cess of our treatment in all other cases, and in view of the large effects of geometry on ^{19}F chemical shifts in saturated fluorides, these correlations seem highly significant. If they are accepted, one must of course conclude that the effects of substituents on chemical properties, and on ^{19}F chemical shifts, present entirely different problems and that attempts to combine the two will prove fruitless.

Experimental and Theoretical Studies of Long-Range H–H Coupling Constants in Ring-Substituted Styrenes

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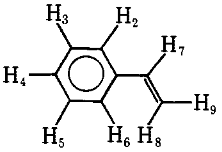
Abstract: Analysis of the proton magnetic resonance spectra of a number of ring-substituted styrenes has yielded the signs and magnitudes of the long-range coupling constants between the protons of the ring and those of the side chain. These parameters are of interest because of their sensitivity to conformational factors and because the relative importance of σ- and π-electron mechanisms in unsaturated compounds of this type is in dispute. To interpret the coupling constant data, theoretical calculations were performed for several values of the dihedral angle between the phenyl ring and the vinyl group. Calculated results for styrene were based on both the semiempirical valence-bond method which includes a sum over triplet states in the second-order perturbation expression for the coupling constants, and by the molecular orbital method which uses finite perturbation theory in the semiempirical INDO approximation. Agreement between experimental and theoretical results is excellent and shows, for example, that the π-electron mechanism is the only important factor for long-range coupling between the vinyl protons and the *p*-hydrogen atom of the ring. On this basis, the experimental and theoretical results permit an estimate to be made of the average angle between the ring and side chain of 2,6-dichlorostyrene.

Although dissection of coupling constants into σ and π contributions is not rigorously valid, this approximation has been found to be useful in both empirical and theoretical studies.[2,3] Proton–proton spin–spin coupling across six or more σ bonds is generally considered to be negligible. However, the relative importance of σ and π contributions to four- and five-bond coupling constants in unsaturated systems is still a subject of debate.[2–6]

Styrene (**1**) and its derivatives would appear to be potentially useful substrates for testing the relative importance of the various possible mechanisms in determining long-range coupling constants. In particular, the use of bulky substituents to vary the relative orientations of the vinyl and phenyl moieties might be expected to yield useful insights. Many proton magnetic resonance studies of ring-substituted styrenes have been reported,[7–11] but few long-range coupling constants[8,9] and no proton–proton signs have hitherto been noted. Recently a complete analysis of perfluorostyrene was reported.[12]



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In this paper we report the experimental signs and magnitudes found for the long-range proton–proton coupling constants in a series of ring-halogenated styrenes, and compare these results with the values predicted theoretically for styrene by previously developed valence-bond (VB)[5,13,14] and molecular orbital (MO)[15–18] formulations.

Experimental Section

Compounds. 3-Bromo-, 3,4-dichloro-, 2,5-dichloro-, and 2,6-dichlorostyrene were obtained from commercial sources and used without further purification. 3-Bromostyrene was used in preference to 3-chlorostyrene because the larger ring-proton chemical shift differences facilitated the spectral analysis. Any slight traces of impurities in these compounds did not obscure the nuclear magnetic resonance (nmr) spectra. Solutions of these compounds had concentrations which were 5 mol % in carbon disulfide and

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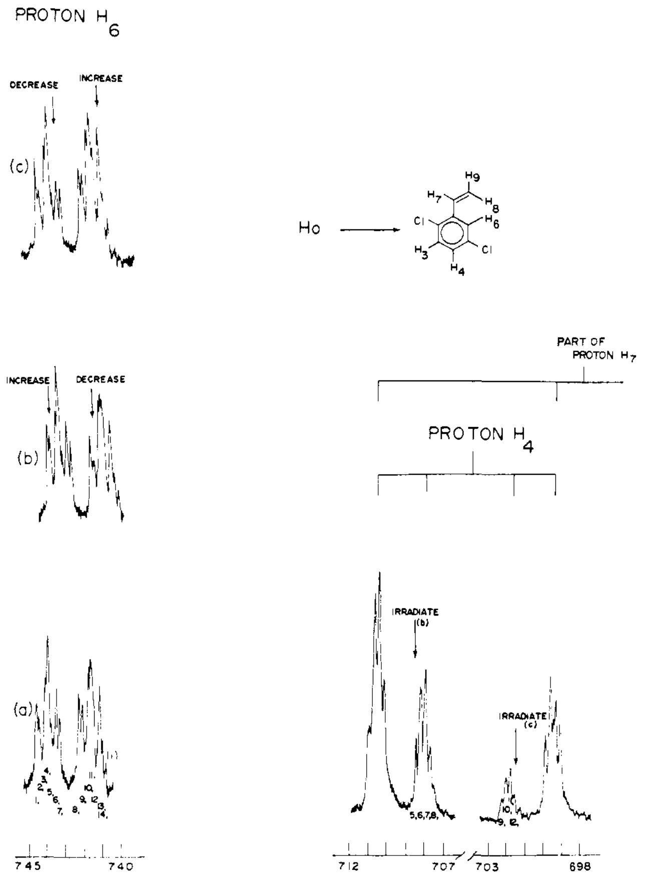

Figure 1. Partial nmr spectrum of 5 mol % 2,5-dichlorostyrene in carbon disulfide at 100 MHz. The scale is in hertz to low field of internal TMS. (a) The single resonance spectrum of protons H_6 and H_4 with the experimental peaks which can be distinguished labeled from low to high field. An impurity peak is designated "(i)". (b) The spectrum of H_6 when very weak tickling irradiation is centered on peak 5 of proton H_4. (c) The spectrum of proton H_6 when very weak tickling irradiation is centered on peak 12 of proton H_4.

included about 3 mol % of tetramethylsilane (TMS). All samples were thoroughly degassed by several freeze–pump–thaw cycles, and sealed.

