Near-Infrared Studies. The Dependence of the Cyclopropyl C–H Stretching Frequency on Inductive Effects

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The first overtone of the fundamental C–H stretching vibration of 58 cyclopropanes has been measured. The position of the absorption was found to be a function of the inductive effect of substituent groups.

Since our initial publication[2] on the use of near-infrared spectroscopy in the identification of cyclopropanes, several articles have appeared which discuss the identification of cyclopropanes by infrared methods.[3–6] Although the utility of this spectroscopic method of identifying cyclopropanes has been firmly established, relatively little is known about the dependence of the cyclopropyl C–H stretching frequency on the nature of substituent groups. On the basis of our early work we reported a correlation of absorption frequency with the Taft σ^* value of substituent groups.[2] Using our published data[2] Charton claimed that the cyclopropyl C–H stretching frequency showed good correlation with σ_m and σ_p, and fair correlation with σ_I.[7] On the basis of much additional data we are now able to evaluate critically this dependence of C–H stretching frequency on inductive effects.

Table I lists the absorption maxima of 37 simple substituted cyclopropanes. Scanning this list quickly illustrates that passing from the strongly electron-withdrawing groups such as cyano down to electron-inducing methyl groups gives a shift in the absorption maximum from 1.624 to 1.650 μ. This systematic increase in the wave length of the first overtone of the fundamental C–H stretching frequency with the decrease in the electron-withdrawing power of the substituents suggested that a dependable correlation should exist between the position of absorption maxima and the substituent-group inductive-effect parameters.

The correlation of substituent constants of functional groups with infrared group frequencies has been of considerable interest in recent years.[8] In the aliphatic series the carbonyl stretch of ketones[9] and amides[10] has been studied as a function of substituent constants. In addition, the OH stretch of acids,[11] the asymmetric nitro stretch,[12] and the nitrile stretching frequency[13] have been correlated with the Taft σ^* constants of substituent groups. A rough correlation of the first overtone of the olefinic C–H stretch in norbornenes with the electron-withdrawing nature of the substituent groups has also appeared recently.[14]

Plots of the near-infrared maxima of simple substituted cyclopropanes *vs.* σ_m, σ_p, and σ^* and σ_I are shown in Figures 1–4. The σ_m plot[15] clearly illustrated that the proposal of Charton,[7] that cyclopropyl C–H stretching frequencies showed good linear correlation with σ_m, could not be substantiated on the basis of extensive data. The σ_p correlation[7,15] also fell victim to the effect of the newly accumulated measurements. In particular, cyclopropylamines were grossly out of place on the σ_p relationship.

A correlation of σ_I[16] with the first overtone of the C–H stretching frequencies of cyclopropanes containing an unsubstituted methylene group in the ring gave the rough plot shown. Although the tendency for a shift to shorter wave length with the increasing electron-withdrawing effect of substituents is obvious, the plot cannot be considered to represent a good linear correlation.

The best over-all correlation was obtained from the σ^* *vs.* C–H stretching frequency plot.[17,18] This plot generally allows the prediction of the near-infrared absorption maximum of new cyclopropanes containing an unsubstituted methylene group in the ring[19] to within ±0.002 μ.

Examination of Table I shows that the phenyl group invariably shifted the cyclopropyl CH_2 absorption to longer wave length as is illustrated in Table II. In view of this consistent effect and the general tendency of groups which are more electron-inducing than hydrogen to show such shifts, it is felt that the phenyl group is electron-inducing relative to hydrogen. A similar conclusion can be reached concerning the $-CH_2OH$ group. On the other hand, the $-NH_2$ group seem to be slightly electron-withdrawing relative to hydrogen. The shift to lower frequency with the introduction of a phenyl group onto the cyclopropyl ring might be construed as a simple conjugation effect. The cyclopropane ring is known to possess a somewhat delocalized character on the basis

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(1) Sinclair Oil Corp. Foundation Fellow, 1964–1965.

