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THE INFRA-RED SPECTRA OF CYCLOBUTANE COMPOUNDS

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Abstract—In an attempt to locate possible characteristic frequencies of the C_4-ring, the I.R. spectra of 191 cyclobutane derivatives have been examined. It appears that from the standpoint of spectroscopic analysis, a distinction must be made between compounds in which all the ring carbons are tetrahedrally co-ordinated, and those in which one or more ring carbons are trigonally co-ordinated. The most useful correlations appear to be a band near 1235 cm^{-1} for cyclobutane compounds with at least one ring methylene group, and a band near 915 cm^{-1} for mono- and 1,1-disubstituted cyclobutanes; both absorptions are thought to arise from ring methylene motions. Less frequently a band is found close to 750 cm^{-1}, which may reflect an in-plane bending of the ring.

INTRODUCTION

TO THE practicing organic chemist, one of the important problems in the area of I.R. spectroscopy has been the search for characteristic frequencies of typical organic ring systems. In the case of the saturated carbocyclic molecules, moderate success has been achieved in the correlation of the spectra of cyclopropane derivatives, although the number of compounds whose spectra have been studied has been relatively small.[1] Investigation of the spectra of four-, five-, and six-membered rings have at best yielded only tentative results. In view of the enhanced interest recently in the chemistry of small rings, identification of such systems by I.R. means has become even more desirable. In this communication, we report on our examination of the spectra of 191 cyclobutane derivatives. In addition, we would like to propose a novel application of a computer technique, which we feel will be of considerable aid in the analysis of large numbers of spectra.

Previous studies in the correlation of the spectra of cyclobutane compounds have been discussed by Bellamy.[2]

Method

Spectra sources. The spectra used in this investigation were available from the I.R. files of these Laboratories. These files consist in part of approximately 36,000 published spectra, which include the following compilations: Sadtler Standard Spectra, Index of the American Petroleum Institute, Index of the National Research Council-National Bureau of Standards, Index of the American Society for Testing Materials, Documentation of Molecular Spectroscopy, and the Coblentz Spectra.[3] At U.C.L.A.

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[1] J. D. Bartleson, R. E. Burk, and H. P. Lankelma, *J. Amer. Chem. Soc.* **68**, 2513 (1946); V. A. Slabey, **74**, 4928, 4930 (1952); V. A. Slabey, 76, 3604 (1954).

[2] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* John Wiley, New York, (1959).

[3] Wyandotte—American Society for Testing Materials, Infra-red Spectral Absorption Data, Philadelphia, Pa.

these spectra have been stored on magnetic tape with the following restrictions: all absorptions which have intensities at least $\frac{1}{10}$ of the maximum intensity are retained, the rest are eliminated; resolution is 0·1 micron over the range 1·0–25·0 microns. Particular spectra are made available by means of a search routine programmed on an I.B.M. 1401 computer. A total of 96 non-fused cyclobutane and cyclobutene spectra were obtained in this manner. In addition, another 131 unpublished spectra of cyclobutane derivatives were courteously made available from the files of Dr. J. D. Roberts' research group at Caltech.[4] Elimination of duplications and of spectra taken in the gas phase left a total of 122 spectra of cyclobutane compounds and 69 of cyclobutene compounds.

Composite spectra. To a first approximation, the vibrational spectrum of a molecule $R\text{-}Z_i$ may be considered as a superimposition of the individual spectra of the groups R- and Z_i-, plus additional absorptions produced by the presence of the $R\text{-}Z_i$ bond(s). Some combinational tones may also be expected. The problem of discovering the characteristic frequencies of R- can then be thought of as one of detecting the R-signal in the presence of the noise spectrum produced by the presence of Z_i-. If R- and Z_i- are both typical organic residues, the signal-to-noise ratio should be of the order of unity, and the signal is indistinguishable from the background activity. Further data is required to extract the desired information. One method of increasing the signal-to-noise ratio is to treat the noise as a random component, and simply average the spectra of several $R\text{-}Z_i$. Such a procedure can be expected to provide an efficient separation of noise and signal, only if the data can be taken as representative of a truly stochastic process.[5,6] In the case at hand, neither the choice of the groups Z_i nor the vibrations that these groups possess can be considered to be strictly random; that is, Z_i is biased to the extent that it is representative of the particularly common organic linkages, such as C—H, C—N, C=O, etc. Nevertheless, the occurrence of combination bands, coupling effects, and frequency shifts due to differences in bond strengths will tend to augment the random behavior of this component.

Our experience indicates that about 2^4 to 2^5 spectra are needed to produce a composite (average) spectrum with sufficient reduction of the noise level to be of interpretive value. Certain prominent features of the composite spectrum may be detectable with fewer spectra, however.

