A CDOE/INDO LMO Study of the Nuclear Spin–Spin Coupling Constants between Directly Bonded C–H and C–C Atoms

C. Van Alsenoy*, H. P. Figeys** and P. Geerlings***

Department of Organic Chemistry, Free University of Brussels (U.L.B and V.U.B.), 50, Ave, F. D. Roosevelt, B-1050 Brussels, Belgium

Müller-Pritchard (MP) type relations are used to study $^1J_{CH}$ and $^1J_{CC}$ coupling constants in a series of unsubstituted as well as in heterosubstituted hydrocarbons. In the case of the coupling constant between two atoms connected by a multiple bond, a generalised MP-type relation is derived.

Key words: CDOE-INDO-Theory – $^1J_{CH}$ and $^1J_{CC}$ coupling constants – Müller–Pritchard relation – Bent's electronegativity rule.

1. Introduction

Until now mainly two types of perturbation methods have been used for the calculation of molecular spin–spin coupling constants in big or medium-sized organic molecules. The first one is the well known Rayleigh–Schroedinger perturbation theory which was used for the first time in this field by Ramsey [1]. The second type are perturbation methods especially adapted for the Hartree–Fock–Roothaan equations [2], either with a finite perturbation (finite perturbation theory [3]) or with an infinitesimal perturbation (coupled Hartree–Fock or Self-Consistent Perturbation theory [4, 5]).

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* "Aangesteld Navorser" of the Belgian National Foundation for Scientific Research (N.F.W.O.), present address: University of Antwerp (U.I.A.) Department of Chemistry, Universiteitsplein, 1, 2610 Wilrijk Belgium.
** Author to whom correspondence should be sent
*** Present address: Vrije Universiteit Brussel, Dienst Algemene Scheikunde, Fakulteit der Wetenschappen, Pleinlaan 2, 1050 Brussel, Belgium.

Using the formulas of these methods all the coupling constants in a molecule, directly bonded as well as long range, can be calculated. For the calculation of coupling constants between directly bonded atoms however, expressions relating the coupling constant and the (%s)-character of the hybrid orbitals forming the bond in question can be used. These relations, which were first derived independently by Müller and Pritchard [6] and by Shoolery [7], have been used in a qualitative way by Frei and Bernstein [8] and by Gunther and Herrig [9]. In the early seventies Maksic et al. [10] and Newton et al. [11, 12] used relationships of this type to make quantitative predictions for nuclear spin coupling constants in hydrocarbons. In this work we will investigate the possibility of using Müller–Pritchard (MP) type relations quantitatively in the study of $^1J_{CH}$ and $^1J_{CC}$ in heterosubstituted hydrocarbons. For the study of the coupling constant between two atoms connected by a multiple bond a generalised MP relation will be derived.

The canonical molecular orbitals (CMO's) for all the molecules in this study are calculated in the INDO approximation using experimental geometries and the previously reported CDOE-technique for the optimalisation of the atomic orbital exponents [13]. This technique which was first used in connection with the CNDO method is based on an iterative variation of Charge-Dependent atomic Orbital Exponents during the conventional SCF procedure. Calculations on a series of H, C, N, O and F containing molecules indicated a smoothing out of the net atomic charges leading to molecular dipole moments which were in much better agreement with experimental data than those obtained via the CNDO/2 SCF method.

In this paper we extend this orbital exponent optimisation to the INDO theory.

This requires a few modifications which will be briefly described. The CMO's are localised using the technique we developed earlier [14] and which is essentially an INDO approximation to the indirect intrinsic [15] localisation method of von Niessen [16]. The applicability of this technique to investigate the correlation between the $^1J_{CH}$ coupling constants in strained hydrocarbons and the (%s)-character of the hybrids involved in the CH bond was investigated in previous work [17]. Finally, the validity of Bent's rule [18] will be investigated for the CH bonds in substituted methanes and aldehydes.