(2) P. G. Gassman, *Chem. Ind.* (London), 740 (1962).

(3) M. Hanack, H. Eggensperger, and S. Kang, *Ber.* **96**, 2532 (1963).

(4) M. Horák, J. Šmejkal, and J. Farkaš, *Collection Czech. Chem. Commun.*, **28**, 2280 (1963).

(5) H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964).

(6) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, submitted for publication.

(7) M. Charton, *J. Chem. Soc.*, 1205 (1964).

(8) For a discussion of these correlations, see C. N. R. Rao and R. Venkataraghaven, *Can. J. Chem.*, **39**, 1757 (1961). See also L. J. Bellamy, *J. Chem. Soc.*, 4221 (1955).

(9) C. N. R. Rao, G. K. Goldman, and C. Lurie, *J. Phys. Chem.*, **63**, 1311 (1959); D. G. O'Sullivan and P. W. Sadler, *J. Chem. Soc.*, 4144 (1957).

(10) T. L. Brown, J. F. Regan, R. D. Schultz, and J. C. Steenberg, *J. Phys. Chem.*, **63**, 1324 (1959).

(11) J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954).

(12) R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); J. Mason and J. Dunderdale, *ibid.*, 759 (1956).

(13) J. P. Jesson and H. W. Thompson, *Spectrochim. Acta*, **13**, 217 (1958).

(14) P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965).

(15) The values for σ_m and σ_p were obtained from H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

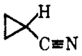
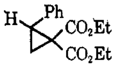
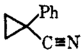
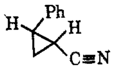
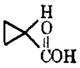
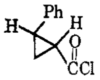
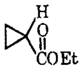
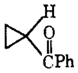
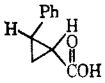
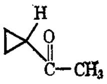
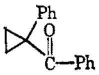
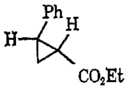
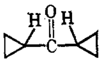
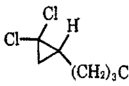
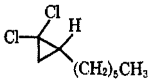
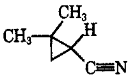
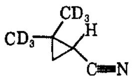
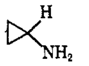
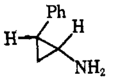
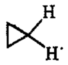
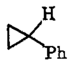
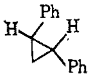
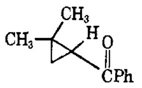
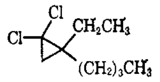
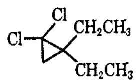
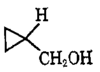
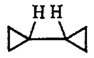
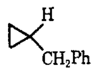
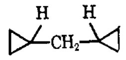
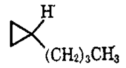
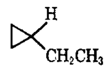
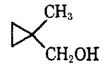
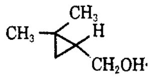
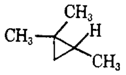
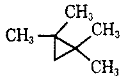
(16) The σ_I values used were obtained from F^{19} shielding values measured in nonprotonic solvents by R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963).

(17) The σ^* values were taken from R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556–675.

(18) The exceptionally good correlation obtained may be due to the absence of accurately measured σ^* values for such groups as NH_2, CO_2H, $-C{\equiv}N$, and Cl.

(19) It should be stressed that cyclopropanes which are substituted on all three positions, such as 1,2,3-trimethylcyclopropane, do not have absorption maxima in the 1.625–1.650-μ region of the spectrum.

