TABLE I

HEAT CAPACITIES (CAL./DEG.-MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
NaF (mol. wt., 41.991)					
54.01	1.659	114.61	6.434	216.14	10.08
58.57	2.025	124.46	7.007	225.80	10.27
62.80	2.380	135.98	7.606	235.96	10.44
67.29	2.770	145.74	8.060	245.66	10.57
71.81	3.165	155.77	8.460	256.40	10.73
76.33	3.555	165.84	8.815	266.20	10.91
80.98	3.955	175.84	9.124	276.20	10.97
85.79	4.355	186.05	9.413	287.15	11.09
95.40	5.110	195.79	9.650	295.86	11.17
105.04	5.808	205.89	9.882	298.15	(11.19)
AlF_3 (mol. wt., 83.98)					
53.65	1.774	114.53	7.268	215.91	14.48
56.69	2.013	124.39	8.131	226.20	15.02
57.89	2.110	135.56	9.077	235.93	15.50
61.01	2.380	145.35	9.879	245.55	15.92
65.62	2.782	155.75	10.68	256.18	16.39
70.32	3.206	165.58	11.38	266.31	16.80
74.88	3.623	175.81	12.08	276.22	17.19
82.19	4.304	185.93	12.75	286.59	17.54
86.30	4.685	195.84	13.35	296.10	17.88
94.60	5.463	206.14	13.93	298.15	(17.95)
104.82	6.404				
Na_3AlF_6 (mol. wt., 209.953)					
53.66	10.10	114.69	27.62	216.05	44.67
57.94	11.39	124.69	29.95	226.06	45.70
62.32	12.76	136.00	32.37	236.20	46.70
66.53	14.13	145.51	34.35	245.81	47.63
70.94	15.54	155.82	36.27	256.33	48.53
75.55	17.00	165.66	37.91	266.23	49.30
80.79	18.55	175.91	39.50	276.24	50.02
84.45	19.61	185.85	40.90	286.47	50.76
94.77	22.46	195.95	42.25	296.00	51.49
105.20	25.24	206.18	43.58	298.15	(51.60)

The curves were extrapolated below 51°K. by means of the following Debye and Einstein function sums, which fit the measured data within the limits of temperature and percentage of the heat capacity shown below

Na_3AlF_6: $D(144/T) + 4E(236/T) + 5E(568/T)$ (51–298°K., 1.7%)
NaF: $D(340/T) + E(391/T)$ (51–115°K., 0.2%)
AlF_3: $D(326/T) + E(385/T) + 2E(767/T)$ (51–298°K., 0.8%)

The entropy values are listed in Table II. The extrapolated portions of the total entropies at 298.15°K. are cryolite, 7.2%; sodium fluoride, 4.1%; and aluminum fluoride, 3.5%.

TABLE II

ENTROPIES AT 298.15°K. (CAL./DEG.-MOLE)

	Na_3AlF_6	NaF	AlF_3
0–51°K. (extrap.)	4.12	0.50	0.56
51–298.15°K.	52.86	11.76	15.33
$S^\circ_{298.15}$	57.0 ± 0.4	12.26 ± 0.07	15.89 ± 0.08

The entropy of formation of cryolite from sodium and aluminum fluorides is 4.3 ± 0.5 cal./deg. mole at 298.15° K.

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[CONTRIBUTION FROM THE WRIGHT AIR DEVELOPMENT CENTER]

Infrared Spectra of Cyclopentamethylenedialkylsilanes[1] in the 2–35–Region

BY GORDON D. OSHESKY AND FREEMAN F. BENTLEY

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The infrared absorption spectra of 21 cyclopentamethylenedialkylsilanes have been obtained from 2–35 μ and empirical assignments made for specific vibrations. The series begins with cyclopentamethylene-silane and ends with cyclpentamethylenedioctadecylsilane. Absorption bands at 10.93 to 11.00 and 20.20 to 20.85 μ are tentatively assigned to vibrations arising from the heterocyclic ring. All the observed absorption bands are given in a table showing their position and relative intensities.

This paper presents infrared absorption spectra of a series of cyclopentamethylenedialkylsilanes in the liquid state from 2 to 35 μ. This series of compounds was studied by this Laboratory for the purpose of correlating various physical properties with molecular structure.[2] This paper will deal solely with the infrared absorption bands of this and mainly with the tentative band assignment of the organosilicon ring vibration.

