Substituent Effects and Long-Range Couplings in Several β,β-Dimethylstyrenes[1a]

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Abstract: We have investigated the proton nmr spectra of a series of para-substituted β,β-dimethylstyrenes, and established the existence of a variety of long-range couplings, including allylic, isopropylidenic, and nine-bond HH couplings. The isopropylidenic couplings are negative in sign, in agreement with theoretical predictions, and possible mechanisms of spin information transfer are discussed. The isopropylidenic couplings correlate closely with corresponding geminal HH couplings, and this observation allows an understanding of the anomalous positive coupling in acetone. The substituent dependence of the couplings is discussed in terms of a qualitative molecular orbital model. Finally, the magnitudes of the nine-bond couplings allow an estimate to be made of the extent of nonplanarity in β,β-dimethylstyrenes.

The 1963 discovery[3] of a 0.54-Hz coupling between the methyl groups of acetone was the first of a large number of examples of isopropylidenic couplings,[4] of which couplings across carbonyl groups are the most familiar and well-studied type.[5–10] By contrast, relatively few examples of such couplings across carbon–carbon double bonds are known. An early investigation[11] of the nmr spectra of β,β-dimethylstyrene derivatives revealed no detectable isopropylidenic couplings.

It thus developed that a chance combination of two factors: the historical accident of their initial discovery and the almost complete lack of data for isopropylidenic couplings in alkenes, conspired to make $^4J_{HH}$ in ketones in general, and acetone in particular, the focus of attention for theorists, with the result that $^4J_{HH}$ in acetone came to be regarded as a prototype for *all* isopropylidenic couplings.

Theoretical estimates of the magnitude of $^4J_{HH}$, most often derived for systems more closely resembling alkenes,[3,6,12,13] but occasionally for acetone itself,[14] are in generally good agreement with experiment. All calculations predicted the sign of the coupling to be negative.

In 1968, the sign of $^4J_{HH}$ in acetone was determined by Dreeskamp[15] and de Jeu and Angad Gaur[16] to be *positive*, in flat disagreement with theoretical predictions raising questions of the adequacy of the theoretical treatments and/or the validity of acetone as a model system.

Based on our own studies[17] of substituent effects on long-range HH couplings, we felt acetone, with its highly polar carbonyl group and unshared electron pairs on oxygen, to be *atypical* and a poor choice for comparison with the results of existing theoretical calculations. In particular, we hypothesized that in acetone, σ electron withdrawal, augmented by back-donation of lone pair electrons into antibonding orbitals in the HCCCH chain, would produce a positive σ-electron contribution capable of overshadowing the estimated -0.5 Hz π-contribution, leading to the observed positive sign. Our discovery that the isopropylidenic couplings in acetone anil and 2-methylpropenyl acetate are 0.00 and -0.49 Hz, respectively, supported our interpretation.[18]

We therefore sought additional verification of our hypothesis and report here results of a reinvestigation of the 60-MHz proton nmr spectra of β,β-dimethylstyrene and several para-substituted derivatives. The results confirm theoretical predictions that the signs of the isopropylidenic couplings are negative, and the substituent-induced variations in $^4J_{HH}$ offer some insight into the manner in which substituents perturb the electronic structures of molecules.

Results

We examined the nmr spectra (in degassed carbon disulfide solutions[19]) of β,β-dimethylstyrene and its *p*-chloro, *p*-methoxy, and *p*-methyl derivatives.

Features common to the spectra of all compounds in-

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(1) (a) Presented in part at the 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., 1971. (b) Taken from the thesis submitted by E. R. C. to the Graduate School of Arts and Sciences in partial fulfillment of the requirements for the degree of Master of Science, 1970.

(2) To whom correspondence should be directed at: Biophysics Research Laboratory, Peter Bent Brigham Hospital, Harvard Medical School, Boston, Mass. 02115

(3) J. R. Holmes and D. Kivelson, *J. Amer. Chem. Soc.*, **83**, 2959 (1963).

(4) The term "isopropylidenic" was suggested by H. C. Beyerman, D. W. Reinholdt, A. Sinnema, and A. Van Veen [*Recl. Trav. Chim. Pays-Bas*, **85**, 347 (1996)] to refer to four-bond couplings in the fragment H–C–C–C–H.

(5) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 121.

