. The infrared active vibration is assigned at 1255 cm.$^{-1}$ and the Raman active mode at 1135 cm.$^{-1}$. For octatetraene, an infrared band at 1229 cm.$^{-1}$ is assigned as the CH_2 asymmetric rocking vibration (ν_{39}) and the Raman band at 1138 cm.$^{-1}$ is assigned as the CH_2 symmetric rocking vibration (ν_{14}).

The last CH_2 modes to be considered are the torsional motions. This frequency for propylene occurs at 578 cm.$^{-1}$. 1,3-Butadiene has two vibrations of this type assigned at 578 cm.$^{-1}$ (infrared) and 580 cm.$^{-1}$ (Raman). The 1,3,5-hexatriene torsion modes are somewhat higher, 658 and 758 cm.$^{-1}$, respectively. It is therefore reasonable to assume that the bands in octatetraene might be even higher in frequency. The CH_2 asymmetric torsional mode (ν_{24}) is assigned to the infrared band at 816 cm.$^{-1}$ and the symmetric torsional mode (ν_{30}) to the Raman band at 722 cm.$^{-1}$.

Other carbon–hydrogen deformations that occur are associated with the vinyl group, the *trans* double-bond group and the central carbon–carbon bond. The selection rules for octatetraene indicate that there would be four modes associated with each of these types of motion. Here again the symmetric vibrations would be Raman active and the asymmetric vibrations infrared active.

Most references give the vinyl and *trans* C–H in-plane deformations in the same frequency range; about 1310–1290 cm.$^{-1}$. For butadiene the vinyl in-plane bending mode occurs at 1309 cm.$^{-1}$ and the out-of-plane mode at 890 cm.$^{-1}$, both of which are Raman active vibrations. For hexatriene the vinyl C–H-in-plane bending mode is assigned to the frequencies at 1429 cm.$^{-1}$ (infrared) and 1280 cm.$^{-1}$ (Raman) corresponding to asymmetric and symmetric motions, respectively. The vinyl out-of-plane vibrations are given as 1011 and 889 cm.$^{-1}$. For octatetraene, the infrared vinyl C–H in-plane bending mode (ν_{47}) is assigned to 1279 cm.$^{-1}$ and the out-of-plane mode (ν_{21}) to 1007 cm.$^{-1}$. The Raman active in-plane bending mode (ν_{15}) for the vinyl group is assigned to 1304 cm.$^{-1}$ while the out-of-plane vinyl bending mode (ν_{31}) is assigned at 883 cm.$^{-1}$.

The *trans* C–H out-of-plane bending mode occurs between 970 and 960 cm.$^{-1}$.[11] However, conjugation shifts this frequency. Allan, Meakins and Whitney[12] state that conjugation of a *trans* double bond with a vinyl group increases the *trans* group frequency. As evidence of this effect Bickford, *et al.*,[13] have shown that for α- and β-eleostearic acid the *trans* frequency occurs at 10.03 μ or 997 cm.$^{-1}$. Jackson, *et al.*,[14] have shown that for a *trans–trans* conjugated linoleate, the *trans* frequency occurs at 988 cm.$^{-1}$, while for the *cis–trans* linoleate two bands are present (948 and 982 cm.$^{-1}$). However, the *trans–trans*- and the *cis–trans* - 1, 4 - diacetyl - 1,3 - butadiene spectra[15] showed a band of medium to weak intensity at 940–945 cm.$^{-1}$, which was not present in the *cis–cis* compound. *trans*-1,3-Pentadiene[16] exhibits a medium band at 949 cm.$^{-1}$ in addition to a very strong vinyl P.Q.R. band at approximately 1017, 1002 and 985 cm.$^{-1}$, respectively, for the vapor. It is possible that this strong band obscures the *trans* band which is increased because of conjugation. Investigations by Allan, *et al.*,[17] on 2,6-

---

(11) Bellamy, ref. 10.

(12) J. L. H. Allan, G. D. Meakins and M. C. Whitney, *J. Chem. Soc.*, 1874 (1955).

(13) W. E. Bickford, E. F. DuPré, C. H. Mack and R. T. O'Connor *J. Am. Oil Chem. Soc.*, **30**, 376 (1953).

(14) J. E. Jackson, R. F. Paschke, W. Tolberg, H. M. Boyd and D. H. Wheller, *ibid.*, **29**, 229 (1952).

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

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

(17) Allan, Meakins and Whitney, ref. 12.

