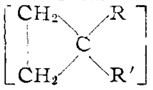
ference, ΔM_r, between the observed and calculated refractions and values for ring contribution determined by Vogel's procedure. It can be seen from the ΔM_r values that a ring contribution determined by the method of reference 2 would have little, if any, meaning. Even if the averaging process were confined to an homologous series, and if the value so obtained were used only for members of that series, the calculated molar refraction would only approximate the observed refraction.

TABLE I

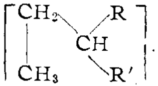
CONTRIBUTION OF THE CYCLOPROPYL RING TO THE MOLECULAR REFRACTION

Cyclopropane derivatives	M_r (obsd.)[a]	ΔM_r[b]	Ring contribution[c]
2-Cyclopropylpropane	28.33	0.45	0.44
2-Cyclopropylbutane	32.85	.32	.44
2-Cyclopropylpentane	37.51	.33	.45
2-Cyclopropylhexane	42.15	.33	.44
2-Cyclopropyl-3-methylbutane	37.37	.19	.44
Dicyclopropyl	26.53	.70	.37
Spiropentane	22.45	1.27	
Vinylcyclopropane	23.60	0.85	.83
2-Cyclopropylpropene	27.98	.58	.62
2-Cyclopropyl-1-butene	32.46	.41	.5
2-Cyclopropyl-1-pentene	37.12	.42	
2-Cyclopropyl-1-hexene	41.75	.41	
2-Cyclopropyl-3-methyl-1-butene	37.06	.36	
2-Cyclopropyl-2-butene, L.B.	32.63	.58	
2-Cyclopropyl-2-pentene, L.B.	37.47	.77	
2-Cyclopropyl-2-hexene, L.B.	42.11	.77	
2-Cyclopropyl-2-butene, H.B.	32.66	.61	
2-Cyclopropyl-2-pentene, H.B.	37.45	.75	
2-Cyclopropyl-2-hexene, H.B.	42.13	.79	
Methylcyclopropylcarbinol	25.12	.37	
Dimethylcyclopropylcarbinol	29.65	.25	
Methylethylcyclopropylcarbinol	34.25	.20	
Methylpropylcyclopropylcarbinol	38.85	.16	
Methylbutylcyclopropylcarbinol	43.48	.14	
Methylisopropylcyclopropylcarbinol	38.64	−.05	
Methyl cyclopropyl ketone	23.94	.60	.75[d]
Diethyl cyclopropane-1,1-dicarboxylate	45.77	.84	.76[e]
Cyclopropyl chloride	19.07	.31	
1,1-Dichlorocyclopropane	24.06	.49	
trans-1,2-Dichlorocyclopropane	24.06	.49	

[a] $(n^2 - 1/n^2 + 2) \times (m/d) = M_r$(obsd.). [b] M_r(obsd.) − M_r(calcd.) = ΔM_r. Atomic and group refractivities of A. Vogel, *J. Chem. Soc.*, 1842 (1948), were used. [c] M_r(obsd.)



$+ 2\ [H_r] - M_r$(obsd.)



. Atomic refractivity of hydrogen (H_r) taken from ref. of footnote *b*. M_r(obsd.) of the acylic hydrocarbons taken from Natl. Bureau Standards Circular C461, U. S. Government Printing Office, Washington, D. C., 1947. [d] M_r(obsd.) of acyclic compound taken from D. M. Cowan, G. H. Jeffery and A. Vogel, *J. Chem. Soc.*, 175 (1940). [e] M_r(obsd.) of acyclic compound taken from A. Vogel, *ibid.*, 643 (1948).

The procedure used in reference 4 could be applied only to the 2-cyclopropylalkanes and to a few additional compounds because reliable physical data were not available for the acyclic structures similar to the remaining compounds. The 2-cyclopropylalkanes gave a "constant" ring contribution, 0.44. However, indiscriminate use of this "constant" for all types of cyclopropane derivatives would give misleading results, because the "constant" changes with the character of the substituents on the ring. This is indicated by the values obtained for the other compounds shown in Table I, and also by the fact that Vogel obtained a ring contribution of 0.614 for the compounds used in his investigation.

It must be concluded that no single value adequately expresses for all structures the contribution of the cyclopropyl ring to molar refraction. This is not entirely unexpected when one considers that the refractivity of the 3-carbon ring reflects the polarization of the electrons of the ring, and that as the substituents on the ring are changed, the degree of polarization of the ring and, hence, the refractivity of the ring, is changed. In neither of the methods of determining ring contribution is this factor taken into consideration; Tschugaeff's method disregards, in addition, the changes in the atomic and group refractivities which occur as the structure varies. Consequently, Vogel's procedure is to be preferred when reliable physical data are available for the appropriate acyclic compounds.

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Characteristic Infrared Absorption Bands of the Cyclopropyl Ring[1]

BY VERNON A. SLABEY

RECEIVED DECEMBER 18, 1953

In the course of investigating the synthesis of cyclopropane derivatives, a method of establishing the presence of the cyclopropyl ring in the synthesis products was desired. The detection of the cyclopropyl ring by chemical means is difficult, and of the physical methods, infrared spectroscopy appeared to be the most promising.

While our investigation was in progress, three papers were published in which the respective authors suggested three different regions of the spectrum between 2 and 16 μ as being useful for determining the presence of the cyclopropyl ring. Bartleson, Burk and Lankelma[2] used absorption bands at 9.75 and 11.55 μ to indicate the rings' presence in 1,1,3-trimethyl- and 1,2-dimethyl-3-ethylcyclopropane. In 1949, Derfer, Pickett and Boord[3] observed that in the infrared spectra of 14 individual cyclopropane hydrocarbons, strong absorption, apparently due to ring deformation, occurred between 9.8 and 10.0 μ, but that the absorption at 11.6 μ used by Bartleson, *et al.*, did not consistently occur in their spectra. More recently,

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[1] Presented before the Organic Division at the 124th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 6-11, 1953.