(6) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

(7) M. S. Gopinathan and P. T. Narasimhan, *J. Magn. Resonance*, **6**, 147 (1972).

(8) P. N. Gates and E. F. Mooney, *J. Chem. Soc.*, 4648 (1964).

(9) K. Takahashi, *Bull. Chem. Soc. Jap.*, 37, 291; 963 (1964).

(10) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(11) H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Aust. J. Chem.*, **18**, 1759 (1965).

(12) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

(13) M. Barfield, *J. Chem. Phys.*, **48**, 4458, 4463 (1968).

(14) W. H. de Jeu, Ph.D. Thesis, Technische Hogeschool Delft, 1969.

(15) H. Dreeskamp, *Z. Phys. Chem.* (*Frankfurt*), **59**, 321 (1968).

(16) W. H. de Jeu and H. Angad Gaur, *Mol. Phys.*, **16**, 205 (1968).

(17) D. J. Sardella, *J. Mol. Spectrosc.*, **31**, 70 (1969).

(18) D. J. Sardella, *Chem. Commun.*, 1613 (1968).

(19) Carbon disulfide was chosen as solvent because it was found that among the solvents tested (acetone, acetonitrile, benzene, carbon disulfide, carbon tetrachloride, chloroform, and *N,N*-dimethylacetamide) it consistently produced the largest shift difference between the nonequivalent methyl groups (0.05 ± 0.02 ppm), a factor of importance in the double irradiation experiments to be discussed. Indeed, in acetone, acetonitrile, chloroform, and *N,N*-dimethylacetamide, the methyl region appeared as a triplet, due to accidental partial overlapping of the methyl doublets.

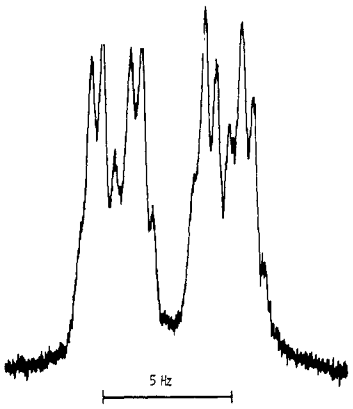

Figure 1. The methyl region of *p*-chloro-β,β-dimethylstyrene, traced on the 50-Hz scale at a sweep speed of 0.10 Hz/sec, illustrating the isopropylidenic coupling.

clude an aromatic multiplet centered at *ca.* δ 6.6–7.21, a methine resonance (*ca.* δ 6.1) split into a septet by near-identical couplings to the β-methyl groups, and non-equivalent methyl absorptions at *ca.* δ 1.79 (cis to phenyl) and *ca.* δ 1.85 (trans to phenyl), each of which was split into a doublet of quartets. In addition, the spectra of *p*-methoxy-β,β-dimethylstyrene and β,β,*p*-trimethylstyrene displayed singlets at δ 3.69 (CH_3O) and δ 2.26 (CH_3), respectively. The chemical shift data are summarized in Table I. Assignments of *cis*- and *trans*-β-methyl resonances followed those of Sternhell, *et al.*[11]

Table I. Chemical Shift Data for Substituted β,β-Dimethylstyrenes in Carbon Disulfide

Substituent	Absorption	Shift in δ, ppm
p-Chloro	*cis*-β-Methyl	1.81
	trans-β-Methyl	1.87
	Methine	6.17
	Aromatic	7.09
None	*cis*-β-Methyl	1.80
	trans-β-Methyl	1.87
	Methine	6.02
	Aromatic	7.08
p-Methyl	*cis*-β-Methyl	1.79
	trans-β-Methyl	1.84
	Methine	6.13
	Aromatic	6.95
	Ring methyl	2.26
p-Methoxy	*cis*-β-Methyl	1.78
	trans-β-Methyl	1.84
	Methine	6.08
	Aromatic[a]	6.58 6.73 6.91 7.06
	Methoxyl	3.69

[a] Positions of the four most intense lines of the AA'BB' aromatic multiplet.

The methyl regions (Figure 1) clearly showed the presence of both allylic (*ca.* 1.5 Hz) and isopropylidenic (*ca.* 0.4 Hz) couplings. In both β,β-dimethylstyrene and its *p*-methyl derivative the couplings were nearly obscured by other, unresolved couplings whose effects, however, were easily removed by decoupling. Figure 2 shows an example of the dramatic increase in resolution which resulted upon irradiation.

