

232. ^{13}C -Chemical Shift/Charge Correlations in Unsaturated Systems as Obtained by Semiempirical MO-Methods: A Reinvestigation

by Harold Baumann and Henrik Olsen

Organisch-Chemisches Laboratorium der ETHZ, Universitätstrasse 16, CH-8092 Zürich

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Summary

The *Spiesecke & Schneider* relationship between charge and ^{13}C -chemical shifts has been widely used in recent years. In the present work a set of 20 organic compounds with a total of 50 different chemical shifts has been investigated with respect to the applicability of this relation. Attempted correlation between ^{13}C -shifts and charges indicated that the proportionality constant highly depends on the MO-method used. In order to circumvent these problems paramagnetic shifts were computed using standard techniques. The effect of including a diamagnetic shift correction is discussed.

Introduction. - The ^{13}C -chemical shift as a probe of charge was originally proposed by *Spiesecke & Schneider* (*S/S*) [1]. In their work *Hueckel* π -charges were linearly correlated with the shifts of **1**, **2**, **10** and **13**. The slope of the averaged line yields the value of 160 ppm/electron.

Theoretical considerations have provided some justification for the empirically found charge-shift relation. The total shielding constant $\sigma_{\text{tot}}^{\text{A}}$ for a particular nucleus A can be approximated as a sum of three terms [2].

$$\sigma_{\text{tot}}^{\text{A}} = \sigma_{\text{d}}^{\text{A}} + \sigma_{\text{p}}^{\text{A}} + \sigma_{\text{r}}^{\text{A}} \quad (1)$$

the diamagnetic contribution $\sigma_{\text{d}}^{\text{A}}$, the paramagnetic term $\sigma_{\text{p}}^{\text{A}}$ and the residual effect term $\sigma_{\text{r}}^{\text{A}}$. *Karplus & Pople* [3] have developed LCAO-expressions for the ^{13}C -shifts in conjugated molecules and demonstrated that the paramagnetic term is charge-dependent. Their method to calculate $\sigma_{\text{p}}^{\text{A}}$ has been extensively applied by other authors [4]. However, the calculations have only led to a qualitative agreement with the experimental shifts. Applying a MO-independent estimation of the diamagnetic term, originally proposed by *Flygare & Goodisman* [5], and correcting the ^{13}C -shifts of aliphatic compounds for this term, *Mason* [6] noted that they become additive for poly-substitution by halogen-, methyl-, methoxy- or phenyl-groups.

The present paper investigates the reliability of the ^{13}C -shift/charge relation. Four different classes of compounds have been used here. Besides the annulenes

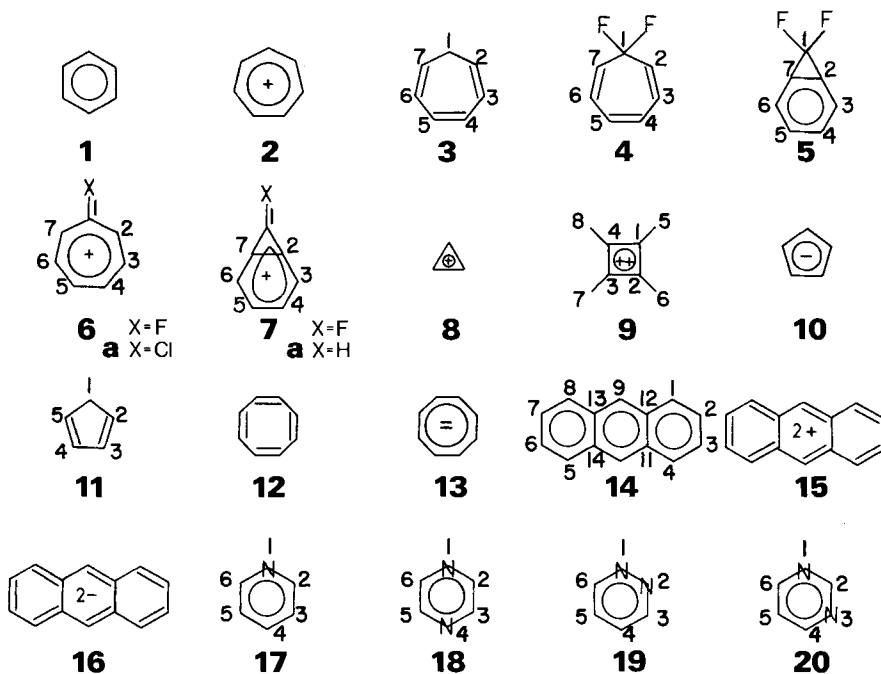


Fig. 1. Structures used for the calculations. The numbering of the structures and the centers corresponds to the first and last column of Table 2, respectively.

