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ABSTRACT

The spectra of tiglic and angelic acids and their methyl esters have been determined and analyzed by first-order perturbation theory. The magnitudes of the long-range coupling constants were found to be greater in each instance for *trans* oriented hydrogens than for *cis* hydrogens. All long-range coupling constants already reported have been examined and found to be consistent with the proposal that *trans* coupling constants are larger than *cis* coupling constants for hydrogens separated by more than three bonds.

Thus far, N.M.R. spectroscopy has been utilized in two ways to assign configuration to a pair of isomeric olefines. The magnitude of the coupling constant between the hydrogens attached to opposite ends of the double bond of a disubstituted olefine has been observed consistently to be larger for *trans* hydrogens than for *cis* hydrogens (1). These observations are in agreement with the theoretical calculation of coupling constants for olefines which were recently reported by Karplus (2). In symmetrically substituted olefines where coupling is not observable due to identical chemical shifts for the two protons on the double bond, the constant has been determined by examination of the peaks produced by interaction of the ethylenic hydrogens with the C¹³ nuclei present in natural abundance (3). The second method, proposed by Jackman and Wiley (4), assigns configuration to olefines on the basis of observations that a substituent β to a methoxycarbonyl group (each attached to one end of a double bond) will appear at a lower field strength when oriented *cis* to the ester group. A third method may be applicable by determination of the relative magnitude of long-range coupling constants between hydrogens *cis* or *trans* to each other.



FIG. 1. Coupling constant nomenclature for tiglic (left) and angelic (right) acids.

Although the magnitude of spin-spin coupling decreases rapidly with increasing distance between the nuclei, the decrease is not so large when one of the intervening bonds possesses unsaturation. In olefines the size of the coupling constant between hydrogens separated by four bonds, hereafter called $J_{1,3}$, generally varies from 0.4 to 2.0 cycles per second (see Fig. 1 for nomenclature). Surprisingly we have observed equally large coupling constants between hydrogens separated by five bonds $(J_{1,4})$ as well. An examination of the literature revealed only relatively few cases where the spectra of a pair of *cis* and *trans* olefines are reported, including the $J_{1,3}$ values. We have measured the spectra of tiglic and angelic acids, and their methyl esters, to determine whether or not a simple relationship exists between the relative magnitude of 1,3 coupling constants and the geometrical relationship of the interacting nuclei. Should such a relationship obtain,

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Can. J. Chem. Vol. 38 (1960)

assignment of configuration to trisubstituted olefines on this basis would be possible. Furthermore, as Muller and Pritchard have pointed out (5) such distant interaction indicates appreciable contribution of hitherto neglected structures to the ground-state wave function of the molecule. Thus the data obtained should be of use in estimating such contributions as was the case for ethylene (2).

Compound	$J_{1,3}$ trans	$J_{1,3}$ cis	Reference
Butene-1	1.3	1.9	(6)
lpha-Methyl styrene	0.7	1.4	(7)
cis-Propenylbenzene trans-Propenylbenzene	1.4	 1.9	(7) (8)
<i>cis–cis</i> -Dimethylmuconate <i>trans–trans</i> -Dimethylmuconate	1.3	0.7	(9) (9)
trans*-1,2,3-Trichloropropene-1 cis-1,2,3-Trichloropropene-1	0.8		(10) (10)
cist-1,3-Dichloropropene-1	0.9		(10)
trans-1,3-Dichloropropene-1	1.2	0.5 1.2	(11) (10) (11)

TABLE I	
Literature values for 1,3 coupling constants in cycles/	sec

*cis and *trans* refer to the orientation of the two chlorine atoms on the double bond.

tcis and trans refer to the orientation of the two chlorine-containing groups.