In order to illustrate this technique, the Sadtler files were searched to obtain the spectra of all monosubstituted benzene compounds, except those containing a substituted or fused-ring aromatic group. A total of 1074 (ca. 2^{10}) different spectra were obtained. These were averaged by an I.B.M. 1401 computer, using the intensity maxima in 0·1 micron "windows" across the spectrum from 1·0–15·0 microns. The resulting composite spectrum is shown in Fig. 1. Since the ordinate axis is best interpreted as a measure of the relative probability of finding a band at a give frequency,

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[4] The preparation of many of these compounds has been described by J. D. Roberts and C. M. Sharts in *Org. React.* **12,** 1 (1962).

[5] For an excellent discussion of the mathematical method and further refinements see W. O. Ash and J. E. Freund, *Randomized Estimates in Power Spectral Analysis* Technical Report No. 31, Dept. of Statistics, Virginia Polytechnic Institute, Blacksburg, Va. (Aug. 1957); also, H. Cramèr, *Mathematical Methods of Statistics*, Princeton University Press, Princeton, N. J. (1957).

[6] For examples of other applications of this method see L. B. C. Cunningham and W. R. B. Hynd, *J. Roy. Statist. Soc.* (Supplement), **8** (1), 62 (1946); H. Press, *J. Amer. Statist. Soc.* **50,** 1022 (1955); H. Press and J. C. Houbolt, *J. Aero. Sci.* **22,** Jan. 1954; M. A. B. Brazier, *Sci. Amer.* **206,** (6), 142 (1962).

the trace has been inverted as is customary in the presentation of power spectra. Of the 14 principal peaks, 9 of these have been considered typically present in monosubstituted benzene systems.[2] The remaining bands (3·00, 7·70, 7·90, 10·90, and 12·00 μ) are less prominent and may not rise sufficiently above the general noise level to be of much interpretive value.

The spectrum of cyclobutane[7] itself indicates that, in addition to specific ring motions, the motions of the ring methylene groups should be important in characterizing the spectra of cyclobutane derivatives (*vide infra*). In view of this, the composite spectrum of the cyclobut*ane* system was prepared from 81 spectra of cyclobutane derivatives, which met the following restrictions: all contained at least one ring methylene group, and none possessed a fused-ring or spirane structure; no cyclopropyl nor cyclopentyl group could be present in the molecule; no cyclobutene compounds were included. The resultant spectrum is shown in Fig. 4. For comparison purposes the corresponding composite spectra of 105 cyclopropane derivatives (Fig. 5), 41 cyclopentane compounds (Fig. 3), and 44 open chain alkanes (Fig. 2) were prepared.

It cannot be overemphasized, that one should not try to extract more information from Figs. 1-5 than the data, from which they were constructed, permit. The pub-

FIGS. 1-5—"Composite Infra-red Spectra"[a]

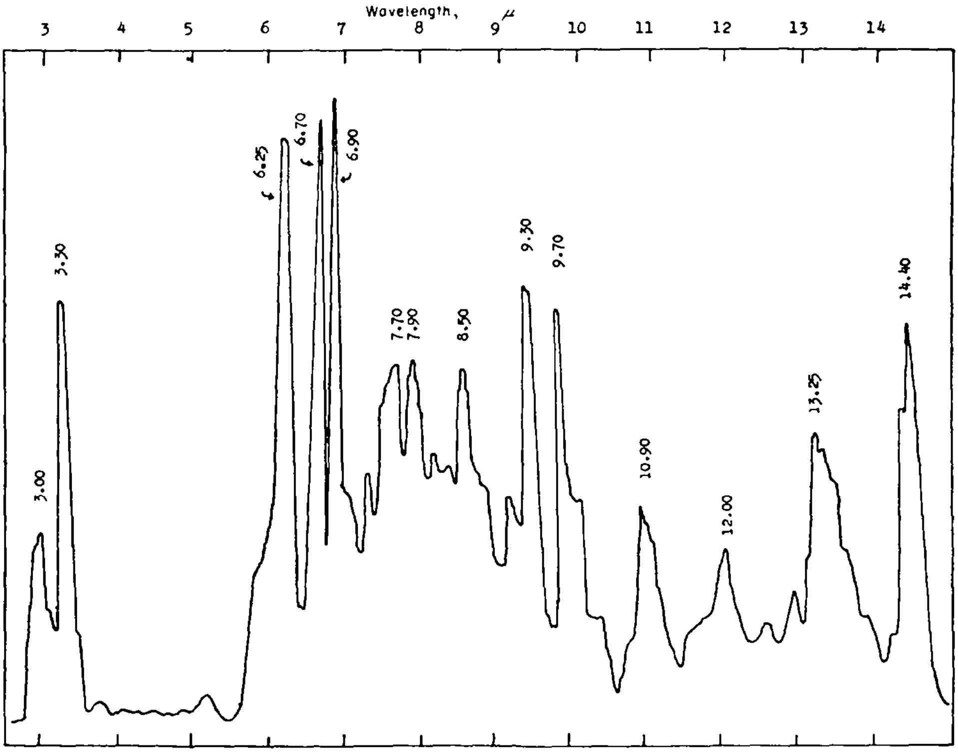

FIG. 1. Monosubstituted benzenes (1074 compounds)
[a] The error in the position of the maxima is ±0·05 μ.

