[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY]

The Infra-red Absorption Spectra of Nitriles

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Introduction

In some earlier investigations a systematic examination of the infra-red absorption spectra of organic derivatives of ammonia[1] was undertaken. The results of these studies which were concerned with the simpler amines of the alkyl, aryl and the mixed alkyl-aryl types were of particular interest in demonstrating that primary, secondary and tertiary amines can be differentiated readily by the intensity (or absence) of the now well-known NH absorption band in the region of 3.0 μ.

The present study deals with another important group of organic nitrogen compounds, *viz.*, the nitriles or organic cyanides. The following substances were selected for examination: acetonitrile, *n*-butyronitrile, *n*-valeronitrile, isocapronitrile, phenylacetonitrile, benzonitrile, α-naphthonitrile and succinonitrile. The infra-red absorption spectra of these compounds in the region between 1.0 and 12.0 μ are presented and discussed in the present paper.

Experimental Part

The absorption spectra were examined by means of a rock salt prism spectrometer. This instrument and the experimental procedure have been previously described.[2]

All of the nitriles were secured from the Eastman Kodak Company. They were examined just as received in original sealed containers without any attempt at further purification.

The absorption cells which were used were constructed from polished rock salt plates and the cell capacity was such that the thickness of the absorbing layer of the material under examination was 0.1 mm. in each case. A description of the preparation of the absorption cells has been given elsewhere.[3]

It will be noted that of the eight nitriles selected two are solids at room temperature, *viz.*, α-naphthonitrile, m. p. 48°, and succinonitrile, m. p. 48°. The former substance was introduced into the absorption cell in the molten condition. On cooling, the α-naphthonitrile failed to crystallize and the spectrum of this compound was therefore examined at room temperature. The specimen of succinonitrile was examined at a temperature of approximately 55° which was maintained by means of an electrical device.[4]

Typical absorption curves are shown in Figs. 1 to 8 in which the percentage transmission has been plotted against the wave length in microns.

Discussion

The nitriles examined may be classified conveniently under several general types. In the first type, for example, we have several representatives of the alkyl cyanides. Benzonitrile and α-naphthonitrile are, to be sure, typical aryl cyanides. Phenylacetonitrile may be regarded as a transition type in which we have the mixed aryl-alkyl hydrocarbon residue. Succinonitrile, or ethylene cyanide, differs radically from the other nitriles in that it contains two CN groups substituted symmetrically in ethane.

The infra-red absorption spectra of acetonitrile and benzonitrile have been previously examined by Coblentz[5] between 1.0 and 15.0 μ. The present curve for acetonitrile is in good agreement with Coblentz' results. Coblentz' band at 6.2 μ was not resolved although its presence is definitely indicated in Fig. 1. The Coblentz spectrum of benzonitrile is also closely checked by the present curve shown in Fig. 6, especially the results obtained by Coblentz with his large spectrometer in the region of the shorter wave lengths.

As might be expected, the most characteristic absorption in the spectra shown in Figs. 1 to 8 is the band due to the CH group which appears consistently in the region from 3.3 to 3.4 μ. Another striking region of absorption which appears to have a "center of gravity" at about 7.0 μ occurs in each spectrum. In most cases this region is poorly defined in the present work, but the presence of two or more bands is clearly indicated. The 6.8 μ band characteristic of the CH linkage is doubtless contributing to this absorption. The absorption spectra of benzonitrile and α-naphthonitrile are well defined in this region of 7 μ. In both of these compounds there are sharp bands at 6.6 to 6.7, 6.9 and 7.2 μ. The bands at 7.2 μ are strikingly similar in location and intensity to those appearing in benzene and naphthalene.[6] The 6.9 μ band in benzonitrile transmits 40% while in α-naphthonitrile, which represents a considerable increase in the molecular weight of the hydrocarbon residue, the transmission is 60%.

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(1) Bell, THIS JOURNAL, **47**, 2192, 2339 (1925); **48**, 813, 818 (1926); **49**, 1837 (1927).

(2) Ref. 1, p. 2194.

(3) Bell, THIS JOURNAL, **50**, 2941 (1928).

(4) Bell, *ibid.*, **47**, 2812 (1925).

(5) W. W. Coblentz, "Investigations of Infra-red Spectra," Carnegie Inst. Pub., 35 (1905).

(6) Ref. 4, p. 2814.

