Nuclear Magnetic Resonance Spectra of *trans*-2-Arylcyclopropanecarboxylic Acids[1]

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Abstract: The nuclear magnetic resonance spectra of a series of *meta*- and *para*-substituted *trans*-2-phenylcyclopropanecarboxylic acids have been studied. A complete computer analysis of the cyclopropyl ring hydrogens has been performed and internal chemical shifts were determined. Comparison of the results with those for analogous saturated and unsaturated compounds both with and without the carboxylic acid group reveals that the cyclopropane ring is intermediate between a dimethylene and an ethylene in its conjugative ability and that the carboxyl group exerts a variable deshielding effect, whereas the phenyl ring at almost comparable distances does not.

The nuclear magnetic resonance spectra of cyclopropanes are potentially useful for the analysis of substituent effects. However, the usefulness is somewhat offset by the fact that the spectra are generally rather complex so that the spectral parameters cannot be obtained without detailed analysis. Computer programs are available which enable one to analyze complex spectra,[3] but in general some estimate of the coupling constants and chemical shifts is needed in order to generate a trial spectrum with which the observed can be compared.

In previously reported analyses of the spectra of cyclopropane derivatives, it has almost always been found that for the vicinal ring protons J_{cis} is larger than J_{trans},[4] in agreement with the dependence on dihedral angle predicted by the theoretical treatments of Karplus[5] and Conroy.[6] A contrary assumption had been made in an early paper by Closs.[7] The J_{cis} values are generally in the range 7–11 cps although values as low as 0.28 cps and as high as 19.6 cps have been reported;[4k] J_{trans} values generally fall in the range 3–7 cps. There has been less agreement on J_{gem} values since some early papers[4b,c] assigned positive values in agreement with theories which predicted like signs for vicinal and geminal coupling constants.[5a,8] The evidence is now overwhelming in support of assignment of negative values to J_{gem} in cyclopropanes;[4a,d–m,9] these generally fall in the range -3 to -9 cps.

The use of coupling constants as a means of evaluating the electronic structure of small-ring compounds leads to conflicting results. Thus, Graham and Rogers conclude that cyclopropanes behave like saturated hydrocarbons because the dependence of J_{cis} and J_{trans} on dihedral angle is similar to that in saturated molecules.[4b] Hutton[9] arrives at a similar conclusion by comparing the dependency of coupling constants on substituent electronegativity to that in ethanes[10] and ethylenes.[11] He also notes the lack of coupling to methyl substituents which is contrary to expectation if there is considerable π character in the ring. On the other hand, Foote finds evidence for much s character in C–H bonds of cyclopropane, based on C^{13}–H coupling constants, and therefore enhanced p character in the ring bonds.[12] Roberts, also from C^{13}–H coupling constant studies, finds values in cyclopropane to be more similar to those in olefins, allenes, and three-membered ring heterocycles and takes this as support for sp^2 hybrid orbitals.[4e] Williamson arrives at an intermediate position from consideration of both coupling constants and internal chemical shifts.[4j] He notes some of the difficulties inherent in the previous studies in which steric factors could have introduced serious complications.

Although the Williamson study of various 2-substituted 1,1-dichlorocyclopropanes has many advantages besides fixed stereochemistry, such as relative simplicity of nmr spectrum (ABX in the Pople system)[13] and wide range of substituent electronegativity, the close proximity of the substituent to the protons under investigation makes it likely that the latter will be affected not only by conjugative effects but also by electric and magnetic field effects. These field effects are, furthermore, solvent dependent. Williamson recognizes this limitation in another study involving a saturated system where he finds a correlation between chemical shift and Hammett σ constants in the absence of field effects but correlation only with nmr-based electronegativities in their presence.[14]

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(1) Taken in part from the Ph.D. dissertation of T. A. Wittstruck.

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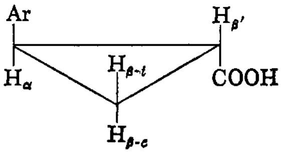
It is the purpose of the present work to investigate the conjugative ability of the cyclopropane ring by use of nmr chemical shifts. As noted above, spin–spin coupling constant data lead to conflicting conclusions; similar lack of agreement is found in other type studies.[15] In order to isolate conjugation effects from various field effects, *trans*-2-phenylcyclopropanecarboxylic acids substituted in the *meta* or *para* positions with various electron-feeding or -withdrawing substituents have been selected for investigation. It has been established from a study of the chemical shifts of the side-chain hydrogens of *meta*- and *para*-substituted styrenes that electric and magnetic field effects of the substituents are negligible compared to induction and resonance.[16] Since the field effects are strongly dependent on distance (inverse cubic relation) and since the distances to the substituents from the side-chain hydrogens of styrenes are similar to those from the cyclopropane ring hydrogens in the systems here studied, it is likely that field effects should again be negligible.