Table I

No.	Compound	$\lambda_{max}^{CCl_4}$ μ	$\lambda_{max}^{CCl_4}$ Cm.$^{-1}$	Molar absorptivity per cyclopropyl CH_2
1		1.624	6158	0.242
2		1.624	6158	0.308
3		1.625	6154	0.361
4		1.625	6154	0.300
5		1.626	6150	0.348
6		1.626	6150	0.285
7		1.626	6150	0.350
8		1.627	6146	0.370
9		1.627	6146	0.309
10		1.628	6142	0.335
11		1.628	6142	0.379
12		1.628	6142	0.285
13		1.629	6139	0.338
14		1.629	6139	0.273
15		1.629	6139	0.260
16		1.631	6131	0.325
17		1.631	6131	0.334
18		1.632	6127	0.279
19		1.632	6127	0.260
20		1.632	6127	0.215
21		1.633	6124	0.258
22		1.6345	6118	0.261
23		1.635	6116	0.328
24		1.636	6112	0.457[a]
25		1.636	6112	0.290
26		1.637	6109	0.306
27		1.637	6109	0.337
28		1.637	6109	0.291
29		1.638	6105	0.281
30		1.638	6105	0.324
31		1.638	6105	0.286
32		1.639	6101	0.285
33		1.639	6101	0.308
34		1.640	6098	0.268
35		1.644	6083	0.317
36		1.647	6072	0.268
37		1.650	6051	0.272

[a] The exceptionally large molar absorptivity for 1,2-diphenylcyclopropane was due to a slight overlap of the first overtone of the cyclopropyl C–H stretching frequency with the first overtone of the aromatic C–H stretching frequency.

of theoretical,[20] ultraviolet,[21,22] infrared,[21] and n.m.r.[23] studies. These delocalized electrons exist in the plane of the ring and have been attributed to the overlap of bent bond orbitals.[24] If a simple conjugative effect was the explanation of our phenomena, it seems rather sur-

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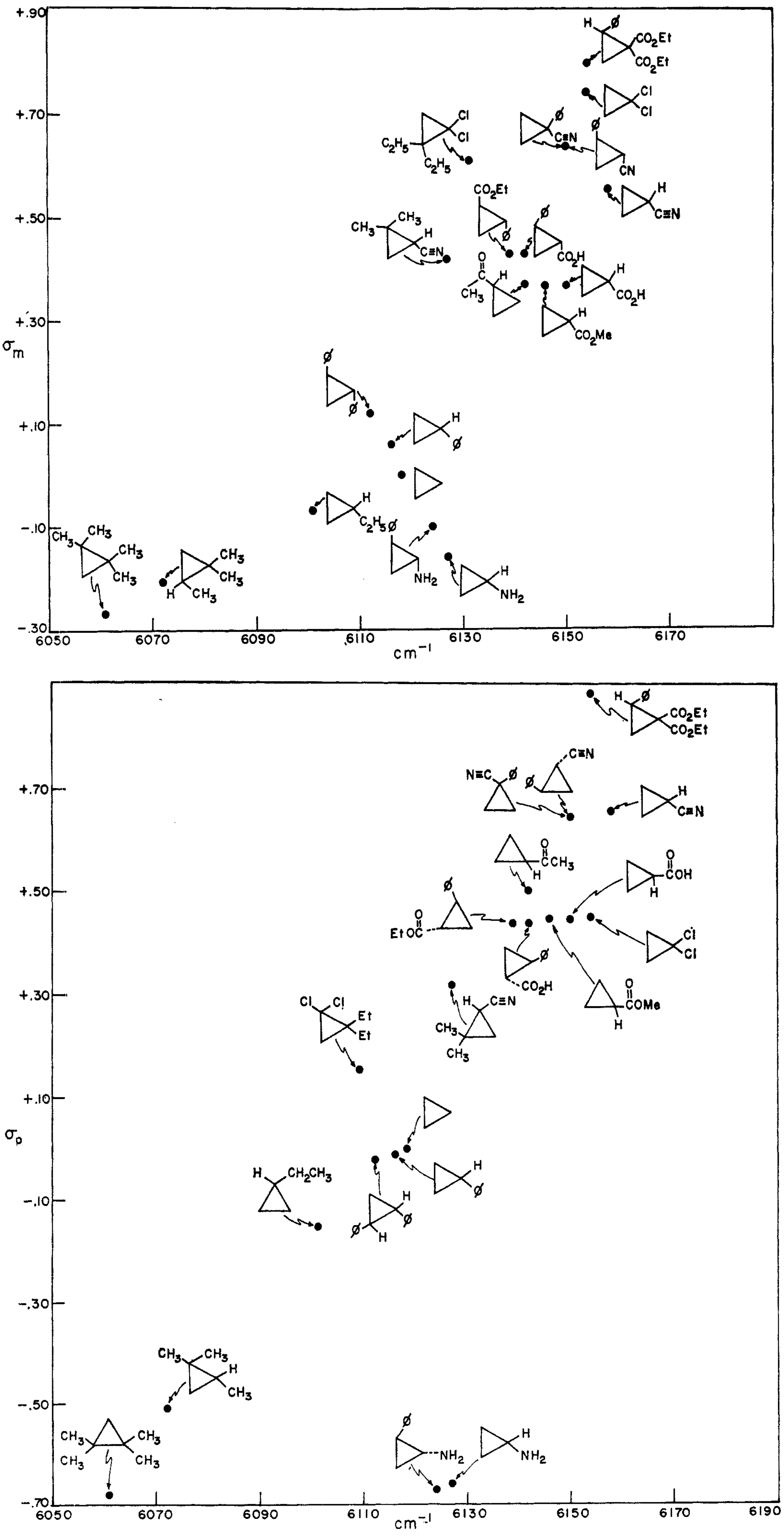
[20] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[21] R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115 (1954); R. H. Eastman and J. C. Selover, *ibid.*, **76**, 4118 (1954); R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955).