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[7] G. W. Rathjens, Jr., *et al.*, *J. Amer. Chem. Soc.* 75, 5634 (1953).

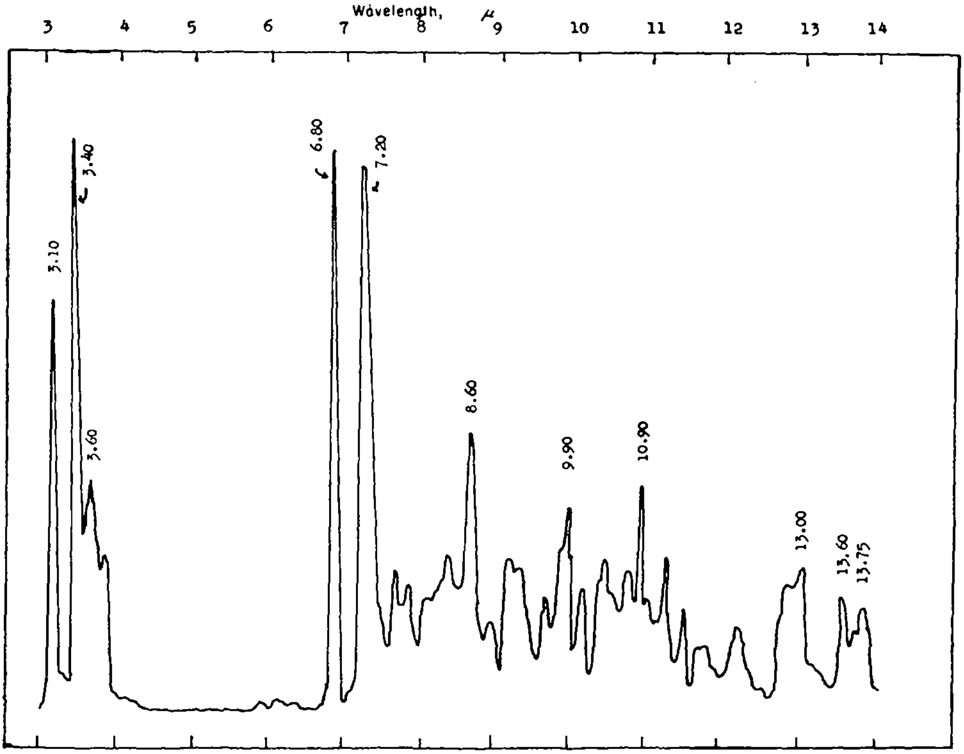

FIG. 2. Alkanes (44 compounds)

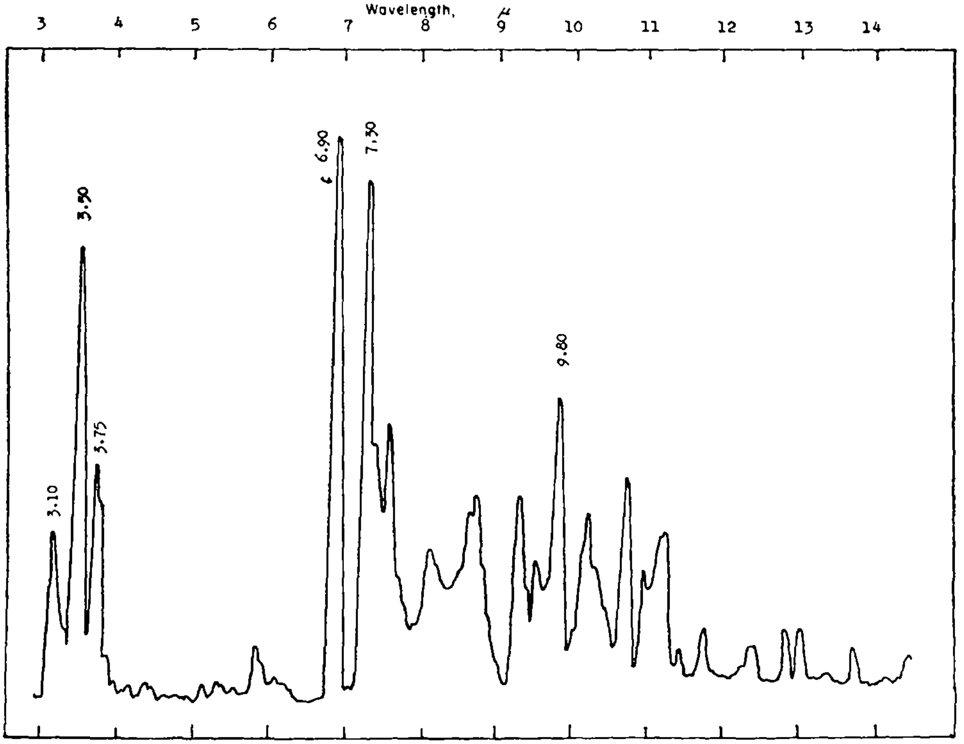

FIG. 3. Cyclopentanes (41 compounds)