2. The CDOE/INDO Method

After the introduction of the INDO approximation [19] and the neglect of penetration, the following expressions are obtained for the HF matrix elements:

$$F_{\mu_A\mu_A} = U_{\mu\mu} + \sum_{\lambda(\in A)} P_{\lambda\lambda}(\gamma^{AA}_{\mu\lambda} - \tfrac{1}{2}e^{AA}_{\mu\lambda})$$

$$+ \sum_{B(\neq A)} \sum_{\sigma(\in B)} (P_{\sigma\sigma} - n_\sigma)\gamma^{AB}_{\mu\sigma}$$

$$F_{\mu_A\nu_A} = P_{\mu\nu}(\tfrac{3}{2}e^{AA}_{\mu\nu} - \tfrac{1}{2}\gamma^{AA}_{\mu\nu})$$

$$F_{\mu_A\nu_B} = H^{AB}_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma^{AB}_{\mu\nu}.$$

Table 1. Damping factors (k) for $U_{\mu\mu}$

	k	Stand. dev. (a.u.)
U_{ss}	0.87320	0.04070
U_{pp}	1.10854	0.04276

$e_{\mu\lambda}^{AA}$ stands for the exchange integral between the AO's χ_μ and χ_λ. The other symbols have their usual meaning [13]. $U_{\mu\mu}$ and $H_{\mu v}$ are calculated theoretically over STO's using the orbital exponents specified in [13].

Subsequently they are multiplied by a damping factor in order to reduce them to a value more suitable for semiempirical calculations. Since the calculation of $H_{\mu v}$ in the CNDO and INDO approximation is identical, the damping factors given in [13] are used for the reduction of this integral. On the contrary, the value for $U_{\mu\mu}$ in the INDO approximation, is, due to the inclusion of one center exchange, different from the corresponding CNDO value. The new damping factors for the elements C, N, O and F are given in Table 1.

The damping parameters for $U_{1s_H,1s_H}$ remain the same as in [13]. The one-center two-electron integrals are calculated using the well known expressions in terms of Slater–Condon parameters [19–21]. The F^0-parameter is calculated as in the CNDO approximation [13].

The remaining F^2 and G^1 parameters are calculated theoretically [20] and then reduced, using an equation of the form

$$y = ax + b$$

The values of the parameters a and b, which are given in Table 2, are obtained from a least-squares regression of the theoretically calculated values versus the experimental ones given by Pople [19]. A comparison of the so obtained values for the Slater–Condon factors with the experimental ones is given in Table 3.

3. Relations Between $^1J_{CH}$ or $^1J_{CC}$ and the Calculated (%s)-Character of the Chemical Bond

For the derivation of their relationship Müller and Pritchard [6] considered the model of two atoms connected by a single bond. When a full Slater determinant of LMO's is used as a molecular wavefunction, a more general expression is obtained

Table 2. Values of the a and b coefficients for the calculation of F^2 and G^1

	a	b	Stand. dev. (a.u.)
F^2	0.81300	−0.05450	0.00144
G^1	1.12259	−0.16483	0.00708

Table 3. Experimental and calculated values of F^2 and G^1 for the elements C, N, O and F (in a.u.)

| Element | F^2 | | G^1 | |
	Exp.	Calcul.	Exp.	Calcul.
C	0.173720	0.172702	0.267708	0.262708
N	0.219055	0.220068	0.346029	0.351045
O	0.266415	0.267425	0.434230	0.439236
F	0.315800	0.314782	0.532305	0.527292

which can equally well be applied to multiple bonded atoms. The final relations, derived in the appendix, can be written as

$$^1J_{AB} = an^2 S_A^2(0) S_B^2(0)(\% s)_A (\% S)_B \tag{1}$$

with n equal to 1, 2 and 3 for a single, double or triple bond respectively. The other symbols have their usual meaning. $S_A^2(0)$ and $S_B^2(0)$ are usually assumed constant for all the molecules under investigation. Many investigators [10, 11, 17] have used a relationship of the type (1) and found that an even better concordance between experimental and calculated coupling constants is obtained when a constant term, b, is added to (1). This term which is usually negative [10, 11, 12, 17] is included to correct some of the deficiencies of the method like the average energy approximation and the fact that coupling is assumed to be only due to the Fermi contact Hamiltonian.