Experimental

Apparatus and Technique.—The infrared spectra in the 2 to 15 μ region were obtained with a Baird Associates, Model B, automatic recording spectrophotometer equipped with a sodium chloride prism. This instrument was calibrated to within ±0.05 μ by using ammonia and polystyrene. The liquid samples were recorded in a 0.028 mm. cell with sodium chloride windows. The thin capillary thicknesses were obtained by placing a drop of liquid between two rock salt plates, which were then fastened tightly together.

The spectra in the 15–35 μ region were obtained on a Perkin-Elmer Model 21, double beam recording spectrophotometer equipped with cesium bromide optics. This prism was calibrated by using atmospheric carbon dioxide and water vapor bands. The accuracy of the wave lengths as recorded here is probably better than ±0.05 μ, which in this region of the spectrum is equivalent to about ±1.5 cm.$^{-1}$. The liquid samples were measured in 0.510 and 0.053 mm. cells with cesium bromide windows. All measurements in the 2 to 35 μ region were made at 24.0 ± 0.5° and at a relative humidity of 35 ± 5%.

Due to insufficient sample the spectra of the diethyl and 2-ethylbutyl derivatives could not be obtained in the 15 to 35 μ region.

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[1] Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

[2] This series of compounds was prepared by Dr. Christ Tamborski, Dr. Harold Rosenberg and Mr. James Groves, and the details of their physical properties and preparation will be published elsewhere.

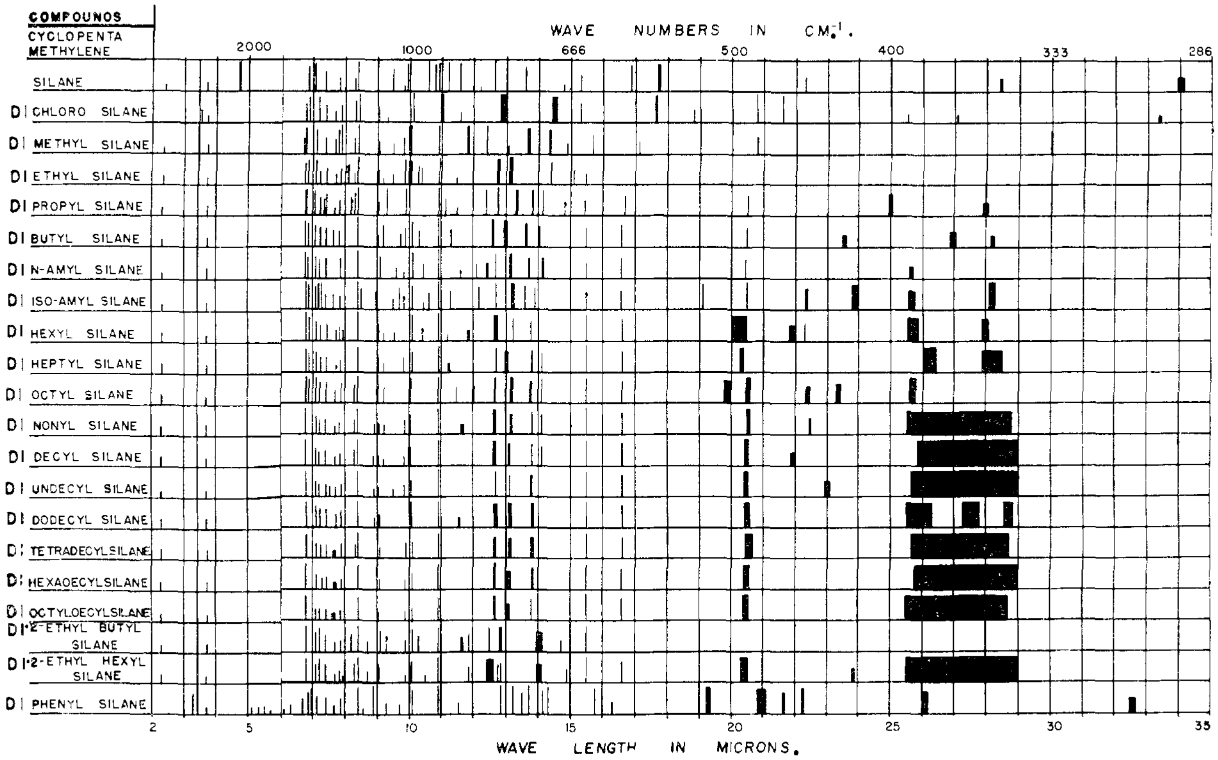

Fig. 1.—Tabulated absorption frequencies of 21 cyclopentamethylenedialkylsilane derivatives.

