

THE INFRARED SPECTRA OF 1-DECENES DEUTERATED ON THE DOUBLE BOND. A COMPARISON WITH THE VINYL HALIDES- d_x

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The absorption spectra ($4000-200\text{ cm}^{-1}$) of the seven species deuterated on the C=C bond were measured in the liquid state. The interpretation of the spectra was focused on behaviour of characteristic group frequencies of the vinyl group after selective deuteration, namely on the out-of-plane deformation =C—H vibrations. The assignment of the strongest bands in the $1000-400\text{ cm}^{-1}$ region was carried out on the basis of analogy with the published results for gaseous vinyl halides and their deuterated species. Moreover, the characteristic and analytical bands were compiled for mono- and di-deuterated *cis* or *trans* internal double bond. This complete set of data affords a tool for analysis of mixtures by infrared spectroscopy which, in this respect, appears superior to mass or $^1\text{H-NMR}$ spectroscopy.

In the course of studies of elimination reactions, a full series of individual 1-decenes deuterated on the double bond was synthesized¹. Up to now, the only studied compounds had been liquid *trans*-1-deuterio-1-hexene, 2-deuterio-1-hexene, *cis*-1,2-dideuterio-1-hexene (Raman, infrared from 200 cm^{-1})², and *cis*-1-deuterio-1-hexene (infrared from 700 cm^{-1})³. Furthermore, *cis*- or *trans*-monodeuteriostyrene (from 700 cm^{-1})⁴, and gaseous⁵ propene- d_6 had been studied in the infrared. The highest possible symmetry of planar molecules of an n-alkene is C_s . Any rotational isomerism in the alkyl substituent of the ethylene moiety causes lowering of molecular symmetry to C_1 , i.e. all vibrations become symmetrical and Raman polarized⁶. Generally, there are three normal out-of-plane (o-o-p) deformation vibrations (A'' for C_s) of the =C—H bonds which are called⁷ the twisting of *trans* HC=CH or C=C, the wagging of =CH₂, and the o-o-p bending of the lone =C—H or recently⁸, the wagging of =CHX where X is a substituent. Strong infrared bands associated with the first two vibrations are classified as characteristic bands or good characteristic group frequencies⁷. This does not hold⁷ for the last vibration because of vibrational coupling with the twisting mode. However, the corresponding frequency (varying in a wide interval, say $650-400\text{ cm}^{-1}$) had been found⁹ to be conformationally sensitive. Two infrared bands observed for liquid n-alkenes have revealed⁹ the presence of at least two rotamers.

The aim of this work was to find and assign analytical infrared bands for alkenes deuterated on the C=C bond.

EXPERIMENTAL

The studied compounds were prepared from 1-decyne- d_0 or 1-deuterio-1-decyne by Brown hydroboration synthesis; the details will be given elsewhere¹. The deuterium isotopic purity of the individual 1-decenes- d_x was determined by mass spectrometry from the intensity of the molecular peak. The results are summarized in Table I. The compound purity (*i.e.* absence of decenes other than 1-decenes) was checked by vapour-phase chromatography (VPC).

It is clear from Table I that the determination of isotopic purity does not reveal the so called "deuterium-atom-position" purity with the species d_1 or d_2 . This characteristic was judged from the overall stereospecificity of the synthetic reaction¹ and from a pattern of the spectrum in the 1000–700 cm^{-1} region. A minimal number of strong bands in this interval was the criterion. In view of this, bands of impurities were searched out in our 1-decenes- d_x in the following order of compounds: III, I and II, V, IV, VI, VII.

The infrared spectra were taken on a Perkin-Elmer grating spectrophotometer, model 621. The precision of wavenumber scale in the 1100–600 cm^{-1} region was checked¹⁰ by NH_3 and CO_2 , being about +0.8 cm^{-1} . The tracking accuracy of recordings was checked with the spectrum 3100–700 cm^{-1} of a polystyrene film¹⁰, recorded at the same conditions as our samples. The overall error in the positions of absorption maxima is believed to be $\pm 1 \text{ cm}^{-1}$ except the bands below 650 cm^{-1} where it amounts to $\pm 2 \text{ cm}^{-1}$. The spectral slit width was about 0.6 cm^{-1} in the 1000–600 cm^{-1} region.