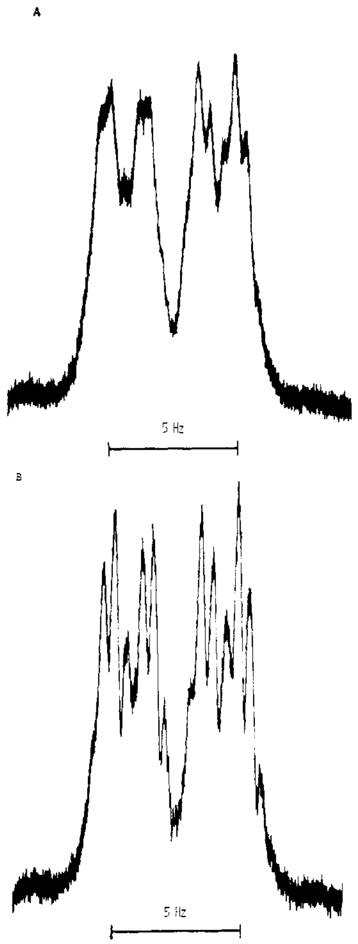

Figure 2. The methyl region of β,β,*p*-trimethylstyrene: (a) undecoupled spectrum, showing broadening due to other, unresolved couplings; (b) spectrum recorded under identical conditions, but with simultaneous decoupling of the ring methyl group.

Sign of the Isopropylidenic Coupling. The spectrum of the isopropylidenyl moiety approximates A_3M_3X and allowed us to determine the relative signs of the allylic and isopropylidenic couplings by series of double irradiation experiments,[20] of which Figures 3 and 4 illustrate typical examples.

Weak irradiation at the low-field side of the vinylic proton resonance caused partial collapse of the lower field quartets of both methyl absorptions (Figure 3b). Similarly, irradiation of the high-field side of the vinylic proton resonance perturbed the higher field quartets (Figure 3c), indicating the allylic couplings to be of like sign.

In another experiment (Figure 4), irradiation of the higher field quartet of the more shielded methyl doublet of quartets caused collapse of the higher field portion of the less shielded methyl absorption. Thus, all three couplings have the same sign. Since recent reviews of long-range couplings[6,10,21] reveal allylic couplings involving methyl groups to be invariably negative, this indicates the isopropylidenic couplings to be negative. The data are summarized in Table II, along with results for the geminal HH couplings in the

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(20) (a) J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963); (b) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962); (c) W. von Philipsborn, *Angew. Chem., Int. Ed. Engl.*, **10**, 472 (1971).

(21) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

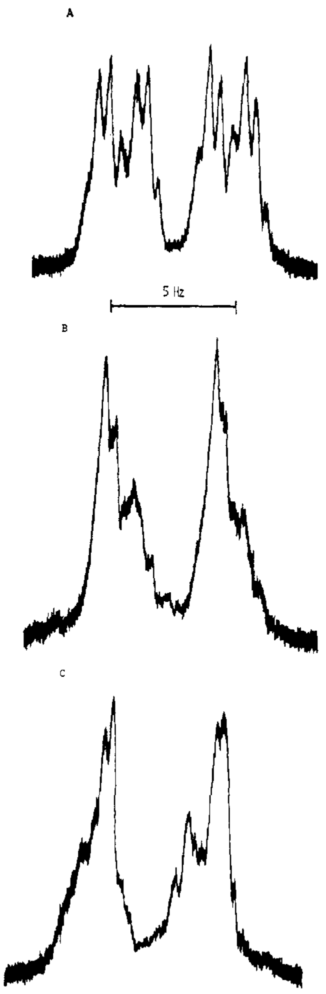

Figure 3. The methyl region of *p*-chloro-β,β-dimethylstyrene: (a) normal spectrum; (b) spectrum recorded with simultaneous irradiation of the lower field portion of the vinylic proton multiplet; (c) spectrum obtained with simultaneous irradiation of the higher field portion of the vinylic proton multiplet.

