[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

Absorption Spectra. VI. The Infrared Spectra of Certain Compounds Containing Conjugated Double Bonds

BY ELKAN R. BLOUT, MELVIN FIELDS AND ROBERT KARPLUS

This investigation is concerned with the infrared absorption spectra of compounds containing conjugated double bonds, and more particularly with the effects of increased conjugation on the spectra in the region of double bond absorption. It has been shown that in the ultraviolet and visible regions the absorption maxima in a series of polyenic compounds shift toward lower frequencies as the conjugation increases.[1,2,3] The question of whether the frequency of maximum absorption in the visible region approaches a limiting value for molecules with very long conjugated systems has not yet been settled.

Compounds containing isolated double bonds, such as butene[4] and squalene,[5] show in the infrared a characteristic absorption in the region 1640–1660 cm.$^{-1}$ attributed to these bonds. Substances such as butadiene and piperylene[4] which contain two conjugated double bonds have also been measured and show absorption at lower frequencies, generally around 1600 cm.$^{-1}$. 2,5-Dimethylhexatriene also shows an absorption maximum in this region.[4] In this paper we wish to report our results with compounds containing as many as ten non-cyclic conjugated double bonds.

1. Aliphatic Polyene Hydrocarbons

The simplest compounds containing conjugated carbon–carbon double bonds are the aliphatic polyene hydrocarbons. Investigation of the infrared spectra of the lower members of this series (Figs. 1–4) in the region 1440–1900 cm.$^{-1}$ shows in addition to the characteristic strong C–H frequency at 1445–1455 cm.$^{-1}$ several other bands of lower intensities. The symmetry of these molecules probably accounts for the lack of intense absorption in this region. Because of the multiplicity of the absorption maxima shown by these compounds in the general neighborhood of C═C absorption it is not possible at this time to interpret these spectra without mathematical analysis. Perhaps it is significant that in the region examined the diene has two, the triene three, and the tetraene four bands which are doublets or even higher multiplets. The strongest of the bands that may possibly be ascribed to double bond vibrations lies for each compound at or near 1650 cm.$^{-1}$; the simpler compounds containing double bonds, such as *cis*-2-butene,[6] also have a band in this region at 1660 cm.$^{-1}$.

2. Aliphatic Polyene Azines

The aliphatic polyene azine series, the lower members of which can be readily prepared from the corresponding aldehydes, offer an opportunity for the spectral examination of compounds containing a larger number of double bonds. In Figs. 5 through 9 are shown the spectra in the region 1440 to 1900 cm.$^{-1}$ for the aliphatic azines containing, respectively, 2, 4, 6, 8 and 10 double bonds. In addition to the characteristic C–H bending frequency around 1450 cm.$^{-1}$,[7] the strongest absorption band in these compounds occurs in the region 1580–1670 cm.$^{-1}$ and is attributable to motions of doubly bonded atoms. The frequency of maximal absorption decreases with increasing chain length. In Fig. 10 we have plotted this frequency as a function of the number of double bonds in the chain.

3. Furyl Polyene Azines

The general characteristics of the spectra in the region of double bond absorption obtained from the polyene azines having terminal α-furyl groups (Figs. 11–14) are similar to those of the corresponding aliphatic azines. The furyl compounds, however, show the C–H bending frequency around 1475 cm.$^{-1}$ rather than at 1450 cm.$^{-1}$. The frequency of the most prominent band decreases with increasing chain length as may be seen from the plot of the position of this maximum against the number of double bonds (Fig. 10). It is observed that the maxima for these bands may be brought into good superposition with the maxima in the aliphatic polyene azine series if each furan ring is weighted as one double bond. It is perhaps worthy of note that both decatetraenal azine (10 double bonds) and 7-furyl heptatrienal azine (10 "double bond equivalents") have very similar spectra in that each compound shows a secondary less intense band at a frequency slightly higher than that of the main band (*cf.* Figs. 9 and 14).