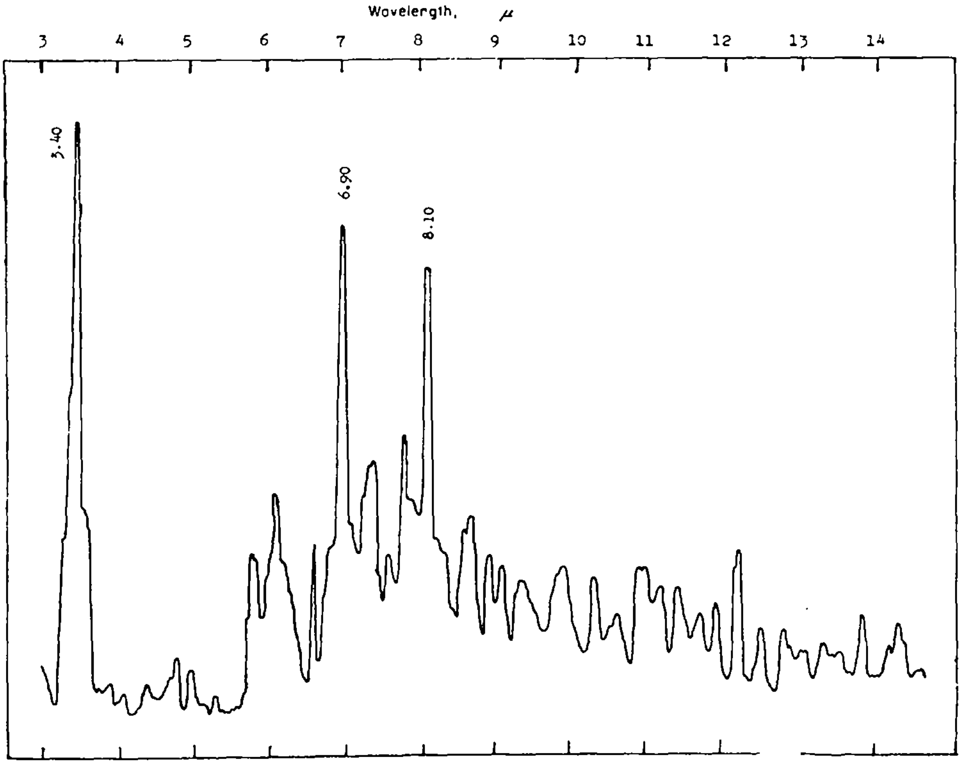

FIG. 4. Cyclobutanes (81 compounds)

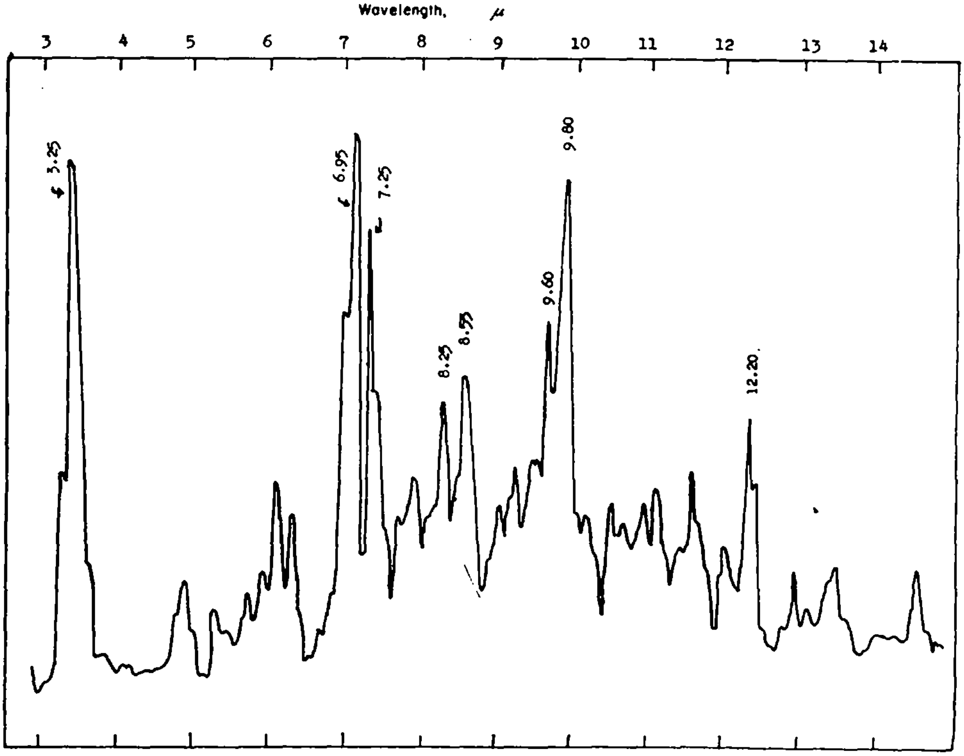

FIG. 5. Cyclopropanes (105 compounds)

lished spectra used in this study were prepared on numerous instruments, under various conditions, using samples (both neat and in solution) of undetermined purity. Consequently, the primary purpose served by the composite spectrum was to indicate where, if anywhere, in the spectra of cyclobutane compounds a characteristic absorption might be found. The discussion below was based then on the examination of the individual spectra, many of which were not used to construct Fig. 4.