considered by *S/S* (1, 2, 10 and 13), aromatic, antiaromatic, and heteroaromatic systems (8, 14, 15, 16, 17, 18, 19 and 20), substituted aromatic systems (6, 7 and 9), and cyclopolyolefines (3, 4, 5, 11 and 12) were studied. The paramagnetic shift and the charges were estimated by well known methods, using CNDO/S [7] wavefunctions based on experimental, computed (OPTMO [8]), and estimated structures.

Method. - The molecular structures used for the computation of the charges and the chemical shifts are divided into the following three groups and are given in Figure 1:

a) Experimentally determined: 1 [9], 3 [10], 5 [11], 11 [12], 12 [13], 14 [14], 17 [15], 18 [16], 19 [17] and 20 [18];

b) Optimized by OPTMO [8]: 2, 6, 7, 13, 15 and 16;

c) Estimated: 4, 8, 9 and 10.

The diamagnetic term in eq. (1) may be estimated using eq. (2) which does not require any MO-calculations [5]:

$$\sigma_d^A = \sigma_d^A(\text{free atom}) + \frac{e^2}{3 m c^2} \sum_{B \neq A} z_B R_{AB}^{-1} \quad (2)$$

whereas for σ_p^A the expression given by *Fraenkel & Tokuhiro* [4] was applied. They are given by eqs. (3) to (8):

$$\sigma_p^A = -2 N^{-1} \chi_p^A \langle r^{-3} \rangle_{2p} \quad (3)$$

$$\chi_p^A = (Ne^2\hbar^2)/(2m^2c^2\langle\Delta E\rangle) \left(Q_{AA} + \sum_{A \neq B} Q_{AB} \right) \quad (4)$$

$$Q_{AA} = \frac{2}{3} (P_{x_A x_A} + P_{y_A y_A} + P_{z_A z_A}) - \frac{1}{3} (P_{y_A y_A} P_{z_A z_A} + P_{z_A z_A} P_{x_A x_A} + P_{x_A x_A} P_{y_A y_A}) \\ + \frac{1}{3} (P_{y_A z_A} P_{z_A y_A} + P_{z_A x_A} P_{x_A z_A} + P_{x_A y_A} P_{y_A x_A}) \quad (5)$$

$$Q_{AB} = -\frac{1}{3} (P_{y_A y_B} P_{z_A z_B} + P_{z_A z_B} P_{x_A x_B} + P_{x_A x_B} P_{y_A y_B}) \\ + \frac{1}{3} (P_{y_A z_B} P_{z_A y_B} + P_{z_A x_B} P_{x_A z_B} + P_{x_A y_B} P_{y_A x_B}) \quad (6)$$

$$\langle r^{-3} \rangle_{2p} = 1/24 (z_A/a_0)^3 \quad (7)$$

$$z_A = 3.25 - 0.35 (q_A - 4) \quad (8)$$

N: Avogadro-Number, e: charge of electron, a_0 : Bohr radius, \hbar : Planck's number $h/2\pi$, m: mass of electron, c: velocity of light, P_{UCVD} : element of bond order matrix, z_A : effective nuclear charge of neutral atom A, q_A : total charge, $(e^2\hbar^2N)/(2m^2c^2\langle\Delta E\rangle) = 6.4468 \cdot 10^{15} \text{ nm}^3$, assumption: $\langle\Delta E\rangle = 10 \text{ eV}$, $e^2/(3mc^2) = 9.3917 \cdot 10^{-7} \text{ nm}$, R_{AB} : internuclear distance A-B.

The experimental ^{13}C -shifts have been linearly correlated with π -charges, total charges and σ_p^A (Table 3: Method I, III and V, respectively). In order to see if the diamagnetic term brings any improvements, the corrected ^{13}C -shifts (δ^{corr}) have likewise been linearly correlated with π -charges, total charges and σ_p^A (Table 3: Method II, IV and VI, respectively).