TABLE IV

COMPARISON OF ASSIGNMENT WITH THAT OF RELATED COMPOUNDS

Vibration type	Activity	C_8H_{10}	C_6H_8	C_2H_4	C_3H_6	C_4H_6	Group freq. range
CH_2 out-of-phase stretch	I.R.	3070	3091	3105.5	3090	3100	3095–3075
	R.	3090	3085	3075	3087		
Vinyl CH stretch	I.R.	3009	3040		3013	3060	3040–3010
	R.	3005	3039		3010		
trans CH stretch	I.R.	2988	3012				3040–1010
	R.	3005	3030		3010		
Center CH stretch	I.R.	2988					
	R.	3005					
CH_2 in-phase stretch	I.R.	2955	2953	2989	2991	3000	
	R.	3005	2989	3019	2990		
Double-bond st.	R.	1608	1623	1623	1648	1643	1640–80
Out-of-phase C=C stretch	R.	1608	1573			(1599)	1600
C=C asymmetric in-phase st.	I.R.	1631	1623		1652		
C=C asymmetric out-of-phase st.	I.R.	1631					
CH_2 bend	I.R.	1405	1443	1444	1419	1484	
	R.	1432	1394	1342	1415	1442	1410–20
Vinyl CH bend	I.R.	1279	1294				1310–1290
	R.	1304	1280	1250		1309	1200–1300
CH_2 rock	I.R.	1229	1255		1229	1290	
	R.	1138	1135				
trans CH in-plane bend	I.R.	1179	1166				1310–1295
	R.	1243	1238				1310–1290
trans center CH in-plane bend	R.	1185					
Asymmetric C–C stretch	I.R.	1138	1130		920	1205	Inc. by conj
	R.	1185	1187		920	1205	
Center CH asymmetric out-of-plane bend	I.R.	1096					
	R.	1080					
Vinyl CH out-of-plane bend	I.R.	1007	1011				995–985
	R.	883	899			890	
trans CH out-of-plane bend	I.R.	954	941				970–960
	R.	958	828				
CH_2 wag	I.R.	897	899	949	912	909	915–905
	R.	905	897	943		911	
trans center CH out-of-plane bend	I.R.	839					
CH_2 torsion	I.R.	816	658		578	520	
	R.	722	758		580	686	
Skeletal terminal angle bend	I.R.	649	590		417		
	R.	528	411		432		
Skeletal middle angle bend	I.R.	627					
	R.	470					
Skeletal central angle bend	I.R.	565	540				
	R.	288	411		432		
Skeletal out-of-plane bend	I.R.	Low	475				
	R.	223	347				
Skeletal in-phase deformation	I.R.	Low					
	R.	223					

NOTE: C_8H_{10}—1,3,5,7-Octatetraene
C_6H_8—1,3,5-Hexatriene
C_2H_4—Ethylene
C_3H_6—Propylene
C_4H_6—1,3-Butadiene

dimethyl-1,3,5,7-octatetraene and 2,5-dimethyl-1,3,5-hexatriene indicated the *trans* C–H band in these compounds occurred at 959 cm.$^{-1}$. For hexatriene, the *trans* C–H in-plane bending vibrations are located at 1166 and 1238 cm.$^{-1}$, while the corresponding out-of-plane vibrations are assigned to the bands at 941 and 928 cm.$^{-1}$.

The spectrum of octatetraene exhibits a medium band at 954 cm.$^{-1}$ and a very strong band at 1007 cm.$^{-1}$, which indicates a similarity to *trans*-1,3-pentadiene. Therefore, the band at 954 cm.$^{-1}$ was assigned to the *trans* C–H out-of-plane band (ν_{22}). The band observed at 1179 cm.$^{-1}$ is assigned to the in-plane *trans* asymmetric vibration (ν_{45}). Raman bands at 1243 cm.$^{-1}$ and 958 cm.$^{-1}$ are assigned to the symmetric in-plane (ν_{13}) and out-of-plane (ν_{28}) *trans* C–H bending vibrations respectively. Another possible assignment, which the authors recognize, is that the *trans* frequency may be high and hidden by the strong band at 1007 cm.$^{-1}$. The band at 954 cm.$^{-1}$ is then assigned to the central C–H out-of-plane bending mode, and the band at 839 cm.$^{-1}$ is assigned to the CH_2 torsional mode. However, we are reluctant to assign a frequency observed near the characteristic *trans* group frequency position to another vibration

A number of bending vibrations occur in octatetraene that would not occur in simpler molecules because there are two *trans* double bonds. Since an out-of-plane mode is lower than a corresponding in-plane mode, the band at 839 cm.$^{-1}$ was assigned as the C–H out-of-plane asymmetric deformation (ν_{25}). The band at 1096 cm.$^{-1}$ was assigned to the C–H in-plane asymmetric deformation (ν_{46}). The 1185 cm.$^{-1}$ band in the Raman spectrum was assigned as the *trans* C–H in-plane symmetric vibration (ν_{16}). The Raman band at 1080 cm.$^{-1}$ was assigned to the corresponding out-of-plane vibration (ν_{32}).