General distribution of absorption maxima. It was suggested to us by Dr. R. M. Badger, that in order to evaluate the significance of the findings discussed below, it would be useful to know the probability of finding an absorption at a particular wavelength in the spectrum of a randomly chosen compound, which does not contain the group in question, i.e., the cyclobutane ring. To obtain a measure of these probability values, the positions of all the maxima (each at least $\frac{1}{10}$th as strong as the most intense absorption) of the spectra in the Sadtler organic index were tallied, and the relative occurrence frequencies were computed for each 0·1 μ (Table 1). Since the compounds in the Sadtler index may be considered to be approximately representative of organic compounds in general, the relative frequencies will be approximately equal to the "actual" probability values. The accuracy of the approximation will depend on the extent to which the Sadtler index may be biased in its sampling. Although the spectra of cyclobutane compounds were included in this tally, their deletion could not change any probability value by more than about 0·6%.

TABLE I. RELATIVE OCCURRENCE FREQUENCIES FOR I.R. ABSORPTION BANDS OVER THE REGION 2·0–14·9 μ BASED ON 17,345 SPECTRA IN THE SADTLER (ORGANIC) INDEX

	0·Y ± 0·05 μ									
X.0 μ	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
2·0	< 0·001	< 0·001	0·003	0·006	0·003	0·001	< 0·001	0·001	0·016	0·145
3·0	0·183	0·107	0·095	0·155	0·414	0·165	0·035	0·026	0·047	0·028
4·0	0·016	0·010	0·006	0·006	0·006	0·136	0·005	0·007	0·005	0·003
5·0	0·002	0·005	0·008	0·008	0·006	0·008	0·017	0·047	0·148	0·147
6·0	0·149	0·175	0·362	0·285	0·138	0·099	0·199	0·255	0·294	0·395
7·0	0·220	0·216	0·230	0·304	0·228	0·210	0·238	0·257	0·252	0·264
8·0	0·246	0·202	0·213	0·173	0·205	0·202	0·202	0·226	0·188	0·182
9·0	0·193	0·174	0·172	0·184	0·168	0·119	0·151	0·193	0·195	0·145
10·0	0·122	0·093	0·099	0·096	0·110	0·087	0·095	0·092	0·108	0·113
11·0	0·109	0·089	0·090	0·086	0·089	0·089	0·099	0·102	0·107	0·104
12·0	0·114	0·100	0·110	0·099	0·097	0·080	0·084	0·079	0·085	0·087
13·0	0·117	0·110	0·144	0·130	0·125	0·093	0·082	0·073	0·087	0·080
14·0	0·061	0·059	0·066	0·089	0·108	0·082	0·065	0·040	0·033	0·026

RESULTS AND DISCUSSION

Cyclobutane. The spectrum of cyclobutane itself has been examined in detail by Rathjens *et al.*[7] It is reported to be complicated by the fact that the barrier to internal rotation about the C—C bond appears small enough to allow an equilibrium to exist between the planar (D_{4h}) and bent (D_{2d}) conformations, both symmetry forms being sufficiently populated at ambient temperatures to be spectroscopically active.[8] The

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[8] Recent evidence from electron diffraction studies give support to D_{2d} as the average symmetry species; O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* **15**, 711 (1961); c.f., J. D. Dunitz and V. Schomaker, *J. Chem. Phys.* **20**, 1703 (1952); high resolution Raman studies also favor this species. R. C. Lord and B. P. Stoicheff, *Canad. J. Phys.* **40**, 725 (1962).

most characteristic vibration, the ring breathing motion of the planar constellation, is unfortunately only Raman active,[9] appearing at 970 cm^{-1} (10·30 μ). This signal is expected to be weak at most in substituted ring systems. For cyclobutane molecules with D_{2d} symmetry, there is an I.R. band at 750 cm^{-1} (13·33 μ), which has been assigned to an in-plane ring bending motion.[7] This absorption should be important in the spectra of substituted cyclobutanes in which bulk and torsional effects tend to favour the non-planar conformation. Another pair of motions, which might be expected to be characteristic of cyclobutane derivatives, also appears in the spectrum of the parent compound. One is the methylene (—CH_2—) twisting movement. This mode is silent in the infra-red for molecules with D_{4h} symmetry, but is active for the lower symmetry form and appears at 1220 cm^{-1} (8·20 μ). Rocking of the methylene group produces a band at 901 cm^{-1} (11·10 μ). In open chain hydrocarbons, the corresponding frequencies are near 1305 cm^{-1} (7·66 μ) and 720 cm^{-1} (13·88 μ).[10]