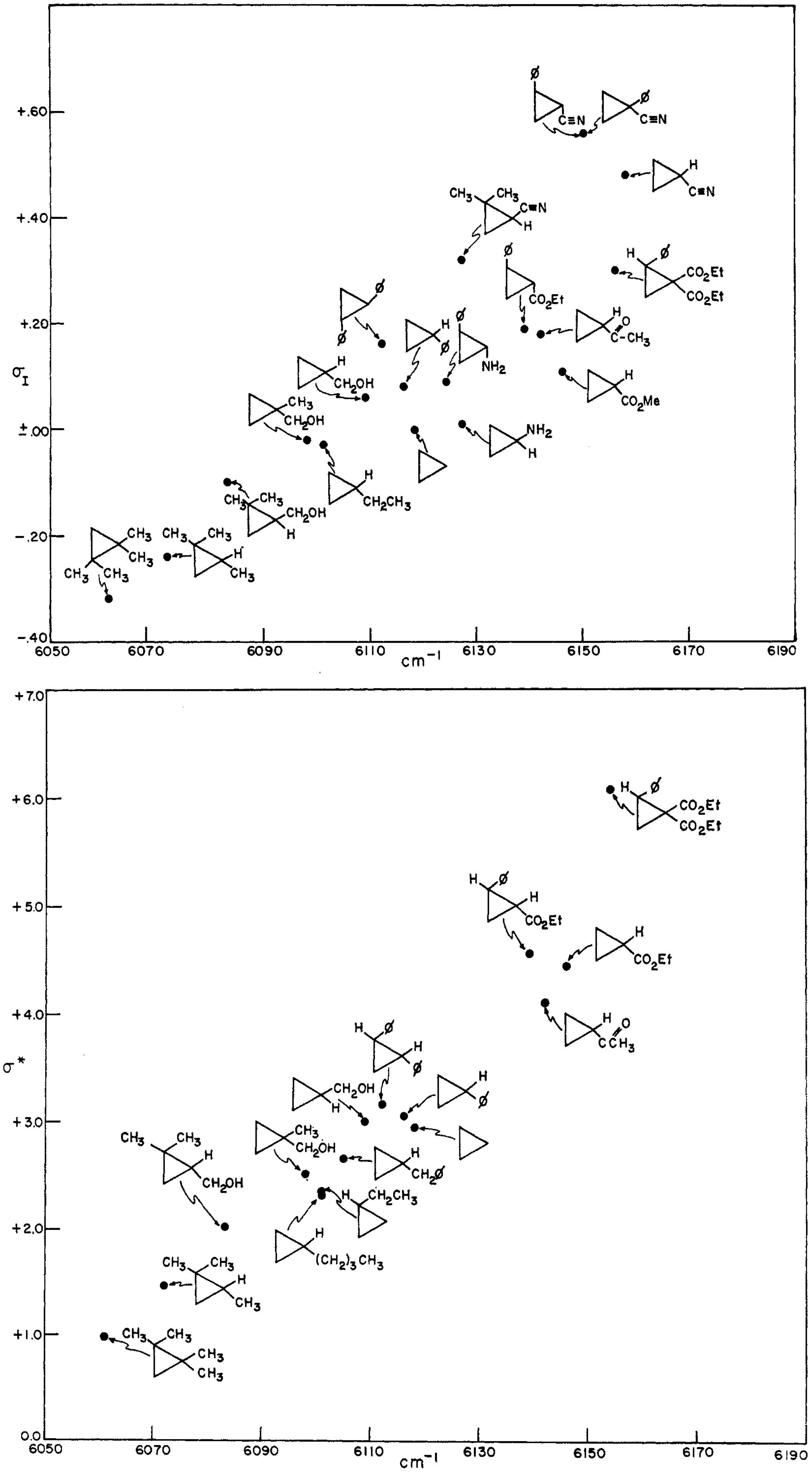
[22] E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962).