According to Mason [6] the diamagnetic term has been added directly to the experimental result. This leads to the expression (9)

$$\delta_{\text{corr}}^A = \delta_{\text{obs}}^A - \sigma_d^A \simeq \sigma_p^A + \sigma_r^A \quad (9)$$

We neglect σ_r^A (theor) and put δ_{corr}^A proportional to σ_p^A

$$\delta_{\text{corr}}^A \simeq \sigma_p^A \text{ (theor)}. \quad (10)$$

Results and discussion. - Recently the ^{13}C -NMR.-spectra of two similar fluorinations **6** and **7** and their precursors **4** and **5** have been measured by Foehlich & Welt [19] (**6** and **7**) and Halton *et al.* [20] (**4** and **5**). The former authors [19] found a perfect correlation between the total MINDO/3 charges [20] and the shifts of **2**, **6**, and the chloro-substituted C-atom of **6a** (correlation coefficient $r=0.99$; slope of $\delta(^{13}\text{C})$ vs. q_{tot} (MINDO/3) equal to 52.5 ppm/electron). The results support the charge-shift relation; the proportionality constant of 52.3 ppm/electron, however, is not in agreement with that found in [1]. Halton *et al.* [20] compared the shift-difference between the neutral compound **5** and the cation **7** with the Self-Consistent-Charge Extended Hueckel (SCC-EH) calculated charge distribution of the model system **7a**. They found likewise that the total downfield shift ($\sum_i \Delta\delta_i = \sum_i (\delta_i(7) - \delta_i(5))$) is less than the 160 ppm signified by the S/S equation.

Table 1. 'Experimental' and calculated charge distributions in cyclopropabenzonium (cpb) cations

Position	Unsubstituted cpb			F-substituted	
	SCC-EH		CNDO/S	$\Delta q(\text{C})^a$	'exp' $\Delta q(\text{C})$
	$\Delta q(\text{H} + \text{C})^a$	$\Delta q(\text{C})^a$	$\Delta q(\text{C})^a$		
1	0.289	0.132	0.068	0.254	0.156
2,7	0.105	0.105	0.070	0.144	0.072
3,6	0.122	0.032	0.032	0.022	0.024
4,5	0.129	0.034	0.023	0.040	0.147
Total ch	1.001	0.474	0.318	0.666	0.642

a) Assumption: $\Delta q(\text{neutral compound}) = 0$ for all centers.

Thus a plot of the ^{13}C - shifts vs. $\Delta q_i(\text{SCC-EH}) = q_i(7a) - q_i(5)$ results in a proportionality constant of 74.3 ppm/electron ($r = 0.63$). To circumvent these problems *Halon et al.* [20] add the hydrogen-charge of the H-atom to the corresponding charge of the C-atom. However, the 'experimental' charge distribution determined by dividing the experimental shifts by the proportionality constant of 160 ppm/electron leads to strong deviations from their calculated values (*Table 1*).

The ^{13}C -shift/charge correlations described above are based on three MO-methods (HMO, MINDO/3, SCC-EH) which estimate the charges differently. The HMO-model does not take into account the H-atoms. Thus, the charge is artificially located on the C-atoms. But neither can SCC-EH and MINDO/3 charges which are computed by including all valence orbitals be compared directly with one another.

Because of the difficulties encountered when comparing the charges obtained from different MO-methods all compounds which were of interest for this work were recomputed by the same method in order to obtain consistent values. The CNDO/S-computed charge densities for 20 compounds are tabulated in *Table 2*. Recorrelation of the ^{13}C -shifts of the four annulenes used in [1] with CNDO/S and MINDO/2 charge densities, results in new proportionality constants, 264 and 295 ppm/electron, respectively, and slightly deteriorated correlation coefficients of 0.947 and 0.953. Unfortunately this relation of the slopes has no general character and is not valid for other groups of molecules.