In the case of CH bonds, n is obviously always equal to one. Eq. (1) reduces with the above mentioned assumptions to

$$^1J_{CH} = a(\% s)_C + b. \tag{2}$$

For the hydrocarbons listed in Table 4 we got via a least-squares analysis, the following relationship
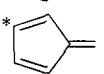
$$^1J_{CH}(Hz) = 6.91(\% s)_C - 72.39 \tag{3}$$

with a standard deviation of 4.98 Hz. Using Pople's original INDO method [19], a standard deviation of 5.12 Hz is obtained. When heteroatomic molecules are however included, the effect of introducing charge dependent orbital exponents becomes more drastic. Collecting the molecules of both Tables 4 and 5, the following relationship is obtained

$$^1J_{CH}(Hz) = 7.09(\% s)_C - 80.77 \tag{4}$$

with a standard deviation of 6.69 Hz. When the CMO's are calculated via Pople's INDO method [19], a standard deviation of 9.85 Hz is found. This improvement clearly illustrates the fact that a better description of changes in polarity of CH bonds is obtained when atomic orbital contractions and expansions are taken into account. Fig. 1 shows a plot of the experimental $^1J_{CH}$ values collected in Tables 4 and 5 against the (% s) character of the carbon hydrids involved in the different
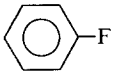
Table 4. Comparison of the experimental and calculated values of $^1J_{CH}$ (in Hz) for hydrocarbons

No.	Molecule[a]	$(\%s)_C$ Calcul.	Theoret. Eq. (3)	Eq. (4)	Exp.	Geom.	$^1J_{CH}$
			$^1J_{CH}$			Reference	
1	CH_3–CH_3	28.90	127.39	123.99	126	22	33
2	CH_3–C≡C–H	45.63	243.03	242.53	247.6	23	33
3	*CH_3–C≡C–H	28.68	125.87	122.43	131	23	33
4	CH_2=CH_2	34.21	164.09	161.62	156.2	24	33
5	CH_2=C=CH_2	34.61	166.86	164.45	168	25	33
6	H–C≡C–H	45.68	243.38	242.88	248.7	26	33
7	(hexagon)	27.73	119.30	115.70	125	27	33
8	(hexagon with inner circle)	32.71	153.72	150.99	159	28	33
9	(square)	29.85	133.95	130.72	136	17	33
10	(triangle)	33.51	159.25	156.66	160.5	29	34
11	exo (bicyclic structure *)	33.91	162.02	159.49	153	30	35
12	endo (bicyclic structure)	34.66	167.20	164.80	169	30	35
13	(bicyclobutane structure *)	40.17	205.29	203.84	205	30	35
14	(triangle fused structure *)	43.66	229.42	228.57	226	31	36
15	(cyclopentadiene structure *)	34.75	167.82	165.44	160	32	37
16	(cyclopentadiene structure *)	35.45	172.66	170.40	170	32	37
17	(cyclopentadiene structure *)	34.45	165.75	163.32	166	32	37

[a] In case of ambiguity the C atom involved in the CH bond is indicated with an asterisk.

CH bonds. It is interesting that in contrast to the conclusions obtained by Pople and Maciel [69] who correlated $^1J_{CH}$ with another measure of the $(\%s)$-character, namely $P^2_{s_C,s_H}$ which is the element of the bond order matrix calculated with the finite perturbation technique [3] and ordinary INDO wave functions, our results for all the molecules investigated can be very well represented by one single straight line. In agreement with our previous work [17] the enhancement of the $(\%s)$-character of the carbon atom hybrid orbital in the CH bond with decreasing ring size is well reproduced. This is particularly evident if closely related

Table 5. Comparison of experimental and caclulated values of $^1J_{CH}$ (in Hz) for heterosubstituted hydrocarbons