Results and Discussion

A series of *meta*- and *para*-substituted *trans*-2-phenylcyclopropanecarboxylic acids have been synthesized. Their nmr spectra have been determined in deuterioacetone at the lowest concentration at which resolution of the 24 lines associated with the cyclopropyl ring hydrogens could be obtained. The chemical shifts in cps from tetramethylsilane (TMS) at 60 Mcps for the cyclopropyl ring hydrogens are given in Table I. In order to perform an exact analysis of this complex portion of the spectrum, which might be called an ABCD system under the classification system of Pople,[17] the computer program, LAOCOON II,[18] was used to calculate theoretical spectra which were then compared to the observed. Based on this detailed analysis, the lowest field absorption is assigned to H_α. This is not surprising since it is dominated by the magnetic anisotropy of the phenyl ring and should be most strongly deshielded. The next upfield signal is assigned to $H_{\beta'}$. The highest field absorptions are due to the geminal hydrogens, $H_{\beta\text{-}c}$ and $H_{\beta\text{-}t}$. The assignments of the latter are in agreement with literature data. Thus, it is known that a carboxyl group shields a *cis* proton less than a *trans* but that the opposite is true for the effect of a phenyl ring.

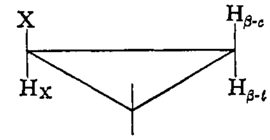
Table I. Chemical Shifts, in cps from Tetramethylsilane, for *trans*-2-Arylcyclopropanecarboxylic Acids



Phenyl substituent	δ(α)	δ(β′)	δ(β-c)	δ(β-t)
p-Methoxy	146.3	107.8	87.2	76.1
p-Methyl	146.3	110.7	88.6	78.0
None	149.5	114.2	91.3	80.6
p-Chloro	147.2	112.8	90.0	79.4
m-Chloro	149.8	117.0	91.7	83.0
p-Nitro	155.0	123.2	95.5	88.2

Nmr data for phenylcyclopropane,[19] cyclopropanecarboxylic acid,[4d] and cyclopropane[20] are available in the literature. From these, one can calculate the substituent effects shown in Table II. As noted above, the carboxyl deshields the β-proton which is *cis* to it to a greater extent than that which is *trans* whereas the effect is reversed for phenyl. If the two groups are present in the same molecule and the effects are additive, one predicts the following chemical shifts in cps from TMS for *trans*-2-phenylcyclopropanecarboxylic acid: H_α, 158.4; $H_{\beta'}$, 122.4; $H_{\beta\text{-}c}$, 94.8; $H_{\beta\text{-}t}$, 85.8. These are in qualitative agreement with the observed values; quantitative correlation would not be expected as the chemical shifts are solvent dependent.

Table II. Substituent Effect on Chemical Shift, in cps, for Cyclopropyl Ring Hydrogens



Substit, X	Δδ(X)	Δδ(β-c)	Δδ(β-t)
COOH	81.6	50.4	45.0
C_6H_5	94.8	27.6	31.2

In a previous paper it was shown that substituent effects can be evaluated by considering a series of related compounds.[16] Chemical shifts were compared for protons within the same molecule and with those of a standard series, *meta*- and *para*-substituted styrenes. Equations were developed to show how plots of appropriate chemical shifts reflect substituent effects. Thus, two hydrogens on the same carbon atom should be equally influenced by inductive and resonance effects and their chemical shifts related as shown by eq 1, where δ(1) and δ(2) are the observed chemical shifts of

$$\frac{d\delta(2)}{d\delta(1)} = 1 + \sum_j \left[\Delta\delta_j{}^{F}(1)\frac{d(G_j{}^{F} - 1)}{d\delta(1)} + (G_j{}^{F} - 1)\frac{d\Delta\delta_j{}^{F}(1)}{d\delta(1)} + \Delta\delta_j{}^{M}(1)\frac{d(G_j{}^{M} - 1)}{d\delta(1)} + (G_j{}^{M} - 1)\frac{d\Delta\delta_j{}^{M}(1)}{d\delta(1)} \right] \quad (1)$$

hydrogens 1 and 2; $\Delta\delta_j{}^{F}(1)$ and $\Delta\delta_j{}^{M}(1)$ are the changes in chemical shifts caused by electric and magnetic field effects of the substituents acting at hydrogen 1; and $G_j{}^{F}$ and $G_j{}^{M}$ are the geometric factors between protons