Materials.—The cyclopentamethylenedialkylsilanes used in this study were fractionated through a 30-cm. short-path Vigreux column. Carbon, hydrogen and silicon analyses were performed on each compound of this series and they were found to be 99% pure. The compounds were analyzed by the Schwarzkopf Microanalytical Laboratory.

Results and Discussion

The difficulty in establishing the presence of a ring in organic molecules by chemical means has promoted interest in identifying the presence of cyclic structures by infrared techniques. Saturated cyclic systems have characteristic frequencies arising from the bond stretching and valence angle modes which occur in the fundamental region. There is a great number of articles in the literature dealing with attempts to characterize alicyclic systems, particularly cyclopropane and cyclobutane, from the infrared spectra, but the situation is still obscure.[3-5] With the possible exception of cyclopropane[6] no certain means of identifying ring systems by the out-of-plane and torsional bending modes beyond 20 μ has so far been realized. A few band assignments for some of the saturated cyclic hydrocarbons are given in Table I.

Tentative frequency assignments have been made for the cyclopentamethylenedialkylsilanes investigated in these studies. Figure 1 lists the 21 compounds recorded and pictorially indicates the band positions and their relative intensities. The infrared spectra of eight of the derivatives of this series are shown in Figs. 2 to 5, inclusively.

TABLE I

Structure	Assigned ring vibrations	Ref.
Cyclopropyl ring	9.8–10.00	7–11
Cyclobutyl ring	10.9–11	12–14
Cyclopentyl ring	10.8–11.3	15, 16
Cyclohexyl ring	9.95–10.5, 9.5–10	15, 16
Cyclopentamethylene silicon ring	10.93–11.00[a]	

[a] Based on the infrared spectra of the cyclic silanes studied in this series.

Carbon–Hydrogen Deformation Frequencies.—Absorption arising from the CH deformation frequencies of these molecules present some interesting correlations. Absorption bands at 6.85 μ in the spectra of cyclopentamethylenesilane and cyclopentamethylenedichlorosilane are apparently due to the CH_2 bending modes of the heterocyclic ring. The position of this band remains constant throughout the series. It is masked to a degree by the CH_2 deformation and CH_3 asymmetrical deformation absorption of the large alkyl substituents on the silicon atom. Absorbance due to the sym-

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(3) E. K. Plyler and N. Acquista, *J. Research Natl. Bur. Standards*, **43**, 371 (1949).

(4) E. K. Plyer, R. Stair and C. J. Humphreys, *ibid.*, **38**, 211 (1947).

(5) R. N. Jones and C. Sandorfy, "Chemical Applications of Spectroscopy," Interscience Publishers, New York, N. Y., 1956, p. 366.

(6) T. K. McCubbin, Jr., and W. M. Stinton, *J. Opt. Soc. Amer.*, **40**, 37 (1950).

(7) J. D. Bartleson, R. E. Burk and H. P. Lankelma, THIS JOURNAL, **68**, 2513 (1946).

(8) J. M. Derfer, E. E. Pickett and C. E. Boord, *ibid.*, **71**, 2482 (1949).

(9) V. A. Slabey, *ibid.*, **74**, 4928 (1952).

(10) S. E. Wiberley and S. C. Bruce, *Anal. Chem.*, **24**, 623 (1952).

(11) M. L. Josien, N. Fuson and A. S. Cary, THIS JOURNAL, **73**, 4445 (1951).

(12) E. B. Reid and M. Sack, *ibid.*, **73**, 1985 (1951).

(13) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(14) J. D. Roberts and H. E. Simmons, Jr., *ibid.*, **73**, 5487 (1951).

(15) L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).

(16) J. Sheppard, *J. Inst. Pet.*, **37**, 95 (1951).