Region near 3000 cm^{-1} (3·4 μ). In cyclobutane[7] the C—H stretching motions give rise to strong bands at 2974 cm^{-1} and 2896 cm^{-1}. Conclusions to be drawn from several previous investigations[2] suggest that for cyclobutane derivatives these motions appear at lower frequencies, namely at 2926 ± 10 cm^{-1} and 2853 ± 10 cm.$^{-1}$ Our investigation of this region was hampered by the lack of good resolution here of many spectra. After an examination of the spectra of 18 cyclobutane compounds possessing a relatively simple band structure in this region, we found that it was possible to identify two bands at 2915–2950 cm^{-1} and 2855–2875 cm^{-1}. Three of the spectra were of the pure liquids and the rest were of carbon tetrachloride solutions. The latter interval coincides with the one reported by Wiberley.[11]

Cyclobutene components usually gave rise to very weak absorptions near 3000 cm^{-1}, and we were unable to obtain much information about them. It appears that the stretching frequencies of the vinyl C—H units are not significantly shifted by the effects of ring strain. A more detailed study of this region, however, should be made.

Region near 1450 cm^{-1} (6·9 μ). The methylene group of saturated hydrocarbons is responsible for a remarkably constant band at 1468 cm.$^{-1}$ This absorption is due to the bending deformation of the H—C—H angle. This so-called "scissoring" motion[12] is readily identified in hydrocarbon spectra, since it is usually the only strong intensity between 1400 and 1500 cm.$^{-1}$ When the polymethylene chain forms a ring, this absorption is shifted to longer wavelengths. Thus, in carbon tetrachloride, the corresponding band of cyclohexane undergoes a significant displacement,[13] falling to 1452 cm.$^{-1}$ In cyclopentane no further shift is observed, and the bands appear at 1453 cm.$^{-1}$ The spectrum of liquid cyclobutane,[7] at ambient temperatures, possesses a doublet at 1453 cm^{-1} and 1450 cm.$^{-1}$ In cyclopropane[14] the methylene deformation

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[9] M. I. Batuev, *Izv. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk.* No. 1, 3 (1947); *Chem. Abstr.* **42,** 4463 (1948).

[10] See R. N. Jones and C. Sandorfy in *Chemical Applications of Spectroscopy* (Edited by W. West) pp. 359 ff. Interscience, New York, (1956).

[11] S. E. Wiberley, S. C. Bunce, and W. H. Bauer, *Analyt. Chem.* **32,** 210 (1960).

[12] When the proportion of methyl groups present in the molecule is large, the asymmetrical vibration near 1460 cm.$^{-1}$ may become more conspicuous; however, it usually provides no more than a shoulder on the more intense methylene absorption under typical resolution. See ref. 2.

[13] R. N. Jones and A. R. H. Cole, *J. Amer. Chem. Soc.* **74,** 5648 (1952); R. N. Jones, A. R. H. Cole, and B. Nolin, *Ibid.* **74,** 5662 (1952).

[14] A. W. Baker and R. C. Lord, *J. Chem. Phys.* **23,** 1636 (1955).

falls sharply to 1434 cm.$^{-1}$ The corresponding in-plane deformation of terminal alkenes[2] (cycloethanes) is found near 1415 cm.$^{-1}$ The cause of this shift to lower frequencies may, as in the case of C—H stretching vibrations, be due to a combination of effects arising from a decrease in ring size. Such factors include bond angle strain, compression of the C—C bond, changes in the state of aggregation of the methylene groups, and changes in the electronegativity of carbon due to differences in bond hybridization.