The maximal absorbances of the analytical bands in the 1000–700 cm^{-1} region were determined by base-line technique. The line was chosen parallel to the abscissa, going through the point of the lowest absorption near 600 cm^{-1} in each spectrum. For the whole series, the position of this line ranged between 91–98% of transmission. Then, the experimental absorbances were re-calculated with the aid of computer to 100% isotopic purity of the individual species. The absorptivities of the analytical bands were calculated under the assumption that density of 1-decene is the same for all the deuterated species. In view of the fact that samples were not thermostated and their temperature could range between 22–35°C during the infrared measurements, the density¹¹ for 1-decene was taken to be 0.733 g/ml. From the molecular weights 140.27, 141.28, 142.28, and 143.29 for d_0 -, d_1 -, d_2 -, and d_3 -species respectively, the corresponding concentrations 5.23, 5.19, 5.15, and 5.12 mol/l were used in calculations. The thickness of the KBr-cell was $0.00183 \pm 0.00002 \text{ cm}$. The apparent maximal molar absorptivities are presented to three significant figures only. The spectrum of non-deuterated 1-decene was also measured and it was identical with that of the standard¹². The numerical separations of overlapped bands were performed on an Elliott 503 digital computer, the program was written in Algol 503 Mk I language.

RESULTS

The infrared spectra of the liquid 1-decenes- d_x (I–VII) are presented in Fig. 1 together with the exact positions of stronger bands. Absorptions belonging to impurities (according to mass spectra) were left in the spectrograms and they are designated by their roman numerals (Table I).

The assignment of the three $=\text{C}-(\text{H,D})$ o-o-p deformation frequencies of the vinyl group in 1-decenes- d_x is given in Table II being based on comparison with the published results for vinyl halides and their deuterated species. The assignment for vinyl chloride⁸ and the approximate mode of vibrations based on the calculated potential energy distribution⁸ (column 2), were taken as the reference data.

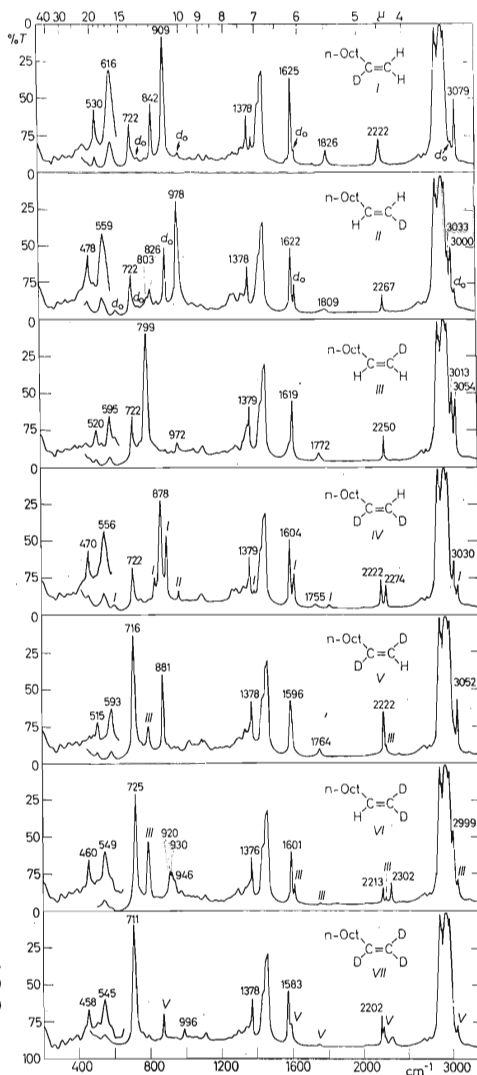


FIG. 1
Infrared Spectra of Liquid
1-Decenes I—VII (3300 to
 450 cm^{-1} for the thickness
 0.00183 cm KBr , $650\text{--}200$
 cm^{-1} for 0.0890 cm CsI)

TABLE I

Isotopic Purity of 1-Decenes- d_x (I--VII) and 1-Decyne- d_1 According to their Mass Spectra

Compound	Type	Isotopic purity, mol. %			
		d_0	d_1	d_2	d_3
I	2- d_1	6.6	93.4	0	0
II	trans-1- d_1	16.4	83.6	0	0
III	cis-1- d_1	0.6	99.4	0	0
IV	cis-1,2- d_2	0.6	26.8	72.6	0
V	trans-1,2- d_2	0.7	9.3	89.4	0.6
VI	1,1- d_2	0.3	22.4	77.3	0
VII	1,1,2- d_3	0.9	1.3	25.7	72.1
VIII	1- d_1	max. 2 ^a	min. 98	0	0

^a According to infrared spectroscopy.