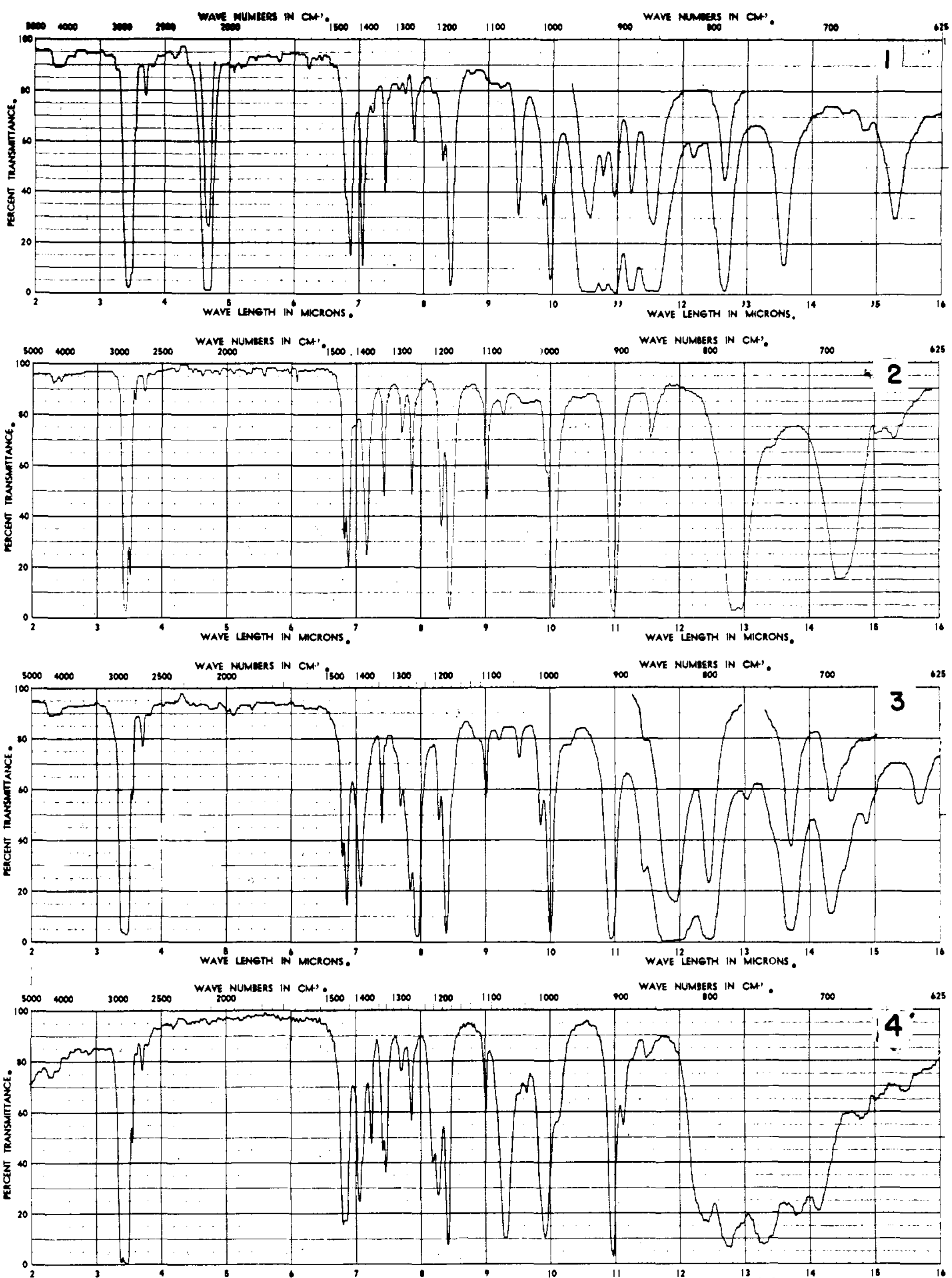

Fig. 2.—Infrared spectra from 2–16 μ of cyclopentamethylene silanes: 1, unsubstituted; 2, dichloro; 3, dimethyl; 4, di-*n*-propyl.

metrical bending vibration of the CH_3–C group at 7.23 μ is clearly present in the spectra of all the molecules of this series containing this group. The intensity of this absorption band gives some indication as to the number of methyl groups present in the molecule. In the spectrum of cyclopentamethylenediisoamylsilane the absorption band is split due to the isopropyl group.[17,18] As would be expected the absorption band at 7.23 μ is not present in the spectrum of cyclopentamethylenedimethylsilane where the methyl group is linked to a silicon atom.

