An Investigation of Long-range Proton–Proton Coupling Constants in Phenylacetylene Derivatives

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Signs and magnitudes of long-range coupling constants in three phenylacetylene derivatives have been determined. Values of the coupling constants are discussed in terms of the McConnell formulation and compared with results of MO–INDO–FPT calculations. Coupling constants are dominated by π contributions. Estimated values of hyperfine interaction constants for acetylene and methylacetylene groups are respectively $Q_{CC\equiv CH} = -12$ and $Q_{CC\equiv CCH} = +12$ G. The theoretical calculations are in excellent agreement with experimental results. Both approaches allow quantitative estimation of nine bond couplings in 4-vinylphenylacetylene.

Les signes et les amplitudes des constantes de couplage à longue distance de trois dérivés du phénylacétylène ont été déterminés. Les valeurs des constantes de couplage sont discutées en terme de la formulation de McConnell et comparées avec les résultats des calculs MO–INDO–FPT. Les constantes de couplage sont dominées par les contributions π. Les valeurs estimées des constantes d'interaction hyperfine pour les groupes acétylène et méthylacétylène sont respectivement $Q_{CC\equiv CH} = -12$ et $Q_{CC\equiv CCH} = +12$ G. Les calculs théoriques sont en excellent accord avec les résultats expérimentaux. Les deux approches permettent une estimation quantitative des couplages de neuf liaisons dans le vinyl-4 phénylacétylène.

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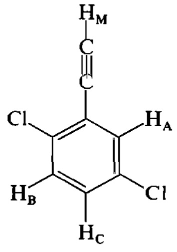
Introduction

The observed magnitudes and signs of long-range couplings between side chain protons and ring protons in styrenes (1) and benzaldehydes (2) are well predicted by theoretical computations using MO–INDO wave functions (3) and finite perturbation theory (MO–INDO–FPT) (4). McConnell's conceptually similar, but much simpler, MO formulation for alternate hydrocarbons (5) has been found to give good agreement with experiment for acenaphthenes (6), toluenes (7, 8), fluorobenzenes (9), pyridines (10), benzaldehydes (11), and xylenes (12). This latter method gives coupling constants in terms of mobile bond orders, mean excitation energies to triplet states, and proton hyperfine interaction constants. Its simplicity makes it attractive when considering more extended coupling paths. However, little data is available to test this extension. Experiments which yielded the signs and magnitudes of long-range coupling constants in the substituted phenylacetylenes **1**, **2**, and **3** are described below. The results are interpreted in terms of the McConnell formulation and are compared with MO–INDO–FPT calculations.



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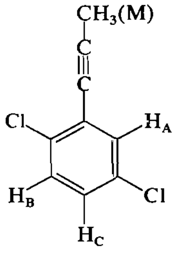

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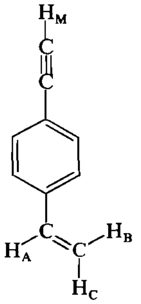

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Experimental

(a) Preparation of Compounds

(2,5-Dichlorophenyl)-acetylene

This compound was synthesized using the method of Drehfahl and Plotner (13). Bromination of the vinyl group of 2,5-dichlorostyrene yielded 1-(2,5-dichlorophenyl)-1,2-dibromoethane. Dehydrobromination using potassium hydroxide in *t*-butanol (13) gave crude (2,5-dichlorophenyl)-acetylene (**1**). Chromatography of the crude product on neutral alumina followed by vacuum sublimation gave **1** as

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white plates, m.p. 40 °C. The structure of **1** was confirmed by its characteristic n.m.r. spectrum. The latter showed a one proton singlet (at low resolution) at δ 3.25 in CCl_4 (δ 4.4 in C_5D_5N), characteristic of an acetylenic proton, and a three proton ABC spectrum in the phenyl region. Detailed analysis in C_5D_5N (see below) showed the presence of one ortho (8.68 Hz), one meta (2.58 Hz), and one para (0.37 Hz) ring proton coupling constant, confirming retention of the 1,2,5-trisubstitution pattern of the phenyl group. These three coupling constants are almost identical with those for the parent 2,5-dichlorostyrene (8.54, 2.53, and 0.34 Hz (1)). The structure was further confirmed by the magnitudes of the long-range coupling constants to the acetylenic proton which are nearly identical to those for phenylacetylene (14) (see below).

