[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH AND FROM MELLON INSTITUTE]

The Infrared Spectra of a Number of Isomeric Normal Acetylenic Compounds

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This paper presents the infrared spectra of twenty-eight straight chain heptynes, heptynyl alcohols, halides, nitriles and *n*-octynoic methyl esters. Most of these compounds have recently been prepared for the first time.[3] Table I provides a list of the compounds and their numbering.

Measurement of the Spectra.—The spectrum of I is available in the A. P. I. catalog of infrared spectrograms,[7] and is not presented here. The spectra of all the other compounds were measured on a Beckman IR-2 infrared spectrometer in the Spectrographic Laboratory of the Department of Chemistry at The Ohio State University. The range 2–15 μ was covered with a sodium chloride prism. Samples were studied as liquids in cells 0.025, 0.10 or 0.40 mm. thick. The spectra are shown graphically in Figs. 1 and 2.

TABLE I

A. NUMBERING OF THE COMPOUNDS DISCUSSED IN THIS PAPER; B. POSITION (IN CM.^{1}) AND INTBNSITY[a] OF THE C≡C BAND

vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Hydrocarbon skeleton	No.	—H Posn.	I	No.	—Cl Posn.	I	No.	—Br Posn.	I
$CH_3—(CH_2)_6—$	I	..	...	...	..	...	VIII	..	...
$H—C≡C—(CH_2)_5—$	II	2100	m	...	..	...	IX	2100	m
$CH_3—C≡C—(CH_2)_4—$	III	2210	vw	V	Missing[b]	...	X	2200	vw
$C_2H_5—C≡C—(CH_2)_3—$	IV	2190	vw	VI	2240	vw	..	..	...
n-$C_3H_7—C≡C—(CH_2)_2—$	IV	2190	vw	...	..	...	XI	2220	w
n-$C_4H_9—C≡C—CH_2—$	III	2210	vw	VII	2240	s	XII	2220	s
n-$C_5H_{11}—C≡C—$	II	2100	m	...	..	...	XIII	2110	w
		—OH			—CN			—$COOCH_3$	
$CH_3—(CH_2)_6—$	XIV	..	...	XX	..	..	XXVII	..	..
$H—C≡C—(CH_2)_5—$	XV	2140	m	XXI	2120	m	XXVIII	2120	m
$CH_3—C≡C(CH_2)_4—$	XVI	Missing[b]	...	XXII	Missing[b]	..	XXIX	Missing[b]	
$C_2H_5—C≡C—(CH_2)_3—$	XVII	2260	vw	XXIII	Missing		XXX	Missing[b]	
n-$C_3H_7—C≡C—(CH_2)_2—$	XVIII	2210	w	XXIV	Missing		XXXI	Missing	
n-$C_4H_9—C≡C—CH_2—$	XIX	2240	s	XXV	2220	s	XXXII	2240	w
n-$C_5H_{11}—C≡C—$	....	..	..	XXVI	2120	w	XXXIII	2210	vs

[a] In estimating intensities, an attempt was made to correct for the effect of the different cell thicknesses. [b] There is a weak or very weak band in the range 2070–2050 cm.$^{-1}$, but this is inordinately low for a C≡C band and probably belongs to a combination tone.

Experimental

Preparation of the Compounds.—The preparation and physical properties of most of these compounds are given in the paper by Newman and Wotiz.[3] The remaining compounds were prepared according to the references cited below. Some physical constants of the infrared-analyzed samples are compared with those in the references: II[4]: b. p. 100° (760 mm.), obs. 97° (745 mm.); n^{20}D 1.4088, obs. 1.4038 (25°); III[5]: b. p. 107–111° (750 mm.), obs. 109° (721 mm.); n^{25}D 1.4220, obs. 1.4199; IV[4]: b. p. 106–107° (?),[6] obs. 104° (748 mm.); n^{25}D 1.415,[6] obs. 1.4165; V[3]: The original sample was found to contain the H—C≡ band at 3270 cm.$^{-1}$, indicating some isomerization during its preparation. The impurity was removed by making a mercury complex. X[3]: impure; contained Br-$(CH_2)_5$-Br. The curve is included because the spectrum of the impurity will add nothing new to the spectrum of X above 1000 cm.$^{-1}$; XII[3]: b. p. 84° (20 mm.), obs. 54° (4 mm.); n^{25}D 1.4878, obs. 1.4844.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.0; H, 6.3; Br, 45.6. Found: C, 48.5; H, 6.2; Br, 45.6.

