The Molecular Structure of Allenes and Ketenes, XII [1]
Four-Bond Proton-Proton Spin-Spin Couplings in Allenes

Wolfgang Runge
Organisch-Chemisches Institut der Technischen Universität München


Four-bond proton-proton coupling constants in allenes are reported. The substituent effects on the coupling constants are discussed on the basis of the dual-substituent parameter approach. Furthermore, the coupling constants are related to quantum-chemical indices (electron densities, overlap populations) obtained from semiempirical CNDO/S and ab initio STO-3G calculations.

The magnitudes of the coupling constants depend upon the polar natures of the substituents as well as upon their charge-transfer abilities (resonance effects) to a comparable amount.

In general, the coupling constants in 1,3-disubstituted allenes are nonadditive in ligand-specific parameters.

1. Introduction

Proton chemical shifts of allenes have been discussed in part XI of this series [1]. The present contribution is concerned with four-bond proton-proton spin-spin coupling constants \( J(\text{HH}) \) in variously substituted allenes (Table I).

The experimental coupling constants are partly from the literature [2–10] and partly from this series of contributions [1, 11].

The substituent effects on the four-bond proton-proton couplings in allenes are discussed on several levels. At first, using the material now being available, it is analyzed whether the coupling constants are additive in ligand-specific parameters as has been suggested in Ref. [5] on the basis of only two independent tests. For this purpose use is made of algebraic (geometrophysical) concepts which have been applied to the general treatments of various molecular properties of allenes [1, 12].

Then, the dual-substituent parameter (DSP) approach [13] serves purposes of semiquantitative insights into the nature of the substituent effect on the four-bond couplings. This treatment is especially concerned with the relative importance of \( \sigma \) and \( \pi \) mechanisms for the transmissions of substituent effects in monosubstituted allenes and, for instance, focusses attention to the question [5] why substituents like Cl and CH\(_3\), which are apparently different with respect to their polar natures and (group) electronegativities, both reduce the (absolute) magnitudes of the four-bond proton-proton couplings in allenes.

Requests for reprints should be sent to Dr. habil. W. Runge, Studiengruppe für Systemforschung, Werderstraße 35, D-6900 Heidelberg.

Table I. Four-bond proton-proton coupling constants of allenes \( R_2HC=CHR_3 \) [in Hz].

| Compound \( R_2 \) | \( R_3 \) | \( J(\text{HH}) \) | Ref.
|-------------------|--------|----------------|-------
| 1 H               | H      | –7.0           | [2]   |
| 2 CH\(_3\)        | H      | –6.67          | [5]   |
| 3 CH\(_2\)Cl      | H      | –6.77          | [5]   |
| 4 CH\(_2\)H\(_5\) | H      | –6.59          | [6]   |
| 5 CH\(_2\)H\(_5\) | H      | –6.95          | [a]   |
| 6 H\(_2\)C\(_=\)CH | H      | –6.64          | [10]  |
| 7 COOH\(_2\)      | H      | –6.65          | [a]   |
| 8 CO\(_2\)H        | H      | –6.50          | [7]   |
| 9 CN               | H      | –6.79          | [3]   |
| 10 CH\(_2\)\(_3\)N\(_2\)H | H | –6.1   | [9]   |
| 11 CH\(_2\)O      | H      | –5.90          | [a]   |
| 12 CH\(_3\)S      | H      | –6.40          | [11c] |
| 13 Cl              | H      | –6.04          | [a]   |
| 14 Br              | H      | –6.06          | [a]   |
| 15 I               | H      | –6.27          | [a]   |
| 16 (CH\(_2\))\(_3\)Si | H | –6.3   | [3]   |
| 17 PO\(_2\)C\(_2\) | H      | –6.61          | [8b]  |
| 18 PO\(_2\)(\text{C}_2\text{H}_4)\(_2\) | H | –6.80 | [8a, 8b] |
| 19 CH\(_2\)OH      | CH\(_3\) | –6.35         | [5]   |
| 20 CH\(_2\)Cl      | Cl     | –5.80          | [4]   |
| 21 CH\(_2\)H\(_5\) | CH\(_3\) | –6.92          | [a]   |
| 22 CH\(_2\)H\(_5\) | COOH   | –6.80          | [a]   |
| 23 CH\(_2\)H\(_5\) | CH\(_2\)O | –6.20          | [a]   |
| 24 CH\(_2\)H\(_5\) | PO(C\(_2\)H\(_2\))\(_2\) | –6.50 | [8a]   |

[a] This work; references in parentheses give hints to other investigations within this series of contributions where other properties of the corresponding compounds are discussed.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung 4.0 Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution 4.0 International License.
At last, the long-range couplings in allenes are related empirically to quantum-chemical indices, such as electron densities or Mulliken overlap populations, in order to corroborate interpretations given on the basis of the DSP approach.

