# Infrared Spectra in Identification of Derivatives of Cyclopropane

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The purpose of this work was to establish more definite criteria for the identification of the cyclopropyl group by use of infrared spectroscopy. A study of the infrared absorption spectra of nine cyclopropyl derivatives obtained with a lithium fluoride prism has shown that bands characteristic of the cyclopropyl group occur at approximately 3.23 and 3.32 microns. The wave-length difference for these two bands is similar to that for cyclopropane gas. Use of these two bands for the identification of the cyclopropyl group in conjunction with the previously reported bands at 9.9 and 10.9 to 11.7 microns yields more conclusive proof of the existence of the cyclopropyl ring system. A study of cyclobutyl and cyclopentyl derivatives in the carbon-hydrogen region of 3.4 microns should yield similar selective assignments for these ring systems.

THE presence of a cyclopropyl group in an organic molecule is difficult to establish by chemical means. By use of infrared absorption spectra Derfer (6) and coworkers have shown that a moderate to strong band at 9.9 microns, ascribed by Herzberg (7)to the symmetric vibration of the cyclopropyl ring, is useful in identifying this ring structure. Recent synthetic studies (14) have used this assignment to aid in establishing the presence of a cyclopropyl group. However, Josien et al. (8) have pointed out that both normal and isosteroids contain so many bands in the 9.9-micron region that this band is not very useful for differentiation purposes. These authors suggest the use of a band at approximately 11.2 microns (890 cm.<sup>-1</sup>), which they ascribe to the asymmetric deformation of the cyclopropane ring, for further evidence of the existence of the cyclopropyl group. Another possibility as indicated by the work of Plyler and Acquista (11) is to study the 3.4-micron region and determine the location of the two CH<sub>2</sub> vibrations.

It would seem that the presence of these two bands, in conjunction with the bands at 9.9 and 11.2 microns previously mentioned, would offer more conclusive spectral proof of the presence of the cyclopropyl group than use of only the 9.9- and 11.2-micron

ladie I. P	roperties of C	yciopropyi	Compounds		
	Boiling Poi	nt, ° C.	Refractive Index at 20° C. n <sup>20</sup> <sub>D</sub>		
Compound	Determined	Literature values	Determined	Literature values <sup>a</sup> $(n_D^{25} - 1.4188)$ (12)	
Cycloprop <b>anecarbonitrile</b>	131.5 69-70 at 80 mm.	133 65 at 75 mm. (12)	1.4204 $(n_{\rm D}^{25} - 1.4184)$		
2-Methylcyclopropanecar- bonitrile	144.5-145.4	144.5-145.5	1.4254	1.4259	
1-Phenylcyclopropanecar- bonitrile	125 at 15 mm.	98-100 at 1 mm. <sup>5</sup>	1.5382	$1.5386^{5}$	
Cyclopropylearbinol	124.0 - 124.5	122 - 123	1.4258	1.426	
Cyclopropyl methyl ketone	111-112	111.6-111.8	1.4251	1.4251	
Cyclopropyl isopropyl ke- tone	140.5-141.5	141.0-141.4	1.4290	1.4299	
Cyclopropyl tert-butyl ke- tone	148.4		1.4380		
Cyclopropyl <i>o</i> -anisyl ke- tone	125 at 7 mm.		1.5552		
1-Phenylcyclopropyl methyl ketone	122.0-122.5 at 25 mm.	• • • •	1.5280		

 $^{\alpha}$  Values of physical constants are those reported in references cited for preparation of each compound, unless indicated otherwise. b In (10), refractive index was, by error. reported as 1.3676. Correct value (9) is  $n_D^{20}$ 1.5386

bands. The purpose of this paper is to present the infrared spectra of nine diversified compounds containing the cyclopropyl group, to show the value of obtaining the wave lengths of the  $CH_2$  vibrations in establishing spectral proof of the presence of the cyclopropyl group.

# **APPARATUS**

The infrared spectra were obtained using a Perkin-Elmer Model 12B recording infrared spectrometer equipped with inter-changeable sodium chloride and lithium fluoride prisms. These prisms were calibrated in the usual manner with the known rotational bands of water vapor, carbon dioxide, ammonia, hydrogen bromide, hydrogen chloride, and carbon monoxide. The measurements were made at  $20.0^{\circ} \pm 0.5^{\circ}$  C. and at a relative humidity of  $30 \pm 1\%$ . The liquid samples were measured in a 0.025-mm. cell with rock salt windows. The broad bands, particularly in the carbon-hydrogen region of 3.4 microns, were resolved into sharp bands with sample thickness less than 0.025 mm. These thin capillary thicknesses were obtained by placing a single drop of liquid between two rock salt windows, which were then fastened tightly together.