Nuclear Magnetic Resonance Spectra. Proton magnetic resonance spectra were recorded on a Varian HA-100 nmr spectrometer operating in the frequency sweep mode, locked to TMS, at a sweep rate of 0.01 Hz/sec. Peak positions, which were calculated by interpolation from at least five traces calibrated at <5 Hz intervals, were obtained with a reproducibility of $\leq$0.03 Hz. Peak widths at half-peak heights were 0.10–0.12 Hz. Double resonance experiments were accomplished using a Hewlett-Packard 4204A oscillator.

Signs of Long-Range Coupling Constants. Most of the relative signs were obtained by the "tickling" technique originally described by Freeman and Anderson.[19] In these experiments a second (perturbing) radiofrequency field is centered on a chosen peak causing connected transitions to be split into doublets. This technique also causes perturbations of any transition which is close ($\Delta\nu$ <0.5 Hz) to the irradiated transition. Since this may have the effect of perturbing the connected transitions associated with these nearby lines, sign determinations by this technique may be unsuccessful. Recently, Bell, Danyluk, and Schaefer have shown[20] that relative sign determinations may be accomplished despite these adverse conditions by making use of the generalized Overhauser experiments of the type described by Kaiser.[21] In these experiments the amplitude of the perturbing field is smaller than in the tickling experiment, and connected transitions change intensity (progressively connected transitions *increase*, regressively connected transitions *decrease*) instead of being split into the doublets of the tickling experiments.

In this work it was found possible to keep the perturbing field small enough so that transitions connected to a peak as close as 0.15 Hz to an irradiated peak were not materially disturbed, while reproducible intensity changes were observed in transitions connected to the irradiated peak. These experiments are illustrated by results obtained for 2,5-dichlorostyrene. The single resonance spectrum of protons H_6 (ortho) and H_4 (para) is shown in Figure 1a with the peaks numbered in an obvious manner (several of the H_4 transitions are overlapped by the H_7 transitions). Figure 1b shows that very weak irradiation centered on peak 5 of H_4 causes an increase in the intensity of peak 2 of proton H_6, and a decrease in peak 9. No change is observed in the relative intensities of peaks 1, 4, 5, 8, 11, and 12 of H_6 which are connected to transitions making up peak 6 of H_4 ($\Delta\nu$ ~0.2 Hz). Knowing the relative *magnitudes* of the coupling constants involved ($J_{47} \approx J_{48} \approx J_{49} \ll J_{46} < J_{34}$; $J_{69} \ll J_{68} < J_{67} \approx J_{36} < J_{46}$), this experiment shows that the signs of J_{47}, J_{67} are the same, whereas the signs of J_{48}, J_{68} are opposite. Confirmation is obtained in the experiment where peak 12 of H_4 is irradiated very weakly. Figure 1c shows a decrease in the intensity of peak 6 of H_6, and an increase in 13, no other peak in H_6 being affected. Other experiments demonstrated that the sign of J_{48} was the same as that of J_{78}, and opposite to that of J_{47}. Since the trans H–H coupling constant in substituted ethylenes is positive,[22] both J_{67} and J_{68} must be negative in 2,5-dichlorostyrene.

Spectral Analyses. The experimental peak positions and relative signs were used as input for iterative fitting using the LAOCN3[23] and LACX[24] computer programs. The nmr parameters derived from these analyses are included with the pertinent computer-fitting data in Tables I and II.

Theoretical Calculations of Long-Range Coupling Constants in Styrene

(1) Valence-Bond Calculations by the Sum over Triplet States (VB–SOT) Method. Valence-bond (VB) calculations of the long-range H–H coupling constants for the parent styrene molecule were based on a previously developed formalism,[13] which uses the generalized product approximation[25,26] with intergroup configuration interaction. This method permits the VB method for coupling constants, which uses[27] a sum over triplet states, to be extended to many electron systems.

Calculated VB long-range coupling constants between the aromatic protons and the H_7 vinylic proton in styrene (**1**) were based on 12 electron fragments. These comprised the eight π-electrons and the two C–H bonds of interest. Coupling constants from the ring protons to the H_8 and H_9 protons were based on 14 electron fragments. A representative 14-electron fragment (the one which was used to calculate J_{49}) is depicted in Figure 2. In all of the VB calculations the π-electron system of eight electrons comprised one group and the σ system of two or three C–H bonds comprised the second group. All exchange integral parameters for the semiempirical VB calculations are given in Table I of ref 5.