Table II. Isopropylidenic Couplings in β,β-Dimethylstyrenes Compared with Geminal Couplings in Styrenes

Sub-stituent	Coupling constant ($^nJ_{\mathrm{HH}}$) β,β-Dimethyl-styrene[a] (n = 4)	Styrene[b] (n = 2)
p-Cl	-0.430 ± 0.02	$+0.83$
None	-0.426 ± 0.01	$+0.95$
p-CH_3	-0.385 ± 0.02	$+1.08$
p-CH_3O	-0.380 ± 0.01	$+0.98$

[a] This work. [b] Reference 22.

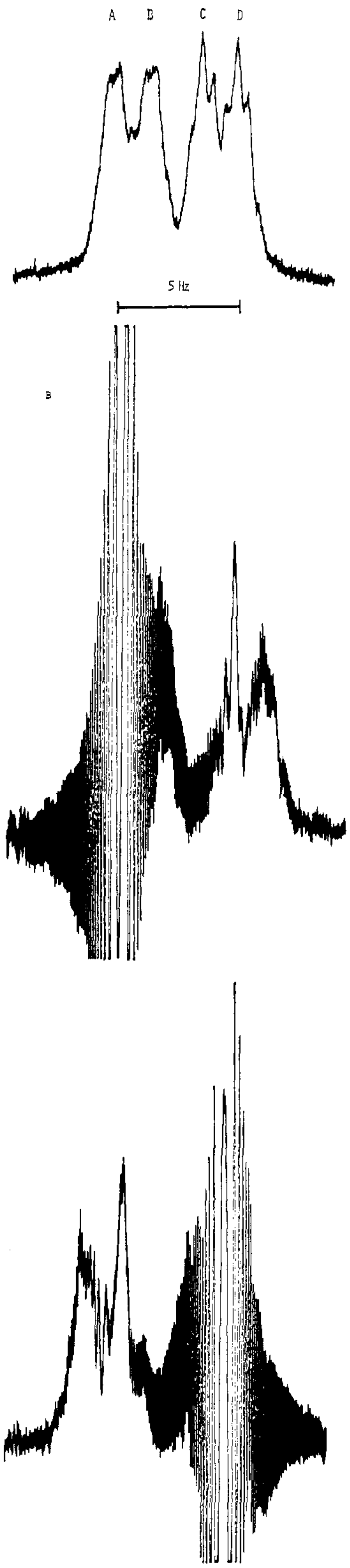

Figure 4. (a) The methyl region of β,β,p-trimethylstyrene; (b) irradiation at point A causes selective decoupling of band C, while leaving D essentially unperturbed; (c) irradiation of D causes collapse of B, leaving A unperturbed. Taken together with the results of an experiment like that shown in Figure 3, this demonstrates the signs of the allylic and isopropylidenic couplings to be negative.

corresponding para-substituted styrenes.[22] These results and our earlier discovery[18] of the -0.49-Hz coupling in 2-methylpropenyl acetate are in agreement with theoretical predictions based on the assumed dominance of the π-electron contribution, and seem to support our assertion of the anomalous position of acetone.

Allylic Coupling. Our values for the allylic coupling constants are uniformly larger by *ca.* 0.1–0.2 Hz than those reported previously by Sternhell and coworkers[11] (Table III). They become more negative with increased substituent electron demand, in agreement with an extensive body of experimental data for allylic couplings,[6] but opposite to the trend reported else-

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(22) Gurudata, J. B. Stothers, and J. D. Talman, *Can. J. Chem.*, **45**, 731 (1967).

Table III. Allylic Couplings in β,β-Dimethylstyrenes

Substituent	J(cis)[a]		J(trans)[a]	
	This work	Ref 11	This work	Ref 11
p-Cl	-1.56 ± 0.05		-1.44 ± 0.04	
None	-1.53 ± 0.03	-1.30 ± 0.02	-1.41 ± 0.01	-1.20 ± 0.02
p-CH$_3$	-1.48 ± 0.05	-1.30 ± 0.02	-1.39 ± 0.02	-1.27 ± 0.02
p-CH$_3$O	-1.50 ± 0.03	-1.35 ± 0.01	-1.39 ± 0.04	-1.35 ± 0.01

[a] Negative signs assumed in accordance with experience (see text).

where.[11] Similar effects appear to be operative in neopentane[23] and phenylacetone[24] derivatives.