| No.	Molecule	$(\%s)_C$ calculated	$^1J_{CH}$ Theoret. eq. (4)	Exp.	Ref. Geom.	$^1J_{CH}$
18	*CH₃–CHO	29.25	126.47	127	38	33
19	*CH₃–COOH	29.26	126.54	130	39	61
20	*CH₃–COCH₃	29.36	127.25	126.5	40	61
21	*CH₃–CN	29.17	125.91	136	41	61
22	*CH₃–F	33.99	160.06	149	42	61
23	*CH₃–NH₂	30.90	138.16	133	43	61
24	*CH₃–OCH₃	32.41	148.86	140	44	33
25	*CH₃–CH₂F	29.39	127.47	126.35	45	62
26	CH₃*CH₂F	31.86	144.97	149.97	45	62
27	CH₂F₂	38.64	193.00	184.5	46	63
28	CHF₃	44.33	233.32	239.1	47	33
29	(CH₃)₂NH	30.70	136.75	132	48	61
30	*HCO–CH₃	37.84	187.33	173.5	38	64
31	*HCO–OH	43.43	226.94	223.5	49	64
32	*HCO–OCH₃	42.59	220.99	227.5	50	64
33	*HCO–F	48.30	261.44	267	51	64
34	*HCO–NH₂	39.63	200.02	187	52	64
35	*HCO–φ	37.64	185.92	175	53	64
36	H–*C≡C–F	50.15	274.55	277.5	54	65
37	H–*C≡C–φ	45.53	241.82	251	55	33
38	△O	37.52	185.07	175.80	56	66
39	△N	35.68	172.03	168.1	57	66
40	□*O	32.94	152.62	148	58	67
41	*□O	31.23	140.50	137.3	58	67
42	o	33.80	159.28	155	59	33
43	φ–F m	32.79	151.55	163	59	33
44	p	33.15	154.55	161	59	33
45	▷*–NH₂	36.07	174.79	173	60	68
46	*▷–NH₂	33.85	159.06	161	60	68
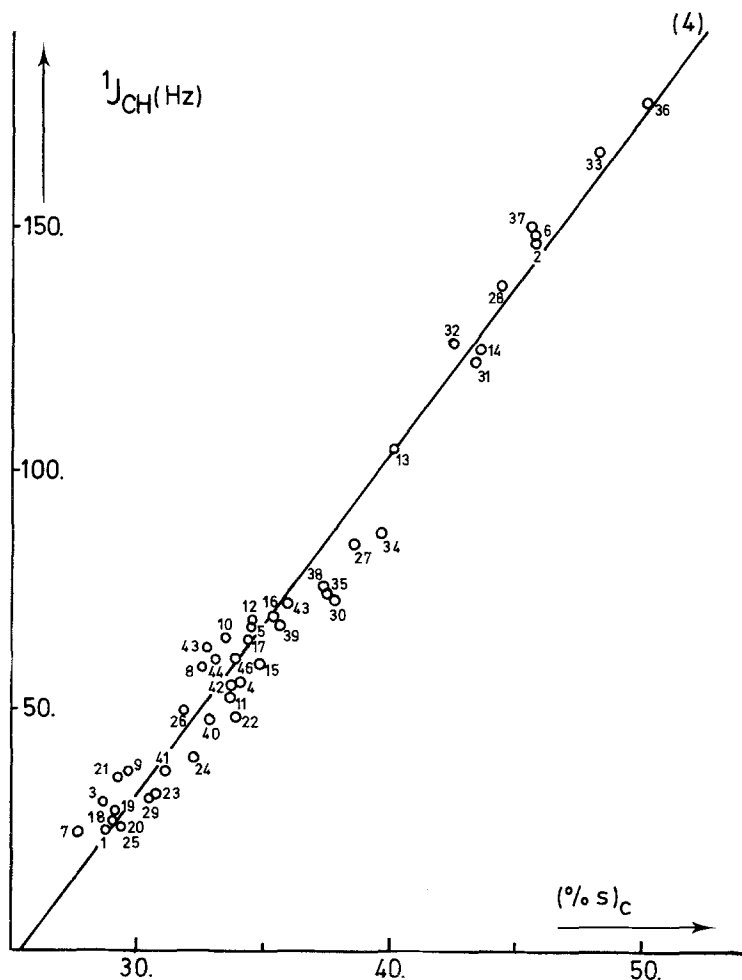
Fig. 1. Least squares relation between experimental $^1J_{CH}$-values and the percentage of s-character in the carbon atom hybrid orbital forming the CH-bond