1-(2,5-Dichlorophenyl)-propyne

This compound was prepared using standard procedures (13, 15). Acylation of *p*-dichlorobenzene with $AlCl_3$/propionyl chloride gave 2,5-dichloropropiophenone. Reaction with PCl_5, followed by dehydrochlorination using potassium hydroxide in *t*-butanol gave 1-(2,5-dichlorophenyl)-propyne (**2**) and other products. Preparative t.l.c. followed by vacuum sublimation gave a small yield of pure **2** as white needles, m.p. 28–30 °C. The compound was characterized by its n.m.r. spectrum which showed a three proton singlet (at low resolution) at δ 2.0 due to the propyne methyl group and a three proton ABC multiplet in the phenyl region. The latter multiplet showed ortho (8.64 Hz), meta (2.59 Hz), and para (0.38 Hz) coupling constants. These are identical, within experimental error, to the values for **1** and confirm the 1,2,5-trisubstitution pattern of the phenyl group.

4-Vinylphenylacetylene

This compound was synthesized as one of a series of 4-substituted styrenes. Full details are provided elsewhere (16).

(b) Nuclear Magnetic Resonance Experiments

Ten mole percent solutions of **1** and **2** in pyridine-d_5 and a 5 mol % solution of **3** in acetone-d_6 (with 3 mol % TMS for lock and reference signal) were degassed by several freeze–pump–thaw cycles and sealed under vacuum in n.m.r. tubes. Pyridine-d_5 was chosen for **1** and **2** since it gave nearly first order spectra. Acetone-d_6 was used for **3** since it collapsed the AA′BB′ spectrum of the ring protons to a sharp singlet (line width $\approx$ 0.3 Hz), allowing complete decoupling of the ring protons at moderate power levels.

Single, double, and triple resonance spectra (frequency sweep, internal lock) were obtained using Varian HA-100 and HA-100D spectrometers and one or more Hewlett-Packard 4204A oscillators. Techniques used were identical to those previously reported (1, 12). Spectra were recorded at a sweep rate of 0.01 Hz/s and calibrated at < 5 Hz intervals with a frequency counter. Line widths of non-degenerate peaks were 0.10–0.12 Hz. The ambient temperature was 30 ± 1 °C.

(c) CNDO/2 and MO–INDO–FPT Calculations

Calculations were performed on an IBM 360/65 computer, using the Quantum Chemistry Program Exchange program no. 141 and standard parameters (17). For the finite perturbation calculations, the program was modified to give a more rigorous convergence criterion (4). The modified program reproduced published results (4).

Results

Proton labelling schemes for **1**, **2**, and **3** have been shown above. They are labelled conventionally, in order of increasing field (decreasing frequency). Final parameters are shown in Table 1. The signs and magnitudes of the long-range coupling constants for **1** are in good agreement with previously reported results for phenylacetylene (14). In that report, signs were determined by analysis. We have confirmed the signs by double-irradiation experiments.

The relative signs of the long-range coupling constants in **1** and **2** were established relative to the known positive signs of intra-ring coupling constants in benzene derivatives (18) and in **3** relative to the known positive signs of the vinyl proton coupling constants in styrene (19). For **1**, the sign determinations involved observation of Overhauser effects caused by very weak "tickling" double irradiation (20, 11*a*),[4] showing J_{AM}, $J_{CM} > 0$, $J_{BM} < 0$. For **2**, double resonance experiments analogous to those used to determine signs in 2-bromo-5-chlorotoluene (21) were employed, showing J_{AM}, $J_{CM} < 0$, $J_{BM} > 0$. In **3**, triple irradiation was employed: strong irradiation to decouple the ring protons and very weak irradiation yielding Overhauser effects (20, 11*a*) or decoupling (12). These showed J_{BM}, $J_{CM} > 0$, with no information about J_{AM}. Slight broadening of the A peaks suggested $|J_{AM}| \approx 0.05$ Hz. A typical experiment for sign determination is shown in Fig. 1. Irradiation of peak B_1 (low field peak of the B octet) decreased C_1 and increased C_3 while irradiation of B_2 decreased C_2 and increased C_4. This experiment proved that J_{BM} and J_{CM} had the same sign. Figure 1 illustrates the usefulness of the Overhauser "tickling" technique for determination of signs of small couplings since B_1 and B_2 are separated by only 0.11 Hz.