[23] T. Shono, T. Morikawa, A. Oku, and R. Oda, *Tetrahedron Letters*, 791 (1964).

[24] R. Parker and N. Issacs, *Chem. Rev.*, **59**, 737 (1959).

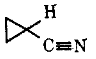
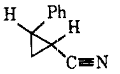
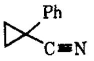
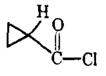
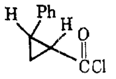
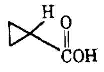
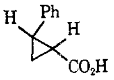
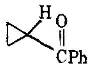
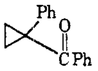
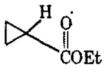
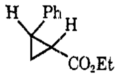
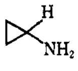
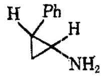
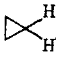
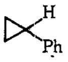
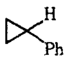
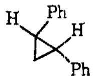


Figures 1 and 2.—Frequency of near-infrared absorption maxima *vs.* σ_m and σ_p, respectively.



Figures 3 and 4.—Frequency of near-infrared absorption maxima *vs.* σ_I and σ^*, respectively.

TABLE II

			Δ, cm.⁻¹
			−8
			−12
			−8
			−3
			−7
			−3
			−2
			−4

prising that 1-cyano-1-phenylcyclopropane (**5**) and 1-cyano-2-phenylcyclopropane (**6**) should show identical absorption maxima and an identical shift from cyanocyclopropane.[25]

The effect of ring strain on the first overtone of the fundamental cyclopropyl C–H stretching frequency was investigated. The effect of strain in spiro compounds was negligible, as shown by compounds **38**, **39**, and **40** (Table III). By comparison, the presence of the cyclopropane in a strained fused-ring system presented a somewhat different result. Examination of the infrared spectra of compounds **41**, **42**, and **43** (Table III) showed that the effect of strain can shift the peak under consideration to a longer wave length.

TABLE III

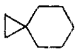
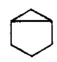
No.	Compd.	λmax μ	λmax Cm.⁻¹	Molar absorptivity per cyclopropyl CH₂
38		1.643	6086	0.243
39		1.645	6079	0.290
40		1.644	6083	0.380
41		1.651	6057	0.300
42		1.642	6090	0.320
43		1.645	6079	0.286