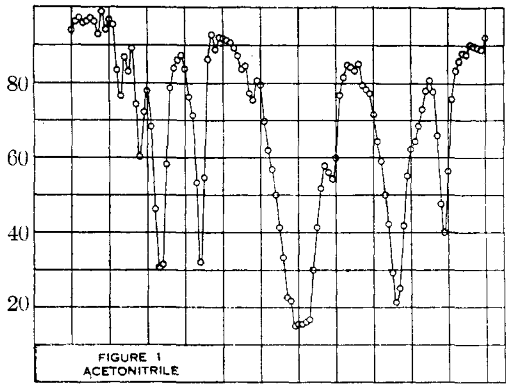

FIGURE 1
ACETONITRILE

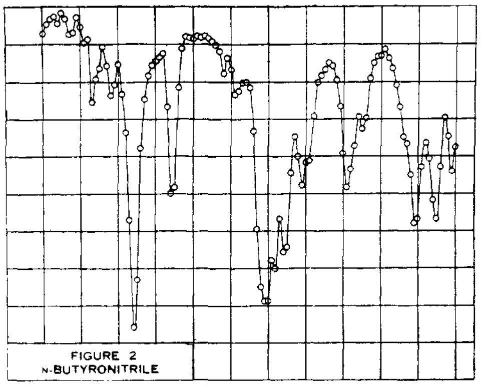

FIGURE 2
N-BUTYRONITRILE

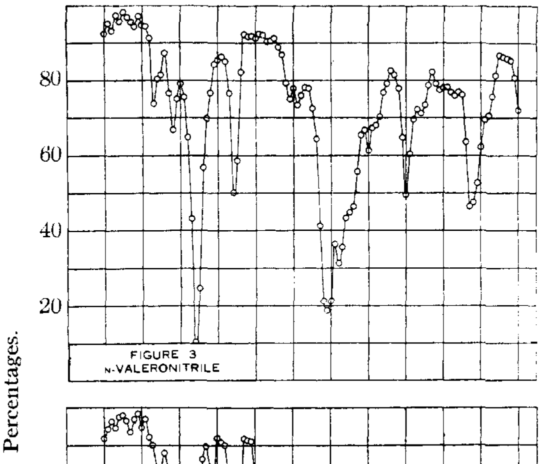

FIGURE 3
N-VALERONITRILE

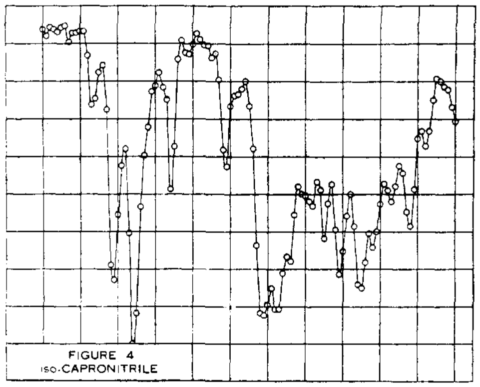

FIGURE 4
ISO-CAPRONITRILE

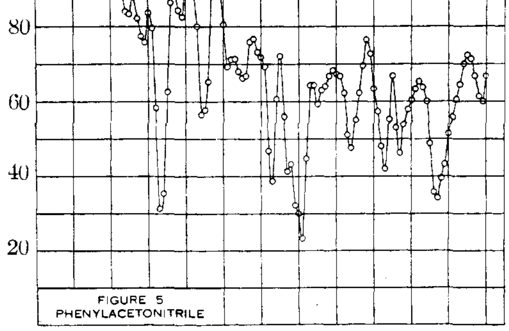

FIGURE 5
PHENYLACETONITRILE

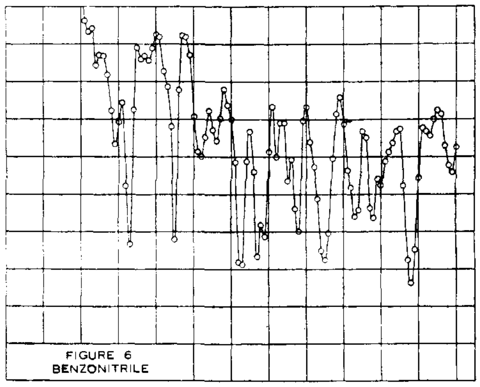

FIGURE 6
BENZONITRILE

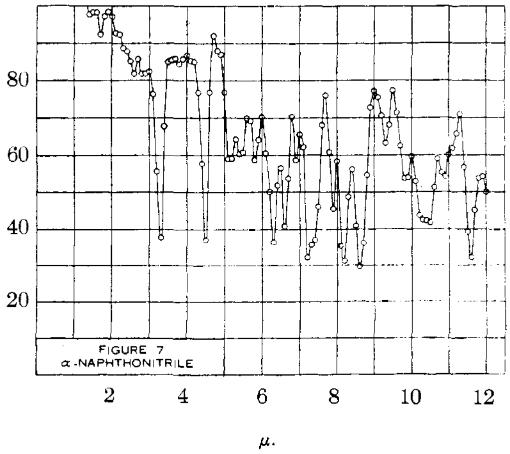

FIGURE 7
α-NAPHTHONITRILE

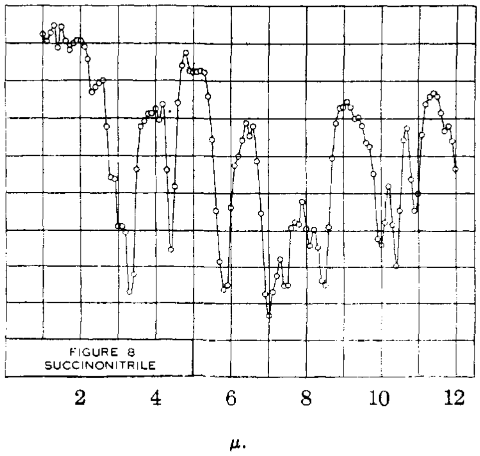

FIGURE 8
SUCCINONITRILE

Although a more detailed examination of this region with considerably higher dispersion is highly desirable, the present results appear to justify the conclusion that there is an absorption at approximately 7 μ which is characteristic of the CN linkage.

In the longer wave lengths attention should be directed to the absorption at 10.9 μ. At this approximate wave length each of the nitriles shows a definite absorption varying in intensity from 25% transmission in benzonitrile to 55% transmission in α-naphthonitrile. The location of the band also shows considerable variation: between 10.65 μ (phenylacetonitrile) and 10.95 μ (*n*-butyronitrile). It should be noted in this connection, however, that Coblentz takes particular notice of the fact[7] that the deep 10.9 μ band of acetonitrile is entirely missing in his absorption spectrum of propionitrile.

Several of the absorption curves given in this paper appear to present an interesting anomaly. It will be recalled that both water and ammonia have an intense and characteristic absorption at very nearly 3.0 μ due, respectively, to the hydroxyl group and the NH group. Similarly, alcohols and compounds containing amino hydrogen show these characteristic bands which, however, may be shifted somewhat toward the shorter wave lengths.