4. Aliphatic Polyene Aldehydes

All the aldehydes examined have one or more very strong bands in the 1500 to 1800 cm.$^{-1}$ region (Figs. 15–21). In addition, these compounds all show a band about 1450 cm.$^{-1}$.[7] The extinction coefficient at the center of this band is about one-

---

[1] For a summary of the work of Kuhn and his school see Kuhn, *J. Chem. Soc.*, 605 (1938).

[2] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

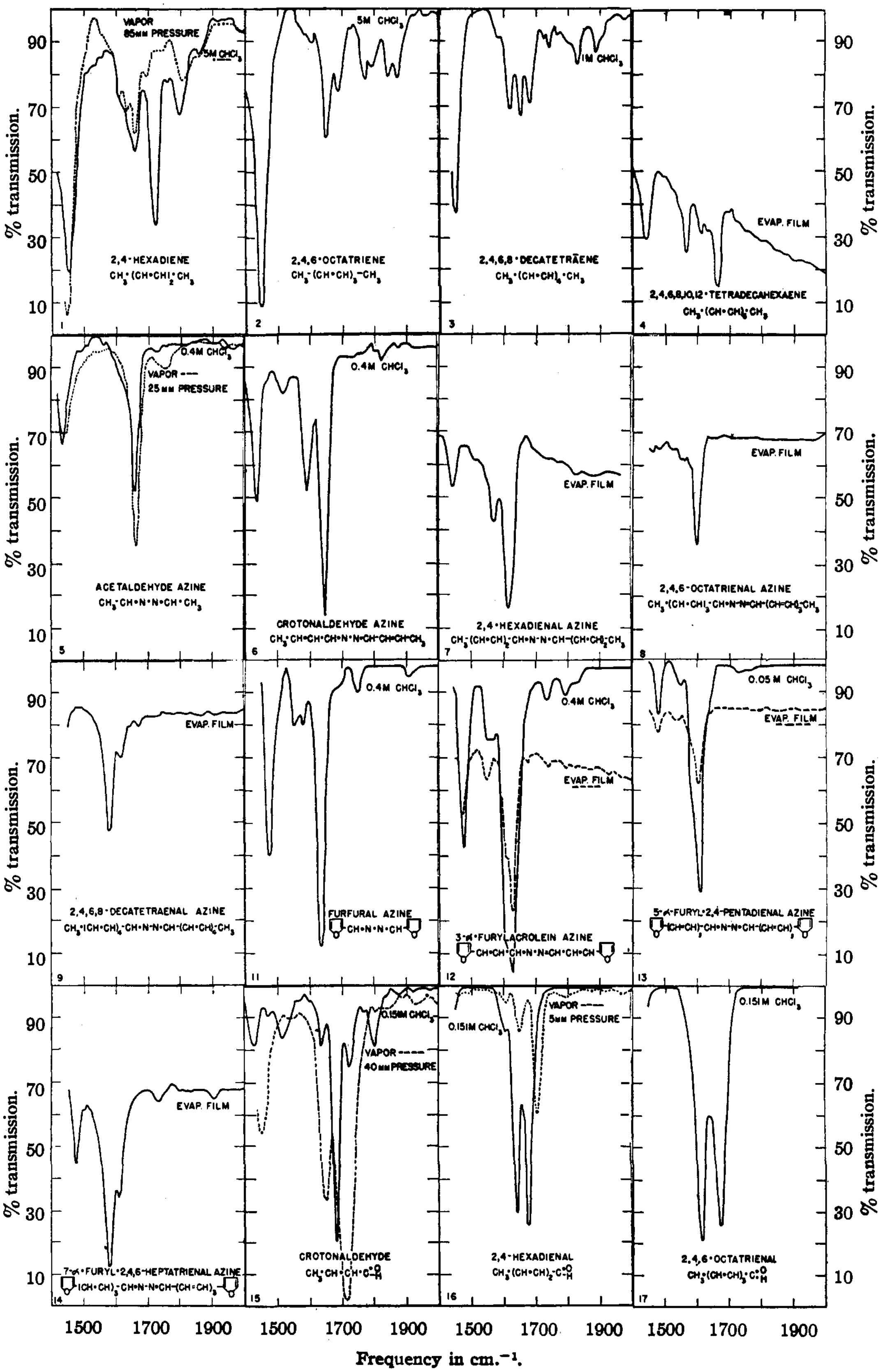
[3] Blout and Fields, THIS JOURNAL, **70**, 189 (1948).