Skeletal deformations comprise the last large group of frequencies to be assigned. This type of vibration is usually found in the low frequency region of the spectrum. The selection rules for octatetraene indicate that there should be eleven observed skeletal deformations, five of which are Raman active and six, infrared active. It is possible, that several of these infrared frequencies lie below the range of available prism materials.

Hexatriene contains terminal and central angle in-plane bending modes which were assigned at 590 and 540 cm.$^{-1}$, in the infrared spectrum, respectively. The Raman active symmetric modes were assigned at 528 and 411 cm.$^{-1}$. The corresponding frequencies for the terminal angle bending motion (ν_{37} and ν_4) of octatetraene were assigned to bands at 649 and 528 cm.$^{-1}$. The central angle bending vibrations (ν_{38} and ν_7) were assigned at 565 and 288 cm.$^{-1}$. The symmetric and asymmetric middle angle bending modes (ν_5 and ν_{36}) were assigned at 470 and 627 cm.$^{-1}$, respectively.

The remaining skeletal deformations are the out-of-plane vibrations. These would be expected at lower frequencies than the in-plane type. The selection rules indicate three out-of-plane deformation frequencies should be observed in the infrared spectrum. Since there are no bands observed below 565 cm.$^{-1}$, it is concluded that these frequencies lie below the range of a CsBr prism. The remaining unassigned bands are three asymmetric skeletal deformation frequencies (ν_{18}, ν_{19} and ν_{20}). The Raman active symmetric skeletal deformations (ν_{26} and ν_{27}) are assigned to the band at 223 cm.$^{-1}$. Schematic diagrams of the modes of vibration of octatetraene are given elsewhere.[1] Tables II and III summarize this tentative frequency assignment. Table IV lists the assignment for this compound along with the assignment for related compounds.

Conclusions

The vibrational spectra of 1,3,5,7-octatetraene indicate that it is the all-*trans* structure. The lack of a sufficient number of coincidences between the infrared and Raman spectra rules out the combination *cis–trans* form and non-planar structures. The strong band in the accepted *trans* C–H frequency range, the lack of evidence for *cis* double bonds and the close relationship to the spectra of 1,3,5-hexatriene indicate but do not conclusively prove the presence of the all-*trans* configuration.

A number of weak bands are unassigned in both the infrared and Raman spectra. It is felt that these do not correspond to any fundamental frequencies of octatetraene. Quite a few are due to overtones and combination and difference tones. It is possible but improbable that some are due to small amounts of impurities in the octatetraene.

Acknowledgment.—The authors wish to express their sincere appreciation to Professor G. Forrest Woods and Frank Scotti for the method of preparation and guidance in the preparation of the sample of 1,3,5,7-octatetraene. A grant in aid from the National Science Foundation is gratefully acknowledged.

College aPrk, Maryland

[Contribution from the Department of Chemistry, Emory University]

Proton Magnetic Resonance Spectra of Propargyl Halides

By E. B. Whipple, J. H. Goldstein, Leon Mandell, G. S. Reddy and G. R. McClure

Received September 23, 1958

A reference procedure for measurement of relative intramolecular proton shieldings based on extrapolation to infinite dilution in saturated hydrocarbon solvents is used to (1) study the effects of solvent on the proton spectrum of propargyl bromide; and (2) measure the relative shieldings and long-range spin couplings in a series of propargyl halides. The medium shifts thus observed show a parallel with infrared stretching frequencies in the same solvents which suggests that intermolecular "H-bonding type" association is largely responsible for n.m.r. medium shifts in non-aromatic solvents. In a series of propargyl halides it is observed that the trans-acetylenic coupling and acetylenic proton shielding are virtually insensitive to the particular halogen substituent, which is taken to indicate that resonance forms involving the acetylenic π electrons are relatively unimportant in the propargyl system.

Following the original work of Meyer and Gutowsky[1] there have been various efforts to correlate nuclear magnetic resonance (n.m.r.) shifts in organic compounds with the qualitative predictions of electronic theory on the assumption that the chemical shielding tensor,[2] σ_i, arises principally from those electrons in the immediate vicinity of the nucleus under observation. More recent theoretical developments point, however, to the importance of "long range" shieldings in proton spectra,[3,4] and the acetylenic bond has been treated as a particular case in point.[5] In spite of the theoretical interest, comparatively few experimental

---

(1) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(2) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **86**, 243 (1952).

(3) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(4) J. A. Pople, *Proc. Roy. Soc. (London)*, **A239**, 541 (1957).

(5) Pople, *ibid.*, **A239**, 550 (1957).