These results indicate that the procedure for calculating the charge from some experimentally determined ^{13}C -shift values using 160 ppm/electron is without a theoretical basis. The value of 155 ppm/electron given by *Tokuhiro & Fraenkel* [4] for the azines computed by $\delta_A(^{13}\text{C})$ vs. $q_{\text{tot}}^A(\text{CNDO/S})$ is close to the HMO-value. We find 269, 280 and 176 ppm/electron for the slopes of $\delta_A(^{13}\text{C})$ vs. $q_{\text{tot}}^A(\text{CNDO/S})$ of **6**, and **15/16**, and **17 to 20**, respectively. The inclusion of 20 organic compounds with a total of 47 different shifts (*Table 2* and *Fig. 2*) leads to a slope of 263 ppm/electron. The slope found correlating CNDO/S π -charges with the measured ^{13}C -shifts of **14** and its dianion and dication is 129 ppm/electron. The $\Delta\langle\delta\rangle_{\text{exp}}$ value of heptalene and its dianion has been determined to be equal to -32.4 ppm. The value obtained by the S/S-relation furnishes -26.7 ppm ($-2/12$ (160 ppm) = -26.7 ppm) [22]. However, given 12 centers this corresponds to a total shift dif-

Table 2. Experimental and theoretical chemical shifts.

Compound	No.	δ_{exp} (TMS) [ppm]	δ_{exp} (benz) [ppm]	Total charge	π^{a} charge	$\langle r^{-3} \rangle$ $\times 10^{-3}$ [nm ⁻³]	$\sum^{\text{B}} Q_{\text{AB}}$	$\Delta\sigma_{\text{p}}^{\text{theor.}}$ (benz) [ppm]	$\Delta\sigma_{\text{d}}^{\text{theor.}}$ (benz) [ppm]	δ_{exp} $-\sigma_{\text{d}}$ [ppm]	n
Benzene (1)	1-6	129.7	0	4.0285	1.0000	9.56	1.27	0	0	0	1
Tropylium (2)	1-7	155.4	26.7	3.9297	0.8571	9.87	1.26	5.0	1.6	25.1	2
Cyclohepta- triene (3)	1	26.8	-101.9	4.0139	-	9.61	1.09	-36.0	-2.6	-99.3	3 ^{c)}
	2	120.0	-8.7	4.0448	-	9.51	1.21	-13.8	1.7	-10.4	4 ^{b)}
	3	125.8	-3.0	4.0368	-	9.54	1.23	-9.0	0.2	-3.2	5 ^{b)}
	4	130.2	1.5	4.0399	-	9.53	1.24	-6.5	0.5	1.0	6 ^{b)}
Difluoro-cyclo- heptatriene (4)	1	-	-	3.6928	-	10.64	1.13	-2.0	-112.7	-	7
	2	124.1	-3.6	4.0031	-	9.64	1.20	-12.2	1.7	-6.3	8 ^{b)}
	3	128.6	-0.1	4.0354	-	9.54	1.23	-8.5	0.2	-0.3	9 ^{b)}
	4	130.4	1.7	4.0330	-	9.55	1.25	-5.7	0.5	1.2	10 ^{b)}
1,1-Difluorocyclo- propabenzene (5)	1	100.7	-28.0	3.7130	-	10.57	1.16	1.7	-112.0	84.0	11 ^{c)}
	2	129.5	0.8	3.9892	0.9672	9.68	1.29	6.3	-31.4	32.2	12
	3	115.9	-12.8	4.0157	1.0143	9.60	1.25	-3.5	-0.4	-12.4	13
	4	135.1	6.4	4.0237	1.0163	9.58	1.27	-0.4	1.3	5.1	14
Fluoro-tropylium (6)	1	179.3	50.6	3.7900	0.8570	10.32	1.31	28.5	-54.0	104.6	15
	2	143.6	14.9	3.9027	0.8910	9.96	1.25	7.0	1.0	13.9	16
	3	156.4	27.7	3.9288	0.8373	9.87	1.25	4.6	1.5	26.2	17
	4	154.8	26.1	3.9297	0.8684	9.87	1.25	4.6	1.6	24.4	18
1-Fluoro-cyclo- propabenzene cation (7)	1	146.2	17.5	3.7235	0.7784	10.54	1.21	13.4	-57.4	74.9	19
	2	139.0	10.3	3.8660	0.7988	10.08	1.27	14.0	-30.2	40.5	20
	3	118.4	-10.3	3.9642	0.9784	9.76	1.24	-0.8	0.4	-10.7	21
	4	156.6	27.9	3.9204	0.8659	9.90	1.26	6.5	1.5	26.4	22
Cyclopropene cation (8)	1-3	176.8	48.1	3.8350	0.6667	10.17	1.20	0.8	0.3	47.8	23
Tetramethyl- cyclobutadiene dication (9)	1-4	209.0	80.3	3.7743	0.5749	10.37	1.29	26.1	-28.2	108.5	24
	5-8	-	-	3.9823	-	9.71	1.07	-38.2	26.6	-	25
Cyclopentadiene anion (10)	1-5	102.1	-26.6	4.1654	1.2000	9.14	1.26	-14.3	0.3	-26.9	26
Cyclopenta- diene (11)	1	41.6	-87.1	4.0144	-	9.61	1.10	-33.1	-2.2	-84.9	27 ^{c)}
	2	132.8	4.1	4.0441	1.0085	9.51	1.22	-11.4	1.5	2.6	28
	3	132.2	3.5	4.0559	1.0295	9.48	1.26	-5.2	0.5	3.0	29
Cyclo-octa- tetraene (12)	1-8	133.0	4.3	4.0215	-	9.58	1.23	-8.8	1.2	3.1	30 ^{b)}
Cyclooctatetra- ene dianion (13)	1-8	85.3	-43.4	4.1626	1.2500	9.15	1.24	-16.7	1.7	-45.1	31
Anthracene (14)	1	130.1	1.4	4.0439	1.0084	9.51	1.26	-3.7	0.1	1.3	32
	2	125.5	-3.2	4.0293	0.9991	9.56	1.26	-1.5	-0.3	-2.9	33
	9	132.6	3.9	4.0642	1.0230	9.45	1.26	-6.1	0.1	3.8	34
	11	132.2	3.5	3.9678	0.9809	9.75	1.34	20.2	-29.5	33.0	35
Anthracene dication (15)	1	165.1	36.4	3.8957	0.7902	9.98	1.25	7.2	0.1	36.3	36
	2	153.5	24.8	3.9197	0.8560	9.90	1.26	7.7	-0.3	25.1	37
	9	187.1	58.4	3.8432	0.6197	10.15	1.24	9.8	0.1	58.3	38
	11	139.4	10.7	3.9896	1.0438	9.68	1.35	18.7	-29.5	40.2	39