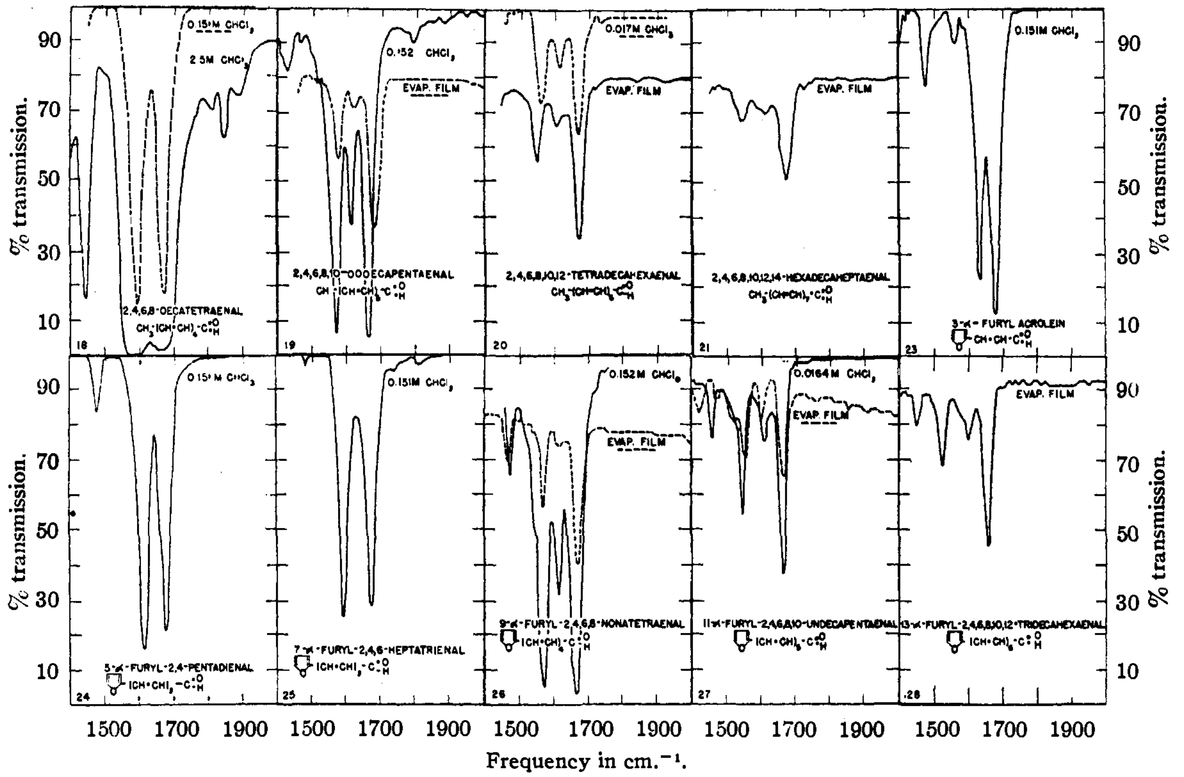
[4] Barnes, Gore, Liddel and Williams, "Infrared Spectroscopy," Reinhold Publishing Co., New York, N. Y., 1944.

[5] Thompson and Torkington, *Trans. Faraday Soc.*, **XLI**, 246 (1945).

[6] A. P. I. Res. Proj. 44, Infrared Absorption Spectrograms, Ser. No. 21, 376.