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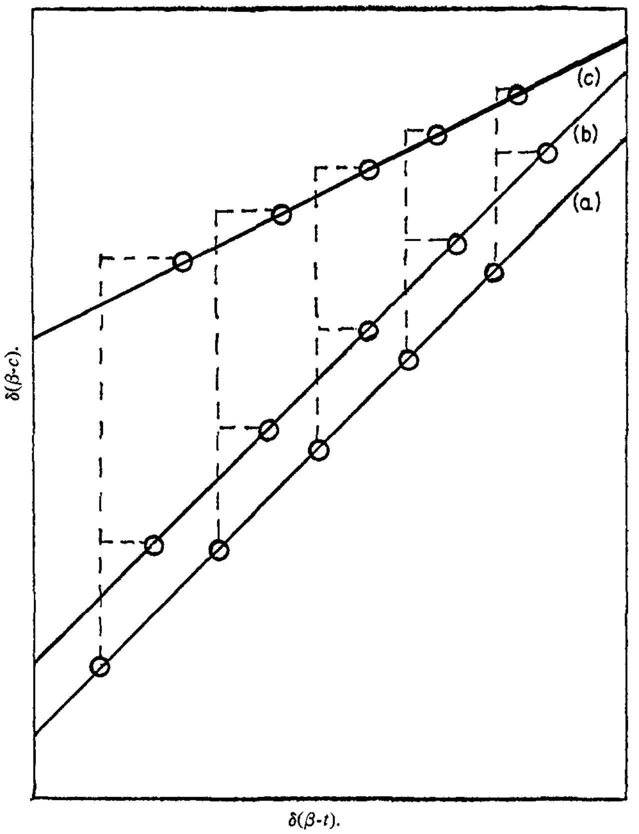

Figure 1. Chemical shifts of $H_{\beta\text{-}c}$ *vs.* $H_{\beta\text{-}t}$ for a hypothetical series. Line a occurs in the absence of carboxyl, slope 1.0. Line b occurs in the presence of carboxyl with constant deshielding effect, slope 1.0. Line c represents variable deshielding effect of carboxyl, slope <1.0. The points represent compounds within a series. For b and c the carboxyl deshields β-*c* to a greater extent that β-*t*.

2 and 1 for electric and magnetic field effects, respectively. The summation is performed over all *j* substituents. In the absence of field effects, eq 1 indicates that the slope of such plots should be unity; nonunit slope indicates the presence of field effects varying with substituent.

For hydrogens on adjacent carbon atoms, the relation between the chemical shifts is expressed by (2) which now includes terms expressing the contribution to the chemical shifts from inductive (I) and resonance (R) effects of the substituents. Here, *F* is the transmittance factor of the bond separating the carbons to which H(1) and H(2) are attached and C_j is a conjugation factor expressing the change in effectiveness of transmission of a resonance effect from the *j*th substituent to H(1) and H(2). In the absence of field effects, eq 2 is considerably simplified.

$$\frac{\mathrm{d}\delta(2)}{\mathrm{d}\delta(1)} = 1 + \sum_j \left[\Delta\delta_j^{\mathrm{F}}(1)\frac{\mathrm{d}(G_j^{\mathrm{F}} - 1)}{\mathrm{d}\delta(1)} + (G_j^{\mathrm{F}} - 1)\frac{\mathrm{d}\Delta\delta_j^{\mathrm{F}}(1)}{\mathrm{d}\delta(1)} + \Delta\delta_j^{\mathrm{M}}(1)\frac{\mathrm{d}(\mathrm{G}_j^{\mathrm{M}} - 1)}{\mathrm{d}\delta(1)} + (G_j^{\mathrm{M}} - 1)\frac{\mathrm{d}\Delta\delta_j^{\mathrm{M}}(1)}{\mathrm{d}\delta(1)} + \Delta\delta_j^{\mathrm{I}}(1)\frac{\mathrm{d}(F - 1)}{\mathrm{d}\delta(1)} + (F - 1)\frac{\mathrm{d}\Delta\delta_j^{\mathrm{I}}(1)}{\mathrm{d}\delta(1)} + \Delta\delta_j^{\mathrm{R}}(1)\frac{\mathrm{d}(C_j - 1)}{\mathrm{d}\delta(1)} + (C_j - 1)\frac{\mathrm{d}\Delta\delta_j^{\mathrm{R}}(1)}{\mathrm{d}\delta(1)} \right] \quad (2)$$