(2) Molecular Orbital Calculations by Finite Perturbation Theory in the INDO Approximation (MO–INDO–FPT). Molecular orbital (MO) calculations of long-range H–H coupling constants in styrene were based on finite perturbation theory[15] in the INDO (in-

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Table I. Long-Range Coupling Constants (in hertz) for Ring-Halogenated Styrenes and Calculated Values for the Coplanar ($\phi = 0°$) and Orthogonal ($\phi = 90°$) Conformations of Styrene

	Experimental[a]				Calculated MO–INDO–FPT[b]		
Coupling constant	2,6-Dichlorostyrene	3,4-Dichlorostyrene	3-Bromostyrene	2,5-Dichlorostyrene	$\phi = 0°$	$\phi = 0°$ (av)	$\phi = 90°$
J_{27}		−0.48	−0.50		−0.27	−0.51	−1.20
J_{67}		−0.53	−0.50	−0.47	−0.75		−1.20
J_{28}		<0.07[c]	<0.07[c]		+0.39	+0.17	+0.28
J_{68}		<0.07[c]	<0.07[c]	−0.15	−0.05		−0.28
J_{29}		+0.18	+0.17		+0.50	+0.35	+0.33
J_{69}		+0.19	+0.19	<0.07[c]	+0.20		+0.33
J_{37}	+0.39			<0.07[c]	+0.22	+0.75	+0.93
J_{57}	+0.39	+0.36	+0.33		+1.28		+0.93
J_{38}	−0.10			<0.07[c]	−0.18	−0.20	−0.14
J_{58}	−0.10	<0.07[c]	<0.07[c]		−0.21		−0.14
J_{39}	<0.07[c]			0.10[d]	+0.12	−0.03	+0.07
J_{59}	<0.07[c]	<0.07[c]	<0.07[c]		−0.18		+0.07
J_{47}	−0.53		−0.25	−0.26	−0.24		−1.05
J_{48}	+0.12		+0.25	+0.26	+0.29		+0.08
J_{49}	+0.13		+0.28	+0.27	+0.29		−0.04

[a] Estimated error limits for coupling constants for which values are quoted is 0.04 Hz. [b] Values reproduced from Table III to facilitate comparison. [c] These values are a conservative upper limit on magnitude. In almost all instances observed line width indicated a value less than 0.05 Hz. [d] Magnitude only.

termediate neglect of differential overlap) approximation[16,17] of self-consistent-field (SCF) MO theory. This method includes all valence electrons and has been used with some success in calculating molecular geometries, dipole moments, and hyperfine and nuclear spin–spin coupling constants.[15,16]

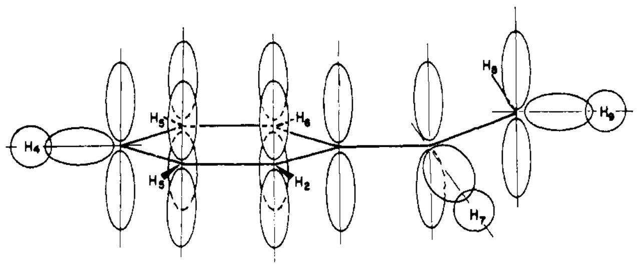

Figure 2. The 14 orbital fragment which was used in the VB calculation for J_{49} in the styrene molecule.

In the finite perturbation method for coupling constants,[15] the Fermi contact perturbation associated with one of the coupled nuclei is added to the diagonal element for the s orbital, which is centered on the specified nucleus, in the Fock matrix corresponding to electrons of α-spin and subtracted from the corresponding matrix element of the Fock matrix for electrons of β-spin. Thus, the contact perturbation has the effect of inducing a small spin density throughout the molecular electronic system. The sign and magnitude of this spin density control the contact interaction at the second nucleus and, therefore, determine the nuclear spin–spin coupling constant.

The major advantage of the INDO approximation in SCF–MO theory over the widely used CNDO (complete neglect of differential overlap) method[28] is the inclusion of the one center interaction integrals. In particular, the one center exchange integrals are essential in providing an adequate description of π-electron effects in nuclear spin–spin coupling.[15] Standard bond lengths and bond angles[29] were used for all of the styrene coupling constant calculations. Since the spin density matrix must be known to great accuracy in order to calculate coupling constants by the finite perturbation method, it was necessary to modify[15,18] the convergence criterion in the usual SCF procedure.[15,17] All of the calculations reported here were performed on a Control Data Corporation 6400 digital computer.

Results and Discussion

(1) Theoretical Predictions. Theoretically calculated values of the long-range H–H coupling constants in styrene, which were obtained by both VB and MO semiempirical methods, are entered in Table III. The VB

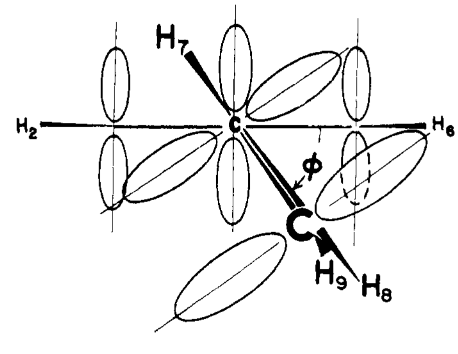

Figure 3. Specification of the dihedral angle, ϕ, in styrene and its derivatives. The angle is measured between the planes of the phenyl and vinyl groups.