Except for the case of terminal alkenes, very little use has been made of the position of the methylene deformation in the infra-red identification of cycloparaffinic structures. Recently,[10,13] however, careful analysis of the spectra of certain steroids has shown that the methylene groups of the D-ring can be distinguished from those of the side-chain and of the six-membered rings. The fact that the position and the intensity of this absorption is strongly influenced by the presence of electronegative substituents has tended to obscure its usefulness in problems of structure identification. This is due largely to the lack of sufficient data on the spectral shifts involved, though other deterrents can also be blamed (*vide infra*). In cyclobutane compounds, this change in position is illustrated by the following series of mono- and 1, 1-disubstituted derivatives: methyl- (1459 cm^{-1}), hydroxy- (1453 cm^{-1}), bromo- (1453 cm^{-1}), amino- (1451 cm^{-1}), phenyl- (1449 cm^{-1}), chloro- (1448 cm^{-1}), l-chloro-l-carboxy- (1418 cm^{-1}), l-fluoro-l-carboxy- (1406 cm^{-1}) and oxo- (1396 cm^{-1}). The shifts are seen to parallel group electronegativities very well. Although the shifts noted here are quite large, it is still often possible to observe the effects of ring size on this absorption within an homologous series of cycloalkyl derivatives. For example, Nolin and Jones[15] have shown that the C—H bending of the α-methylene groups of ketones is displaced down to 1430–1410 cm.$^{-1}$ The values of the corresponding cyclic systems are 1422 cm^{-1}, 1404 cm^{-1} and 1396 cm^{-1} for neat cyclohexanone, cyclopentanone and cyclobutanone[16] respectively. A similar trend is observed in the analogous *exo*-cyclic methylene derivatives (1457 cm^{-1}, 1447 cm^{-1}, and 1428 cm^{-1}; neat). This shift to longer wavelengths is further illustrated in the spectra of the cycloalkyl bromides and chlorides published by Roberts and Chambers,[17] as well as in the A.P.I. spectra[18] of mono- and 1, 1-dialkylcycloalkanes. The spectra of the cycloalkylbenzenes and the cycloalkyl carboxylic acids do not follow the usual trend. The observed deviations may be due to a coupling of the scissoring mode with the 1450 cm^{-1} skeletal motion of the aromatic ring, and with a C—O motion near 1440 cm^{-1} respectively. Although coupling of this kind should be weak, this belief is strengthened by the fact that the proper order is restored when the benzene ring is partially hydrogenated and when the carboxyl group is reduced to an aldehyde function.

Examination of this region of the spectrum showed that 93% (26/28) of the cyclopentane structures absorbed over 1460–1430 cm^{-1}, 76% (84/111) of the cyclobutanes over 1450–1420 cm^{-1}, while 80% (84/105) of the cyclopropane derivatives displayed bands in the region 1430–1390 cm.$^{-1}$ Nevertheless, except within a series of

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[15] B. Nolin and R. N. Jones, *J. Amer. Chem. Soc.*, **75**, 5626 (1953).

[16] A higher value of 1402 cm.$^{-1}$ has been reported for cyclobutanone; Von Kl. Schäffer, *et al.*, *Z. Elektrochem.* **65**, 2 (1961).

[17] J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.* **73**, 5031 (1951).

[18] American Petroleum Institute, Index of Infra-red Absorption Data, published by the A.P.I. Research Project 44 and the Manufacturing Chemists Association, National Bureau of Standards.

analogously substituted cycloalkanes, the position of the methylene deformation is not sufficiently characteristic of ring size to be used as a means of identification.

We have observed, however, that in the monosubstituted cyclopropane spectra, the methylene scissoring band is invariably split by about 10–15 cm^{-1}, while in monosubstituted cyclobutane spectra splitting appears in about $\frac{2}{3}$rds of the cases. Cyclopentane compounds less frequently (ca. $\frac{1}{3}$ of the time) possess a sharp absorption with a shoulder on the higher frequency slope, but seldom have the well defined doublet structure found in the smaller rings. Six-membered rings and open chain systems possess a single band as long as the methylene groups are not rendered greatly unequivalent by the presence of strong electron withdrawing groups. Inasmuch as the cyclopropane ring structure can usually be identified by reference to bands near 1020 cm^{-1} (9·8 μ) and 3050 cm^{-1} (3·27 μ), the absence of these bands along with the 10–15 cm^{-1} splitting of the methylene band may be evidence for the cyclobutane ring. Since the cause of this splitting is not clear, such interpretations should be made with caution, and one should be aware, in so far as possible, of those structural features which are likely to complicate the analysis of this region of the spectrum. In this connection, it may be mentioned, that the presence of one or more fluorine atoms on the cyclobutane ring may give rise to a band between 1430 cm^{-1} and 1330 cm.$^{-1}$ Bands of similar contour and intensity below 1350 cm^{-1} have been observed by Thompson *et al.*[19] in a variety of fluorinated substances, although the group motions responsible for them have not yet been determined.

In addition, 31 spectra of cyclobutene compounds containing the ring methylene group were examined. An absorption was invariably found below 1445 cm.$^{-1}$ It was not always clear whether this kind was due to the ring methylene unit or to some other group.

Region near 1235 cm^{-1} (8·10 μ). According to the composite spectrum of 81 cyclobutane compounds (Fig. 4), an absorption occurs near 1235 cm^{-1} frequently enough to merit consideration as a possible characteristic vibration. No absorption is noted here for the cyclopropane and cyclopentane compounds examined. Since this band is very likely associated with the methylene twisting motion on the four-membered ring,[7] the spectra of derivatives containing this group were examined in detail in this region. A medium to strong signal appeared in 55% (61/111) of the cases at 1235 ± 10 cm.$^{-1}$ In 87% (96/111) of the spectra, a band was found over 1235 ± 20 cm^{-1}, while the interval 1200–1260 cm^{-1} contained a band in 93% (103/111) of the cases. Polysubstituted cyclobutanes generally represented the exceptions. Some caution must be exercised in interpreting these figures, however, since this is a region of high spectral activity (Table 1). It may be that some of the observed absorptions should be ascribed to strong C—O motions. Nevertheless, the relative constancy of the 1235 cm^{-1} band in a large number of compounds indicates that it should be very useful in identifying the cyclobutane ring.

