The Molecular Structure of Allenes and Ketenes, XIII [1]

Correlations of Carbon-Proton Spin-Spin Coupling Constants in Allenes with \textit{ab initio} STO-3G Overlap Populations

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Allenes, Carbon-Hydrogen Coupling Constants, Substituent Effects

It is shown that substituent effects on one-bond and long-range carbon-proton spin-spin constants in monosubstituted allenes parallel quantitatively \textit{ab initio} STO-3G carbon 2s-hydrogen 1s overlap populations, irrespectively of whether the substituents are bonded to the allenic skeleton via first-row (C, O) or second-row (Si, S, Cl) atoms.

Substituent effects on molecular properties often may be characterized and predicted by quantum-chemical indices, such as electron densities and/or bond orders (or related qualities).

It is the intention of the present note to show that substituent effects on (one-bond and long-range) carbon-proton spin-spin coupling constants \( W_{\text{J}(13\text{CH})} \) of monosubstituted allenes (Table I)

\[
\begin{align*}
\text{Table I. One-bond carbon-proton coupling constants [in Hz] and STO-3G overlap populations of monosubstituted allenes RCH} &= \text{C}=\text{CH}_\text{a,b},
\end{align*}
\]

may be adequately related to \textit{ab initio} STO-3G carbon 2s-hydrogen 1s overlap populations \( Q_{\text{SCSH}(1)} \).

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\[
\begin{align*}
Q_{\mu\nu} &= \sum_{\mu \neq \nu} P_{\mu\nu} S_{\mu\nu} & (1a) \\
P_{\mu\nu} &= 2 \sum_{i} c_{\mu} c_{\nu} & (1b)
\end{align*}
\]

In eqs. (1a) and (1b) \( S_{\mu\nu} \) is the overlap integral between the atomic orbitals \( \mu \) and \( \nu \) and \( P_{\mu\nu} \) is the atom \( \alpha \mu \)-atom \( \beta \nu \) element of the first-order density matrix.

In this approach we follow a suggestion [2] which is based upon empirical observations that spin-spin couplings may be related to overlap populations obtained from \textit{ab initio} procedures. In case of the allenes it has been shown recently that also four-bond proton-proton couplings \( 4J(\text{HH}) \) correlate with STO-3G overlap populations \( Q_{\text{SCHS}}(1) \).

In Tables I and II experimental one-bond and long-range \( 13\text{CH} \) couplings from this series of contributions [3a] and the literature [4] as well as the corresponding STO-3G overlap populations are summarized.

In Fig. 1 it is seen that both kinds of one-bond carbon-proton couplings for all the molecules under investigation may be related to the carbon 2s-hydrogen 1s overlap populations (with a linear correlation coefficient of \( \rho = 0.9330 \) for eq. (2)).

\[
1J(13\text{CH})(\text{RCH} = \text{C}=\text{CH}_2) = 1064.9 Q_{\text{SCSH}(1)} - 142.0
\]

Most remarkably, correlation (2) (involving indices from \textit{ab initio} procedures) holds for allenes with substituents bonded to the allenic moiety via first-row (C, O) as well as second-row atoms (Si, S, Cl). In corresponding correlations of one-bond coupling constants with the squares of the carbon 2s-hydrogen 1s bond orders \( P_{\text{SCSH}}^2 \) (eq. (1b)) obtained from semiempirical quantum-chemical methods, "second-row groups" exhibit large deviations from the correlations or even give a separate correlation valid for these last groups [3a, 5]. Our findings corroborate the assumptions [3a, 5] that in the above types of correlations of couplings with \( P_{\text{SCSH}}^2 \)

Exper. [3a] measured in CDCl3; details of the STO-3G MO calculations may be found in refs. [3b] and [3c]; from ref. [4] measured on the neat liquids with 10% C6D6 and 5% TMS as the couplings for 9 in ref. [3a] are erroneous.
Table II. Long-range carbon-proton coupling constants\(^a\) [in Hz] and STO-3G overlap populations\(^c\) of mono-