The experimental A'' -frequencies for vinyl fluorides- d_x ¹³ and bromides- d_x ¹⁴ were re-grouped (columns 3,5) by us according to vinyl chloride (column 4). An obvious trend (column 6) of the frequencies for each vibration in the series F → Cl → Br* makes the starting point for our assignment of the bands from the 1000–400 cm⁻¹ region of the published spectra of vinyl iodide, 1-hexenes- d_x , propene- d_6 (column 7), and of our 1-decenes- d_x . The planar structure of the vinyl halides is doubtless fact, the assumption⁹ of this symmetry for one of the rotamers (methyl group in *cis*-position with respect to the C=C bond) was confirmed by the microwave study¹⁵ of 1-butene. The other conformer(s) are non-planar. Such a distinction between the planar and non-planar carbon skeleton C₍₈₎—C=C is made in columns 8,9 on the basis of the decreasing trend of the lowest frequency for each species. To check the assignment of the wagging =CH₂ vibration, the frequency of its first overtone was also included in the Table II (column 10 denoted 2 × *wag*). The last column collects very weak bands which we interpret as a binary combination frequency wagging + twisting (measured in the thicker cell).

With the first compound, the non-deuterated species, there are no difficulties with the assignment, despite the uncertainty in the trend for the twisting vibration. The re-assignment of the experimental frequencies¹⁶ for vinyl iodide had been already proposed^{7,8}.

With compound I, our assignment is supported by that of Hoffmann² for 2-deuterio-1-hexene. The infrared value² for the 2 × *wag* is 1826 cm⁻¹.

* The chosen order from F to Br and further to n-octyl group stems from the expectation that trends of the frequencies will follow the decreasing polarity of the substituent and not the increasing mass (it should also be valid for lighter alkyl groups, e.g. in 1-hexenes- d_x).

Our assignment of the twisting mode for compound *II* is again confirmed by Hoffmann's one and also by a strong characteristic band at 978 cm^{-1} for *trans*-1-deuterio-2-phenylethylene⁴. As to the wagging $=\text{CH}_2$ motion, here exists the only case where the trend of frequencies is opposite to that with the other compounds (column 6). However, it is necessary to point out here that the experimental positions of Q-branches for $\text{DHC}=\text{CHF}$ and $\text{DHC}=\text{CHBr}$ had not been read^{13,14} from the spectra of individual species but of gaseous mixtures of the isomers *cis* and *trans*. The frequencies therefore can be badly influenced by overlapping of an increased number of bands. There are two weak infrared bands at 833 and 805 cm^{-1} for *trans*-1-deuterio-1-hexene³. The first of them is preferred² as the wagging frequency. This is supported by the characteristic band⁴ at 845 cm^{-1} for the above mentioned styrene- d_1 . We incline to the Hoffmann's suggestion² of the higher frequency which we support by the summation band $978 + 826 = 1804$, being closer to our experimental value 1809 cm^{-1} (corresponding infrared band in the 1-hexene- d_1 is at 1813 cm^{-1})².

With compound *III*, difficulties with the trend of the twisting frequency seem to exist again. The explanation is in footnote^h in the Table. There are two weak, unassigned bands at 917 and 975 cm^{-1} in the spectrum³ of the hexene- d_1 . We prefer the value at higher wavenumbers. Our assignment of the wagging frequency is supported by the band at 808 cm^{-1} for *cis*-1-deuterio-2-phenylethylene⁴. Another supporting evidences are the shoulder at 1605 cm^{-1} ($2 \times \text{wag}$) and the summation band 1772 cm^{-1} (in the corresponding 1-hexene³ at 1764 cm^{-1}).

Compound *IV* represents the first puzzle in searching the third o-o-p frequency, the twisting one (*cf.* also²), for the assignment of the wagging mode is straightforward through $2 \times \text{wag}$ band (in the 1-hexene- d_2 at 1748 cm^{-1})². See footnoteⁿ. The absence of any band may preclude appearance of a band for ($\text{tw} + \text{wag}$).

With compound *V* the assignment of the $\text{H}_2\text{C} = \text{wag}$ is clear through the trend and the band of $2 \times \text{wag}$. The summation band at 1610 cm^{-1} is uncertain because of isotopic impurity *III*.

Compound *VI* is the second puzzle (*cf.* *IV* above). The assignment of the wagging mode is possible only with the aid of the trend. See footnotes^{l,p}.