This band is not seen in the spectra of perdeuterocyclobutane and nine other cyclobutane compounds in which the ring methylene units are missing. On the other hand, cyclobutane and cyclobutane systems, which contain fluorine attached to the ring, e.g. perfluorocyclobutane itself, are quite likely to possess a strong absorption near 1235 cm.$^{-1}$

[19] P. Torkington and H. W. Thompson, *Trans. Faraday Soc.* **41**, 236 (1945); H. W. Thompson and R. B. Temple, *J. Chem. Soc.* **1948**, 1422.

It is interesting that all of fourteen compounds containing one *exo*-cyclic double bond attached to the ring (either $=CR_2$ or $=O$) presented an absorption near 1235 cm^{-1}, while as a rule cyclobutene derivatives did not. Some exceptions were noted. In particular, eleven derivatives of l-phenylcyclobutene absorbed near 1240 cm.$^{-1}$ In simple systems, it appears that the 1235 cm^{-1} band may be of some value in distinguishing between *endo*- and *exo*-cyclic double bonds, if the presence of the C_4-ring has already been established.

Region near 900 cm^{-1} (11 μ). Earlier investigators have observed a band at 910–920 cm^{-1} in a number of cyclobutane spectra, and they have identified it with a methylene rocking mode.[20] Our investigation revealed that this band occurs frequently (82%, 40/49) in the spectra of mono- and l, l-disubstituted cyclobutanes over the interval 910–925 cm.$^{-1}$ It is, however, comparatively rare (22%, 16/73) in the spectra of cyclobutane compounds which possess a different substitution pattern, but which still retain at least one ring methylene group. It should be pointed out, that the behavior of the methylene rocking motion, unlike the other bending modes of the methylene group, is in general considerably more susceptible to the influence of neighboring groups.[10] The incidence of absorptions over the range 890–925 cm^{-1} was 53% (39/73). Cyclopentane compounds have been reported[21] to absorb near 890 cm^{-1} as well as near 930 cm.$^{-1}$ Fig. 3 displays bands near these values (11·2 μ and 10·8 μ).

We are not able to concur with Marrison[22] that a characteristic signal appears at 960–1000 cm^{-1} for cyclobutane systems. We observed an absorption in this interval only 31% (38/122) of the time; many of these were very weak bands. It may be significant that eleven of these compounds contained fluorine, although the C—F bond usually produces peaks at frequencies above 1000 cm^{-1}[2].

Deformation of the C—H bond of the terminal methylene group of alkenes produces a band at 890 ± 5 cm.$^{-1}$ In methylenecyclobutane compounds, this band appears to be shifted to slightly longer wavelengths. For non-conjugated methylene groups, the band shifts to 875 ± 5 cm^{-1} (six compounds), while for conjugated systems, the peak is at 845–850 cm^{-1} (nine compounds). As examples: methylenecyclobutane (879 cm^{-1}), 3-methyl-l-methylenecyclobutane (876 cm^{-1}), 1, 3-dimethylenecyclobutane (870 cm^{-1}); 3, 4-dimethylenecyclobutene (848 cm^{-1}), l-phenyl-3, 4-dimethylenecyclobutene (847 cm^{-1}), 2-chloro-1-phenyl-3,4-dimethylenecyclobutene (846 cm^{-1}), and l-phenyl-3-methylenecyclobutene (850 cm^{-1}). In allenes[23] (methylenecycloethanes) this band is near 860 cm.$^{-1}$

Region near 750 cm^{-1} (13·3 μ). Use of solvents blocked out the region near 750 cm^{-1} in most of the spectra available to us. However, a band at 745 ± 5 cm^{-1} was observed in 70% (19/27) of the cases. This may result from the low frequency inplane bending of the four-membered ring.[7]

Acknowledgments—We are particularly indebted to Dr. Robert A. Sparks for writing the computor programs essential to this study, and for making his infra-red files available to us. Also we are extremely grateful to Dr. Richard M. Badger, whose valuable criticisms were an asset in the preparation of this manuscript.

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[20] T. P. Wilson, *J. Chem. Phys.* **11**, 369 (1943); J. M. Derfer *et al.*, *J. Amer. Chem. Soc.* **71**, 2482 (1949); E. B. Reid and M. Sack, *Ibid.* **73**, 1985 (1951).

[21] N. Sheppard, *J. Inst. Petrol.* **37**, 95 (1951).

[22] L. W. Marrison, *J. Chem. Soc.* **1951**, 1614.

[23] R. S. Rasmussen and R. Brattain, *J. Chem. Phys.* **15**, 131 (1947).