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(17) S. A. Francis, *J. Chem. Phys.*, **18**, 861 (1950).

(18) H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

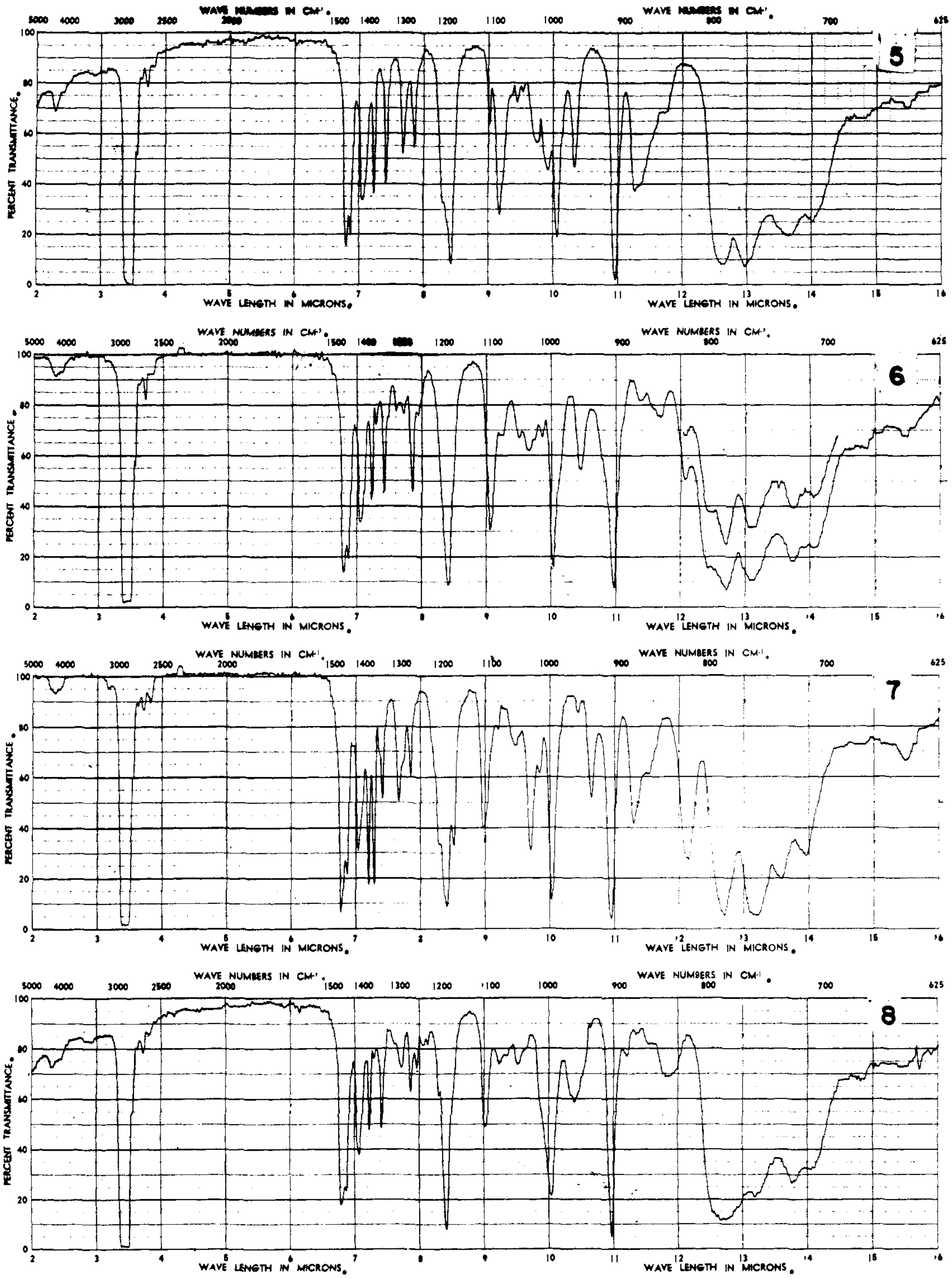

Fig. 3.—Infrared spectra from 2–16 μ of cyclopentamethylene silanes: 5, di-*n*-butyl; 6, di-*n*-amyl; 7, diisoamyl; 8, di-*n*-hexyl.