The Raman spectra of II,[8,9] III[10] and XXXIII[8] have been reported earlier. They provide values for the bands above 2000 cm.$^{-1}$ which are higher than ours by 20–40 cm.$^{-1}$. This is probably due to the poor dispersion of rocksalt in this region, and the Raman values are to be preferred.

Discussion of Results

A number of the observed bands can be attributed immediately to various structural groups in the molecule. These bands occur in their expected positions so that no discussion is needed.[11] We shall therefore confine our remarks to two topics: the intensity and position of the C≡C band,

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(3) Newman and Wotiz, THIS JOURNAL, **71**, 1292 (1949).

(4) Henne and Greenlee, *ibid.*, **67**, 484 (1945).

(5) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **3**, 1 (1937).

(6) "Handbook of Chemistry and Physics," 29th ed., 1945, p. 816.

(7) American Petroleum Institute Research Project 44, National Bureau of Standards, Washington, D. C.; curve 637.

(8) M. Bourgel and P. Daure, *Bull. soc. chim.*, **47**, 1349 (1930).

(9) M. J. Murray and F. F. Cleveland, THIS JOURNAL, **63**, 1718 (1941).

(10) B. Gredy, *Ann. chim.*, [XI] **4**, 5 (1935).

(11) See, for example, Barnes, Gore, Stafford and Williams, *Anal. Chem.*, **20**, 402 (1948).