Other Long-Range Couplings. As we noted above, the spectra of all four compounds, but especially that of β,β,p-trimethylstyrene (Figure 2), suggested the occurrence of very small unresolved long-range couplings. The resulting line broadening hinders resolution of the larger couplings, may introduce errors into the magnitudes of coupling measured directly from spectra (note the reversal of the substituent effect on allylic couplings shown in Table III), and is undoubtedly the factor which allowed the isopropylidenic couplings to elude detection in earlier work.

Irradiation of the relatively narrow aromatic proton multiplet of β,β,p-trimethylstyrene caused noticeable sharpening of the vinylic proton septet and a slight improvement in the appearance of the β-methyl resonances. No significant change occurred in the ring methyl absorption. The other compounds gave similar results.

In the only case where it was possible to distinguish between protons ortho and meta to the 2-methylpropenyl side chain,[25] p-methoxy-β,β-dimethylstyrene, decoupling experiments showed the β-methyl protons to be more strongly coupled to the ortho (lower field) protons.

The dramatic sharpening (Figure 2) of the β-methyl resonances of β,β,p-trimethylstyrene upon irradiation of the ring methyl proton resonance signalled the presence of a coupling between nonspatially proximate methyl protons *separated by nine chemical bonds*, and to the best of our knowledge, this is only the second reported example of a nine-bond HH coupling.[26] Previously Barfield and Chakrabarti had predicted[6] that the π-electron contribution to the coupling in a molecular fragment such as $CH_3C{=}CC{=}CC{=}CCH_3$ would be +0.17 Hz (*i.e.*, small, but nonnegligible and nonstereospecific). We estimate by line-shape analysis that $^9J_{HH}$ = 0.05–0.15 Hz, in reasonable agreement with the prediction. Seven-bond couplings of similar magnitudes in chlorinated styrenes have recently been reported.[27]

Discussion

The observation that the isopropylidenic couplings in the β,β-dimethylstyrenes are detectable and negative is in accord with the expectation that the couplings are dominated by the π contribution.[3,6,13,14,17] The discrepancy between the value of −1.2 Hz predicted by valence-bond calculations[6] and the −0.4-Hz couplings we observe seems to imply a contribution of about +0.8 Hz from some other sources. This is qualitatively consistent with our experience that couplings between geminal methyl groups across sp^3-hybridized carbon atoms range from +0.2 to +0.7 Hz.[17]

Similarly, the relative magnitudes of the allylic couplings (*cis*, −1.52 ± 0.03; trans, −1.40 ± 0.02 Hz) support the interpretation of a −1.7-Hz π contribution (nonstereospecific) superimposed upon unequal σ contributions. The results support our original contention that $^4J_{HH}$ in acetone occupies the same anomalous position with respect to isopropylidenic couplings that $^2J_{HH}$ in formaldehyde (+42.2 Hz)[28] does for geminal HH couplings (typically +1 Hz), and for the same reasons.[29]

In molecules of the type $(CH_3)_2C{=}X$, the increased electronegativity on changing X from carbon (alkenes) to oxygen (acetone) can be expected to increase the polarities of both the C–X σ and π bonds, thereby altering both the σ and π contributions to $^4J_{HH}$.

Polarization of the C–X σ bond results in withdrawal of σ electrons from the HCCCH chain. In 2-substituted propanes, such changes cause an algebraic increase in $^4J_{HH}{}^{\sigma}$ and should thus make $^4J_{HH}$ in acetone less negative.[6,16] The four-bond coupling in $(CH_3)_2CX_2$ is +0.35 Hz in neopentane (X = CH$_3$) and +0.65 Hz in 2,2-dimethoxypropane (X = OCH$_3$).[17]

Polarization of the C–X π bond can be predicted to reduce the negative π contribution, and de Jeu[14] has estimated $^4J_{HH}{}^{\pi}$ in acetone to be −0.6 Hz. Combining the predictions, we anticipate $^4J_{HH}$ in acetone to be near zero or positive, probably in the range of +0.2 to +0.4 Hz, in reasonable agreement with experiment.[3] A similar argument can account for the lack of coupling in acetone anil.[18]

Solvent effects on $^4J_{HH}$ are consistent with this explanation. Increased hydrogen bonding of acetone to solvent molecules should increase the π polarization, further reducing $^4J_{HH}{}^{\pi}$, causing a positive shift in the isopropylidenic coupling. de Jeu reports $^4J_{HH}$ to increase from +0.56 Hz in pure acetone to +0.72 Hz in water.[14,30]

Substituent Effects on Long-Range Couplings. The effect of substituents on the allylic couplings is unexceptional, agreeing with the general observation[6,23,24] that withdrawal of σ electrons from the terminal carbons of an HCCCH chain reduces the positive σ contribution to the coupling making $^4J_{HH}$ more nega-

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(23) D. J. Sardella, *J. Amer. Chem. Soc.*, **94**, 5206 (1972).