[7] Although this band is not shown in Figs. 8, 9, 16, 17, 20 and 29, since measurements were not extended to low enough frequencies, it is undoubtedly present.


% transmission.
90
70
50
30
10
1
VAPOR 85MM PRESSURE
5M CHCl₃
2,4-HEXADIENE
CH₃·(CH=CH)₂·CH₃
2
5M CHCl₃
2,4,6-OCTATRIENE
CH₃·(CH=CH)₃·CH₃
3
1M CHCl₃
2,4,6,8-DECATETRAENE
CH₃·(CH=CH)₄·CH₃
4
EVAP. FILM
2,4,6,8,10,12-TETRADECAHEXAENE
CH₃·(CH=CH)₆·CH₃
5
0.4M CHCl₃
VAPOR ---- 25MM PRESSURE
ACETALDEHYDE AZINE
CH₃·CH=N·N=CH·CH₃
6
0.4M CHCl₃
CROTONALDEHYDE AZINE
CH₃·CH=CH·CH=N·N=CH·CH=CH·CH₃
7
EVAP. FILM
2,4-HEXADIENAL AZINE
CH₃·(CH=CH)₂·CH=N·N=CH·(CH=CH)₂·CH₃
8
EVAP. FILM
2,4,6-OCTATRIENAL AZINE
CH₃·(CH=CH)₃·CH=N·N=CH·(CH=CH)₃·CH₃
9
EVAP. FILM
2,4,6,8-DECATETRAENAL AZINE
CH₃·(CH=CH)₄·CH=N·N=CH·(CH=CH)₄·CH₃
11
0.4M CHCl₃
FURFURAL AZINE
CH=N·N=CH
12
0.4M CHCl₃
EVAP. FILM
3-α-FURYLACROLEIN AZINE
CH=CH·CH=N·N=CH·CH=CH
13
0.05 M CHCl₃
EVAP. FILM
5-α-FURYL-2,4-PENTADIENAL AZINE
(CH=CH)₂·CH=N·N=CH·(CH=CH)₂
14
EVAP. FILM
7-α-FURYL-2,4,6-HEPTATRIENAL AZINE
(CH=CH)₃·CH=N·N=CH·(CH=CH)₃
15
0.15M CHCl₃
VAPOR ---- 40MM PRESSURE
CROTONALDEHYDE
CH₃·CH=CH·C=O H
16
0.15M CHCl₃
VAPOR ---- 5MM PRESSURE
2,4-HEXADIENAL
CH₃·(CH=CH)₂·C=O H
17
0.15M CHCl₃
2,4,6-OCTATRIENAL
CH₃·(CH=CH)₃·C=O H
1500
1700
1900
Frequency in cm.⁻¹.



sixth as large as those at the centers of the strong bands between 1500 and 1700 cm.$^{-1}$.

If the frequencies of the strong lines are plotted against the total number of double bonds in the molecule (Fig. 22), two different curves are obtained for compounds containing up to five double bonds, whereas three curves are obtained for higher members of the series. The position and intensity of the high frequency band around 1672 cm.$^{-1}$ is essentially constant for aldehydes having more than two double bonds in the chain. The maximum absorption of the lowest frequency band, however, shifts with increasing chain length. It may be seen from Fig. 22 that this shift is always in the same direction (toward lower frequencies with increasing chain length) but the increment per double bond decreases for the longer molecules so that this curve of the lowest frequency band may also become asymptotic with sufficiently long chains of conjugated double bonds.

5. ω-Furyl Polyene Aldehydes

The infrared spectra of these compounds are very similar to those of their aliphatic analogs. They are characterized by the same band system (Figs. 23–28) consisting of a strong band around 1672 cm.$^{-1}$ whose position remains unchanged as the chain length is increased, a second strong band whose frequency decreases as the number of double bonds increases, and a weaker band whose position is constant around 1475 cm.$^{-1}$. In addition, as in the aliphatic series, a third band appears in the higher molecular weight compounds. The salient features of the spectra of this group of compounds can perhaps best be seen by referring to the plot of the frequency of maximal absorption *vs.* the number of double bonds (Fig. 29). It is of interest to observe that the contribution of the furyl group in the aldehyde series as in the azine series is again equivalent to approximately one aliphatic double bond.