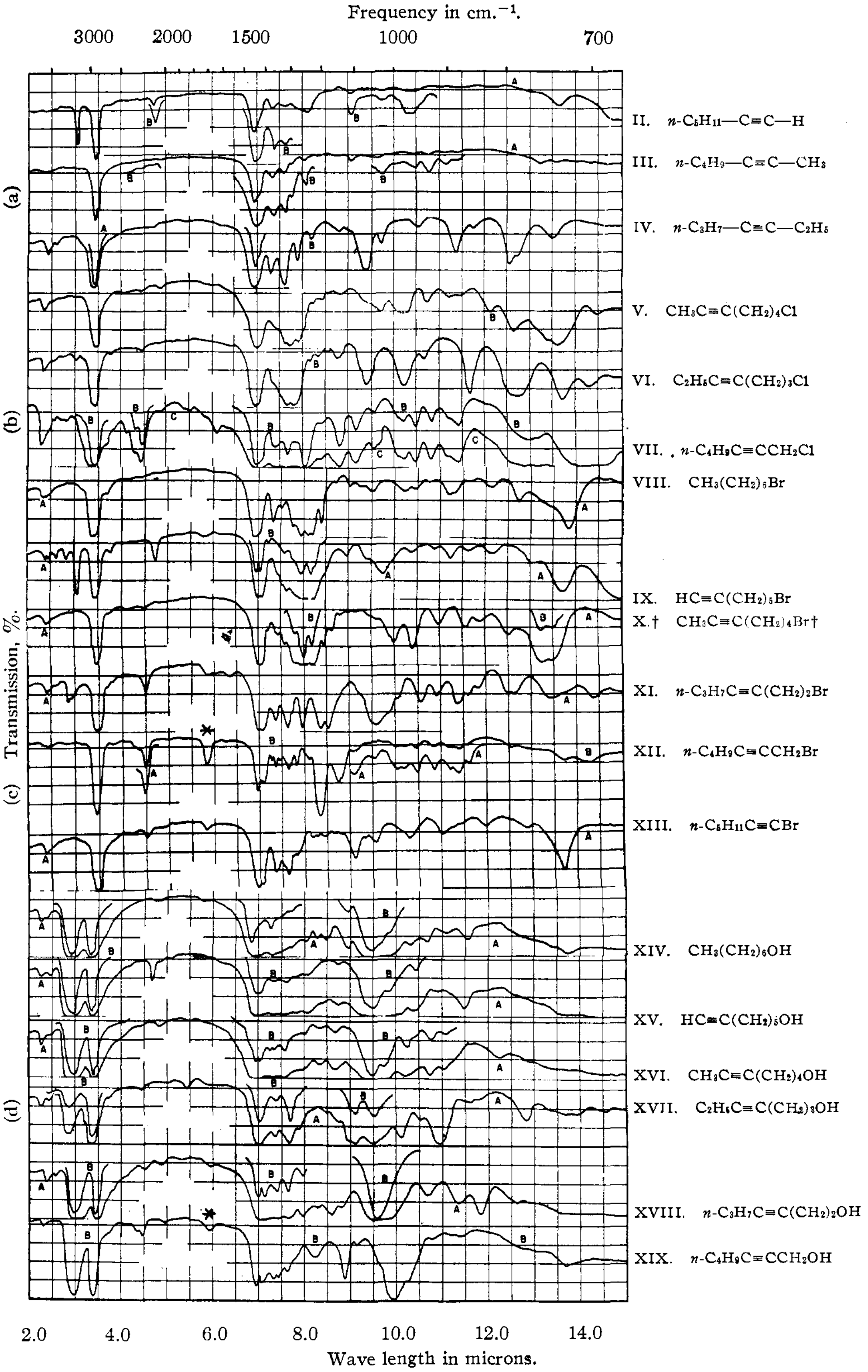

Fig. 1.—Infrared spectra of (a) *n*-heptynes, (b) *n*-heptynyl chlorides, (c) *n*-heptynyl bromides and (d) *n*-heptynyl alcohols: cell thicknesses, curves II–VII, A = 0.025 mm., B = 0.10 mm., C = 0.40 mm.; curves VIII–XIX, A = 0.10 mm., B = 0.025 mm. * See discussion of anomalous bands. † Sample impure. See "Experimental."