<table>
<thead>
<tr>
<th>Compound</th>
<th>(2^\text{J}^{(13}\text{C}_2\text{H}_2)) ((10^{-2}))</th>
<th>(Q_{\text{SCSH}}(2' 2))</th>
<th>(2^\text{J}^{(13}\text{C}_3\text{H}_3)) ((10^{-2}))</th>
<th>(Q_{\text{SCSH}}(2' 3))</th>
<th>(3^\text{J}^{(13}\text{C}_3\text{H}_3)) ((10^{-4}))</th>
<th>(Q_{\text{SCSH}}(1' 3)) ((10^{-4}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-3.9</td>
<td>-1.1569</td>
<td>-3.9</td>
<td>-1.1569</td>
<td>+7.7</td>
<td>1.5417</td>
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<td>2</td>
<td>0(^b)</td>
<td>-1.2216</td>
<td>0(^b)</td>
<td>-1.1671</td>
<td>+8.8</td>
<td>1.4174</td>
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<tr>
<td>4</td>
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<td>-4.4</td>
<td>-1.1612</td>
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<td>-1.1011</td>
<td>-3.4</td>
<td>-1.1885</td>
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<td>1.4254</td>
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<td>-1.1799</td>
<td>-4.4</td>
<td>-1.1643</td>
<td>+6.8</td>
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<tr>
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<td>-1.2882</td>
<td>-4.5</td>
<td>-1.1520</td>
<td>+6.5</td>
<td>1.6597</td>
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<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) From ref. [4]; \(^b\) from ref. [3a]; \(^c\) MO calculations from refs. [3b] and [3c].

the differentiations between first-row and second-
row groups are due to deficiencies in the semi-
empirical MO parametrizations.

Furthermore, it should be noted that the sub-
stituent effects on the couplings \(1^\text{J}^{(13}\text{C}_2\text{H}_2)\) within
the allenic methylene group are adequately desc-
bred by changes in the corresponding CH 2s-ls
bond orders \(P_{\text{SCSH}}(3' 3)\) are practically
unaffected by substitutions at the remote carbon
atom \((\text{C}_1)\).

Using the CNDO/S scheme with regard to long-
rage CH couplings of allenes, there cannot be
observed any correlations of two-bond and three-
bond CH couplings with the squares of the bond
orders, though such correlations may be found for
other molecular systems using the CNDO/2 method
[5]. If plotted \textit{versus} the corresponding STO-3G
overlap populations (in units of \(10^{-4}\)), both the
two-bond carbon-proton couplings in allenes show
a fair correlation \((r = -0.9339)\)

\[
2^\text{J}^{(13}\text{CH})(\text{RCH} = \text{C} = \text{CH}_2) = 64.35 \ Q_{\text{SCSH}} - 78.61 \quad (3)
\]

However, this relationship is only relevant for the
couplings \(2^\text{J}^{(13}\text{C}_2\text{H}_2)\) which exhibit sensitive sub-
stituent dependencies, whereas the couplings
\(2^\text{J}^{(13}\text{C}_2\text{H}_2)\) do not depend upon the substituents
(Table II). The last types of couplings all have values
which are similar to that of allene \((1)\). The situation
is different for the three-bond CH couplings of allenes.
Both the three-bond CH couplings cannot be incor-
porated into only one correlation. The couplings
\(3^\text{J}^{(13}\text{C}_3\text{H}_3)\) (Table II) give a moderate correlation
\((r = -0.7557)\) with \(Q_{\text{SCSH}}(3' 2)\). If, however, as in
the case of the four-bond proton-proton couplings of
allenes \([1]\), the cyano group is omitted in the re-
gression analysis, one finds an acceptable correlation
\((r = -0.9890)\) of \(3^\text{J}^{(13}\text{C}_3\text{H}_3)\) with the corre-
sponding STO-3G overlap population (in units of \(10^{-4}\)).

\[
3^\text{J}^{(13}\text{C}_3\text{H}_3)(\text{RCH} = \text{C} = \text{CH}_2) = -8.19 \ Q_{\text{SCSH}} + 20.02 \quad (4)
\]

On the other hand, the coupling \(3^\text{J}^{(13}\text{C}_1\text{H}_3)\) in-
volving the substituted carbon atom exhibits a fair
correlation \((r = 0.9316)\) which includes all the
molecules in Table II.

As a resume one may deduce that for predictive
purposes correlations of coupling constants with ab
initio overlap populations seem to be superior to
correlations with squares of semiempirical bond
orders, irrespective of the fact that there is no direct
quantum-chemical justification for the first types
of correlations, but that there is one for the corre-
sponding couplings with \(P_{\text{SCSH}}(6)\).

\[
3^\text{J}^{(13}\text{C}_1\text{H}_3)(\text{RCH} = \text{C} = \text{CH}_2) = 22.43 \ Q_{\text{SCSH}} - 27.00 \quad (5)
\]
    b) J. Kroner, W. Kosbahn, and W. Runge, Ber. Bunsenges. Phys. Chem. 81, 826 (1977);
    b) R. Radeglia and E. Gey, J. Prakt. Chem. 314, 43 (1972);
    c) R. Radeglia and E. Gey, Z. Physik. Chem. (Leipzig) 252, 345 (1973);