The last compound *VII* represented the greatest difficulty. Whilst the trends for the d_3 -species enable to re-assign the published⁵ *twist* and *wag* frequencies for propene- d_6 , there is no such a guide for 1-decene- d_3 because both combination bands are obscured. The single band at 711 cm^{-1} must be clearly composed of the three components (*tw* and *wag* $\text{H}_2\text{C} =$ plus *rock* $(\text{CH}_2)_7$; Fig. 2).

1-Deuterio-1-decyne (*VIII*) has only two interesting frequencies: stretching (2597 cm^{-1}) and bending (491 cm^{-1}) $\equiv \text{C}-\text{D}$.

It follows from Table II that the pair of the lowest frequencies is mass-dependent. It had been noted⁹ that this pair is connected with vibrational motions of the terminal $\text{H}_2\text{C} =$ group only, for one band only is present in the spectra of 2,2-dialkyl-

TABLE II
Assignment of the o-o-p Frequencies (cm^{-1}) of the Vinyl Group in 1-Decenes- d_x

Com- pound ^a	Vibr. mode ^b	F^c, d	Cl^e	Br^c, f	Trend ^g	Others ⁱ	n - Octyl				
							C_s^m	C_1^m	$2 \times \text{wag}^r(\text{tw} + \text{wag})^v$		
d_0	<i>tw</i>	931	943	942	?	946 ^c	991				
	<i>wag</i>	863	897	902	up	909 ^c	909		1 825	1 980	
	<i>out</i>	711	621	583	down	(435)	551	633	[1 818]	[1 900]	
I	<i>tw</i>	791	803	802	?	846	842				
	<i>wag</i>	867	900	906	up	910	909		1 826	1 750	
	<i>out</i>	683	590	551	down	530, 613	530	616	[1 818]	[1 751]	
II	<i>tw + out</i>	926	937	940	up	985	978				
	<i>wag</i>	815	815	811	down	805, 833	809, 826		— ^s	1 809	
	<i>tw + out</i>	576	511	485	down	477, 554	478	559	{1 618} {1 652}	{1 787} {1 804}	
III	<i>tw + out</i>	910	922	(918)	up? ^h	917, 975	972				
	<i>wag</i>	785	790	793	up	799	799		sh 1 605 ^f	1 772	
	<i>out + tw</i>	642	573	541	down	NM ^j	520	595	[1 598]	[1 771]	
IV	<i>out + tw</i>	726	722	719	down	?	? ⁿ				
	<i>wag</i>	844	866	872	up	877	878		1 755	?	
	<i>out + tw</i>	575	506	476	down	468, 548	470	556	[1 756]	[?]	
V	<i>tw + out</i>	695	690	691	?	— ^k	716 ^o				
	<i>wag</i>	844	850	856	up	— ^k	881		1 764	1 610	
	<i>out + tw</i>	639	567	531	down	— ^k	515	593	[1 762]	[1 597]	
VI	<i>out + tw</i>	888	882	871	down	? ^l	? ^p				
	<i>wag</i>	693	717	724	up	728 ^c	725		— ^u	— ^s	
	<i>tw + out</i>	564	494	465	down	NM ^j	460	549	[1 450]	[?]	
VII	<i>tw</i>	675	690	691	up	712 ^c	} 711 ^o				
	<i>wag</i>	728	730	732	up	734 ^c				— ^u	— ^u
	<i>tw + out</i>	563	491	462	down	434 ^c		458	545	[1 422]	[1 422]

^aSymbol d_0 represents the non-deuterated species for the substituents in columns 3—5 and 7—11; for roman numerals see Table I. ^bStrictly valid for vinyl chlorides- d_x only; based on their calculated⁸ potential energy distribution. Meaning of abbreviations: *tw*, twisting C=C, *wag*, wagging (D,H)₂C=C or HDC=C, *out*, out-of-plane deformation of the lone (D,H)C=C. The sum *tw + out* means the coupled vibrations. ^cExperimental infrared frequencies for gas, positions of Q-branches. ^dRef.¹³ ^eProbable values estimated from the experimental and calculated data⁸. ^fRef.¹⁴; numbers in parentheses generally mean the frequency of a Raman line of liquid. ^gIt denotes the obvious trend of the frequencies in the series vinyl-F→Cl→Br. ^hRef.¹⁶: In the series of vinyl halides it "is often found that the Raman frequencies of the liquid tend to be slightly

ethylenes¹⁷. We agree with this statement, with the stipulation, that if the third H or D atom is attached to a C=C bond (*i.e.* in 1-alkenes) then its o-o-p vibrational motion is also involved in the corresponding mode of the terminal H₂C= group.