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Table II. The Remaining Nmr Parameters[a] Derived for the Ring-Halogenated Styrenes at 5 Mol % Solutions in Carbon Disulfide

Parameter	Compound 2,6-Dichlorostyrene	 3,4-Dichlorostyrene	 2,5-Dichlorostyrene	 3-Bromostyrene
ν_2[b]		−735.18		−741.52
ν_3	−720.22		−717.17	
ν_4	−700.19		−706.41	−724.83
ν_5	−720.22	−726.27		−707.33
ν_6		−711.52	−742.78	−718.32
ν_7	−662.46	−654.26	−695.42	−654.89
ν_8	−572.94	−566.80	−567.48	−565.49
ν_9	−562.75	−525.48	−535.74	−521.17
J_{23}[c]				
J_{24}				1.98
J_{25}		0.34		0.40
J_{26}		2.07		1.66
J_{34}	8.06		8.54	
J_{35}	Indeterminate			
J_{36}			0.35	
J_{45}	8.06			7.94
J_{46}			2.53	1.04
J_{56}		8.92		7.72
J_{78}	17.82	17.47	17.41	17.49
J_{79}	11.72	10.84	10.96	10.84
J_{89}	1.38	0.66	0.87	0.77
Number of peaks fitted	116	192	192	435
Worse fit of any, Hz	0.043	0.029	0.056	0.036
Rms error of fitting peaks, Hz	0.014	0.012	0.019	0.018
Computed "probable errors," Hz	0.002–0.003	0.002	0.002–0.003	0.002–0.003

[a] The estimated maximum errors are 0.04 Hz. [b] Chemical shifts in hertz relative to internal tetramethylsilane. [c] Coupling constants in hertz.

Table III. Calculated Results for Long-Range Coupling Constants (in hertz) for Styrene[a]

Coupling constant	VB-SOT ϕ[b] = 0°	 ϕ = 30°	 ϕ = 60°	 ϕ = 90°	MO-INDO-FPT ϕ = 0°	 ϕ = 90°
J_{27}[c]	−0.51	−0.75	−1.21	−1.45	−0.27	−1.20
J_{67}[c]	−0.51	−0.75	−1.21	−1.45	−0.75	−1.20
J_{28}[d]	+0.59	+0.44	+0.16	+0.05	+0.39	+0.28
J_{68}[d]	+0.59	+0.44	+0.16	+0.05	−0.05	+0.28
J_{29}[d]	+0.59	+0.44	+0.16	+0.05	+0.50	+0.33
J_{69}[d]	+0.59	+0.44	+0.16	+0.05	+0.20	+0.33
J_{37}[c]	+0.39	+0.59	+0.98	+1.18	+0.22	+0.93
J_{57}[c]	+0.39	+0.59	+0.98	+1.18	+1.28	+0.93
J_{38}[d]	−0.45	−0.33	−0.13	−0.04	−0.18	−0.14
J_{58}[d]	−0.45	−0.33	−0.13	−0.04	−0.21	−0.14
J_{39}[d]	−0.45	−0.33	−0.13	−0.04	+0.12	+0.07
J_{59}[d]	−0.45	−0.33	−0.13	−0.04	−0.18	+0.07
J_{47}[c]	−0.43	−0.63	−1.04	−1.25	−0.24	−1.05
J_{48}[d]	+0.51	+0.37	+0.14	+0.04	+0.29	+0.08
J_{49}[d]	+0.51	+0.37	+0.14	+0.04	+0.29	−0.04

[a] Values quoted are for the numbering depicted in **1**. [b] The dihedral angle, ϕ, is measured from the plane of the phenyl and vinyl groups as depicted in Figure 3. [c] VB calculations were based on 12 electron fragments which included the π-electron system with eight electrons and a group of four electrons consisting of a C–H bond at the α-carbon atom and a C–H bond at either the ortho, meta, or para position of the ring. [d] VB calculations were based on 14 electron fragments, which in addition to the 12 electron fragments described in footnote *c* included a C–H bond at the β-carbon atom. Calculated values for coupling constants to H_8 were approximately 0.005 Hz greater than those to the H_9 proton.

results, which are based on the sum over triplet states (VB–SOT) method, are given for 30° intervals of the dihedral angle, ϕ. The MO results, which are based on INDO wave functions and finite perturbation theory (MO–INDO–FPT), are given only for $\phi = 0°$ and $\phi = 90°$ for reasons of computational economy. To facilitate comparison with experimental data, the MO–INDO–FPT results are also given in Table I. The dihedral angle, ϕ, is measured between the plane of the phenyl ring and the plane of the vinyl group as shown in Figure 3. It should be noted that the calculated VB results in Table III refer only to π-electron contributions arising from σ–π configuration interaction and π-electron delocalization in the previously mentioned 12- and 14-electron fragments. In contrast, the MO–INDO–FPT results in Table III are based on all valence electrons and, therefore, may be expected to include almost all types of effects arising in the total electronic framework.