Table III gives values for the internal chemical shifts for the cyclopropyl ring protons of *trans*-2-phenylcyclopropanecarboxylic acids, as well as the relative sensitivity of the α-hydrogens to phenyl substitution compared to that in styrene. The fact that $H_{\beta\text{-}c}$ and $H_{\beta\text{-}t}$, which are both on the same carbon atom, give different values for the internal chemical shift indicates that some functional group exerts a variable field effect. It was previously demonstrated in the styrenes that direct field effects are negligible at the distances involved in these molecules.[16] The same was found to be the case for any possible variation in field effect of the phenyl ring itself. It thus appears likely that this variation in field effect must arise from the carboxyl group. If the carboxyl were to exert a constant field effect throughout the series, this would change the intercept but not the slope of a plot of internal chemical shifts, as is indicated schematically in Figure 1 (line b) even though the deshielding from the carboxyl is greater at $H_{\beta\text{-}c}$ than at $H_{\beta\text{-}t}$. A question immediately arises as to why the field effects of the carboxyl should vary in this series of compounds. If the electron density at carboxyl changes throughout the series, there would be a variable deshielding effect. One way in which the electron density could be altered is by a direct, *i.e.*, through space, electric field effect of the substituents on the aromatic ring. However, this does not appear to be reasonable at the distances involved, which exceed those in similarly substituted styrenes in which such field effects were demonstrated to be absent. A more likely explanation is conjugation between the carboxyl and the phenyl substituent. When the deshielding effect of the carboxyl is variable, both the intercept *and the slope* of a plot of internal chemical shifts will change (line c, Figure 1).

Table III. Internal Chemical Shifts of Cyclopropyl Ring Hydrogens

Hydrogen	dδ(H)/dδ(α)
β-*t*	1.27 ± 0.14
β-*c*	0.85 ± 0.10
β′	1.56 ± 0.22
α[a]	0.58 ± 0.09

[a] Relative sensitivity compared to H_α of styrene.

By the same token, it would be expected that H_α should be similarly affected by the carboxyl, and if H_α and $H_{\beta\text{-}c}$ are symmetrically disposed with respect to this group, comparison of their chemical shifts should cancel out the effect due to the carboxyl. The substituent effects at $H_{\beta\text{-}c}$ are somewhat smaller than those at H_α indicating that the carbon–carbon bond attenuates these effects. Were it not for the field effect of the carboxyl, $H_{\beta\text{-}t}$ should also show this same value.

This same effect should be even more pronounced at $H_{\beta'}$ since the maximum deshielding of the carboxyl will occur at this position. If one corrects for this variable effect of local anisotropy, one would get an even higher value for the internal chemical shift between $H_{\beta'}$ and H_α. In Table IV are shown the values for the internal chemical shift between a hydrogen on a car-

Table IV. Comparison of Internal Chemical Shifts

Acid series	Internal chemical shift
trans-2-Phenylcyclopropanecarboxylic acid	1.56 ± 0.22
trans-Cinnamic acid[a]	3.89 ± 1.10
Dihydrocinnamic acid[b]	0.71 ± 0.07

[a] Reference 16. This value is for cinnamic acids substituted with electron-feeding groups in the *meta* and *para* positions. [b] Reference 16.

boxyl-bearing carbon and a benzylic hydrogen in three analogous series.

It is clear from the discussion above that it would not be valid to interpolate the internal chemical shift value for the cyclopropane system between those for the saturated and unsaturated cases to arrive at an estimate of the double bond character of the three-membered ring. One must first correct that value upwards, and one cannot determine from these data how large a correction this must be. However, a similar correction must also be applied to the other two reference compounds and this correction must be least for the dihydrocinnamic acid and greatest for the cinnamic acid. The net result of applying all necessary corrections will be to place the internal chemical shift of the cyclopropyl compound closer to the saturated case than is indicated in Table IV. The conclusion then is that the cyclopropyl group is intermediate between saturated and unsaturated systems in its conjugative power.