Discussion

There are two causes from which one might derive these observations. First, with increasing conjugation, the apparent order[8] or double-bond character[9] of the double bonds decreases. This in turn results in a decrease in the force constants of the vibrations involving the double bonds, while an increase would be expected in the force constants appropriate to vibrations primarily involving single bonds. The decrease in force constants with unchanged or increased reduced masses is then responsible for the decrease in the normal vibration frequency. Second, the normal modes will be different. That is, the frequencies no longer correspond to the vibration of an individual bond as in ethylene; instead, for two identical double bonds, for instance, the normal modes would be in the in-phase and opposite-phase simultaneous vibration of the two bonds. Where there are more double bonds, the interactions become

---

(8) Penney, *Proc. Roy. Soc.* (*London*), **A158**, 306 (1937).

(9) Pauling, Brockway and Beach, THIS JOURNAL, **57**, 2705 (1935); Pauling and Brockway, *ibid.*, **59**, 1223 (1937).

more complicated. Where, finally, the bonds are no longer alike, as is the case with the polyene aldehydes and the polyene azines, the assignment of the vibrations to the oscillation of individual structures, or even to certain combinations of such oscillations, becomes impossible.

One can, however, in the case of the polyene aldehydes, say that the higher frequency band, the one that is almost unaffected by increasing chain length, is associated more with the carbonyl bond, while the other strong bands contain more carbon–carbon double bond vibration. It is sur-

TABLE I

The relative intensities for the different maxima are shown on a 1 to 10 scale by the figures in parentheses. They were calculated by determining the ratios of the absorptions of the less intense peaks to the most intense peak in any compound and multiplying these values by 10.

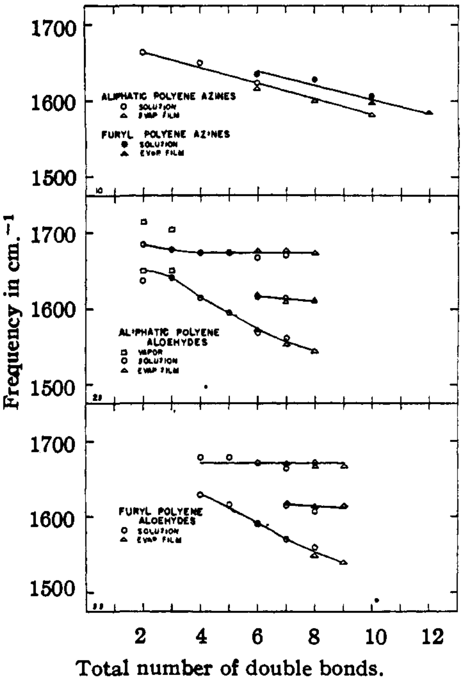
Compound	Physical state of spectral sample	Positions (cm.$^{-1}$) and relative intensities of main absorption maxima								
2,4-Hexadiene	Vapor, 85 mm.	1452 (10)			1656 (5)	1717 (8)		1795 (4)		
	5.0 *M* $CHCl_3$ soln.	1445 (10)	1608 (3)	1635 (3.5)	1656 (4)	1693 (2)		1805 (2)		
2,4,6-Octatriene	5.0 *M* $CHCl_3$ soln.	1445 (10)	1601 (1)		1646 (4)	1685 (2)	1763 (1.5)	1785 (1.5)	1804 (2)	1867 (1.5)
2,4,6,8-Decatetraene	7.0 × 10^{-1} *M* $CHCl_3$ soln.	1450 (10)	1615 (6)		1646 (5.5)	1677 (5.5)	1733 (3)		1825 (4)	1890 (3.5)
2,4,6,8,10,12-Tetradecahexaene	Evaporated film	1444 (8)	1567 (10)	1611 (4)	1635 (4)	1664 (10)				