Generally, the in-plane bending modes of the vinyl group were not found and

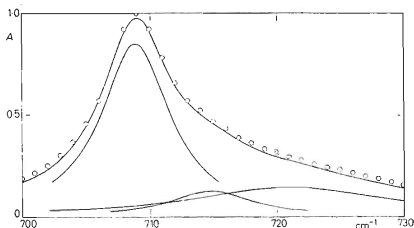


FIG. 2

Numerically Resolved Band of VII near 710 cm^{-1} (cell thickness 0.00183 cm)

○ Sums of the resolved bands.

Continued from p. 3754.

smaller than the corresponding frequencies in the infrared.”. ⁱData for the d_0 -species belong to vinyl iodide¹⁶, I, II, IV (ref.²), III (ref.³) are for liquid 1-hexenes- d_x , VI (ref.²⁸) is for propene-1,1- d_2 , VII (ref.⁵) is for propene- d_6 . ^jNM — not measured. ^kNo available data. ^lDespite the trend, there is no band near 850 cm^{-1} . Farina had found²⁹ unexpected strong band at 900 cm^{-1} and compared it with the band at 820 cm^{-1} of trialkylethylenes. ^mSymbols C_s and C_1 denote the respective point groups of symmetry. The first two numbers for each species are common for both symmetries. ⁿAccording to the trend, a band should be near 720 cm^{-1} where is the band of the rocking vibration of $-(\text{CH}_2)_7-$ at 722 cm^{-1} . The latter has “usual” intensity (Fig. 1) in the contrary to the other cases (Fig. 1). ^oSuperimposed on the band at 722 cm^{-1} . The bands could not be resolved even at a higher resolution but they were separated by computer (Table IV and Fig. 2.) ^pSee Fig. 1: There is no band in the 900—800 cm^{-1} region, however, the three unexpected bands 920, 930, and 946 cm^{-1} not corresponding to the trend are present. *Cf.* footnote^l. ^rThe number in square brackets means the twice of the experimental wagging frequency, the first is the experimental band position. ^sThe band is obscured by the C=C band. ^tSymbol sh means the shoulder 1610—1600 cm^{-1} on the C=C band, (Fig. 1), resolved by computer at 1599 cm^{-1} . ^uIf the band exists then is obscured by the band at 1450 cm^{-1} . ^vThe number in square brackets means the sum of experimental frequencies ($tw + wag$), the first is the experimental band position, measured at the cell thickness 0.0890 cm CsJ.

searched in the spectra 1-7.* These are (all wavenumbers for d_0 -species): scissoring $\text{H}_2\text{C}=\text{C}$ (near 1420 cm^{-1} , after deuteration could be obscured by the 1378 cm^{-1} band), deformation $\begin{matrix} \text{C} \\ \diagup \\ \text{H} \end{matrix} \text{C}=\text{C}$ (between $1300\text{--}1200\text{ cm}^{-1}$, clearly too weak), rocking $\text{H}_2\text{C}=\text{C}$ (somewhere near 1000 cm^{-1} , very weak), and deformation $\text{C}=\text{C}=\text{C}$ (about 430 cm^{-1} , very weak in higher 1-alkenes).

It is clear from the spectra that the $\text{C}=\text{C}$ stretching mode (near 1600 cm^{-1}) is to some extent also mass-dependent. From this follows that the $\text{C}=\text{C}$ frequency is coupled with the stretching motion of the $=\text{C}-\text{D}$ bonds. The problem had been treated in more detail by Bellamy¹⁸. Conclusions from the position and number of the $=\text{C}-\text{D}$ stretching bands can be drawn directly from our spectra.

The o-o-p vibrations of $=\text{C}-(\text{H}, \text{D})$ were found to have characteristic frequencies for the isotopically substituted vinyl group. The corresponding strongest peaks ($1000\text{--}600\text{ cm}^{-1}$) were chosen as a tool for quantitative analysis of mixtures of 1-decenes- d_x during studies of elimination reactions¹. A computer program for maximal absorbances was written for this purpose¹. The experimental absorbances, apparent maximal molar absorptivities, and shapes of these analytical bands are summarized in Table III, along with their half-band widths, $\Delta\nu_{1/2}$, for the Lorentzian ones (column 6). If the band is asymmetrical (\swarrow or \searrow), the two numbers are presented. For instance, the half-band width $-5 + 10$ means $\Delta\nu_{1/2} = 15\text{ cm}^{-1}$, 5 cm^{-1} being from lower wave numbers to the band axis, 10 cm^{-1} from the axis to the higher wave number wing. From combination of all these data and from the mass analysis of the isotopic species, the stereospecificities of the preparative reactions were backward estimated numerically¹.