Spectra were analyzed by the iterative computer programs LAOCN3 (22) and LAME (23), giving the parameters in Table 1. The only point worthy of note concerns **1**. Proton B gave sharp peaks with no observed coupling to M. (The line width at half height was $\approx$0.12 Hz, almost identical to that for known singlet peaks.) However, the iterative computer fit gave $J_{BM} = -0.07$ Hz. In calculations where J_{BM} was fixed

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[4] A typical H_2 power level was 2 mV under load (measured on the oscilloscope).

TABLE 1. The n.m.r. parameters of 2,5-dichlorophenylacetylene (**1**), 1-(2,5-dichlorophenyl)-propyne (**2**), and 4-vinylphenylacetylene (**3**)*

Parameter	Compound 1	Compound 2	Compound 3
δA	7.549	7.455	6.744
δB	7.304	7.297	5.838
δC	7.226	7.170	5.290
δM	4.428	1.989	3.621
J_{AB}	+0.37	+0.38	+17.64
J_{AC}	+2.58	+2.59	+10.96
J_{BC}	+8.68	+8.64	+0.89
J_{AM}	+0.29 (+0.27)†	−0.30	<0.10‡
J_{BM}	−0.07 (−0.11)	+0.15	+0.11
J_{CM}	+0.33 (+0.24)	−0.26	+0.14
Program	LAOCN3	LAME	LAOCN3
No. of peaks fitted	32	52	32
Worst fit (Hz)	0.030	0.016	0.023
R.m.s. deviation (Hz)	0.011	0.007	0.009
Probable errors of parameters	0.006–0.011	—	0.003–0.004
Standard deviation of parameters	—	0.001–0.002	—

*Chemical shifts on δ scale, coupling constants in Hz ($\pm$0.03 Hz).
†Results from ref. 14.
‡Magnitude only.

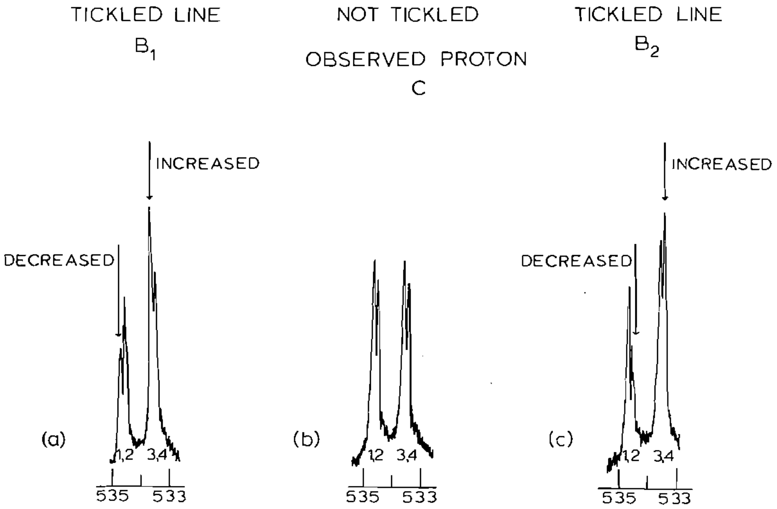


FIG. 1. Triple resonance Overhauser experiments used to determine relative signs of J_{BM} and J_{CM} in 4-vinylphenylacetylene. Ring protons are decoupled in all three spectra. (*a*) Lowfield quartet (C_1–C_4) of C proton octet with triple resonance frequency at B_1 (592.28 Hz); (*b*) C_1–C_4 without triple resonance; (*c*) C_1–C_4 with triple resonance frequency at B_2 (592.17 Hz).

at 0.00 Hz or +0.07 Hz, the fit between calculated and experimental spectra was significantly worse, particularly in the M proton region. The computed sign is consistent with the double resonance experiments and with previous results for phenylacetylene (14).

Results of MO–INDO–FPT calculations of long-range coupling constants are given in

TABLE 2. Long-range coupling constants (in Hz) obtained from MO–INDO–FPT calculations

	Compound		
Coupling constant*	Phenylacetylene	1-Phenylpropyne	4-Vinylphenylacetylene (**3**)
J_{AM}	+0.46	−0.38	−0.08
J_{BM}	−0.09	+0.27	+0.11
J_{CM}	+0.20	−0.26	+0.11

*Labelling of protons is identical to that previously given for **1**, **2**, and **3**.