As expected,[2] the predicted conformational dependence of the semiempirical VB results is dominated by two mechanisms. In the planar conformation the important mechanism is delocalization in the extended π-electron system. This mechanism has a $\cos^2 \phi$ dependence on dihedral angle, ϕ. For the out-of-plane conformations, increasingly important contributions to the coupling between the ring proton and the H_7 vinylic proton occur *via* a σ–π configuration interaction (exchange) mechanism, and this has a $\sin^2 \phi$ dependence on dihedral angle. The very small coupling constants between the ring protons and the H_8 and H_9 protons for $\phi = 90°$ indicate that this type of long-range coupling is ineffectively transmitted by the σ-electron framework of the vinyl group. Because the mechanism of transmission of the coupling through the vinyl group is analogous to the three-bond vicinal coupling in which the trans value is greater than the cis value, it is predicted and found that the coupling constants between the ring protons and the H_8 proton are somewhat greater than to the H_9 proton for the out-of-plane conformations.

Since only two mechanisms dominate the calculated VB results in Table III, these values are very well represented by the following equations.

$$J_{27} = J_{67} = -0.51 \cos^2 \phi - 1.45 \sin^2 \phi$$

$$J_{37} = J_{57} = 0.39 \cos^2 \phi + 1.18 \sin^2 \phi$$

$$J_{47} = -0.43 \cos^2 \phi - 1.25 \sin^2 \phi$$

$$J_{28} = J_{29} = J_{68} = J_{69} = 0.59 \cos^2 \phi + 0.05 \sin^2 \phi$$

$$J_{38} = J_{39} = J_{58} = J_{59} = -0.45 \cos^2 \phi - 0.04 \sin^2 \phi$$

$$J_{48} = J_{49} = 0.51 \cos^2 \phi + 0.04 \sin^2 \phi$$

Best agreement between the calculated VB results and experimental data is expected for coupling constants in which the nuclei are separated by more than five bonds because the contributions from the σ-electron framework should be effectively damped out over as many as six bonds.

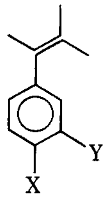
The semiempirical MO results in Table III are based on a computational and parameterization scheme which is significantly different from that used in the VB calculations. Since the MO method includes all valence electrons, the calculated values reflect contributions transmitted *via* the σ- and π-electron systems as well as direct interactions associated with the proximity of the bonds containing the coupled nuclei. Unfortunately, in the finite perturbation method there is no obvious way of sorting out the contributions of the various coupling constant mechanisms to the calculated values. However, the VB results reported here and previous theoretical studies of long-range coupling constants provide a basis for interpreting most of the factors which are involved.

The calculated VB and MO results in Table III are quite similar. The only differences in sign are those which occur for J_{68} and J_{39}. It seems likely that the disparity between the two sets of results for J_{68} may be attributable to some type of direct interaction arising because of the proximity of the H_6 and H_8 protons. The factors which are responsible for the disparity in the J_{39} coupling are less clear, but they may be related to small, positive σ-electron contributions along the extended zigzag path which links these two protons. With two exceptions the VB results for the planar conformation are larger in magnitude than the MO results. The larger magnitudes for J_{67} and J_{57} in the MO calculations are almost certainly attributable to σ-electron contributions along the four-bond path and the all-trans five-bond path, respectively. The other disparities between the two sets of calculations for the planar conformation may be attributable to intrinsic differences in parameterization schemes, different treatment of correlation effects by the two methods, etc.

The identity of the MO results for J_{48} and J_{49} in the planar comformation clearly shows that any type of σ-electron contribution is damped out over as many as seven bonds. The remarkable correspondence between the VB and MO results for the 90° twisted geometry in Table III provides a very strong argument for the importance of the σ–π configuration interaction mechanism described previously.

(2) Expected Conformations of Ring-Substituted Styrenes. Little quantitative data are available on the preferred conformations of styrene and its derivatives. The available evidence indicates that nonplanar conformations are preferred by bulky 2,6-disubstituted styrenes, and perhaps also by bulky 2-substituted styrenes, but that 3- and 4-substituted styrenes are planar.[7,30–35] These results suggest a fairly close parallel between the conformations adopted by many substituted styrenes and the corresponding benzaldehydes, for which more quantitative data are available.[4,20,36–39]

In the absence of any evidence to the contrary, it appears reasonable to assume that, at room temperature, 3- and 4-halostyrenes exist as the rapidly interconverting (approximately equal populations) conformers **2** and **3** and that 2-chlorostyrenes exist predominantly as either the planar conformer **4** or a slightly twisted conformer **5**, whereas nonplanar conformation **6** is preferred by 2,6-dichlorostyrene.