In his earlier work,¹⁹ Hoffmann had published some data on maximal absorbances of 1-hexenes- d_x at the cell thickness $50\ \mu$. Under the assumption of uniform density value for 1-hexenes- d_0 , $-d_1$, and $-d_2$ (cf. Experimental, $d = 0.664\text{ g/ml}$, m.w. $85.17(d_1)$ and $86.17(d_2)$), we re-calculated his data for the sake of comparison. The results are summarized in Table III together with some Jones' data²⁰ for 1-hexene and 1-decene (column 7).

DISCUSSION

Although the types of vibrational modes (Table II) for vinyl chloride can be taken as only approximate ones for the other compounds, it is clear from the Table that this approximation is not too far out. Namely the trends of wagging frequencies prove that this mode is practically free of vibrational coupling with the remaining A'' -vibrations. The opposite statement holds for the twisting motion which is not a "pure" mode. The data for 1-decenes- d_1 (I-III) indicate that deuterium atom on the

* The only exception is the scissoring $=\text{CH}_2$ in I which was found at 1401.5 cm^{-1} (for d_0 is at 1413 cm^{-1})¹².

TABLE III

Analytical Bands, their Intensities, Shapes, and Half-Band Widths

1-Decene	Band ^a	Absorbance ^b	$a_{\max}^{(a)}$ ^c	Shape ^d	$\Delta\nu_{1/2}$ ^e	$a_{\max}^{(a)}$ ^{c,f}
d_0	993	0.4527	48.1	\searrow	-5.5 + 8.5	45 ^g
	911	1.1672	124	sym	10	113 ^g
I	909	1.0040	107	sym	10	>39 ^h
	842	0.2294	24.6	\swarrow	-6 + 4.5	18 ^h
II	978	0.8022	85.9	\searrow	-5 + 7	>39 ^h
III	799	0.9476	101	sym	15	strong ⁱ
IV	878	0.7882	85.0	sym	13	>39 ^h
V	881	0.4047	43.6	sym	9	- ^j
	716	0.9293	100	sym	11	- ^j
VI	725	0.7993	86.2	\swarrow	-6 + 5	very strong ^k
VII	711	1.1674	127	\searrow	-3.5 + 5	very strong ^l

^aIn (cm^{-1}) . ^bExperimental value re-calculated for the 100% isotopic purity. ^cApparent maximal molar absorptivity in $(\text{cm}^{-1} \text{mol}^{-1})$. For the calculation procedure see Experimental. ^dAbbreviation sym. means symmetrical, *i.e.* a Lorentzian band. The other symbols see p. 3756. ^eIn (cm^{-1}) . Explanation in the text. ^fPublished data for 1-hexenes- d_x . ^gRef.²⁰. The corresponding values for 1-decene are 46 and 148 respectively. Jones²⁰ quotes: "These intensities, computed from curves in the A.P.I. collection, are not all measured under the same experimental conditions." ^hRef.¹⁹. ⁱRef.³. ^jNo available data. ^kRef.²⁹, propene-1,1- d_2 . ^lRef.⁵, propene- d_6 .

TABLE IV

Characteristic Frequencies of the o-o-p Deformation Vibrations in Alkenes with an Internal (D,H)C=C(D,H) Moiety

Configuration	Interval ^a	IR Intensity	Ref.
<i>cis</i> - d_0	730-675	strong	7,28
<i>cis</i> - d_1	641 ^b	strong	2,19
<i>cis</i> - d_2	603 ^c	strong	2,19
<i>trans</i> - d_0	near 965	strong	7
<i>trans</i> - d_1	875 ^d	medium	} this work
<i>trans</i> - d_2	714 ^e	strong	
	709 ^f	strong	

^aIn (cm^{-1}) . ^bFor 3-deuterio-3-hexene; the experimental² absorbance had been about 0.7 at the cell thickness 0.0050 cm. ^cFor 3,4-dideuterio-3-hexene; the experimental² absorbance had been 0.5 at the cell thickness 0.0050 cm. ^dFor 5-deuterio-5-decene. ^eFor compound V; the calculated absorbance was 0.81 at the cell thickness 0.00183 cm. ^fFor compound VII; the calculated absorbance of the separated band was 0.85 (Fig. 2).