Table 2 (continued).

Compound	No.	δ_{exp} (TMS) [ppm]	δ_{exp} (benz) [ppm]	Total charge	π^{a} charge	$\langle r^{-3} \rangle$ $\times 10^{-3}$ [nm $^{-3}$]	$\sum_{\text{B}} Q_{\text{AB}}$	$\Delta\sigma_{\text{p}}^{\text{theor.}}$ (benz) [ppm]	$\Delta\sigma_{\text{d}}^{\text{theor.}}$ (benz) [ppm]	δ_{exp} $-\sigma_{\text{d}}$ [ppm]	n
Anthracene dianion (16)	1	101.1	-27.6	4.1542	1.2168	9.18	1.25	-15.3	0.1	-27.7	40
	2	114.2	-14.5	4.1420	1.1436	9.22	1.26	-11.9	-0.3	-14.2	41
	9	75.1	-53.6	4.2127	1.3928	9.00	1.24	-20.8	0.1	-53.7	42
	11	150.0	21.3	4.0098	0.9433	9.62	1.34	16.4	-29.5	50.8	43
Pyridine (17)	2, 6	150.4	21.7	3.8416	0.8824	10.15	1.27	16.6	-8.8	28.4	44
	3, 5	124.1	-4.6	4.0923	1.0559	9.37	1.27	-5.6	-0.1	-4.5	45
	4	136.1	7.4	3.9386	0.8947	9.84	1.28	8.6	-0.1	7.5	46
Pyrazine (18)	2, 3	145.8	17.1	3.9359	0.9337	9.85	1.28	10.0	-6.8	23.9	47
	5, 6										
Pyridazine (19)	3, 6	153.0	24.3	3.9233	0.9071	9.89	1.29	12.2	-6.8	31.1	48
	4, 5	127.8	-0.9	3.9917	0.5911	9.68	1.27	2.8	0	-0.9	49
Pyrimidine (20)	2	159.7	31.0	3.8192	0.7812	10.23	1.29	22.5	-13.5	44.5	50
	4, 6	157.7	29.0	3.8817	0.8126	10.02	1.28	14.8	-6.7	35.7	51
	5	122.3	-6.4	4.0502	1.0755	9.50	1.27	-1.7	0	-6.4	52

a) These are the π -charges of the 40 centers referred to in column 3 of Table 3.

b) These are the 7 centers added in column 4 of Table 3.

c) These are the 3 centers added in column 5 of Table 3.