The strong absorption in the 7.03 to 7.10 μ region is attributed to the deformation vibrations of the CH_2 group linked to the silicon atom. The CH bending vibration of the $Si–CH_3$ group was observed by Wright and Hunter[19] and all the tetraalkylsilanes (more than 30) studied in this Laboratory absorb in this region. Young and co-workers[20] also observed an absorption band at 7.08 μ in the spectra of cyclic disubstituted siloxanes containing $Si–CH_3$ and $Si–CH_2CH_3$ linkages. They tentatively assigned this band to the carbon-hydrogen

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(19) N. Wright and M. J. Hunter, This Journal, **69**, 805 (1947).

(20) C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

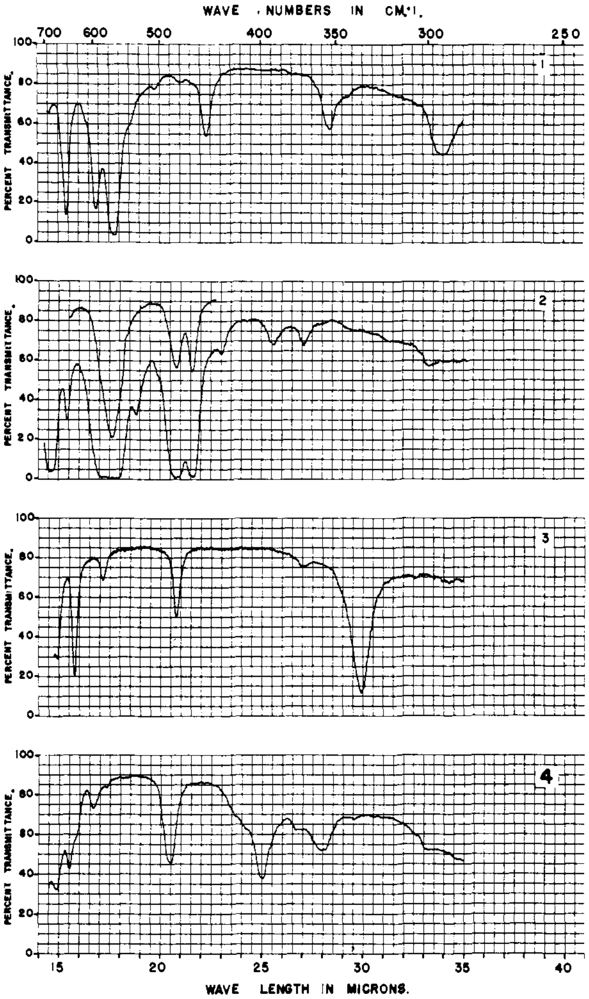

Fig. 4.—Infrared spectra from 15–35 μ of cyclopentamethylene silanes: 1, unsubstituted; 2, dichloro; 3, dimethyl; 4, di-*n*-propyl.