Table 2. For **1** and **2**, calculations were performed for the parent compounds, phenylacetylene and 1-phenylpropyne, for reasons of computational economy. For **1** and **2**, the perturbation was placed on the acetylenic proton. A repetition of the calculation for **1** with the perturbation on the four proton, C, gave a value of J_{CM} which differed by less than 0.001 Hz from the original value. For **2**, four calculations were performed for two conformations of the methyl group (see Fig. 2). The results in Table 2 are a weight average (allowing for the number of equivalent protons) of the four calculations.

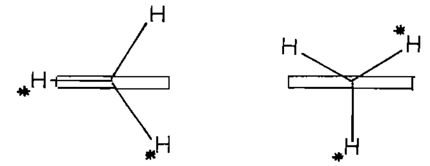


FIG. 2. Conformations of methyl group in 1-phenylpropyne for which MO–INDO–FPT calculations were performed. Protons on which pertubations were placed are marked with asterisks.

TABLE 3. Bond orders (CNDO/2 calculations) between carbon to which substituent is attached and carbon para to substituent

Compound	Bond order $\rho_{NN'}$
Toluene	−0.3266
p-Xylene	−0.3206
Styrene	−0.3193
Phenylacetylene	−0.3225
1-Phenylpropyne	−0.3212
4-Vinylphenylacetylene	−0.3089

Discussion

The McConnell relationship for calculation of π contributions to coupling constants in benzene is (5):

$$[1] \qquad J_{HH'} = \beta^2 \rho^2_{NN'} Q_{CH} Q_{CH'}/h\Delta E$$

where β = Bohr magneton, $\rho_{NN'}$ = mobile bond order between carbon atoms to which hydrogens are bonded, Q_{CH} is the proton hyperfine splitting constant, and ΔE is an average excitation energy to low-lying triplet states. This approach has been extended to several benzene derivatives (6–12). For example, for toluene, [1] may be written (6, 10)

$$[2] \qquad J_{H,CH_3} \propto Q_{CH} Q_{CCH}$$

where Q_{CCH} is the methyl hyperfine splitting constant.

If it is assumed that the same proportionality constant can be used for different compounds, then possible σ and π contributions to long-range coupling constants can be discussed in terms of equations of the same type as [2] (9–12). This assumption requires that $\rho^2_{NN'}/\Delta E$ must be constant for the compounds under investigation. Bond orders for a series of compounds which are relevant to this discussion have been estimated by CNDO/2 MO calculations (see Table 3). $\rho_{NN'}$ is nearly constant. The observation that J_{H,CH_3} values in toluene derivatives are nearly substituent independent (19, 21) suggests that the variation in $1/\Delta E$ must also be small. Therefore, it is reasonable to use the same proportionality constant for different compounds.

The McConnell relationship applies specifically to π electron contributions. For toluene, $J^p_{H,CH_3} = -0.6$ Hz (21, 24) while $Q_{CCH} = +25$ G (10). It has been shown that J^p_{H,CH_3} contains a negligible σ contribution (12). If it is assumed that J_{CM} for **1** also contains only π contributions, then $Q_{CC\equiv CH}/Q_{CCH} = J_{CM}/J^p_{H,CH_3}$. The average of J_{CM} from the two sets of experimental results is +0.28 Hz. Consequently, the estimated value of

$Q_{CC\equiv CH}$ is $(0.28 \times 25/(-0.6)) = -12$ G. This value can be checked by calculating the long-range coupling constants for **3**. The corresponding long-range coupling constants for the para proton to the vinyl group in styrene derivatives are $J_A^p = -0.24$, $J_B^p = +0.26$, and $J_C^p = +0.28$ Hz. Assuming $Q_{CH} = -23$ G (10), $Q_{CC\equiv CH}/Q_{CH} = 12/23$ and estimated coupling constants for **3** are $J_{AM} = -0.12$, $J_{BM} = +0.13$, and $J_{CM} = +0.14$ Hz. The magnitude of J_{AM} is slightly overestimated but J_{BM} and J_{CM} are in excellent agreement with the experimental values. This strongly suggests that the estimated value of $Q_{CC\equiv CH}$ is accurate and that J_{CM} for **1** is dominated by π effects. Consequently the acetylenic linkage appears to be about half as effective as a methyl group in transmitting spin information from a phenyl π electron system. It is almost equal in effectiveness to a vinyl group since in the latter case, the corresponding para to β hydrogen coupling constants (which are also dominated by π effects (1)) are identical in sign and magnitude to J_{CM} for **1** (see above).