TABLE IV

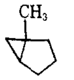
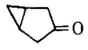
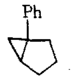
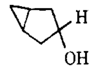
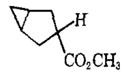
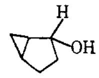
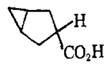
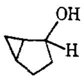
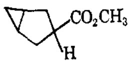
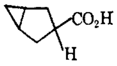
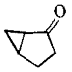
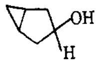
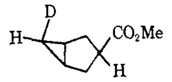
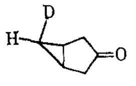
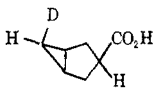
No.	Compd.	λmax μ	λmax Cm.⁻¹	Molar absorptivity
44		1.646	6075	0.250
45		1.643	6086	0.345
46		1.642	6090	0.308
42		1.642	6090	0.320
47		1.642	6090	0.357
48		1.642	6090	0.345
49		1.641	6094	0.359
50		1.641	6094	0.447
51		1.639	6101	0.415
52		1.639	6101	0.270
53		1.639	6101	0.378
54		1.636	6112	0.291
55		1.636	6112	0.291

TABLE V

No.	Compd.	λmax μ	λmax Cm.⁻¹	Molar absorptivity
56		1.643	6086	0.106
57		1.643	6086	0.132
58		1.642	6090	0.182

Compounds **44**–**55** (Table IV) illustrate that the inductive effects noted in the case of simple cyclopropanes carry over to bridged cyclopropanes. However, in the rigid bicyclo[3.1.0]hexane system the correlation is far poorer than in the simple substituted cyclopropanes. One aspect of Table IV which merits discussion is the curious phenomenon that bicyclo[3.1.0]hexanes with substituents *cis* to the cyclopropane ring have their absorption maxima at shorter wave length than those compounds with *trans* substituents. This is illustrated by a comparison of compounds **47**, **48**, **49**, and **50** with **55**, **52**, **51**, and **53**, respectively. The epimeric bicyclo[3.1.0]-hexan-3-ols show a particularly large difference. It is felt that this shift is probably due to a spatial electronic interaction of the nonbonding electrons on oxygen with the cyclopropane ring. This type of "electrostatic field effect" has been noted in other systems.[14] Compounds **56**, **57**, and **58** (Table V) present an additional point of interest. Here the deuterium of the cyclopropyl methylene group has little effect on the position of absorption (a slight shift to longer wave length can be

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[25] In general our data indicate that the cyclopropyl group acts as an "electron sink" into which charge can be induced or withdrawn. This results in the inductive effects of various substituent groups being unusually additive.

detected), but as expected the molar absorptivity is somewhat more than halved.

Experimental Section

Near-Infrared Spectral Procedure.—Near-infrared spectra were measured on an Applied Physics Corp. Cary Model 14 recording spectrophotometer. The instrument was calibrated using didymium glass and polystyrene. Slit width was automatically controlled at 0.1 mm. at 2.000 μ.

Carbon tetrachloride was used as the solvent in all cases. Most of the compounds studied were at a concentration of either 0.500 or 1.000 *M*. These measurements were made using 1-cm. matched silica cells. Molar absorptivities were reproducible when the concentrations were varied by a factor of 10. Wavelength precision in the region 1.600 to 1.700 μ was of the order ±0.0005 μ.

Sources of Compounds.—Compounds **19**, **34**, and **35** were supplied by Dr. Dionis E. Sunko. The other monocyclic cyclopropanes were synthesized, purchased, or obtained from various members of the faculty at The Ohio State University. Compounds **41–58** were synthesized as part of a separate study. The preparation of these compounds will appear in a future publication.

Acknowledgment.—Support of this research by National Science Foundation Grant NSF-G25221 is acknowledged with appreciation. The authors are indebted to many individuals who supplied samples of certain cyclopropanes.