The values of 1,3 coupling constants reported in the literature are given in Table I. At first glance no clear-cut relationship is obvious. Each set of values, however, must be critically appraised. The constants reported by Alexander (6) were obtained after a complete analysis of the spin wave functions for a system of five nuclei. The purpose of his analysis was to determine the relative signs of $J_{1,2}$ and $J_{1,3}$ and he found by testing various values for nine adjustable parameters that the best fit with the observed spectrum was obtained with the indicated values. An inversion of the magnitudes of $J_{1,3}$ cis and $J_{1,3}$ trans was not tested for comparison with the observed spectrum and could well be as acceptable. The relative magnitude of the coupling constants listed for α -methylstyrene depends on the assignment of peaks to the two ethylenic hydrogens. Pople, Bernstein, and Schneider (7) have only tentatively assigned the peak at high field to the hydrogen cis to the methyl group. The opposite assignment, perhaps even more acceptable,* would reverse the values for $J_{1,3}$ trans and $J_{1,3}$ cis. The results for the isomeric propenyl benzenes are more difficult to assess as details of the analysis of the cis isomer have not been reported. Should the values listed for the first three systems prove erroneous then the general rule $J_{trans} > J_{cis}$ would be obeyed.

Similar uncertainties exist in the remaining reported values in Table I with the exception of the trichloropropenes, which gave a simple spectrum. The most reliable values can only be obtained from spectra which can be analyzed by first-order perturbation theory. Such spectra have been obtained for tiglic and angelic acids and their methyl esters. The

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^{*}The effect of the benzene ring on its cis hydrogen can be either diamagnetic or paramagnetic depending on its orientation with respect to the rest of the molecule (12). The ultraviolet spectrum of α -methylstyrene shows a K-band maximum at lower wavelength with diminished intensity compared with that of styrene (13). Such a shift is most likely attributed to deviation of the aromatic ring from coplanarity with the ethylene system, the amount of which determines the strength of the paramagnetic effect.

FRASER: N.M.R. SPECTRA OF OLEFINES

spectra for tiglic acid and methyl tiglate were first measured in carbon tetrachloride and showed complications in structure due to lack of a difference in chemical shift between the two methyl groups. When the spectra were measured on 10% solutions in benzene, solute-solvent interactions caused a preferential shift of the β -methyl group by 20 cycles/sec to high field thus allowing first-order analysis to be applied. Figure 2 shows the



FIG. 2. Spectra due to ethylenic hydrogen (low-field peak) and methyl groups of tiglic acid. (A) 10% solution in carbon tetrachloride; (B) 10% solution in 93% deuterated benzene. (The 7% of benzene protons obscures the first quartet of the ethylenic absorption.)

absorption peaks for the ethylenic hydrogen and the two methyl groups of tiglic acid in carbon tetrachloride and deuterobenzene solutions. Assignment of the two quartets at highest field to the β -methyl group is made on the basis of the assumption that the larger CH₃—C—H coupling will occur between hydrogens on adjacent carbon atoms. Exceptions to this assumption are known but are not likely here. The reverse assignment for the two methyl groups would require $J_{1,3}$ to be 7.11 cycles/sec and $J_{1,2}$ to be 1.43 cycles/ sec, a highly improbable situation. Any doubt as to the structures of tiglic and angelic acids has recently been removed by the irrefutable evidence of X-ray analysis (14).

The measured values for the chemical shifts and coupling constants are given in Table II. The results obtained show $J_{1,3}$ trans > $J_{1,3}$ cis in both pairs of isomers. In addition $J_{1,4}$ trans > $J_{1,4}$ cis. The only other pair of geometrical isomers whose $J_{1,4}$ values have been

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TABLE II

Chemical shifts* and coupling constants† for tiglic and angelic acids and their methyl esters

