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

Correlations of Carbon-Proton Spin-Spin Coupling Constants in Allenes with *ab initio* STO-3G Overlap Populations

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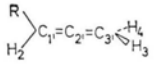
It is shown that substituent effects on one-bond and long-range carbon-proton coupling constants in monosubstituted allenes parallel quantitatively ab initio STO-3G carbon 2s-hydrogen 1s overlap populations, irrespectively of whether the substituents are bonded to the allenic skeleton *via* first-row (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 $^{n}J(^{13}CH)$ of monosubstituted allenes (Table I)



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

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$$Q_{\mu\nu} = \sum_{\mu \neq \nu} P_{\mu\nu} S_{\mu\nu} \qquad (1a)$$

$$P_{\mu\nu} = 2 \sum_{i}^{\text{occ.}} c_{\mu i} c_{\nu i} \qquad (1b)$$

In eqs. (1a) and (1b) $S_{\mu\nu}$ is the overlap integral between the atomic orbitals μ and ν and $P_{\mu\nu}$ is the atom A μ-atom B ν-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 *ab initio* procedures. In case of the allenes it has been shown recently that also four-bond proton-proton couplings $^{4}J(HH)$ correlate with STO-3G overlap populations Q_{SHSH} [1].

In Tables I and II experimental one-bond and long-range ^{13}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 $r = 0.9330$ for eq. (2)).

$$^{1}J(^{13}CH)(RCH{=}C{=}CH_2) = 1064.9\, Q_{SCSH} - 142.0 \qquad (2)$$

Most remarkably, correlation (2) (involving indices from *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^2_{SCSH} (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^2_{SCSH}

Table I. One-bond carbon-proton coupling constants [in Hz] and STO-3G overlap populations of monosubstituted allenes $RCH{=}C{=}CH_2$[a, b].

Compound	R	$^{1}J(^{13}C_1{'}H_2)$	$Q_{SCSH}(1'2)$	$^{1}J(^{13}C_3{'}H_3)$	$Q_{SCSH}(3'3)$
1	H	+ 168.2	0.2932	+ 168.2	0.2932
2	C_2H_5	+ 158.0	0.2866	+ 164.0	0.2907
3	$H_2C{=}CH$	+ 168	0.2966	+ 168	0.2928
4	$COOCH_3$	+ 172.5	0.2984	+ 171.6	0.2938
5	CN	+ 180.0	0.3081	+ 167.1	0.2922
6	CH_3O	+ 191.4	0.3109	+ 167.5	0.2893
7	$(CH_3)_3Si$	+ 148.0	0.2646	+ 169.0	0.2916
8	CH_3S	+ 181.3	0.2980	+ 165.2	0.2904
9	Cl	+ 206.9[c]	0.3182	+ 170.1[c]	0.2912

[a] Experimental values from ref. [3a] measured in $CDCl_3$; [b] details of the STO-3G MO calculations may be found in refs. [3b] and [3c]; [c] from ref. [4] measured on the neat liquids with 10% C_6D_6 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 monosubstituted allenes.

Compound	$^2J(^{13}C_2'H_2)$	$Q_{SCSH}(2'2)$ (10^{-2})	$^2J(^{13}C_2'H_3)$	$Q_{SCSH}(2'3)$ (10^{-2})	$^3J(^{13}C_3'H_2)$	$Q_{SCSH}(3'2)$ (10^{-4})	$^3J(^{13}C_1'H_3)$	$Q_{SCSH}(1'3)$ (10^{-4})
1	— 3.9	— 1.1569	— 3.9	— 1.1569	+ 7.7	1.5417	+ 7.7	1.5417
2		— 1.2713		— 1.1507	+ 6.0[b]	1.6152		1.5234
4	0[b]	— 1.2216	0[b]	— 1.1671	+ 8.8[b]	1.4174	+ 12.7	1.7371
5	— 5.7	— 1.1826	— 4.2	— 1.1533	+ 6.4	1.5267	+ 7.6	1.5750
6	+ 8.0	— 1.3686	— 4.4	— 1.1612	+ 6.2	1.7523	+ 8.1	1.5847
7	— 8.5	— 1.1011	— 3.4	— 1.1685	+ 8.4	1.4254	+ 6.7	1.4929
8	+ 1.3	— 1.1799	— 4.4	— 1.1643	+ 6.8	1.5534	+ 8.8	1.5533
9	+ 6.3	— 1.2882	— 4.5	— 1.1520	+ 6.5	1.6597	+ 9.3	1.6578

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

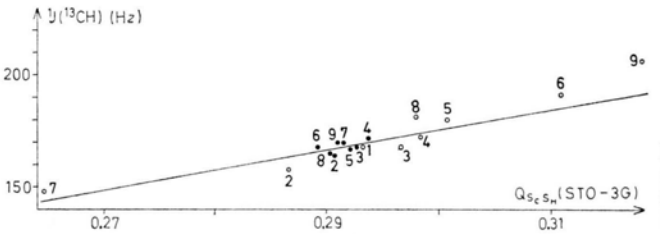

Fig. 1. Correlation of one-bond carbon-proton coupling constants of allenes RCH=C=CH_2 and STO-3G overlap populations (○ ○ $^1J(^{13}C_1'H_2)$, ● ● $^1J(^{13}C_3'H_3)$).

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

Furthermore, it should be noted that the substituent effects on the couplings $^1J(^{13}C_3'H_3)$ within the allenic methylene group are adequately described by changes in the corresponding CH 2s–1s overlap populations. On the other hand, using CNDO/S calculations [3a], the substituent effects on $^1J(^{13}C_3'H_3)$ must be related to variations in the carbon and hydrogen electron densities, as the CNDO/S bond orders $P_{SCSH}(3'3)$ are practically unaffected by substitutions at the remote carbon atom (C_1').

Using the CNDO/S scheme with regard to long-range 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 *versus* the corresponding STO-3G overlap populations (in units of 10^{-2}), both the two-bond carbon-proton couplings in allenes show a fair correlation (3) (r = —0.9339)

$$^2J(^{13}CH)(RCH{=}C{=}CH_2) = 64.35\ Q_{SCSH} - 78.61 \quad (3)$$

However, this relationship is only relevant for the couplings $^2J(^{13}C_2'H_2)$ which exhibit sensitive substituent dependencies, whereas the couplings $^2J(^{13}C_2'H_3)$ do not deqend 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 incorporated into only one correlation. The couplings $^3J(^{13}C_3'H_2)$ (Table II) give a moderate correlation (r = —0.7557) with $Q_{SCSH}(3'2)$. If, however, as in the case of the four-bond proton-proton couplings of allenes [1], the cyano group is omitted in the regression analysis, one finds an acceptable correlation (4) (r = —0.8989) of $^2J(^{13}C_3'H_2)$ with the corresponding STO-3G overlap population (in units of 10^{-4}).

$$^3J(^{13}C_3'H_2)(RCH{=}C{=}CH_2) = -8.19\ Q_{SCSH} + 20.02 \quad (4)$$

On the other hand, the coupling $^3J(^{13}C_1'H_3)$ involving the substituted carbon atom exhibits a fair correlation (5) (r = 0.9316) which includes all the molecules in Table II.

As a resumé 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 correlations of couplings with P^2_{SCSH} [6].

$$^3J(^{13}C_1'H_3)(RCH{=}C{=}CH_2) = 22.43\ Q_{SCSH} - 27.00 \quad (5)$$

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