TABLE II

Compound	Physical state of spectral sample	Positions (cm.$^{-1}$) and relative intensities of main absorption maxima				
Acetaldehyde azine	Vapor, 25 mm. pressure	1442(5)			1664(10)	1755(2)
	4.0 × 10^{-1} *M* $CHCl_3$ soln.	1432(7)			1664(10)	
Crotonaldehyde azine	4.0 × 10^{-1} *M* $CHCl_3$ soln.	1439(6)	1521(2)	1592(6)	1650(10)	
2,4-Hexadienal azine	3.8 × 10^{-1} *M* $CHCl_3$ soln.	1438(4)	1573(4)		1624(10)	
	Evaporated film	1445(6)	1573(7)		1618(10)	
2,4,6-Octatrienal azine	Evaporated film	1443(1.5)	1558(2)		1601(10)	
2,4,6,8-Decatetraenal azine	Evaporated film				1583(10)	1615(4)
Furfural azine	4.0 × 10^{-1} *M* $CHCl_3$ soln.	1473(7)	1552(2)	1579(2)	1635(10)	1750(1)
3-α-Furylacrolein azine	4.0 × 10^{-1} *M* $CHCl_3$ soln.	1477(6)	1561(3)		1628(10)	1737(1)
	Evaporated film	1475(3)	1549(1)		1628(10)	
5-α-Furyl-2,4-pentadienal azine	5.0 × 10^{-2} *M* $CHCl_3$ soln.	1479(2)	1546(1)		1608(10)	
	Evaporated film	1477(2)	1538(1)		1601(10)	
7-α-Furyl-2,4,6-heptatrienal azine	Evaporated film	1477(4)			1583(10)	1611(6)

TABLE III

Compound	Physical state of spectral sample	Positions (cm.$^{-1}$) and relative intensities and main absorption maxima				
Crotonaldehyde	Vapor, 40 mm. pressure	1449(5)		1650(7)		1715(10)
	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1429(2)	1520(2)	1638(2)		1685(10)
2,4-Hexadienal	Vapor, 5 mm. pressure		1608(1)	1650(4)		1705(10)
	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1447(7.5)	1608(2)	1642(9.5)		1677(10)
2,4,6-Octatrienal	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1445		1615(10)		1674(9.5)
2,4,6,8-Decatetraenal	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1445(6)		1592(10)		1673(9.5)
2,4,6,8,10-Dodecapentenal	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1429(2)		1570(9.8)	1615(6)	1664(10)
	Evaporated film			1573(5)	1618(3)	1677(10)
2,4,6,8,10,12-Tetradecahexaenal	1.7 × 10^{-2} *M* $CHCl_3$ soln.			1561(7.5)	1615(4)	1671(10)
	Evaporated film			1555(5.5)	1611(3)	1677(10)
2,4,6,8,10,12,14-Hexadecaheptaenal	Evaporated film			1546(4)	1611(3)	1674(10)
3-α-Furylacrolein	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1472(3)	1558(1)	1628(9)		1677(10)
5-α-Furyl-2,4-pentadienal	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1477(2)		1615(10)		1677(9.5)
7-α-Furyl-2,4,6-heptatrienal	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1477(1)		1591(10)		1672(9.5)
9-α-Furyl-2,4,6,8-nonatetraenal	1.5 × 10^{-1} *M* $CHCl_3$ soln.	1477(4)		1570(9.5)	1615(7)	1667(10)
	Evaporated film	1467(3)		1570(6)	1618(1.5)	1671(10)
11-α-Furyl-2,4,6,8,10-undecapentaenal	9.6 × 10^{-2} *M* $CHCl_3$ soln.	1477(4)	1528(6)	1558(8.5)	1608(5)	1671(10)
	Evaporated film	1462(3)		1549(8)	1614(3)	1668(10)
13-α-Furyl-2,4,6,8,10,12-tridecahexaenal	Evaporated film	1463(2)		1539(5)	1613(3)	1668(10)