The spectrum of isocapronitrile (Fig. 4) between 2.5 and 4.0 μ presents a typical absorption of an alcohol or a primary amine due, of course, to the presence of the sharp band at 2.9 μ. In acetonitrile and benzonitrile the same condition is observed less pronounced. The spectrum of succinonitrile (Fig. 8) is especially interesting. The bands have not been resolved, but absorption is definitely indicated at both 2.8 and 3.0 μ. The pronounced and broad absorption at 5.85 μ is probably the resultant of two bands bearing an harmonic relation to the 2.8 and 3.0 μ bands.

The most obvious explanation of these observations may be based on the assumption of the presence of impurities in the substances examined. Before attempting to attach any further significance to these results it is planned to make a further study of the absorption spectra of these substances with respect to the effect of impurities.

With regard to the general problem of the differentiation and identification of organic compounds by their infra-red absorption spectra, the region of 4.5 μ is highly important in the present curves. Each of the substances examined shows a well-defined absorption band at that wave length. This band is particularly significant in that it occurs in a region where almost all organic compounds display a relatively high degree of transparency.

The band occurs at 4.5 μ in the spectra of the two aryl nitriles and closely parallels in intensity that of the corresponding CH band at 3.3 μ. In the alkyl nitriles it appears at 4.4 μ and in phenylacetonitrile at 4.45 μ. The conclusion that this band is characteristic of the CN linkage in nitriles appears to be amply justified.

Summary

1. The infra-red absorption spectra of acetonitrile, *n*-butyronitrile, *n*-valeronitrile, isocapronitrile, phenylacetonitrile, benzonitrile, α-naphthonitrile and succinonitrile have been examined between 1.0 and 12.0 μ.

2. The nitriles are characterized by a well-defined absorption band at 4.4 μ in alkyl nitriles and at 4.5 μ in aryl nitriles. This band is attributed to the CN linkage.

3. The possibility that 7.0 μ may also be a region of characteristic absorption has been indicated.

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(7) Ref. 5, p. 60.