#### **COMPOUNDS**

All the cyclopropyl compounds measured except cyclopropyl methyl ketone were prepared bv

various investigators in this laboratory. Cyclopropanecarbonitrile (3) and 2-methylcyclopropanecarbonitrile (4) were prepared by the reaction of sodium anide with 4-chlorobutyroni-trile and 3-methyl-4-chlorobutyronitrile. 1-Phenylcyclopropanecarbonitrile (10) was prepared from phenylacetonitrile and ethylene dichloride with sodium amide. Cyclopropylcarbinol was prepared by West (15) by the method subsequently reported by Smith and McKenzie (13). Cyclopropyl methyl ketone (2) obtained from the Matheson Co., was purified by fractional distillation

The preparation of the other cyclopropyl ketones used will be separately reported. The physical properties of cyclopropyl isopropyl ketone prepared by another method (2) were available for comparison. The structure of cyclopropyl tert-butyl ketone was confirmed by the synthesis from it of cyclopropylmethyl-tertbutylcarbinol, which had also been prepared in this laboratory from cyclopropyl methyl ketone and tert-butyl magnesium chloride. Cyclopropyl o-anisyl ketone and 1-phenylcyclopropyl methyl ketone were converted to the corresponding amides by reaction with hydrazoic acid, and the

Table II. Carbon-Hydrogen Frequencies of Cyclopropyl Compounds<sup>4</sup>

		0.0	<b>P</b> = =======						
Compound	A	В	С	D	E	F	D - F		
Cyclopropanecarbo- nitrile	3.471 w			3.300 s	3.263 s	3.224 w	0.076		
2-Methylcyclopro- panecarbonitrile	3.469 w	3.39 <b>8</b> m	3.361 s	<b>3.308</b> m		3.288 w	0.080		
1-Phenylcyclopro- panecarbonitrile	3.489 w	3.406 w		3.295 s	3.261 s	3.228 m	0.067		
Cyclopropylcarbinol Liquid Vapor	$^{3.478}_{3.467}$ m	3.420 m 3.408 m	· · ·	3.315 m 3.303 m		3.237 w 3.226 w	$0.078 \\ 0.077$		
Cyclopropyl methyl ketone	3.469 w	3.404 m	3.361 m	3.318 s		3.226 m	0.092		
Cyclopropyl isopro- pyl ketone	3.471 m	3.404 m	3.361 s	3.318 m		3.226 m	0.092		
Cyclopropyl tert- butyl ketone	3.471 m	'3.39 <b>8</b> m	3.359 s	3.312 m	3.258 w	3.226 w	0.086		
Cyclopropyl <i>o</i> -anisyl ketone	3.520 s	3.392 s	3.368 w	3.320 s		3.247 m	0.073		
1-Phenylcyclopropyl methyl ketone	3.501 w	3.415 m		3.316 s	3.298 s	3.237 m	0.079		
Cyclopropane(vapor)	• • •			3.307 s		3.233 s	0.084		
<sup>a</sup> w, m, and s for weak, moderate, and strong have been used to indicate relative band in- tensity. All these bands would normally be classified as strong.									

products of hydrolysis of each amide were identified. In addition, semicarbazones and 2,4-dinitrophenylhydrazones of these four ketones were prepared, and the nitrogen analyses of these derivatives checked with the calculated values.

The boiling points and refractive indices of the cyclopropyl compounds used are listed in Table I, together with the corresponding values previously reported.

# DISCUSSION

Figure 1 contains the spectra obtained with a sodium chloride prism of the nine cyclopropyl compounds listed in Table I.

A detailed assignment of band frequencies for each compound whose spectrum is presented is not attempted here. It is possible to recognize the presence of certain absorption bands which are characteristic of structural features of each of the compounds  $(\delta)$ .