prising, even in view of the resolving power of the spectrometer used in this investigation, that a greater number of distinct bands are not observed in the region examined. Since one would expect all the double bond vibrations to yield bands of comparable intensity (the molecules have no symmetry), the weak bands that appear above 1700 cm.$^{-1}$ in the more concentrated solutions must be assigned to overtones or combinations. Finally, one must consider the possibility that each of the observed strong bands in the region 1550—1700 cm.$^{-1}$ is actually a group of several unresolved bands. The ultimate solution to this problem awaits mathematical analysis.

Acknowledgment.—We wish to acknowledge the valuable assistance of Messrs. Claude Valle and Marshall Kane in the preparation of many of the compounds, and the aid of Mr. Dwight Merrill and other members of the spectrophotometric group in determining many of the spectra.

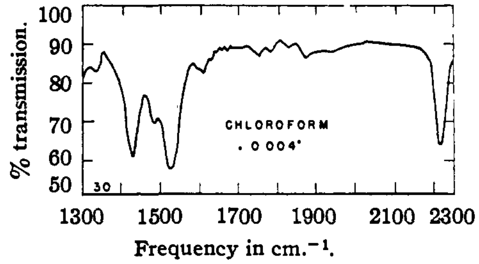
Experimental

The aliphatic polyene hydrocarbons were prepared according to the method of Kuhn and Grundmann.[10] The polyene azines and aldehydes were prepared according to the procedures described or referred to in a previous paper.[3]

The spectral measurements were made on a Perkin-Elmer infrared spectrometer Model 12-A using a 40 cycle chopper, a Strong[11] bolometer, an a.c. amplifier, and a Brown Instrument Company potentiometer. The data were obtained on a point-to-point basis, the points being taken from 5 to 10 cm.$^{-1}$ apart in the 1440 to 1900 cm.$^{-1}$ region. In the vicinity of the absorption maxima points were taken every 2 to 4 cm.$^{-1}$.

The vapor measurements were made in an 80-mm. cell having plane parallel rock salt windows. A second identical cell evacuated to 2 mm. was used to correct for reflection losses.

Chloroform, a useful solvent for spectral measurements in this region,[12] was purified by drying over phosphorus pentoxide followed by distillation; the material used gave the spectral curve shown in Fig. 30. As can be seen from Tables I–III and the figures, the lower members of each series were measured in chloroform solution. The cell used was constructed from two rock salt plates and had a thickness of 0.004″.[13] To correct for reflection and absorption losses the measurements were made against an identical cell containing only C. P. chloroform.



The decrease in solubility with the increasing number of double bonds in the higher molecular weight compounds made it necessary to use films of the less soluble materials which had been evaporated in high vacuum (<10^{-4} mm. of mercury) on rock salt discs. No measurements of film thickness were made. Evaporated films of the more unstable compounds, the aliphatic polyene aldehydes and 2,4,6,8,10,12-tetradecahexaene, were measured in a specially constructed evacuated cell.

Summary

The infrared spectra of twenty-six compounds containing two or more conjugated double bonds were determined in the region of double bond vibrational absorption. Polyene aldehydes and polyene azines show at least one strong absorption maximum which shifts toward lower frequencies as the length of the conjugated system is increased.

CAMBRIDGE 39, MASSACHUSETTS RECEIVED APRIL 2, 1947

---

[10] Kuhn and Grundmann, *Ber.*, **71**, 442 (1938).

[11] The nickel-strip bolometer used was kindly supplied to us by Professor John Strong of Johns Hopkins University.

[12] Torkington and Thompson, *Trans. Faraday Soc.*, **41**, 184 (1945).

[13] Halford and Schaeffer, *J. Chem. Phys.*, **14**, 141 (1946).