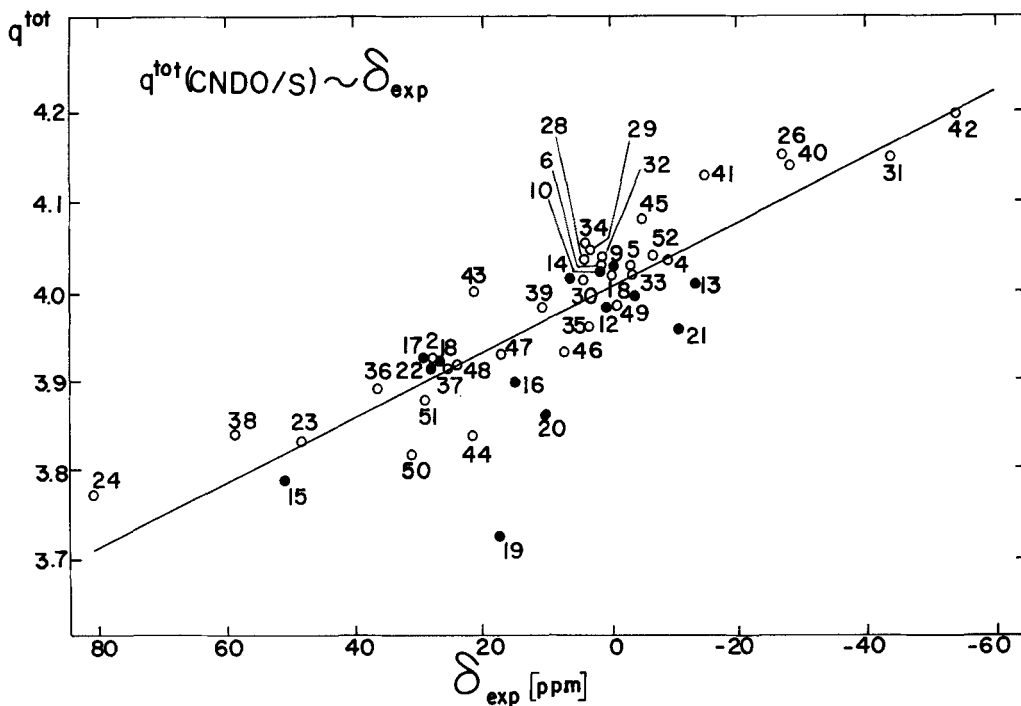
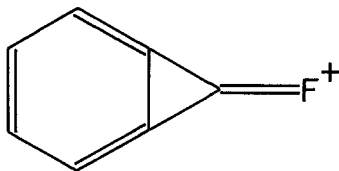


Fig. 2. Linear correlation between $q_{\text{tot}}(\text{CND0/S})$ and δ_{exp} . Numeration corresponds to the last column of Table 2. ●: Fluoro compounds. (Method III of Table 3.) $r=0.8602$.

ference of 68.4 ppm which does not seem to be negligible. In fact, here the S/S-relation would predict that 2.43 electrons are added to the π -system. Another example which provides insight into the problems associated with the understanding of experimentally determined ^{13}C -shifts is given by the attempted correlation of charge density distributions and the chemical shifts of cyclopropa-arene cations and their 1,1-dihalogeno precursors [20]. As already mentioned the total down-field shifts for these benzocyclopropabenzene ions are significantly less than 160 ppm/electron. In order to elucidate this apparent 'discrepancy' Halton *et al.* [20] proposed that a perturbation effect of the charge distribution of the chlorine and fluorine atoms in **7** (1-chloro- and 1-fluoro-2,5-diphenyl-cyclopropabenzene cation) was operative. The following resonance structure was considered to contribute significantly:



CNDO/S calculations show that the backdonation in **7** is only 0.089 electrons which is too small an effect to account for the deviation. Assuming the applicability of the S/S-relation this calculated charge corresponds to 15 ppm. Consulting *Table 2* it may be concluded that the diamagnetic shift contribution (see later) in this case plays a dominant role. Neglecting such effects can easily lead to wrong conclusions. Also the argument that the large (C, F)-coupling constant is indicative of the contribution of the given resonance structure should be taken with care. In contrast to (C, C)-coupling constants (C, F)-coupling constants require in addition to the *Fermi* contact interaction the consideration of the orbital and spin dipolar interaction in order to obtain agreement with the experiment [23].