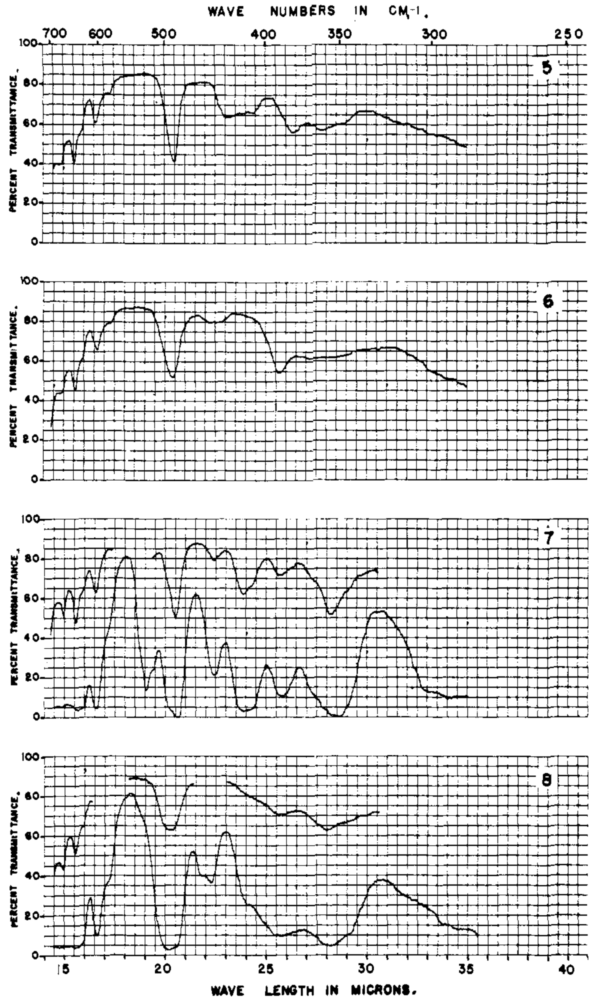

Fig. 5.—Infrared spectra from 15–35 μ of cyclopentamethylene silanes: 5, di-*n*-butyl; 6, di-*n*-amyl; 7, diisoamyl; 8, di-*n*-hexyl.

bending vibrations of the methylene group linked to the silicon atom.

Vibrations Attributed to the Heterocyclic Ring.—Analysis of the spectra of the cyclic silanes led to empirical assignments for the characteristic vibrations of the heterocyclic ring. Absorption bands at 10.93 to 11.00 μ and 20.20 to 20.85 μ in the spectra of these compounds are tentatively assigned to this structure. The sharp absorption band at 10.93 to 11.00 μ appears to be the most promising band for determining the presence of the heterocyclic ring. It is a strong band and is very constant in wave length position throughout this series of compounds. The second band absorbs strongly at 20.20 to 20.85 μ and is present in the spectra of all the cyclic silanes except cyclopentamethylenesilane and cyclopentamethylenediphenylsilane. In the latter spectrum the band is at 21.00 μ, just outside the above range, but in the spectrum of the silane it has shifted to longer wave lengths at 22.30 μ. This band is attributed to the out-of-plane bending mode of the heterocyclic ring.

Several other absorption bands in the spectra of these cyclic silanes appear to be characteristic of the cyclopentamethylene silicon ring, and serve to identify this class of compounds. A weak absorption band at 3.70 to 3.75 μ is present in the spectra of all the cyclic silanes in this series, and most of the cyclopentane and cyclohexane derivatives in the API spectra. It appears to be a characteristic feature of these aliphatic ring systems. A study in the 3 to 4 μ region with a lithium fluoride prism would probably disclose a band characteristic of the C–H vibration of the heterocyclic ring.

The weak absorption band at 7.83 to 7.90 μ is present in the spectra of all the cyclic silanes in this series and appears to be characteristic of the heterocyclic ring. Since Si–CH_3 always absorbs in this region, however, this band is a risky one for other correlations. Cyclohexane has an absorption band at 7.95 μ and most of its derivatives absorb in this region. The 7.83 to 7.90 μ band appears to be associated with the vibrations of the methylene linkage in the heterocyclic ring.

The strong absorption band at 9.95 to 10.05 μ decreases in intensity as heavier alkyl substituents are linked to the silicon atom. The relative position of this band is constant throughout the series. Marrison[15] has noted that most of the published spectra of cyclohexane derivatives show bands in the 9.95 to 10.50 μ and 9.48 to 10.00 μ region, and cyclopentane and cyclopropane[8,9] derivatives absorb in the 10 μ region. Absorption in the 10 μ region also appears to arise from vibrations of the methylene group in the heterocyclic ring.

Vibrations Attributed to the Alkyl-Silicon Linkage.—There has been some dispute over the assignment of absorption bands arising from vibrations of the methylene groups bonded to a silicon atom as to whether it should be assigned to the 11.6 or 8 μ region[21,22] and as to whether it is a deformation or rocking vibration.[19,20] A strong absorption band at 8.42 μ was observed in the spectra of all the cyclic silanes studied. The relative intensity and position of this band is constant throughout the series. This band was also observed in the spectra of alkyl silanes by Kaye and Tannenbaum[23] and it was attributed to the symmetrical deformation vibration of the methylene groups attached alpha to the silicon atom.