Nuclear Magnetic Resonance Studies of Enolizable Cyclic β-Keto Esters[1]

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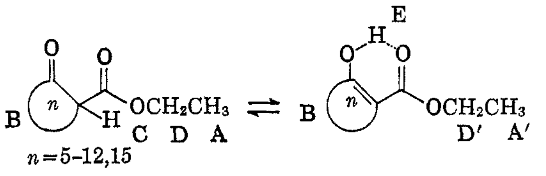
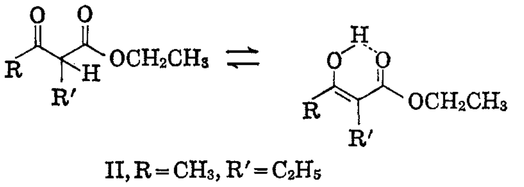
N.m.r. studies have been made of 2-carbethoxycyclanones of 5–12 and 15 ring members and of two acyclic β-keto esters, ethyl α-ethylacetoacetate and ethyl 2-hexyl-3-ketodecanoate. Within the cyclic series, trends in the chemical shift values and splitting patterns of the enolic hydrogen and of the α-hydrogen of the ketonic species are noted and discussed in terms of the partial geometries and conformations of these molecules. Enol contents are recorded for the tautomeric systems measured as 2.5 *M* solutions in carbon tetrachloride.

The advantages of the n.m.r. technique in studies of tautomeric phenomena have been amply demonstrated in recent years.[2] In keto–enol equilibria, in which the tautomers are only slowly interconverted at room temperature, the proton signals of the individual isomers are clearly distinguishable. Within a systematically varied series of compounds, analysis of these signals with respect to intensity, position, and splitting pattern might be expected to furnish significant information concerning the influence of a regular structural change on the geometries of the isomers and on the tautomeric equilibria. This paper reports the results of a preliminary study undertaken to test the potentiality of this approach.

In this study, 2-carbethoxycyclanones of 5–12 and 15 ring members, IK ⇄ IE, and two acyclic analogs, ethyl α-ethylacetoacetate (II) and ethyl 2-hexyl-3-ketodecanoate (III), have been examined at 60 Mc. as 2.5 *M* solutions in carbon tetrachloride. The signals of the enolic proton, E, the α-proton of the ketonic species, C, and the methylene, D and D′, and methyl, A and A′, protons of the carbethoxy function are clearly separated in the spectra of these compounds. The methylene hydrogens of the ring, B, including the γ-hydrogens of the keto species ($-CH_2CO-$) and the allylic hydrogens of the enol species ($-CH_2\overset{|}{C}{=}\overset{|}{C}CH_2-$), produce a complex set of overlapping signals at high field (~1–2.5 p.p.m.); no attempt was made to analyze this region in detail. Table I summarizes the chemical shift data for the protons A–E as well as the enol contents for these systems under the conditions studied. Typical spectra, illustrative of the points to be discussed, are displayed in Figure 1.



IK IE



II, R = CH_3, R′ = C_2H_5
III, R = C_7H_{15}, R′ = C_6H_{13}

Attention is first directed to the effect of ring size on the chemical shift parameters of the enolic hydrogen, E, and the α-hydrogen, C, of the keto species. Rather definite and roughly parallel trends are discernible in the two sets of signals.

The strong deshielding effect of internal hydrogen bonding in enolic chelates is well recognized and it is generally accepted that the magnitude of the displacement of the OH signal to lower field is related to the strength of the hydrogen bond.[2f,3,4] In the series at hand, the downfield shift of the signal of proton E increases sharply from the five- to the six-membered ring enol and then changes more slowly through the series to reach a position of maximum deshielding with

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[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964.

[2] (a) See J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 433 ff, for a review of early work in this area. Recent studies include (b) M. T. Rogers and J. Burdett, *Can. J. Chem.*, **43**, 1516 (1965); (c) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964); (d) E. W. Garbisch, Jr., *ibid.*, **87**, 505 (1965); (e) E. W. Garbisch, Jr., *ibid.*, **85**, 1696 (1963); (f) S. Forsen, F. Merenyi, and M. Nilsson, *Acta Chem. Scand.*, **18**, 1208 (1964); (g) R. W. Hay and P. P. Williams, *J. Chem. Soc.*, 2270 (1964).

[3] Reference 2a, p. 400 ff.

[4] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1959, p. 143.