Bloor & Breen [24] in their original work, concerning the relationship between ^{13}C -chemical shifts of polyatomic molecules and charges obtained from the CNDO/2 method, emphasized that the total but not the π -charges are linearly related to ^{13}C -shifts. Surprisingly this does not seem to be the case in the systems treated here. Thus, if the ^{13}C -shifts are correlated with the CNDO/S π -charges the deviations decrease significantly (see *Table 3*). *Jones et al.* [25] have suggested that for alternant and nonalternant hydrocarbons both π - and σ -electronic variations must be taken into account in the form of the relationship

$$\begin{aligned} \delta^{13}\text{C} &= 100 \Delta Q_{\pi} + 67 \Delta Q_{\sigma} - 76 \Delta P \\ \Delta Q_{\pi} &= Q_{\pi}(\text{Benzene}) - Q_{\pi}; \Delta Q_{\sigma} = Q_{\sigma}(\text{Benzene}) - Q_{\sigma} \\ \Delta P &= P(\text{Benzene}) - P; P: \text{Sum of the } \pi\text{-bond orders} \end{aligned}$$

It seems reasonable that the three terms have variable weight in different classes of compounds and that the two last terms even could cancel.

As already shown by *Tokuhiro et al.* [4] mainly the $\langle r^{-3} \rangle_{2p}$ values are proportional to the charges. This means that in general we can only get good results with the simple charge proportionality method when the other effects (χ_p^A , σ_r) are

Table 3. Correlation coefficients of different correlations

Method	Proportionality	r(40 ctrs.) only planar parts of molecules	r(47 ctrs.)	r(50 ctrs.)
			non planar parts included	no sp ³
I	$q^\pi \sim \delta_{\text{exp}}$	0.9364	-	-
II	$q^\pi \sim \delta_{\text{exp}} - \sigma_d$	0.8423	-	-
III	$q^{\text{tot}} \sim \delta_{\text{exp}}$	0.8576	0.8602	-
IV	$q^{\text{tot}} \sim \delta_{\text{exp}} - \sigma_d$	0.8792	0.8842	-
V	$\sigma_p \sim \delta_{\text{exp}}$	0.7755	0.7700	0.8296
VI	$\sigma_p \sim \delta_{\text{exp}} - \sigma_d$	0.8852	0.8813	0.9160 (0.8868)

of minor importance. In order to shed further light on this matter we have studied the chemical-shift differences using the more detailed model of *Karplus & Pople* [3]. The results using CNDO/S calculations are given in *Table 2*. Comparing the charge with the $\langle r^{-3} \rangle_{2p}$ column clearly reveals that they are proportional as already pointed out by *Tokuhiro & Fraenkel* [4]. Binomial expansion of expression (7) leads to equation (11)

$$b(4.65 - x)^3 = (100.54 - 64.87x + 13.95x^2 - x^3)b \quad (11)$$

$$b = (24 a_0^3)^{-1}; x = 0.35 q_A.$$

It is seen that for small x-values (which always occur for organic molecules) the third and fourth term are of minor importance, leading to a linear dependence of q_{tot} vs. $\langle r^{-3} \rangle_{2p}$. In contrast to $\langle r^{-3} \rangle_{2p}$ the $\sum_B Q_{AB}$ values reflect changes in the bonding situation of the centers. Particularly instructive are the q_{tot} and the $\sum_B Q_{AB}$ term changes for the shifts 3, 6, 15 and 26 (see *Table 2*). With a total of 50 shifts we find by means of the methods I-VI applied in this work the correlation coefficients given in *Table 3*.

Methods V and VI are considered with and without sp³-hybridized C-atoms which can not be treated by method I to IV. In **5** the fluoro-substituted C-atom experiences a σ_r -effect (neighboring benzene ring). When the ¹³C-shift of the latter C-center is included in the correlation, a different r-coefficient is obtained. This is given in parenthesis in *Table 3*.