compounds are considered, i.e. the saturated cyclic hydrocarbons cyclohexane $(7)^1$ cyclobutane $(9)^1$ and cyclopropane $(10)^1$. We also note an enhancement of the $(\%s)$-character of the CH bonds α to the heteroatom in small saturated heterocyclic compounds. This is particularly evident in the series: cyclopropane $(10)^1$, ethylene oxide $(38)^1$ and aziridine $(39)^1$ and when going from cyclobutane $(9)^1$ to oxetane $(40)^1$. Due to the fact that we calculated the $(\%s)$-character of the hybrid orbital on the C atom engaged in the CH bond in a pure quantum chemical fashion, we find ourselves in an excellent position to check Bent's rule [18] which states that: "Atomic s-character concentrates in orbitals directed towards electropositive substituents." Our results, together with Hinze and Jaffé's group

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[1]   These figures refer to the numeration in Fig. 1 and Tables 4 and 5.

| X | $(\% s)_C$ in CH bond | | | |
	H–CH_2–X	H–CO–X	χ_g
CH_3	28.90	37.84	2.30
CH_2F	29.39	—	2.61
NH_2	30.90	39.63	2.82
OCH_3	32.41	42.59	3.53 (OH)
OH	—	43.43	3.53
F	33.99	48.30	3.90

Table 6. Comparison of $(\% s)$-character in CH-bonds with Hinze and Jaffé's electronegativities (χ_g) for the substituent X

electronegativities [70], are collected in Table 6. The agreement is remakable. Contrary to the conclusions of Grant and Litchman [71] and Rock and Hammaker [64] we see that there is indeed a significant change in hybridisation of the C-atom hybrid forming the CH bond upon substitution in the direction predicted by Bent's rule.

This is especially the case for the aldehydes where an increase of more than 10% in $(\% s)$-character is obtained upon substitution of a CH_3 group by an F atom.

A similar investigation has also been carried out for $^1J_{CC}$ coupling constants; in this case (5) has been used

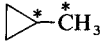$$^1J_{C_1C_2} = an^2(\% s)_{C_1}(\% s)_{C_2} + b. \tag{5}$$

As expected on the basis of electronegativity arguments, the influence of the charge-dependent orbital exponents on the $(\% s)$-character of the hybrid orbitals forming the C–C bonds we studied is not as important as it was in the case of CH bonds. Consequently, there is only a slight improvement of the results with the use of the CDOE technique. Schulman and Newton [12] have recently shown that, except for bonds common to two or more small rings, the contributions to the coupling constant, $^1J_{CC}$, from the orbital-dipole (OD) and the spin-dipolar (SD) Hamiltonians are in most cases opposite in sign and in all cases much smaller than the contribution from the Fermi-contact (FC) Hamiltonian. A theory for the prediction of coupling constants based on the use of the FC Hamiltonian alone should thus be valuable in most cases. For simple C–C bonds in hydrocarbons (Table 7) we calculated, via a least squares analysis, the following equation:

$$^1J_{C_1C_2} (Hz) = 0.0635(\% s)_{C_1}(\% s)_{C_2} - 19.36 \tag{6}$$

with a standard deviation of 3.19 Hz which compares very well with the 2.4 Hz obtained by Newton et al. [11], who localised INDO-CMO's by the unapproximated but time consuming Edmiston–Rüdenberg procedure [15]. From Table 7 we remark that the increase in $^1J_{CC}$ in small bicyclic ringsystems is very well reproduced (e.g. compare cyclopropane $(7)^2$ to bicyclopentane $(10)^2$ and bicyclobutane $(8)^2$). The relative increase in $^1J_{CC}$ in going from cyclopropane $(7)^2$ to spiropentane $(11)^2$ and methylenecyclopropane $(6)^2$ is also well reproduced but too small in absolute value. Using Eq. (6) we calculated -15.29 Hz for the

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[2]   These figures refer to the numeration used in Table 7 and Fig. 2.