An absorption band in the 11.6 μ region was not observed in the cyclopentamethylenedialkylsilane series, but strong bands in the 12 to 13 μ region were observed. These bands are attributed to the methylene groups in the alkyl radical which are bonded to the silicon atom. Young, Koehler and McKinney[24] observed an absorption band at 11.5 μ in the spectrum of tetramethylsilane and assigned this band to a methyl rocking vibration. A strong absorption band is observed at slightly longer wave lengths, 11.90 μ, in the spectrum of cyclopentamethylenedimethylsilane. This band is attributed to a methyl rocking vibration. Absorption bands at 7.97 μ in the latter spectrum and at 8.03 μ in the spectrum of cyclopentamethylenediethylsilane apparently are due to symmetrical deformation vibrations of the methyl and ethyl groups bonded to the silicon atom.

Absorption Characteristic of Disubstituted Silanes.—An absorption band in the 10.6 to 10.7 μ region, characteristic of disubstituted silanes, was observed and reported by West and Rochow,[25] but no frequency assignments were made in that paper. A strong band in this region was also observed by Opitz[26] in the spectra of monosubstituted silanes. He assigned the 10.60 to 10.90 μ region, which is common to disubstituted silanes, to a deformation mode of the $SiH_2=$ group. An absorption band has been observed at 10.58 μ in the spectrum of cyclopentamethylenesilane. This band is in agreement in frequency and intensity with the band for the $SiH_2=$ bending frequency occurring at 10.50 μ for dichlorosilane[27] and 10.62 μ for dibromosilane.[28] This band has been observed to remain essentially constant throughout the spectra of 38 compounds containing two and three hydrogens on silicon.[29,30]

Two strong absorption bands are present in the spectra of the cyclic silanes at 10.0 and 11.0 μ. These bands occur at wave lengths which have been assigned to the terminal vinyl linkage, $-C=CH_2$, in the litarature.[31,32]

Spectra of the Cyclic Silanes in the Long Wave Length Region.—The infrared spectrum of most materials in the wave length region beyond 8 μ is quite sensitive to change in structure, as pointed out many times in the literature.[33] The spectra of this series of cyclopentamethylenedialkylsilanes exhibits this sensitivity to a degree. A noticeable change can be observed in the spectra up to the dinonyl derivatives. Beyond the dinonyl derivative the change may be considered negligible.

Several absorption bands in the wave length region beyond 15 μ are of interest. The medium band at 15.4 to 15.8 μ is very consistent in wave length position in the dialkyl derivatives, and may be related to vibrations of the heterocyclic ring. The medium band at 16.6 μ and the strong broad band at 26 to 29 μ in the spectra of the dialkyl silanes are apparently due to vibrations arising from the alkyl substituents linked to the silicon atom. Similar absorption bands are observed in the spectra of long chain esters studied in this Laboratory. The presence of these bands gives some indication as to the size of the alkyl groups in this type of molecule. The strong band at 29.9 μ in the spectra of cyclopentamethylenedimethylsilane is observed in the spectra of toluene and other cyclic systems containing methyl groups and may be indicative of this group.

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DAYTON, OHIO

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(21) W. F. Edgell and C. H. Ward, THIS JOURNAL, **77**, 6486 (1955).

(22) D. H. Rank, B. D. Saksena and E. R. Shull, *Disc. Faraday Soc.*, **9**, 187 (1950).

(23) S. Kaye and S. Tannenbaum, *J. Org. Chem.*, **18**, 1750 (1953).

(24) C. W. Young, J. S. Koehler and D. S. McKinney, THIS JOURNAL, **69**, 1410 (1947).

(25) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

(26) H. E. Opitz, J. S. Peake and W. H. Nebergall, THIS JOURNAL, **78**, 292 (1956).

(27) J. A. Hawkins and M. K. Wilson, *J. Chem. Phys.*, **21**, 360 (1953).

(28) J. A. Hawkins, S. R. Polo and M. K. Wilson, *ibid.*, **21**, 1122 (1953).

(29) J. S. Peake, W. H. Nebergall and Chen Yun-Ti, THIS JOURNAL, **74**, 1526 (1952).

(30) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(31) F. A. Miller, "Organic Chemistry," Vol. III, Edited by H. Gilman, John Wiley and Sons, New York, N. Y., 1953, p. 138.

(32) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1954.

(33) K. Dobriner, *et al.*, *J. Biol. Chem.*, **172**, 241 (1949).