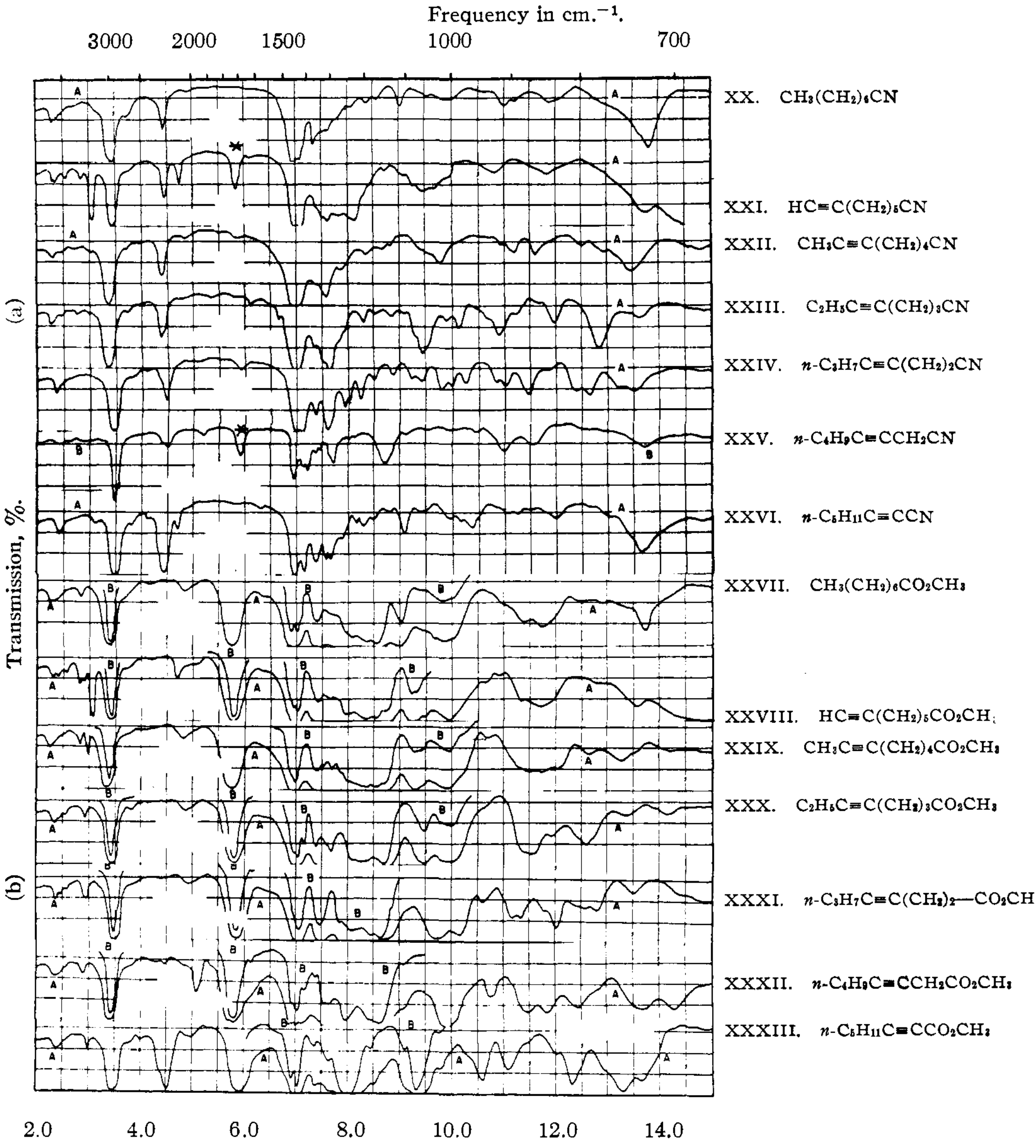

Fig. 2.—Infrared spectra of (a) *n*-heptynyl nitriles, and (b) *n*-octynoic methyl esters: cell thicknesses, A = 0.10 mm., B = 0.025 mm. * See discussion of anomalous bands.

and the presence of some anomalous bands in several of the spectra.

C≡C Band.—One of the interesting features of these spectra is the variable intensity of the C≡C band at 2100–2240 cm.$^{-1}$. In the infrared this intensity is appreciable only if the triple bond is near either end of the chain. As it is moved toward the center of the chain the corresponding band weakens and virtually disappears. This is shown in detail in Table I. The only exceptions occur in the bromide and nitrile series, where the band is more intense for $n\text{-}C_4H_9\text{—}C{\equiv}C\text{—}CH_2\text{—}$ than for $n\text{-}C_5H_{11}\text{—}C{\equiv}C\text{—}$. The reason for these two exceptions is not apparent to us, but the explanation of the general behavior seems fairly simple. As the triple bond is moved toward the interior of the molecule, the change in the dipole moment during the valence vibration of the triple bond diminishes. Since (classically) the intensity of infrared absorption is proportional to the square of the rate of change of the dipole moment,[12] the intensity rapidly decreases. It is as though a pseudo center of symmetry were produced at the center of the triple bond. The stretching of the triple bond is symmetric toward this pseudo symmetry center, and so the vibration is inactive in the infrared. It is evident, then, that the infrared spectrum is not an infallible test for the absence

[12] Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 240.

of a triple bond even when the geometric symmetry is so low that there are no formal selection rules.[13]

A similar effect is known in the infrared spectra of olefinic compounds, where the $C=C$ frequency is notorious for its variable intensity. For example, Kletz and Summer[14] have shown that the strength of this band in octenes decreases as the symmetry of substitution about the double bond increases. They explained these results in essentially the same way. It is not unexpected to find that Cl, Br, OH, CN and $COOCH_3$ are all much more effective than alkyl groups in enhancing the intensity of the $C\equiv C$ band when substituted nearby.