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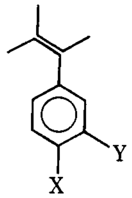

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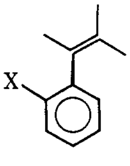

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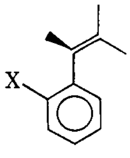

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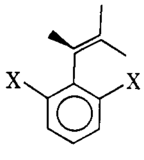

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Some doubt exists as to the exact conformation adopted by 2,5-dichlorostyrene. If conformation is the major factor causing coupling constant variations, then the similarity of J_{47}, J_{48}, and J_{49} values in 2,5-dichlorostyrene and 3-bromostyrene, and their dissimilarity to the values in 2,6-dichlorostyrene, suggest that 2,5-dichlorostyrene exists as a planar or nearly

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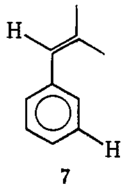
planar conformer. The J_{37} coupling constant cannot be observed in 2,5-dichlorostyrene (<0.1 Hz) and in 2-bromostyrene ($J_{37} < 0.1$ Hz, $J_{57} \sim 0.7$ Hz[40]). Analogy with previous nmr results for benzaldehydes[41,42] and α-substituted toluenes[43,44] then indicates that H_7 is syn to H_3, *i.e.*, 2,5-dichlorostyrene exists predominantly as, or close to, the trans-planar conformer **4**. Support for this conclusion is found on calculating the nonbonded repulsions in styrene and 2,5-dichlorostyrene by the method of Scott and Scheraga.[45] Conformer **4** for 2,5-dichlorostyrene is predicted to be only about 0.8 kcal/mol less stable than the planar conformation of styrene itself.[46] Further support for conformer **4** is given by the low value of J_{89},[7] and by the marked deshielding of proton H_7 (Table II) presumably by the proximate chlorine atom. Finally, the MO calculations provide support for conformer **4** since they predict a negative sign for J_{68} (as observed experimentally) in this conformer but not in the other conformer.

(3) Substituent Effects on Coupling Constants. Substituents can affect coupling constants by perturbing the electronic energy levels.[2] For example, the marked substituent dependence of $^4J_{H,CHO}{}^o$ in para-substituted benzaldehydes has been attributed largely to perturbation of the σ-electron contributions.[4] A similar sensitivity is found for $^4J_{H,CH\alpha}{}^o$ in para-substituted styrenes.[47] For example, $^4J_{H,CH\alpha}{}^o = -0.5 \pm 0.1$ Hz in p-$Me_2NC_6H_4CH{=}CH_2$, and -0.2 ± 0.1 Hz in p-$NCC_6H_4CH{=}CH_2$. Therefore, some care is required in drawing conclusions based on comparisons between coupling constants for a series of styrene derivatives. In this work chlorine substituents, which have a weak perturbing effect as measured, for example, by Swain and Lupton's "R" parameter,[48] were used where possible to try to mitigate these effects. Some support for the success of this stratagem may be taken from the approximate constancy of $^4J_{H,CH\alpha}{}^o$ values in Table I. On the basis of these arguments long-range coupling constant variations observed in this study are assumed to be dominated by conformational rather than substituent factors.

(4) Comparison of Experimental and Theoretical Results. (a) Signs. In all cases, the long-range coupling constants whose signs were determined (*i.e.*, those with magnitudes >0.1 Hz) were found to have the signs predicted by the theoretical treatments. In addition, the signs of the coupling constants associated with the H_7 proton are identical with those found for analogous coupling constants in toluenes[49,50] and benzaldehydes.[20,51] Coupling constants J_{39}, J_{69}, and J_{49} have the same signs as the corresponding values in phenylacetylene[52] and 2,5-dichlorophenylacetylene.[53] More detailed consideration of the results, however, indicates a few discrepancies between some of the theoretical predictions and experimental observations.

(b) Four-Bond Coupling Constants. In all of the molecules studied the two four-bond coupling constants (J_{27} and J_{67}) are equal within experimental error, even for the preferred conformation found for 2,5-dichlorostyrene. The average value of the MO results for J_{27} and J_{67} is 0.51 Hz, which is identical with the VB result in Table III, and both are nearly identical with the experimental results. These values could be interpreted in terms of a preponderant π-electron contribution with only small contributions from the σ-electron framework. Although this conclusion is consistent with previous results in acyclic conjugated systems such as butadiene,[2,54] similar magnitudes for $^4J_{HH'}$ are well known in saturated systems.[2,18] Experimental results in toluenes[6] and benzaldehydes[4] have indicated the possibility of appreciable contributions to four-bond coupling constants from the σ-electron framework in these compounds. From the calculated and experimental data in Tables I and III, it would appear that any σ-electron contributions to the four-bond coupling constants in styrene are quite a bit smaller than those found in the saturated molecules.[18] Since σ-electron effects are not implicit in the VB method used here, the apparent agreement between the theoretical and experimental results is probably the result of a somewhat fortuitous choice of parameters. Experiments designed to explore the importance of σ-electron contributions to ^4J in styrenes are currently in progress.