Table 7. Experimental and calculated values of $^1J_{CC}$ (in Hz) for single bonds in hydrocarbons (Fig. 2: ○; Eq. 6)

No.	Molecule	$\dfrac{(\%s)_{C_1}(\%s)_{C_2}}{100}$	$^1J_{CC}$ Calcul. Eq. (6)	Exp.	Ref. Geom.	Ref. $^1J_{CC}$
1	CH_3–CH_3	9.02	37.95	36.6	22	9
2	(cyclopropyl)*–*CH_3	9.46	40.74	44.0	72	78
3	CH_3–$CH{=}CH_2$	10.33	46.27	41.9	73	79
4	(structure)	11.54	53.96	53.7	74	80
5	CH_3–$C{\equiv}CH$	13.25	64.82	67.4	23	9
6	(structure)	6.08	19.27	23.2	75	9
7	(cyclopropane)	4.87	11.58	10.0	29	78
8	(structure)	6.46	21.68	21.0	30	9
9	(structure)	8.80	36.55	36.7	76	9
10	(structure)	6.10	19.40	16.0	76	9
11	(structure)	5.64	16.47	20.2	77	9
	(structure)	2.38	−4.26		76	
	(structure)	0.64	−15.29		30	
	(structure)	4.26	7.69		77	
	(structure)	4.23	8.14		75	
	(cyclobutane)	7.08	25.57		17	

bridgehead–bridgehead $^1J_{CC}$ coupling constant in bicyclobutane. This value is in close agreement with the $^1J_{CC}$ for the corresponding bond in [1-cyanobicyclobutane] ($|^1J_{CC}| = 16$ Hz) [81] but not with the measured value in diethyl, 1-methyl, 3-phenyl bicyclobutane-2,4-dicarboxylate [82] ($^1J_{CC} = -5.4$ Hz). We also remark that the calculated value for the coupling constant in cyclobutane is in excellent

Table 8. Experimental and calculated values of $^1J_{CC}$ (in Hz) for single bonds in heterosubstituted hydrocarbons (Fig. 2: $\triangle$; Eq. 7)

No.	Molecule	$\dfrac{(\%S)_{C_1}(\%S)_{C_2}}{100}$	$^1J_{CC}$ Eq. (7)	Eq. (9)	Exp.	Refs. Geom.	$^1J_{CC}$
12	CH_3COOH	12.62	47.20	47.87	56.7	[39]	[4]
13	CH_3CHO	12.28	45.89	46.53	39.4	[38]	[4]
14	CH_3COCH_3	11.16	41.57	42.12	40.6	[40]	[78]
15	CH_3CN	14.48	54.37	55.19	57.3	[41]	[8]
16	$^*CH_2{}^*CH_2CN$	8.14	29.93	30.25	33.0	[83]	[86]
17	$CH_3{}^*CH_2{}^*CN$	14.06	52.75	53.54	55.2	[83]	[86]
18	⬦=O	10.13	37.60	38.08	29.7	[84]	[78]
19	⬦=O	7.52	27.54	27.81	28.5	[84]	[78]
20	⬠=O	10.89	40.53	41.07	37.2	[85]	[78]
21	⬠=O	7.69	29.34	29.54	34.4	[85]	[78]

accord with the value of 27 Hz predicted by Weigert and Roberts [78] on an experimental basis. The calculated coupling constants for a few other analogous compounds using Eq. (6) are also given at the end of Table 8.

An equation of the form (5) has also been applied to the correlation between $^1J_{CC}$ and the $(\%s)$-characters of multiple bonded atoms in hydrocarbons and for single bonded atoms in heterosubstituted derivatives. For all the molecules of Tables 7, 8 and 9 we calculated the following equation

$$^1J_{C_1C_2}(Hz) = 0.0385n^2(\%s)_{C_1}(\%s)_{C_2} - 1.45 \tag{7}$$

with a standard deviation of 7.87 Hz. This standard deviation can be reduced if we do not represent all the points by a single line. For the calculations of $^1J_{CC}$ between multiple bonded atoms in hydrocarbons (Table 9) we calculated the following equation

$$^1J_{CC}(Hz) = 0.0454n^2(\%s)_{C_1}(\%s)_{C_2} - 25.14 \quad (SD = 6.42\ Hz) \tag{8}$$

while for the calculation of $^1J_{CC}$ between singly bonded atoms in heterosubstituted hydrocarbons (Table 8) we calculated

$$^1J_{CC}(Hz) = 0.0393(\%s)_{C_1}(\%s)_{C_2} - 1.78 \quad (SD = 5.65\ Hz). \tag{9}$$

Using Eq. (8) we calculated 51.15 Hz for the experimentally unknown coupling constant between the two olefinic carbon atoms in cyclopropene. This value compares very well with the 47 Hz obtained by Schulman and Newton [12] for the contribution of contact term using Santry's SCP theory [4].