The spectra of the first three compounds contain a strong, sharp band at 4.45 microns characteristic of the nitrile group. Cyclopropylcarbinol contains a strong, broad band at 3.01 microns characteristic of the bonded hydroxyl group of alcohols. The three aliphatic ketones, cyclopropyl methyl ketone, cyclopropyl isopropyl ketone, and cyclopropyl tert-butyl ketone, have strong absorption bands at 5.87, 5.87, and 5.93 and at 8.35, 8.35, and 8.34 microns, respectively, characteristic of the carbonyl frequencies of aliphatic ketones. The strong bands at 7.01, 6.92, and 6.74 microns in these three compounds can be attributed to the terminal methyl group. The bands at 7.20, 7.47, 7.59, 8.47, 8.89, and 11.05 microns can probably be assigned to the isopropyl group in cyclopropyl isopropyl ketone; similarly, bands at 7.25, 8.17, 8.34, and 11.31 microns can be assigned to the tert-butyl group in cyclopropyl tert-butyl ketone.

Cyclopropyl *o*-anisyl ketone has bands at 6.27, 6.74, 8.27, 8.98, 9.49, 9.75, 10.10, 13.32, and 14.24

microns characteristic of ortho disubstituted benzene derivatives. 1-Phenylcyclopropyl methyl ketone has bands at 6.33 and 6.68 microns, three sharp bands at 8.70, 9.12, and 9.72 microns, and two strong broad bands at 13.16 and 14.24 microns characteristic of monosubstituted benzene derivatives. The aromatic ketone bands appear at 7.79 and 5.86 microns in the spectrum of this compound, while in cyclopropyl-o-anisyl ketone these bands appear at 8.02 and 6.01 microns; the shift of the 6.01-micron band is attributed to the fact that the carbonyl group is conjugated with the aromatic ring.

All the cyclopropyl compounds contain a strong band at 9.9 microns in agreement with the assignment of Derfer, Pickett, and Boord  $(\beta)$ . With the exception of cyclopropanecarbonitrile, these



Figure 1. Infrared Absorption Spectra of Cyclopropyl Compounds



compounds also contain a moderate to strong band in the region of 10.9 to 11.7 microns in agreement with the assignment of Josien, Fuson, and Carv (8).

In order to determine how effective these two assignments are in establishing the presence of the cyclopropyl group, a punch card sort was made of 175 spectrograms of hydrocarbons of other types (1). The first punch was made between 9.52 and 10.00 microns and 121 cards dropped out. A second sort was then made on these 121 cards between 10.81 and 12.12 microns and 113 cards dropped out. These wave-length intervals were selected so that the nine cyclopropyl compounds studied would be included. Hence, use of both assignments does not yield selective sorting.

In an effort to obtain additional useful bands, the spectra of the nine cyclopropyl compounds were obtained using a lithium fluoride prism from 3.067 to 3.580 microns. Table II contains the wave lengths of the bands obtained. Data (7) on cyclopropane gas are included for reference. An inspection of Table II shows that all the cyclopropyl compounds contain bands at 3.23 and 3.32 microns characteristic of the CH<sub>2</sub> vibrations of the cyclopropyl ring system. The wave-length difference for these two bands is similar to that for cyclopropane gas (7). For comparison purposes cyclopropylcarbinol was measured in both the liquid and vapor state.

As an additional check on the selectivity of the band assignments at 3.23 and 3.32 microns, the spectra of methyl *n*-propyl ketone and methyl isopropyl ketone were also measured in this region. These ketones, obtained from the Matheson Co., were purified by fractional distillation and the boiling points and refractive indices were checked with the reported values. The methyl isopropyl ketone sample required treatment with potassium permanganate solution before distillation.

Figure 2 shows a plot of this wave-length region for these two ketones and for methyl cyclopropyl ketone. Only methyl cyclopropyl ketone has the two characteristic bands at 3.23 and 3.32 microns.

If these latter two bands are used for a further punch card sort, of the 113 cards previously left, only 35 now drop out. A further inspection of the individual wave-length tables of these compounds shows that only two compounds of this group contain two bands in this region.

Many compounds contain harmonic and overtone bands in the 3.3-micron region. If more data in the carbon hydrogen region were available for compounds measured with a lithium fluoride prism, undoubtedly more compounds other than cyclopropyl derivatives would be found in a punch card sort between 3.23 and 3.33 microns (3000 to 3100 cm. $^{-1}$ ). However, the probability that such compounds would contain a band in the region of 3.22 to 3.25 microns and another in the region of 3.29 to 3.32 microns as well as the other two cyclopropyl assignments (6, 8) is slight. The value of obtaining infrared absorption data on cyclopropyl compounds in the carbon hydrogen region is therefore shown by this investigation.

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