[2] J. D. Bartleson, R. E. Burk and H. P. Lankelma, THIS JOURNAL, 68, 2513 (1946).

[3] J. M. Derfer, R. E. Pickett and C. E. Boord, *ibid.*, 71, 2482 (1949).

Wiberley and Bunce[4] investigated the CH absorption between 3.2 and 3.5 μ of several non-hydrocarbon derivatives of cyclopropane, using a lithium fluoride prism to resolve these bands. They found that in the nine compounds investigated, CH vibrational bands at 3.23 and at 3.32 μ were indicative of the ring.

These three regions are considered in the present report in the light of the infrared spectra we have obtained of 34 cyclopropane derivatives.[5]

Apparatus and Materials

The syntheses of the compounds employed in this investigation have already been reported.[6]

The infrared spectra were obtained with a Baird Associates model B automatic recording infrared spectrophotometer, employing a sodium chloride prism and 0.1-mm. rock salt sample cells. The spectra were obtained both on undiluted samples and on samples diluted 1:10 with either carbon tetrachloride or carbon disulfide. The calibration of the instrument was frequently checked with ammonia gas and polystyrene, and found to be consistently within ±0.02 μ of the correct wave length.

Discussion

For critical examination of the 3.2 to 3.5 μ C–H vibrational absorption bands, the sodium chloride prism used in determining the spectra is, unfortunately, not suitable, because the resolution is insufficient. In general, a broad absorption in this region "blacks out" the detail of the band structure. However, in many of the 34 spectra, a sharp band or a shoulder was observed at about 3.23 μ, slightly less than the wave lengths of the broad absorption. By diluting the samples it was possible, also, to detect shoulders at about 3.32 μ, within the region of the broad absorption. Bands at both the 3.23 and 3.32 μ wave lengths were clearly discernible in spectra of those compounds having a predominance of ring C–H bands.

All 34 compounds showed strong absorption between 9.5 and 10.0 μ (Table I). Of the 30 compounds which had only one substituent on the ring, all but two had maxima at 9.79 ± 0.04 μ. The remaining compounds, in which two ring hydrogens were replaced, had maxima at lower wave lengths.

Table I

Characteristic Absorption in the Infrared for the Cyclopropyl Ring

Cyclopropane derivative	Wave length, μ
Dicyclopropyl	9.82
2-Cyclopropylpropane	9.82
2-Cyclopropylbutane	9.82
2-Cyclopropylpentane	9.82
2-Cyclopropylhexane	9.82
2-Cyclopropyl-3-methylbutane	9.83
Vinylcyclopropane	9.77
2-Cyclopropylpropene	9.77
2-Cyclopropyl-1-butene	9.78
2-Cyclopropyl-1-pentene	9.78
2-Cyclopropyl-1-hexene	9.79
2-Cyclopropyl-3-methyl-1-butene	9.78
2-Cyclopropyl-2-butene, L.B.	9.82
2-Cyclopropyl-2-pentene, L.B.	9.80
2-Cyclopropyl-2-hexene, L.B.	9.82
2-Cyclopropyl-2-butene, H.B.	9.80
2-Cyclopropyl-2-pentene, H.B.	9.80
2-Cyclopropyl-2-hexene, H.B.	9.80
Methylcyclopropylcarbinol	9.75
Dimethylcyclopropylcarbinol	9.78
Methylethylcyclopropylcarbinol	9.77
Methylpropylcyclopropylcarbinol	9.76
Methylbutylcyclopropylcarbinol	9.80
Methylisopropylcyclopropylcarbinol	9.75
Methyl cyclopropyl ketone	9.69
Ethyl cyclopropyl ketone	9.78
Propyl cyclopropyl ketone	9.80
Butyl cyclopropyl ketone	9.75
Isopropyl cyclopropyl ketone	9.78
Cyclopropyl chloride	9.73
1,1-Dichlorocyclopropane	9.66
trans-1,2-Dichlorocyclopropane	9.58
Spiropentane	9.54
Diethyl cyclopropane-1,1-dicarboxylate	9.70

Examination of the spectra between 11 and 12 μ indicated that this region was of little value for determining the presence of the cyclopropyl ring. In many of the spectra the absorption was considerably displaced from the position 11.55 μ reported in reference 2, and in others the band was so broadened by interfering absorption that the positions of the maxima were indeterminate.

It was concluded that the 9.5 to 10.0 μ region was the most suitable for determining the presence of the cyclopropyl ring, at least for molecules no greater in complexity than those encountered in the present work. When adequate resolution can be obtained, the 3.23 and 3.32 μ ring C–H bands offer confirming evidence of the ring's presence.

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(4) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

(5) Pertinent parts of the spectra referred to in this article have been deposited as Document number 4226 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(6) (a) V. A. Slabey, This Journal, **68**, 1335 (1946); (b) V. A. Slabey and P. H. Wise, *ibid.*, **71**, 3252 (1949); (c) **74**, 1473 (1952); (d) **74**, 3887 (1952); (e) V. A. Slabey, *ibid.*, **74**, 4928 (1952); (f) **74**, 4930 (1952); (g) **74**, 4963 (1952); (h) Hydrocarbon and Nonhydrocarbon Derivatives of Cyclopropane, V. A. Slabey, P. H. Wise and L. C. Gibbons, National Advisory Committee for Aeronautics, Technical Report 1112.