(24) T. W. Proulx and D. J. Sardella, unpublished observations.

(25) Assignments were made on the basis of chemical shift additivity relations. Introduction of a 2-methylpropenyl group causes an upfield shift of all protons in benzene of *ca.* 0.3 ppm, whereas a methoxyl substituent causes shifts of 0.1 (meta) and 0.6 (ortho and para to methoxyl). Hence the predicted aromatic shifts for p-methoxy-β,β-dimethylstyrene are: ortho to the side chain, 7.0 (found, 7.0); and meta, 6.5 (found, 6.6).

(26) E. I. Snyder and J. D. Roberts [*J. Amer. Chem. Soc.*, **84**, 1582 (1962)] report the coupling in octa-2,4,6-triyn-1-ol to be 0.4 Hz.

(27) M. Barfield, C. J. Macdonald, I. R. Peat, and W. F. Reynolds, *J. Amer. Chem. Soc.*, **93**, 4195 (1971).

(28) B. L. Shapiro, personal communication.

(29) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(30) W. H. de Jeu, H. Angad Gaur, and J. Smidt, *Recl. Trav. Chim. Pays-Bas*, **84**, 1621 (1965).

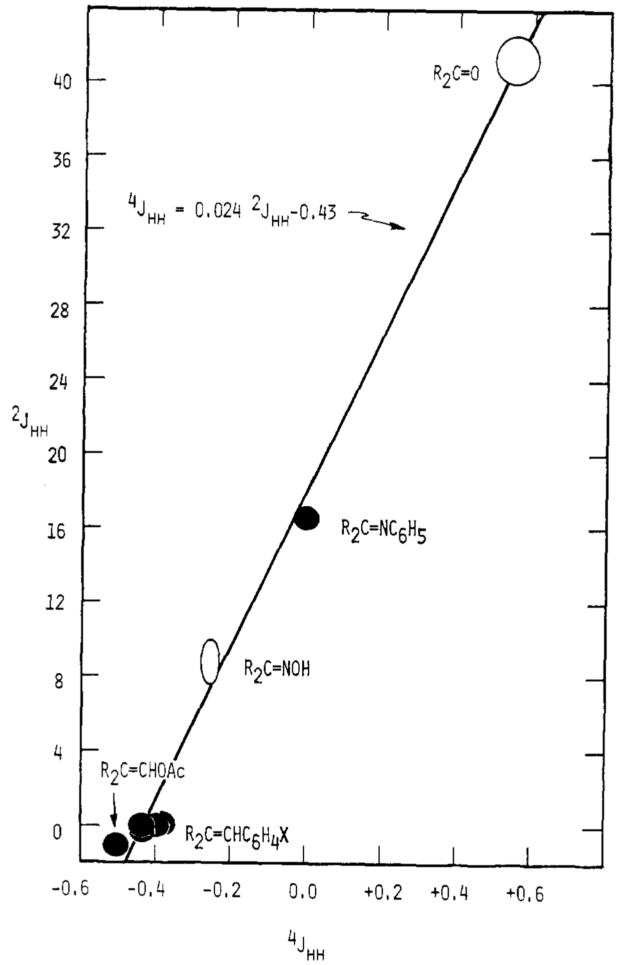


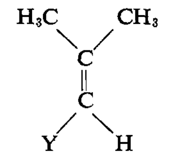
Figure 5. $^2J_{HH}$ in $H_2C{=}X$ plotted against $^4J_{HH}$ in $(CH_3)_2C{=}X$. A negative sign has been assumed for $^4J_{HH}$ in $(CH_3)_2C{=}NOH$. Open circles indicate the range of solvent-induced variations in $^2J_{HH}$.

tive, as observed. By contrast, removal of σ electrons from the central carbon causes $^4J_{HH}$ to become more positive.