Ditchfield et al. [26] using their *Hartree-Fock*-perturbation theory [27] have calculated the diamagnetic and paramagnetic contribution in a variety of organic compounds. An important feature of this work is that the calculated σ_d -terms vary up to 80 ppm. It is of interest to compare the σ_d values, estimated with the formula of *Goodisman & Flygare* [5] with those of [26]. For methane, ethane, propane, allene, and tetrafluoromethane the two methods yield 295, 296.2; 311, 320.2; 355, 363.2; 306, 304.3; 461, 501.9, respectively. It is seen that the agreement is satisfactory, except for tetrafluoromethane. In *Table 2* the σ_d values are listed. As expected the correlation of the paramagnetic shifts vs. δ_{exp} improves considerably when the latter is corrected by the diamagnetic term (see *Table 3* and *Fig. 3*).

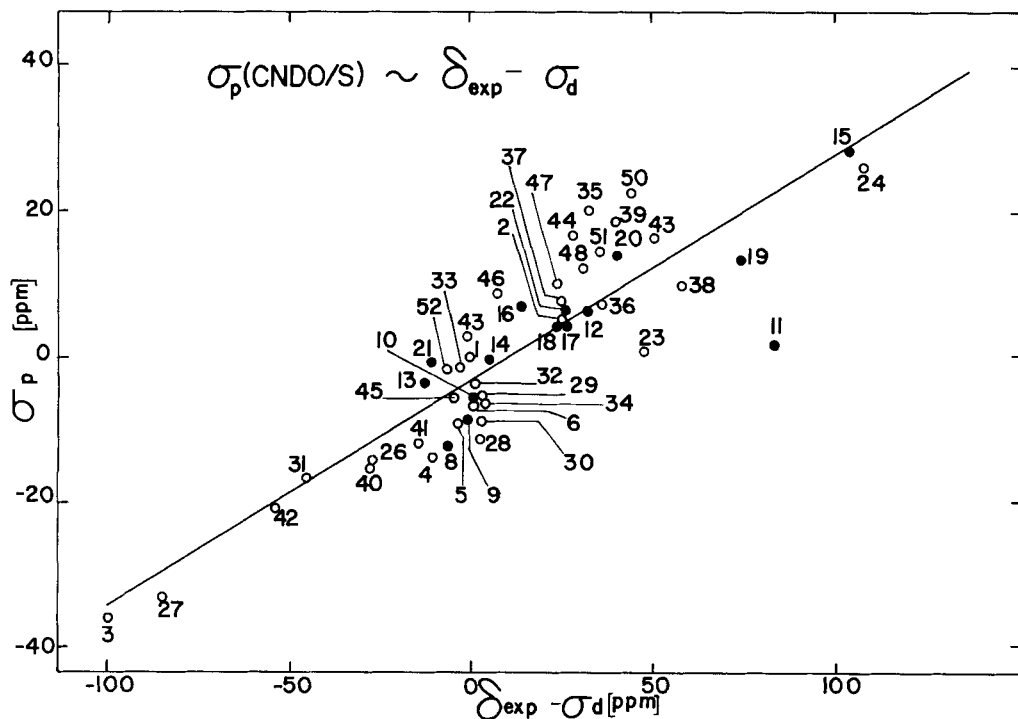


Fig. 3. Linear correlation between $\sigma_p(\text{CNDO/S})$ and $\delta_{\text{exp}} - \sigma_d$. Numbering corresponds to the last column of Table 2. ●: Fluoro compounds. Shift No. 11 undergoes a strong σ_r -effect (benzene ring). (Method VI of Table 3.) $r = 0.9160$.

Conclusion. - In summary we conclude that the often used value of 160 ppm/electron, proposed on the grounds of HMO-calculations, is not of general validity and should only be applied with extreme care [28]. The correlation of the experimental shift with the charge q_π is superior to the one with the total charge q_{tot} which must be applied for non-planar systems. Consequently, these systems call for more elaborate theoretical shift calculations. A first inspection of Table 3 suggests that all methods are of the same quality level. However, changes in the bonding situation, substitution effects, and non-planarity can not be treated by simple charge correlations. (The values of these correlation coefficients are for this reason left out in Table 3.) Our results show that in order to get consistent results for a large class of molecules it is necessary to estimate σ_p 's and σ_d 's. A clear example is provided by the fluoro compounds 4, 5, 6 and 7.

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