Compound	Form	ula	$J_{1,3}$	J _{1,4}	$J_{1,2}$
Tiglic acid	(8.13) CH ₃	(8.13) CH ₃	$1.43 (\sigma = 0.03)$ $\sigma = \text{standar}$	1.17 ($\sigma = 0.06$) rd deviation	$7.11 (\sigma = 0.05)$
	H (3.03)	COOH (-2.62)			
Angelic acid	(7.94) CH ₃	(-2.75) COOH	$1.28 (\sigma = 0.05)$	$1.46 (\sigma = 0.06)$	$7.16(\sigma = 0.11)$
	H (3.82)	CH₃ (8.10)			
Methyl tiglate	(8.25) CH ₃	(8.20) CH ₃	$1.37 (\sigma = 0.04)$	$1.20(\sigma = 0.04)$	$7.18(\sigma = 0.14)$
	H (3.28)	COOCH ₃ (6.35)			
Methyl angelat e	(8.05) CH ₃	(6.35) COOCH;	$1.22(\sigma = 0.03)$	$1.51(\sigma = 0.05)$	$6.96(\sigma = 0.14)$
	C== H (4.03)	C CH ₃ (8.13)			

*Determined from 10% solutions in carbon tetrachloride containing 1% of tetramethylsilane and reported in parentheses as τ values (parts per million with tetramethylsilane assigned a value 10.00). †In units of cycles per second.

determined are the butene-2 isomers. There, too, $J_{1,4}$ trans was found to be greater than $J_{1,4}$ cis (15). Demonstration that such a general relationship is true for long-range coupling constants in all olefines must await the accumulation of sufficient empirical and theoretical evidence. Work is continuing in this direction. Finally, it is interesting to note that our chemical shift data agree with the findings of Jackman and Wiley (4).

EXPERIMENTAL

The spectra were measured with a Varian V-4302 high resolution N.M.R. spectrometer. Peak separations in each multiplet were measured by the side band technique (16) employing a Hewlett-Packard wide-range oscillator. The accuracy of the oscillator was checked with a Hewlett-Packard standardized frequency counter and the error was found to be less than 0.5% in the range employed for coupling constant determinations and less than 0.75% when used for determination of chemical shifts. Each coupling constant is reported as the average of at least four determinations and the standard deviation is reported with each value. The spectrum of angelic acid was measured on a 10% solution in carbon tetrachloride. Those for tiglic acid and its methyl ester were obtained from 10% solutions in deuterobenzene and benzene respectively. Methyl angelate was run as the pure liquid. All chemical shifts were measured from 10% solutions in carbon tetrachloride containing 1% of tetramethylsilane as internal standard (17).

552

FRASER: N.M.R. SPECTRA OF OLEFINES

Tiglic Acid

This compound was prepared by the oxidation of tiglaldehyde by a modification of the method of Goldberg and Lindstead (18). A mixture of 52 g (0.6 mole) of tiglaldehyde, b.p. 114-115°, and 260 g (1.6 mole) of silver nitrate in 840 ml of 28% ethanol in a 3-1. flask was stirred for 4 hours. After standing for 12 hours the mixture was filtered. The filtrate was acidified and treated with 34 g (0.3 mole) of calcium chloride in 75 ml of water. The precipitated calcium salt was filtered off, and converted to the sodium salt by boiling with an excess of 10% sodium carbonate. The solution of the sodium salt was acidified, extracted with ether, and the dried extracts upon evaporation gave 32.5 g (53%) of tiglic acid, m.p. 64-65° (literature m.p. 64° (19)).

Methyl Tiglate

The methyl ester was obtained by esterification according to the method of Buckles and Mock (20). Methyl tiglate, b.p. 133-135°, $n_{\rm D}^{24}$ 1.4360 was obtained in 91% yield (literature b.p. 137.5–139°, $n_{\rm D}^{20}$ 1.4371 (20)).

Angelic Acid

Tiglic acid was converted to angelic acid by the procedure of Buckles and Mock (20). The over-all yield of angelic acid, m.p. 42-44°, was 39% (literature m.p. 44-45.2° (21)).

Methyl Angelate

Angelic acid was esterified by the procedure of Buckles and Mock (20). From 2.5 g of acid was obtained 1.5 g (52%) of methyl angelate, b.p. 125-126°, $n_{\rm D}^{24}$ 1.4307 (literature b.p. 127.2–128°, $n_{\rm D}^{20}$ 1.4330 (20)).

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