Table 9. Experimental and calculated values of $^{1}J_{CC}$ (in Hz) for multiple bonds in hydrocarbons (Fig. 2: ◇; Eq. 8)

No.	Molecule	$\dfrac{n^{2}(\%s)_{C_1}(\%s)_{C_2}}{100}$	$^{1}J_{CC}$ Calculated Eq. (7)	Eq. (8)	Exp.	Refs. Geom.	$^{1}J_{CC}$
22	▷=	24.80	94.15	87.55	95.2	[75]	[9]
23	$CH_3-CH=CH_2$	21.72	82.28	73.55	70.0	[73]	[33]
24	$CH_2=CH_2$	22.41	84.94	76.69	67.2	[24]	[9]
25	=\—	21.30	80.66	71.64	68.8	[74]	[9]
26	$CH_2=C=CH_2$	25.80	98.01	92.09	98.7	[25]	[9]
27	$HC\equiv CH$	44.20	168.93	175.70	171.5	[26]	[9]
28	$\phi-C\equiv CH$	43.62	166.70	173.06	175.9	[55]	[33]
29	⬡	17.42	65.70	54.01	57.0	[28]	[9]
	$CH_3-C\equiv CH$	43.72	166.87	173.35		[23]	
	△	16.80	63.23	51.15		[31]	
	$HC\equiv CF$	46.62	178.04	186.51		[54]	

From Table 8 we see that the increase in $^{1}J_{CC}$ is reproduced when going from the C_2-C_3 bonds to the C_1-C_2 bonds both in cyclobutanone (*18, 19*) and in cyclopentanone (*20, 21*), although much too great in absolute value.

Finally we investigated the influence of possible variations of $S_x^2(0)$ on our results. To this purpose we calculated this quantity analogous to Pople *et al.* [69] as

$$S_x^2(0) = k^3/k_0^3 \qquad (10)$$

where k and k_0 stand for the s orbital exponents calculated with the obtained molecular and atomic charge distributions. Contrary to Pople's observations using finite perturbation theory [69] no significant improvement of the results was observed when the CDOE/INDO exponents where used.

Appendix: *Derivation of the Relation*

$$^{1}J_{AB} = an^{2}S_A^2(0)S_B^2(0)(\%s)_A(\%s)_B.$$

Let us start from Ramsey's second-order perturbation expression [1] for the contribution to the coupling constant between nuclei A and B due to the
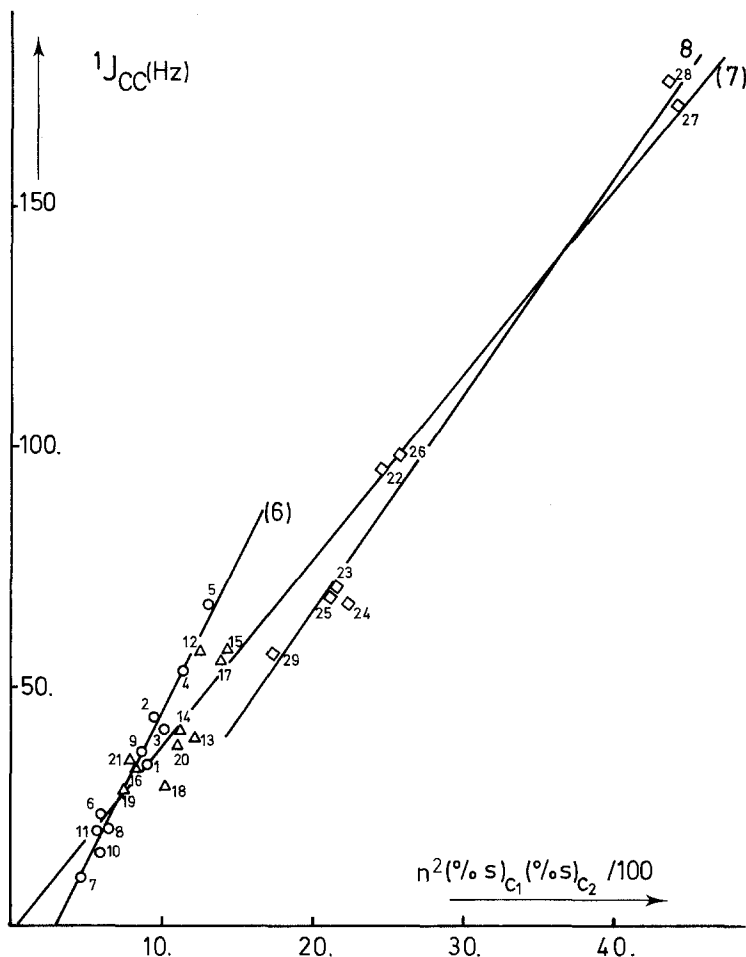
Fig. 2. Comparison of experimental and calculated values of $^1J_{CC}$ for single bonds in hydrocarbons ($\bigcirc$; Fig. 6), in heterosubstituted derivatives ($\triangle$; Eq. 7) and for multiple bonds in hydrocarbons ($\diamond$; Eq. 8)