2. Results and Discussions

2.1. Nonadditivity of substituent effects on the four-bond couplings

In Table I experimental four-bond proton-proton coupling constants of allenes are summarized. These values reveal that there is a small, but significant substituent effect on the four-bond couplings. The overall variation of the couplings amounts to 1.10 Hz. It may be assumed that the experimental errors of the individual values do not exceed ±0.07 Hz. Considering all the couplings in Table I the suggestion that the four-bond proton-proton couplings in allenes are additive in ligand-specific parameters [5] cannot be supported. Though the coupling constants of 19 and 20 are correctly predicted using eq. (1) (κ(H) = 0; τ = −7.00 Hz from 1; χ(CH3) = +0.33 Hz from 2; χ(Cl) = +0.96 Hz from 13)

\[ 4J(HH) = \tau + \kappa(R_2) + \kappa(R_3) \] (1)

the couplings of the phenylallenes 21–24 cannot be reproduced with such a simple procedure to within ±0.16 Hz. 0.16 Hz represent about 15% of the overall observable variation of the couplings and may be assumed to be a limit for an acceptable deviation between calculated and observed couplings.

Therefore, one may conclude that, in general, four-bond proton-proton coupling constants of allenes are nonadditive in one-particle functions (ligand-specific parameters).

For scalar molecular properties of allenes, such as carbon electron densities [12c], 13C chemical shifts [12a, 12b], and 1H chemical shifts [1], interactions between substituents attached to the same carbon atom (geminal substituents) have proven essential for an understanding of the observable phenomena. The results for the four-bond coupling constants, i.e., the nonadditivity in substituent effects, suggest that there may exist distinct interactions between the two substituents R2 and R3 attached to different carbon atoms of the allenic skeleton. Such types of interactions may be immediately deduced if one refers to the geometric models for the treatments of point-properties of allenic systems [1, 12].

The four-bond coupling may be viewed as a molecular property which depends simultaneously upon point-properties p of the two protons H1 and H4. Therefore, the coupling \( 4J(H_1H_4) \) is factored into functions depending only upon one argument, i.e., \( 4J(H_1H_4) \) is separated into a product of equivalent functions \( p(H_1) \cdot p(H_4) \).

\[ 4J(H_1H_4|R_2, R_3) = p(H_1|R_2, R_3, H_4) \cdot p(H_4|R_2, R_3, H_1). \] (2)

In its simplest form p is additive in ligand-specific parameters (p corresponds to P, a point-property of an allene proton in a three-site pyramidal Cs situation discussed in Ref. [1]; cf. eq. (1) in Ref. [1]). Then, from eq. (3) \( \gamma'(H) = 0 \) it is easily seen that the simplest ansatz for the description of the four-bond proton-proton couplings in allenes must contain an interaction term \( \pi(R_2, R_3) = \pi(R_2, R_3) \).

\[ p(H_1|R_2, R_3, H_4) = \beta' + \alpha'(R_2) + \gamma'(R_2) + \gamma'(H_4). \] (3)

\[ 4J(H_1H_4|R_2, R_3) = \tau + \kappa(R_2) + \kappa(R_3) + \pi(R_2, R_3). \] (4)

Therefore, in general, an addition of substituent effects (eq. (1)) can only give rough numerical estimates of the observable four-bond couplings in 1,3-disubstituted allenes. Within the above approach additivity in substituent effects, as is observed in case of 19 and 20, must be viewed as accidental. It cannot be predicted on the basis of any group theoretical or quantum theoretical arguments.

As a concluding remark it should be noted that, on the basis of any purely algebraic model, there is no a priori justification for an ansatz like eq. (2). The most general form of a two-variable function \( f(x_1, x_2) \) should involve a correlated pair-function [14] \( j(x_1, x_2) \) \( f(x_1, x_2) = g(x_1) \cdot h(x_2) + j(x_1, x_2) \). The roots for eq. (2), however, may be found in physics, as the energy of interaction of two nuclei A and B (in the spin Hamiltonian), is directly proportional to the dot product of the corresponding nuclear spin operators, namely \( E_{AB} \sim J_{AB} \bar{I}_A \cdot \bar{I}_B \), where \( \bar{I}_A \) and \( \bar{I}_B \) do not depend upon the electronic wavefunctions [15, 16].