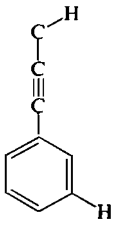
Further information concerning π contributions to coupling constants can be obtained by the methyl group replacement technique (25). If a coupling constant to a proton is transmitted through the π system, then replacement of the proton by a methyl group should give a coupling constant opposite in sign but nearly equal in magnitude (since $Q_{CH} \approx -Q_{CCH}$). For example, J_{H,CH_3}^p in toluene $= -0.6$ Hz while J_{CH_3,CH_3}^p in *p*-xylene $= +0.6$ Hz (12). It is not obvious, *a priori*, that the methyl group replacement technique will work when the methyl group is bonded to an acetylenic linkage rather than directly to a phenyl group. However, the averaged values for the two sets of coupling constants for **1** ($J_{AM} = +0.28$, $J_{BM} = -0.09$, $J_{CM} = +0.28$ Hz are nearly identical in magnitude and opposite in sign to those for **2**. This strongly suggests that the methyl group replacement technique can be applied to this system and that the observed long-range coupling constants in **1** and **2** are all transmitted primarily through the π system. All of the determined signs of coupling constants are entirely consistent with π contributions.

Assuming $Q_{CC\equiv CH} = -12$ G, the observed coupling constants for **2** indicate that $Q_{CC\equiv CCH} = +12$ G. By comparing hyperfine e.p.r. coupling constants for γ-phenylpropargyl and benzyl radicals, Kochi and Krusic (26) concluded that the interposition of an acetylenic linkage reduced the transmission of spin density from a methylene group to a phenyl group by 47%. Since this corresponds to $Q_{CC\equiv CCH} = (0.47 \times 25) = +12$ G, our conclusions are in quantitative agreement with those obtained from e.p.r. measurements.

The MO–INDO–FPT calculations were performed to determine whether they could reproduce the long-range coupling constants for **1**–**3** and consequently provide insight into the mechanism of transmission of these coupling constants. For **1**, J_{CM} and J_{AM} are respectively under- and overestimated but the overall agreement between calculation and experiment is very good. The agreement is even better for **2** although J_{AM} and J_{BM} are slightly overestimated. The agreement for **3** is excellent, assuming that J_{AM} has the expected negative value. The overall agreement for the three compounds is extremely good with four of the eight long-range coupling constants whose signs were determined estimated within the probable experimental error (0.03 Hz).

The conformational dependence of the calculated long-range coupling constants for **2** provides insight into the mechanism of transmission of these interactions. J_{CM} varied from -0.05 Hz for the C—H bond coplanar to the phenyl group to -0.46 Hz for the C—H bond perpendicular to the phenyl group with a $\sin^2 \phi$ dependence (defining ϕ as the projection angle between the C—H bond and the phenyl group). Similar behavior has been noted for α C—H bonds in toluene (27), styrene (1), and benzaldehyde (11) and attributed to a σ–π configuration interaction (27). The fact that the same behavior is noted for a methyl group bonded to an acetylenic linkage suggests that the spin information is only transmitted through the extended π system. This could account for both the success of the methyl group replacement technique for **2** and the conclusion that vinyl and acetylenic linkages are equally effective in transmitting spin information.

J_{AM} and J_{BM} showed similar, although less marked conformational dependence. For the planar forms ($\phi = 0°$), J_{BM} was predicted to have a slightly larger value for conformation I (+0.24 Hz) than for conformation II (+0.17 Hz). For α proton couplings, an enhanced positive con-



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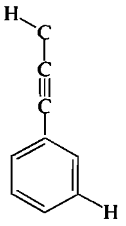

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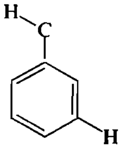

III

tribution has been found for the all-*trans* conformation III (28, 29, 1). It would be difficult to check the prediction concerning I and II.

In summary, the McConnell formulation has proved useful for extended coupling paths, since starting from results for a six bond coupling constant in toluene it has proved possible to derive Q values which quantitatively predict the nine bond couplings, J_{BM} and J_{CM} in **3**. MO–INDO–FPT also predict these couplings accurately. Even more extended coupling paths are under investigation.

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