vinyl group behaves as an alkyl group, *i.e.* 1-alkenes- d_1 can be treated as dialkylethylenes^{2,7} (Table III). According to the literature⁷ all dialkyl derivatives have only one strong band in the 1000–650 cm^{-1} region, namely: about 965 cm^{-1} for *trans*-1,2 (*twist, cf. II*), from 730 to 675 cm^{-1} for *cis*-1,2 (*twist, cf. III*), and about 890 cm^{-1} for 2,2-dialkyl (*wag, cf. I*). However, an additional strong band (842 cm^{-1}) is found for the twisting vibration of $\begin{array}{c} \text{C} \\ \diagup \\ \text{D} \end{array} = \text{H}$

in *I* which is down-shifted due to the isotopic substitution. It is necessary to point out that the twisting vibration has an interesting feature: although compound *IV* contains the same moiety as *I*, no band for the vibration can be found in *IV* at all (Table II). Analogously, whilst *III* and *VI* contain the same $\begin{array}{c} \text{C} \\ \diagup \\ \text{H} \end{array} = \text{D}$ grouping, only

for *III* a weak band is observed. From these facts it can be concluded that 1-decenes- d_2 (*i.e.* 1-alkenes- d_2 generally) should be considered as a trialkylethylene. For this derivative one band for the lone $=\text{C}-\text{H}$ is observed in the spectra⁷ near 820 cm^{-1} . Keeping in mind that only one position possibility exists for trialkylsubstitution of ethylene in contrast with the three isomers of 1-decene- d_2 (*IV-VI*), we actually find one band for o-o-p vibrations of $=\text{C}-\text{H}$. In all three cases the band is assigned to the wagging mode, frequency of which is mass-dependent (881 for $=\begin{array}{c} \text{H} \\ \diagup \\ \text{D} \end{array}$ (*V*) \rightarrow 878 for $=\begin{array}{c} \text{H} \\ \diagup \\ \text{D} \end{array}$ (*IV*) \rightarrow 725 for $=\begin{array}{c} \text{D} \\ \diagup \\ \text{D} \end{array}$ (*VI*)). The only exception is *V* where the second strong band is found for the twisting of $\begin{array}{c} \text{C} \\ \diagup \\ \text{D} \end{array} = \text{D}$ grouping.

It follows from these facts that the twisting frequency corresponds to a vibration depending not only on the mass but also on the position of respective deuterium atom (s). Its appearance or its infrared intensity has no general feature as it is suggested by the data for the cases *I-VII*.

All these considerations are very important for an estimation of stereospecificities of the alkene-forming deuterioboration reactions. For instance, if we assume that the small 972 cm^{-1} band is the band of impurity *II* in *III* (regardless the 6 cm^{-1} of difference, Table II) then the stereospecificity for a *trans*- d_1 synthesis is lowered by several per cents. Conversely, such a lowered stereospecificity should be the same for a *cis*- d_1 synthesis. In this case, the compound *III* would figure as the impurity in *II*. The strongest 799 cm^{-1} band of *III* could be represented in *II* by the small band at 809 cm^{-1} , a shift to higher wavenumbers being explained by overlapping with the 826 cm^{-1} band of *II*. For these reasons, the correct assignment of the doublet 826, 809 cm^{-1} in *II* is much desired.

The expression for the Redlich-Teller product rule is identical²¹ for both compounds *II* and *III*. Provided that the needed moments of inertia I_x and I_y are numerically close together due to geometrical reasons ($=\text{CHD}$ vs $=\text{CDH}$ only), we can calculate and thus may decide between the wagging frequencies 826, 809 cm^{-1} for *II*

from the equation

$$(\omega_{tw} \cdot \omega_{wag} \cdot \omega_{out})_{cis} = (\omega_{tw} \cdot \omega_{wag} \cdot \omega_{out})_{trans}, \quad (1)$$

where ω denotes the frequencies in cm^{-1} . Using the values 972, 799, 520 cm^{-1} for *III* and 978, 478 cm^{-1} for *II*, the searched wagging frequency for the *trans*-compound *II* is $\omega_{wag}^{trans} = 864 \text{ cm}^{-1}$. This result thus also substantiates the assignment of the higher frequency 833 cm^{-1} for *II* as the wagging mode.