The position of the $C\equiv C$ band depends upon the number of substituents. For the series $H—C\equiv C—R$ the band is at 2100–2140 cm.$^{-1}$; for $R'—C\equiv C—R''$ it is at 2190–2260 cm^{-1}.[15] This is known, through studies of the Raman spectra, to be a general result for acetylenic compounds.[16,17] It is interesting to note that this holds even when R equals Br (XIII). The Raman work has also shown that the compounds $H—C\equiv C—R$ have a single line in the $C\equiv C$ region, whereas in the series $R'—C\equiv C—R''$ there are two or more lines in this region, the "extra" ones being due to overtones or combination tones whose intensity has been enhanced by resonance with the fundamental. These same frequencies are observed in the infrared for those disubstituted acetylenes possessing a $C\equiv C$ band of good intensity. In some cases these satellite bands appear only as weak inflections or shoulders on the $C\equiv C$ band. Several of these spectra were redetermined on a Baird double-beam spectrometer, and the bands were then clearly resolved.

It is well known that the group $\equiv C—H$ has a stretching frequency of about 3270 cm.$^{-1}$. It is therefore simple to distinguish between a monosubstituted and a disubstituted acetylene from the position of either the $C—H$ or the $C\equiv C$ stretching frequency as follows[18]

	$\equiv C—H$	$C\equiv C$
$H—C\equiv C—R$	3270	2100–2140
$R'—C\equiv C—R''$	..	2190–2260 (plus nearby satellites)

Anomalous Bands.—Several of the spectra exhibit unexpected bands that warrant mention. For example, all the esters have some absorption at 3350–3500 cm.$^{-1}$, which may indicate a small amount of free acid. The strong band of XXXII at 1960 cm.$^{-1}$ is probably a combination tone; its intensity is partially illusory because the sample was much too thick.

Some of the nitriles seem to contain a carbonyl impurity. Compound XXI, for example, has a strong band at 1720 cm.$^{-1}$. Another sample was later prepared by an entirely different method—dehydration of the corresponding amide—and the carbonyl band was then much weakened.

The series n-$C_4H_9—C\equiv CH_2—$ also contains evidence of a carbonyl group in the band at 1650–1710 cm.$^{-1}$, which ranges in intensity from very weak to strong. However, the existence of a carbonyl-containing impurity is open to question. The conversion of XII into XXV was done in the absence of an oxygen-containing reagent and solvent, and yet the "carbonyl" band has maintained its intensity in spite of an appreciable difference in physical properties of the two compounds and the resulting ease of separating them. Furthermore no evidence for an aldehyde or ketone could be found in the ultraviolet spectrum of bromide XII.[19] (This is admittedly not as sensitive a test as the infrared spectrum, however.) One must therefore consider the possibility that this band may be characteristic of compounds where the functional group is removed from the acetylenic linkage by one methylene group. A further investigation of such compounds is under way to determine whether this band is due to an impurity (perhaps an azeotropic mixture), or whether it is indeed characteristic of this type of molecule. If the latter proves to be true, it will be a surprising result.

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Summary

The infrared spectra of twenty-eight normal acetylenic compounds and four substituted normal heptanes are presented. The intensity of the $C\equiv C$ band is observed to vary greatly. The band is most intense when the triple bond is near the end of the chain. If the triple bond is three or more positions from the end, the band is scarcely detectable.

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[13] By contrast, the $C\equiv C$ frequency appears with good intensity in the Raman spectra of all acetylenic compounds regardless of where the triple bond is located. References 16 and 17 provide many such examples.

[14] T. A. Kletz and A. Summer, *J. Chem. Soc.*, 1456 (1948).

[15] Compound XXVI is an exception to this, since for it the $C\equiv C$ band is at 2120 cm.$^{-1}$. However, the $C\equiv C$ is conjugated with $C\equiv N$ in this case. Since the "normal" frequencies of these groups are close together, it is probable that Fermi resonance has lowered the $C\equiv C$ band below its "normal" position.

[16] J. H. Hibben, "The Raman Effect and its Chemical Application," Reinhold Publishing Corp., New York, N. Y., 1939, p. 200 ff.

[17] Reference 9 and earlier papers cited therein.

[18] Hibben states (ref. 16, p. 208) that a Raman line at 1380 cm.$^{-1}$ is quite generally present in the disubstituted acetylenes. This is not a useful criterion in the infrared because this frequency is characteristic of a methyl group.

[19] An isoöctane solution of XII was studied with a Cary spectrophotometer. The only band observed had $\lambda_{max.}$ at 216 mμ, with a molecular extinction coefficient ϵ = 3300.