Using the factorization \( J(XH) = p(H) \cdot q(X) \) one may immediately conclude that, for instance, one-bond couplings \( 1J(XH) \) in tetrahedral systems
HXR\textsubscript{1}R\textsubscript{2}R\textsubscript{3} (X = C, Si) are nonadditive in substituent effects and that in treating one-bond couplings $^{1}J(^{13}\text{CH})$ in allenes one must take geminal interactions and interactions across the allenic system into consideration. Both these deductions are established by experiments [17, 18].

2.2. Discussions of substituent effects

From monosubstituted allenes, i.e. from the ligand-specific parameters $\chi(R)$, some insights into the physical effects underlying the mechanisms for the transmissions of the substituent effects on the four-bond proton-proton couplings may be obtained.

Usually, for spatially fixed orientations of the relevant protons substituent effects on long-range proton-proton couplings are discussed in terms of factors which influence primarily the $\sigma$ electronic structures of the molecules under consideration, i.e. they are related to (group) electronegativities or polarity effects [2, 5, 19]. In LCAO expansions for the descriptions of the electronic structures of planar unsaturated systems (ethylenes, benzenes, etc.) the hydrogen $1s$ atomic orbitals (AOs) can only be part of the $\sigma$ electronic structures. In monosubstituted allenes, however, the hydrogen $1s$ AOs of the methylene group protons may be involved in the allenic $\pi$ system ("hyperconjugation") [11a, 11c, 12c] and thus may undergo direct $\pi$ resonance interactions with the substituents.

Therefore, one may expect that the variations of the couplings do not only originate from the substituent (or substituent-carbon bond) polarity, but also from its charge-transfer ability. Adopting the DSP approach [13] for a semiquantitative discussion of the substituent effects $\chi(R)$ it has turned out that $\chi(R)$ correlates with the polar substituent constant $\sigma_{I}$ [13, 20] and the resonance substituent constant $\sigma_{R}^{\pi}$ [13] (linear correlation coefficient $r = 0.967$ omitting the groups $\text{C}_6\text{H}_5$ and CN) (Fig. 1).

$$\chi(R) = 1.10 \sigma_{I} - 1.38 \sigma_{R}^{\pi} + 0.11 \text{ (in Hz)} \quad (5)$$

The $\lambda$-value ($\lambda = q_{R}/q_{I} = -1.25$) of correlation (5) clearly demonstrates that polar and resonance factors are of comparable importance for an understanding of the substituent effects on the four-bond couplings in allenes. Furthermore, eq. (5) reveals that for mesomeric acceptors, such as COOCH\textsubscript{3}, COCH\textsubscript{3}, CN, the resonance contribution counteracts the polarity influence, which explains the relatively small substituent effects of these strongly polar groups. For the nonpolar groups (e.g. CH\textsubscript{3} and H\textsubscript{2}C=CH) the effect on $^{1}J(\text{HH})$ results almost entirely from resonance contributions.

This interpretation of the substituent effects is corroborated qualitatively by the correlation (6) ($r = 0.912$) of $\chi(R)$ with the difference in the CNDO/S electron densities [11c, 12c] ($\text{PHH}(1)-\text{PHH}(4)$) (in $10^{-3}$ e) of the hydrogen atoms involved in the coupling (Fig. 2).

$$\chi(R) = 0.0431 (\text{PHH}(1)-\text{PHH}(4)) + 0.11 \text{ (in Hz)} \quad (6)$$

The cyano and the chloro groups show larger deviations from the correlation. The group POCl\textsubscript{2} exhibits a serious discrepancy. All these three groups have been omitted in the regression analysis.

![Fig. 1. Correlation of the substituent effect on the allenic four-bond proton-proton coupling constant and the polarity and resonance substituent constant within a DSP approach.](image1)

![Fig. 2. Correlation of the substituent effect on the four-bond proton-proton coupling and the difference in electron densities of the corresponding hydrogen atoms.](image2)
Correlation (6) has the same structure as eq. (5). Though of inferior quality than eq. (5) correlation (6) is conceptionally illustrative as it relates the couplings \( J(H_1H_4) \) directly to point-properties of the corresponding hydrogen atoms \( H_1 \) and \( H_4 \), respectively. On the other hand, it contains a corresponding information like eq. (5), as the electron density variations at \( H_4 \) are essentially determined by \( \pi \) resonance (hyperconjugative) effects [12c], whereas the electron densities at \( H_1 \) are determined by \( \sigma \)-type mechanisms.