Fermi-contact Hamiltonian

$$J_{AB} \simeq - \sum_{n=1}^{\infty} (E_n - E_0)^{-1} \langle 0| \sum_i \delta(r_{iA})s_i |n\rangle .$$

$$\text{(A1)}$$

$$\langle n| \sum_j \delta(r_{jB})s_j |0\rangle .$$

E_0 and $|0\rangle$, E_n and $|n\rangle$ represent respectively for the ground and the nth excited state the molecular energy and the molecular wavefunction. We take as ground state wavefunction a single *Slater* determinant built up with LMO's. For brevity we note

$$\sum_i \delta(r_{iA})s_i = A \qquad \sum_j \delta(r_{jB})s_j = B.$$

Assuming $E_n - E_0 = \Delta E = $ constant for all n and making use of the relation

$$\sum_{n=0}^{\infty} |n\rangle\langle n| = 1$$

(A1) reduces to

$$^1J_{AB} \simeq (\Delta E)^{-1}\{\langle 0|\boldsymbol{A} \cdot \boldsymbol{B}|0\rangle - \langle 0|\boldsymbol{A}|0\rangle \cdot \langle 0|\boldsymbol{B}|0\rangle\} \tag{A2}$$

where the second term of the right-hand side vanishes because of the assumed closed-shell structure of the molecules under consideration. The product $\boldsymbol{A} \cdot \boldsymbol{B}$ can be written as follows:

$$\boldsymbol{A} \cdot \boldsymbol{B} = \sum_i \delta(r_{iA})\delta(r_{iB})S_i^2 + \sum_{i \neq j}\sum \delta(r_{iA})\delta(r_{jB})\boldsymbol{S}_i \cdot \boldsymbol{S}_j. \tag{A3}$$

We know from the properties of the Dirac delta function that

$$\delta(r_{iA})\delta(r_{iB}) = \delta(r_{iA} - r_{iB})$$

which in our case will always vanish because we assumed A and B to be two distinct nuclei. Consequently we are left with the second term of the right-hand side of (A3) which has the typical structure of a two-particle operator. Using Slater's rules [21] for the calculation of matrix elements and using the fact that we consider only closed-shell molecules, we obtain for (A3)

$$^1J_{AB} \simeq \sum_{k,l} \langle\phi_k|\delta(r_A)|\phi_l\rangle\langle\phi_l|\delta(r_B)|\phi_k\rangle \tag{A4}$$

where ϕ_k and ϕ_l are LMO's. Introducing the LCAO expansion in (A4) and retaining only one-center terms we obtain for J_{AB}

$$^1J_{AB} \simeq \sum_{k,l} C_{S_A,k}C_{S_A,l}S_A^2(0)C_{S_B,l}C_{S_B,k}S_B^2(0) \tag{A5}$$

When we assume atoms A and B to be direct neighbours bounded by n perfectly localised identical LMO's we obtain immediately

$$^1J_{AB} \simeq an^2 S_A^2(0)S_B^2(0)(\%s)_A(\%s)_B. \tag{A6}$$

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