Of the various systems studied here and in the previous paper,[16] only two contain distinguishable geminal hydrogens. Interestingly, the two β-hydrogens of styrene show an internal chemical shift of 0.98 ± 0.02 indicating the absence of field effects, but the two geminal β-hydrogens of *trans*-2-phenylcyclopropanecarboxylic acid have an internal chemical shift of 0.67 ± 0.04 indicating the presence of field effects. Since the distance to the phenyl ring of the hydrogens in question is quite comparable in both compounds, it is safe to assume that the phenyl is not giving rise to such effects in either case and that it is the carboxylic acid acting as a dependent variable which is responsible for this anomaly. Two explanations suggest themselves. Part of the effect may be due to the slightly shorter distances involved between the hydrogens in question and the carboxyl group. Since both electric and magnetic field effects on the chemical shift have an inverse cubic dependence, even small displacements can prove significant. A more important factor may be that substitution of electron-feeding or -withdrawing groups has a greater effect on the anisotropy of the carboxyl (if there is conjugation to it) than on the phenyl ring itself. In other words, the large ring current of the benzene may not be as sensitive to substitution (essentially a cross-conjugation) as would be the anisotropy of a carboxyl.

It should be noted that any variable effect which a carboxyl causes in *trans*-2-phenylcyclopropanecarboxylic acid should also manifest itself in *trans*-cinnamic acid and other compounds whose protons are located at like distances. Examination of the data for them could not have shown such an effect since there are no distinguishable geminal hydrogens. Nonetheless, the variable deshielding of the carboxyl should exist and should, indeed, be more pronounced if conjugation from the phenyl substituents to the carboxyl is more effective.

Experimental Section

Reagents. The 2-phenylcyclopropanecarboxylic acids were prepared by the reaction of ethyl diazoacetate with the appropriate styrene. The styrenes required were obtained from commercial sources. The ethyl diazoacetate was prepared by the method of Smith and McKenzie.[21] The reaction of ethyl diazoacetate with styrenes to yield a mixture of ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylates and their saponification into the isomeric acids has previously been reported.[22] The only departure from this procedure was that the ethyl esters of the *m*- and *p*-chloro acids were separated into the *cis* and *trans* isomers by gas chromatography with a $^3/_8$ in. × 10 ft column packed with 3% SE-30 on Gas Chrom Z. The recovered esters were then saponified to give the appropriate acids, whose melting points are listed in Table V.

Table V. Melting Points, °C, of Substituted *trans*-2-Phenylcyclopropanecarboxylic Acids

Substituent	Found	Lit.	Ref
p-Methoxy	112–113	113.2–114.2	*a*
p-Methyl	119–120	119.5–120.5	*a*
None	91.5–92.0	93	*b*
p-Chloro	115–116	115.8–116.7	*a*
m-Chloro	108.0–108.5	108–109	*a*
p-Nitro	198–199	197–199	*c*

[a] E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4015 (1958). [b] Reference 22. [c] D. G. Markees and A. Burger, *J. Am. Chem. Soc.*, **70**, 3229 (1948).

Spectra. The nmr spectra were obtained on a Varian Associates HA-60 spectrometer operating at a frequency of 60 Mcps. The samples were weighed into tared 5-mm o.d. precision-bore Pyrex tubes and diluted to 0.25 ml with deuterioacetone containing tetramethylsilane (TMS) as internal standard. While the spectra were being obtained, the sample tubes were spun at 1800 rpm. The field was swept at a rate of approximately 1 cps/sec. In order to minimize errors, the spectra were obtained by both increasing and then immediately decreasing the field through the whole spectrum while maintaining all instrumental settings constant. The average frequency of the peaks observed for these two consecutive runs was taken to represent the value for that particular sample. Frequent checks on duplicate runs showed that the variation in frequency with respect to TMS for a given peak was less than 0.5 cps. Hence, this is taken to represent the average uncertainty in peak position.

The spectra were obtained with side bands occurring at a known frequency (usually 500 cps) which were introduced by the use of a Hewlett-Packard audiooscillator, Model 200 CDR. The individual frequencies of the peaks of a spectrum were then measured by interpolation. The average values of the frequency with respect to TMS for each peak taken from the two consecutive runs were then tabulated. Expanded portions of the spectra with a sweep width of 250 cps were obtained for the cyclopropyl ring protons of each compound. The chemical shifts of these protons were then obtained by LAOCOON II spectral analysis.[18]

Acknowledgments. The authors wish to thank the Worcester Foundation for Experimental Biology, Shrewsbury, Mass., for use of their nmr spectrometer and the Computation Center at the Massachusetts Institute of Technology for use of their IBM 7094 computer.

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