The isopropylidenic couplings display a slight, but statistically significant, variation with substituent, becoming more negative with increasing electron withdrawal. Inspection of Table I indicates that $^4J_{HH}$ and $^2J_{HH}$ in styrenes respond similarly to substitution, consistent with the parallel behavior we have noted for $^2J_{HH}$ and $^4J_{HH}$ in other molecular systems.[17,18] This parallel behavior extends well beyond styrenes. Data for $^2J_{HH}$ (in molecules of the type $H_2C{=}X$), plotted in Figure 5 against $^4J_{HH}$ in $(CH_3)_2{=}X$, reveal an excellent linear correlation (correlation coefficient 0.997). This implies that the same mechanisms of spin information transfer are operative in both series of molecules and display proportionate variations along the series.

The coupling constant variations within the β,β-dimethylstyrene series cannot be explained in terms of changes in either the σ or π contributions. Increased electron withdrawal *via* the σ framework would correspond to removal of electrons from the central carbon of a propanic fragment and thus lead to an algebraic increase in $^4J_{HH}$,[3,17] whereas the opposite trend is observed. Similarly, increased π electron withdrawal should also cause a positive shift in $^4J_{HH}$.

The results are, however, consistent with the following mechanism. The +42-Hz coupling in formaldehyde has been ascribed[28] to the combined effects of σ-bond polarization and back-donation of electrons from the oxygen lone pairs into antibonding orbitals of the same symmetry type in the HCCCH fragment, and, on symmetry grounds, it seems reasonable to expect a similar contribution to $^4J_{HH}$ in acetone. The attempted dissection of the acetone coupling in the preceding section neither supports nor precludes this possibility. The antisymmetric character of a lone pair is retained in a bound pair, but the degree of back-donation should be drastically reduced, the extent being determined by the polarization of the CY bond in



Increased electron demand at Y should further reduce the positive contribution, leading to a more negative isopropylidenic coupling, as observed. The change in $^4J_{HH}$ from *ca.* −0.40 Hz in the β,β-dimethylstyrenes to −0.49 Hz in 2-methylpropenyl acetate further illustrates the effect. Pople and Bothner-By, in their theory of substituent effects on geminal HH couplings, termed such effects β effects.[29]

Conformations of β,β-Dimethylstyrenes. Topologically, a *cis*-β-methyl group in β,β-dimethylstyrene is equivalent to an *o*-methyl group, so that some degree of molecular nonplanarity might be anticipated to relieve steric strain. Although no conclusions about the degree of nonplanarity can be drawn from either the allylic or the isopropylidenic couplings, some tentative deductions can be made from the magnitudes of the unresolved nine-bond couplings in β,β,p-trimethylstyrene. Inspection of Figures 3a and 3b reveals, qualitatively, unequal nine-bond couplings. We have estimated their magnitudes by digitizing the decoupled methyl absorptions and constructing multiplets using assumed values for the nine-bond couplings. We estimate the couplings to the β-methyl groups to be: trans, (±0.10–0.15 Hz); cis, ±(0.05–0.10) Hz.

Barfield, Reynolds, and coworkers[27] have calculated the π-electron contributions to the corresponding seven-bond couplings in styrenes as a function of the twist angle. Since replacement of a proton on a π system by methyl inverts the sign, but does not affect the magnitude, of a long-range coupling to it,[31] their results are applicable to our series.

The angle of twist can be related to the observed long-range coupling by the equation[27]

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

where $J(\theta)$ is the observed coupling, and $J(0°)$ and $J(90°)$ refer to $^4J_{HH}$ for hypothetical planar and orthogonal conformations, respectively. Using Barfield's calculated value of 0.04 Hz[27] for $J(90°)$ and $^7J_{HH}$ in styrene (0.26 Hz)[27] for $J(0°)$, then an average value for $^9J_{HH}$ of 0.10 Hz leads to $\theta \simeq 40°$. This number is, of course, very imprecise and we regard it as no more than a general indication of the degree of molecular nonplanarity.

(31) (a) A. D. McLachlan, *Mol. Phys.*, 1, 233 (1958); (b) M. Karplus, *J. Chem. Phys.*, 33, 1842 (1960).