Now, it remains to settle the question of origin of the small bands 972 cm^{-1} in *III* and 809 cm^{-1} in *II*. The band at 809 cm^{-1} is also present in the spectra of *trans*-1-deuterio-1-hexene^{2,19} and in *trans*-1-deuterio-2-phenylethylene and is almost equally intense for all these compounds in spite of preparation by different reactions^{22,4} under different reaction conditions. Therefore, we can exclude the corresponding *cis*-compound as the impurity causing the appearance of the band. The same arguments will hold for the band at 972 cm^{-1} in *III*, *i.e.* we do not suppose this band to belong to the *trans*-impurity *II*. Our conclusion is: the stereospecificity of the synthetic reactions for the *cis*- or *trans*-compounds is very high¹.

The only infrared band at about 630 cm^{-1} in solid *n*-alkenes had been assigned to non-planar carbon skeleton rotamers⁹. As it was noted the Raman counterpart of this band should be polarized. Results of the polarization measurements² for liquid 1-hexenes- d_x fulfil this condition. The values of the depolarization ratio are²: 0.34 for *I*, 0.25 for *II*, and 0.21 for *IV*. Unfortunately, the second frequency at about 550 cm^{-1} in liquid *n*-alkenes is too weak in Raman spectra^{2,23} of 1-hexenes- d_x^2 to measure the ratio. Despite this, our assignment of both bands to planar (C_s) and non-planar (C_1) rotamers is in part confirmed.

Usefulness of infrared spectroscopy for analyses of mixtures of 1-alkenes- d_x is apparent from Table III. However, when multicomponent mixtures are to be analyzed some difficulties due to overlapping of bands can arise. The aliphatic $(\text{CH}_2)_n$ chain is characterized by the medium intense band in the $780\text{--}720 \text{ cm}^{-1}$ region, its position depending²⁴ on n . This band just badly interferes in mixtures of *V*–*VII* because of the $(\text{CH}_2)_7$ chain in *n*-octyl substituent (band at 722 cm^{-1}). This complication does not evidently exist for propene, 1-butene (a band of the rocking $(\text{CH}_2)_1$ should be near 770 cm^{-1}), and 1-pentene ($\sim 740 \text{ cm}^{-1}$), or in 1-alkenes with a branched alkyl chain.

Problems of locating the $\text{C}=\text{C}$ or $=\text{C}-(\text{H}, \text{D})$ bonds in an alkene molecule are usually encountered in studies of isomerization of alkenes or of partial hydrogenation of alkynes. In experiments with deuterated species, the most frequently used analytical methods are mass spectrometry and/or PMR-spectroscopy. Neither of the two methods alone can yield unambiguous results. Mass spectra afford the concentration sums of $d_{0,1,2,3}$ species, PMR-spectra give only indirect information on the position of deuterium atoms. Infrared spectroscopy had been used in few cases, namely

for studies of isomerization^{25,26} but only for distinguishing between the saturated C—D and the =C—D bonds in the interval of the stretching frequencies 2400 to 2200 cm^{-1} . However, it is clear from Fig. 1 that the intensities of bands favour the 1000–700 cm^{-1} region, increasing the detection limit of alkenes- d_x . For instance, the most intense band of the =C—D stretching vibration is that for *V* (Fig. 1), having $a_{\text{max}}^{(a)} = 16$ only (cf. Table III).

The region of the o-o-p deformation frequencies has not been explored because the infrared data for *trans*-1,2-dialkylethylenes deuterated on the C=C bond are still lacking. To complete the information needed, we separated numerically the superimposed bands in *V* and *VII* containing the *trans* grouping DC=CD. In the first approximation, these values can be used as model data for *trans*-alkenes- d_2 , for such individual compounds have not yet been synthesized.* The value for the *trans*- d_1 configuration is wavenumber for *trans*-5-deuterio-5-decene measured by us in the mixtures with *trans*-5-decene- d_0 . All these data, together with the published information for the remaining configurations, are summarized in Table IV. The numerical separations of overlapped bands were carried out by the damped least squares method modified by Meiron²⁷, under the assumption of Lorentzian shape of bands. The treatment of the single band at 711 cm^{-1} for *VII* (Fig. 2) gave three components, namely 708.9, 714.8, and 721.1 cm^{-1} with the absorbances 0.85, 0.13, and 0.15, respectively. The frequency at 721 cm^{-1} is clearly the $(\text{CH}_2)_7$ rocking mode, according to its position and intensity.

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* Methyl *trans*- d_2 -crotonate absorbs³⁰ at 718 cm^{-1} .

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