(c) Five-Bond Coupling Constants. The five-bond coupling constants between ring and side chain protons in styrene may be divided into two sets: J_{37}, J_{57}, J_{28}, J_{29}, J_{68}; J_{69}. The agreement between calculated and experimental results is generally good. Best agreement is found with the MO–INDO–FPT results in Table I, which is indicative of the fact that the marked orientation dependence of these coupling constants is undoubtedly dominated by the σ-electron mechanism. For example, the calculated value of +1.28 Hz for J_{57} occurs for the all-trans arrangement, **7**, but the calculated value for the cis–trans arrangement, **8**, for J_{37} is only +0.22 Hz. The small magnitude of J_{37} in 2,5-dichlorostyrene, values of 0.35 Hz for J_{57} in 3,4-dichlorostyrene and 3-bromostyrene, and values of 0.7 Hz for J_{57} and <0.1 Hz for J_{37} in 2-bromostyrene all provide experimental support for the stereospecificity of J_{37} and J_{57} in the planar conformation. Similar results have been observed in toluenes,[43,44] benz-



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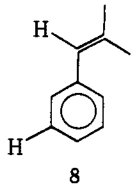

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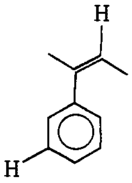
aldehydes,[41,42] phenols,[55] and anilines.[56] A comparison of calculated (MO–INDO–FPT) and experimental results suggests that the theoretical results somewhat overestimate the magnitudes of the σ-electron effect. The calculated value of J_{37} may represent an upper limit for the π-electron contributions in these systems.

The J_{68} coupling in 2,5-dichlorostyrene is particularly interesting in that both calculated and experimental values for this coupling constant are negative in sign. The negative value calculated for J_{68} may be the first indication of a mechanism which gives negative contributions to the coupling over five bonds. This would help to resolve the apparent paradox regarding the relative importance of σ- and π-electron mechanisms in these systems by leading to smaller values for these coupling constants than would be otherwise expected by summing the σ- and π-electron contributions. As previously mentioned, the negative coupling constant may be due to direct interactions between the proximate C–H groups.

Of the remaining five-bond coupling constants in Table I, the calculated average value for J_{28} and J_{68} is smaller than that for J_{29} and J_{69}, in agreement with the experimental results, although the calculated values are slightly larger than the experimental results.

(d) Six-Bond Coupling Constants. It is convenient once again to divide the coupling constants into two groups: J_{38}, J_{39}, J_{58}, J_{59}, and J_{47}. On the basis of the VB calculations for the π-electron mechanism alone, the two sets are predicted to have approximately equal magnitudes and the same signs. Unfortunately, the first set is only observable in the planar conformations of 2,5-dichlorostyrene ($|J_{39}| = 0.10 \pm 0.04$ Hz), and in the nonplanar conformation of 2,6-dichlorostyrene ($J_{38} = J_{58} = -0.10 \pm 0.04$ Hz). All of the other coupling constants in this group are too small to be observed (<0.07 Hz). The smallness of these coupling constants and the paucity of data make it difficult to assess the effect of twisting the vinyl group out of the plane of the phenyl group. It does appear that J_{39} is a maximum for the all-trans arrangement, **9**. This is in accord with the observation of a stereospecific $^6J_{HH'}$ ($\sim$1 Hz) in the extended "W" conformation of rigid saturated molecules.[57] The calculated MO results for J_{39} are of particular interest as they are of opposite sign to the other six-bond coupling constants. Therefore, the theoretical results are consistent with experimental observations and strongly suggest a stereospecific σ-electron mechanism for coupling over six bonds. (It is unfortunate that the unresolved couplings, J_{37}, J_{38}, and J_{69}, made it impossible to experimentally determine the sign of J_{39} for 2,5-dichlorostyrene.) Presumably this coupling constant would be positive in sign and have its maximum value of 0.1–0.3 Hz in the all-trans arrangement, **9**. In terms of the qualitative VB bond order formulation developed previously,[58] such contributions could arise from a number of third-order mechanisms. The optimum coupling paths would probably involve both the σ- and π-electron frameworks.



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The calculated value for J_{47} in the planar conformation is in excellent agreement with the experimental values. The large increase in the magnitude of J_{47} for 2,6-dichlorostyrene is also consistent with the theoretical predictions for substantial deviations from planarity.

(e) Seven-Bond Coupling Constants. As expected for coupling over as many as seven bonds, agreement between theory and experiment is excellent. Thus, J_{48} and J_{49} are very nearly equal to one another in both planar (+0.26 ± 0.04 Hz) and nonplanar (+0.12 ± 0.04 Hz) conformations. In addition, in the planar conformations J_{48} and J_{49} have approximately the same magnitude as (and opposite sign to) J_{47} (−0.25 ± 0.04 Hz). Both the MO and VB results are identical for J_{48} and J_{49}, indicating the complete absence of any type of σ-electron contributions. The observed halving of the magnitudes of J_{48} and J_{49} on twisting the vinyl moiety out of the plane of the ring in 2,6-dichlorostyrene is also well predicted by both the MO and VB results.