We also estimated the twist angle from the hypochromic effect of twisting on the molar absorptivity of the longest wavelength electronic absorption band in β,β-dimethylstyrene using the relation[32]

$$\epsilon/\epsilon_0 = \cos^2 \theta$$

As the reference compound, we chose styrene (ϵ 15,600),[22] generally regarded as planar. From the molar absorptivity of β,β-dimethylstyrene (ϵ 11,750), we calculate a twist angle of about 30°, in reasonable agreement with the data for 2-methylstyrene[22] and 2,5-dichlorostyrene,[27] and with our concusions based on the magnitude of $^9J_{HH}$.

Experimental Section

Nmr spectra were recorded at ambient temperature on a Varian Associates Model HA-60-IL spectrometer, operating in the frequency swept mode. Chemical shifts were measured from spectra run on the 500-Hz scale at a sweep speed of 1 Hz/sec, and are the average of two to three upfield sweeps. Coupling constants were determined from spectra traced on the 50-Hz scale at a sweep speed of 0.1 Hz/sec. Under these conditions, the precision (standard deviation of 20 separate determinations) exceeded ±0.03 Hz. Inaccuracies in chart calibration are less than +0.01 Hz. Isopropylidenic couplings were determined from spectra from which line broadening due to unresolved long-range couplings had been eliminated by decoupling.

Decoupling experiments were also done in the frequency swept mode, using either a Hewlett-Packard Model 200AB signal generator or a General Radio Model 1304B audio oscillator.

Nmr samples contained approximately 10 vol % of the appropriate β,β-dimethylstyrene in spectroquality carbon disulfide, with about 5 vol % of tetramethylsilane added to serve as both internal reference and lock signal. Samples were degassed by repeated freeze-pump-thaw cycles, and sealed under vacuum to ensure optimum resolution. No degradation of samples was evident over a 3-year period.

Compounds were prepared by the method of Sternhell, *et al.*,[11] described below for β,β-dimethylstyrene.

A solution of benzaldehyde (0.2 mol in 60 ml of anhydrous ether) was added dropwise to 0.4 mol of isopropylmagnesium bromide in 150 ml of ether. After being heated under reflux for 3 hr, the reaction mixture was cooled and poured onto a mixture of 10% H_2SO_4 and ice. The aqueous layer was extracted with ether, the extracts were combined with the original ether layer and dried (Na_2SO_4), and the solvent was removed *in vacuo*. A mixture of isopropylphenylcarbinol and unreacted benzaldehyde resulted.

The mixture was heated under reflux with 30% H_2SO_4 for 4 hr, yielding a mixture of β,β-dimethylstyrene and benzaldehyde. Chromatography on neutral alumina (activity I) with low-boiling petroleum ether afforded β,β-dimethylstyrene, which was further purified by preparative vapor phase chromatography (Varian Aerograph Model 1700; 6 ft × 0.25 in. column packed with 30% SE-30 on firebrick). Sample purity was checked with refractometry, vpc, ir, and nmr spectroscopy.

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(32) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962.

Carbon-13 Magnetic Resonance. XXIV.[1]
The Perhydroanthracenes and Perhydrophenanthrenes

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Abstract: The proton-decoupled, carbon-13 magnetic resonance (cmr) data have been determined for all of the five possible perhydroanthracene structural isomers and for four of the six possible perhydrophenanthrene compounds. The former are of known configuration, but the latter are unidentified in the chemical literature prior to the present work. The data are initially assigned to specific carbon positions using a parameter set derived from the methyldecalins. The calculated spectra are then refined by least-squares, regression analysis. New chemical shift parameters associated with boat and skew pentane conformations are discussed.

The first tetradecahydroanthracene (or perhydroanthracene, abbreviated for convenience to PHA) isomer was synthesized about the turn of the century.[2-4] It was soon recognized that other geometric isomers were possible[5] and as many as 20 were suggested.[6] Fries and Schilling ultimately delineated the correct number as being five,[7] the last of which was synthesized only in recent years.[8] Many workers contributed to the synthesis and characterization of the several isomers.[7,9-14] X-Ray[15] and electron diffraction[16,17] work demonstrated that the individual six-member rings in these compounds normally exist as chair forms, with the exception of the center ring of the trans-anti-trans compound, which is locked in a boat conformation.

Table I portrays the compounds which are conformationally locked by at least one trans ring fusion. The isomers which have two cis ring junctions may interconvert between all-chair forms; they are diagrammed in Table II. The nomenclature for the PHA isomers is

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