Direct quantum-chemical calculations of long-range coupling constants are complicated owing to the question of whether only the Fermi contact term [15] or also the orbital [15] and spin dipolar term [15] contribute to the overall spin-spin coupling mechanism. Furthermore, the results of such quantum-chemical calculations depend sensitively upon the basis set. These difficulties manifest in the numerical results for four-bond couplings (including results for allene (1)) obtained with different quantum-chemical procedures [22].

Therefore, empirical or semiempirical correlations of long-range couplings with quantum-chemical indices continue to be of practical and theoretical value for discussions of substituent effects.

MO treatments of Ramsey’s perturbation formula [15] for the Fermi contact term invoking an “average energy approximation” relate the coupling constant of the nuclei A and B to the square of the atom A–atom B element of the first-order density matrix, i.e. the bond order \( P_{AB} \) [23]. Neglecting problems associated with the signs of the coupling constants variations in \( P_{AB} \) often reflect substituent effects on long-range couplings [24]. Using CNDO/S wavefunctions for the allenes [11c, 12c] no correlation of \( J(H_1H_4) \) and \( P_{AB} \) for the differently substituted molecules is found. On the other hand, it has been suggested [25] recently that coupling constants may be related to Mulliken overlap populations \( Q_{AB} \) obtained from ab initio procedures. In Fig. 3 the four-bond coupling constants of monosubstituted allenes are plotted \textit{versus} the hydrogen 1s-hydrogen 1s overlap populations resulting from ab initio STO-3G MO calculations [12c].

If one neglects the points for the cyano and the chloro groups, these groups showing also deviations from the correlation with the CNDO/S qualities in Fig. 2, there is indeed a correlation (7) \( r = -0.932 \) between \( J(HH) \) and \( Q_{HH} \) (in units of \( 10^{-3} \))

\[
J(HH) = -1.035 Q_{HH} - 13.258 \quad (\text{in Hz}) \quad (7)
\]

### 3. Experimental and Quantum-Chemical

The proton NMR spectra of the allenes have been measured with a Varian A 60 spectrometer in CCl\(_4\) and analyzed as outlined in Ref. [1]. The Mulliken overlap populations \( Q_{HH} \) related to the protons \( H_1 \) and \( H_4 \) obtained from STO-3G calculations in Ref. [12c] are given below.

<table>
<thead>
<tr>
<th>( Q_{HH} \times 10^{-3} )</th>
<th>6.04</th>
<th>6.47</th>
<th>6.20</th>
<th>6.41</th>
<th>5.65</th>
<th>7.07</th>
<th>6.51</th>
<th>6.14</th>
<th>6.36</th>
</tr>
</thead>
</table>

The CNDO/S electron densities for the monosubstituted allenes with the groups CH\(_2\)Cl and POCl\(_2\) are as follows:

<table>
<thead>
<tr>
<th>( R )</th>
<th>( P_{CC}(1') )</th>
<th>( P_{CC}(2') )</th>
<th>( P_{CC}(3') )</th>
<th>( P_{HH}(2) )</th>
<th>( P_{HH}(3) )</th>
<th>( P_{CC}(1') )</th>
<th>( P_{CC}(2') )</th>
<th>( P_{CC}(3') )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)Cl</td>
<td>4.038</td>
<td>3.955</td>
<td>4.100</td>
<td>0.959</td>
<td>0.965</td>
<td>1.127</td>
<td>0.931</td>
<td>0.973</td>
</tr>
<tr>
<td>POCl(_2)</td>
<td>4.075</td>
<td>3.856</td>
<td>4.046</td>
<td>0.950</td>
<td>0.943</td>
<td>1.202</td>
<td>0.728</td>
<td>0.988</td>
</tr>
</tbody>
</table>
The enumerations of the atoms correspond to those used in Refs. [11c, 12c]. The calculations have been performed including d atomic orbitals for the chloro and phosphorus atoms.

Note added in prove

Only after submission of the manuscript the author became aware of the fact that in a paper on carbon-proton coupling constants of allenes (N. J. Koole and M. J. A. de Bie, J. Magn. Reson. 23, 9 (1976)) $J$ values for $1, 9, 11-14, 16$ are given. With the exception of $9$ [3] these values agree with those in Table I to $\pm 0.10$ Hz.