(5) Calculated Nonplanarity of 2,6-Dichlorostyrene. The above arguments provide good evidence that the coupling constants between the vinylic protons and the aromatic H_4 proton are largely determined by the π-electron mechanism. With this assumption the angular dependence given for the VB results in section 1 can be used to estimate an average intergroup angle (ϕ in Figure 3) for 2,6-dichlorostyrene. A similar approach has been given by Bell, Danyluk, and Schaefer.[20] Rearrangement of the equations in section 1 gives

$$\cos^2 \phi = [J(\phi) - J(90°)]/[J(0°) - J(90°)]$$

where ϕ is the average deviation from planarity, $J(\phi)$ is the observed coupling constant, and $J(0°)$ and $J(90°)$ are the respective coupling constants for the coplanar and the 90° twisted conformations of the vinyl and phenyl moieties. For J_{48} and J_{49} the theoretical VB result for the π-electron contribution is $J(90°) = 0.04$ Hz, which is in good agreement with the MO results. The coupling constant in the planar conformation is given by the experimental result in Table I, $J(0°) = 0.26 \pm 0.04$ Hz. It follows, therefore, from the observed values for J_{48} and J_{49} in 2,6-dichlorostyrene that $\phi = 30$–$50°$. An analogous calculation with J_{47} gives $\phi = 30$–$40°$, which is in the same range as the previous calculation. This value for the average deviation from planarity may be compared with the value of 55–60° calculated[46] for 2,6-dichlorostyrene using Scott and Scheraga's nonbonded energy calculations[45] together with an assumed torsional energy of 5 kcal/mol; $\phi = 20$–$25°$ for 2,6-dichlorobenzaldehyde derived from its proton nmr spectrum,[20] $\phi = 10$–$18°$ in 2,6-dichloroacetophenone derived from ^{13}C chemical shift measurements,[59] and $\phi = 54°$ for 2,6-dimethylstyrene derived from its uv spectrum.[31]

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Acknowledgments. This work was supported in part by grants from the National Science Foundation (M. B.) and the National Research Council of Canada (W. F. R.). Computational assistance of Miss Carol Browdy and the services of the University of Arizona Computer Center are gratefully acknowledged.

Conformational Preferences of Bridged Aromatic Compounds. I. Ortho-Substituted Diphenylmethanes[1]

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Contribution from the Institute of Industrial Chemistry of the University, Catania, Italy. *Received October 5, 1970*

Abstract: Dipole moments and nmr data are reported for a series of ortho-substituted diphenylmethanes. The results obtained indicate that, depending on the substitution pattern in the four ortho positions, different conformational preferences can arise. The preferred conformations are discussed for each case and good agreement is found between dipole moments and nmr data.

We have been interested in the study of conformational properties of ortho-substituted diphenylmethanes[1] and dibenzylbenzenes[1,2] as a way of exploring the conformational behavior of bridged aromatic compounds[3] and of providing useful models for macromolecular systems.[4]

In our approach, we have coupled dipole moment and nmr measurements to study the conformational preferences eventually induced by ortho substituents in the above mentioned compounds.

Dipole moments, being conformation dependent, are very useful in the study of this kind of molecule, but sometimes do not provide unequivocal information. In fact, due to the angular geometry of these molecules, it may occur that two or more different conformations are calculated to have the same dipole moment value.

We have found[1] that nmr spectra also may provide useful data regarding the conformations of the above compounds. In fact, due to the proximity of the two aromatic rings, the shielding of the ring current[5] of the adjacent nucleus at the ortho position is a function of the molecular conformation. This effect has been systematically investigated by us and the results have been found complementary with those obtained by dipole moments.

In this paper we discuss some data concerning variously substituted diphenylmethanes. The results obtained indicate that, depending on the substitution pattern in the four ortho positions, different conformational preferences can arise.

Stereochemistry of Diphenylmethanes

Diphenylmethane is not a planar molecule in the solid state, its phenyl rings being rotated about 52° out of the plane containing the two C_{Ar}–C bonds.[6,7] This spatial arrangement also seems preferred by other bridged aromatic systems.[8,9]

On the other hand, it is generally agreed that diphenylmethane does not have a fixed conformation in solution at room temperature.[10–13] Four possible forms involved in its conformational equilibrium are shown in Figure 1. In form A, the two rings are coplanar with each other and with the C_{Ar}–C–C_{Ar} plane. In form B, the rings are perpendicular to the C_{Ar}–C–C_{Ar} plane. In form C, one ring is coplanar and the other perpendicular to the C_{Ar}–C–C_{Ar} plane. Form D stands for the intermediate (skew) conformation.

Although all these forms may be conveniently generated by internal rotation of the phenyl rings around the two C_{Ar}–C axes, structures A and B seem energetically disfavored because of repulsive interactions between nonbonded atoms.[9,10,14] Ortho substitution certainly enhances the energy barrier to internal rotation, and the question arises as to whether it causes this rotation to become restricted, or whether it induces a given conformation to become preferred on steric grounds.[15]

Internal rotation is kinetically restricted in the cyclic compound **1**.[17] Inspection of molecular models indicates that the cycle is unstrained, but the internal rotation of the duryl rings can occur only through an energetically disfavored pathway involving close contacts of the bulky methyl substituents. In open-chain com-

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(1) For a preliminary communication, see G. Montaudo, S. Caccamese, P. Finocchiaro, and F. Bottino, *Tetrahedron Lett.*, 877 (1970).

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