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The Effect of Ionicity and Hybridization on the Calculation of Spectroscopic Coupling Parameters and Dipole Moments

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Calculations have been carried out in order to calculate the *s*-character and ionicity of the carbon-halogen bonds in eight halomethanes from experimental values of (1) ^{13}C–H couplings, (2) nuclear quadrupole couplings, and (3) dipole moments. Two sets of results were obtained based on the use, first, of (1) and (2) and, second, on the use of (1) and (3). The two sets of results show a reasonable degree of consistency, under the assumptions and methods involved, and tend to support the need for considering both hybridization and charge transfer in accounting for substituent effects on the properties studied.

Es wurden Rechnungen zur Bestimmung des *s*- und des Ionencharakters von Kohlenstoff-Halogen-Bindungen in acht Halogenmethanen aus den experimentellen Daten von (1) ^{13}C–H-Koppelungen, (2) Kernquadrupolkoppelungen und (3) Dipolmomenten durchgeführt. Zwei Sätze von Ergebnissen wurden erhalten, die auf der Benutzung von (1) und (2) bzw. (1) und (3) basieren. Die Ergebnisse der beiden Rechnungen sind im Rahmen der Annahmen und Methoden konsistent und ergeben die Notwendigkeit, sowohl Hybridisierung als auch Ladungsübergang bei der Betrachtung von Substitutionseffekten auf die zu untersuchenden Eigenschaften zu berücksichtigen.

On a calculé le caractère *s* et l'ionicité des liaisons carbone-halogène dans huit halogénométhanes à partir des valeurs expérimentales (1) des couplages ^{13}C–H, (2) des constantes de couplage quadrupolaire nudéaire (3), des moments dipolaires. Deux ensembles de résultats ont été obtenus à partir de (1) et (2) et de (1) et (3). Ces deux ensembles de résultats montrent un degré raisonnable de consistance, étant données les hypothèses et les méthodes utilisées, et sont en faveur d'une intervention simultanée de l'hybridation et du transfert de charge pour rendre compte des effets de substituants sur les propriétés étudiées.

Introduction

In studying and characterizing chemical bonds, one has available a variety of experimental properties such as, e.g., dipole moments, stretching frequencies, etc. Interpretation of the latter is, however, complicated by the difficulty of relating them in a clear and unequivocal manner to the parameters (whether theoretical or empirical) which are often employed to characterize bonds. This problem is evident in the extended discussions which have centered around the relation between the character of carbon-halogen bonds and the effect of the halogen substituent on such properties as the ^{13}C–H and nuclear quadrupole couplings (*eQq*).

In their original studies of bond character based on the use of *eQq* data, DAILEY and TOWNES first assigned halogen hybridization on the basis of electronegativity differences, and then proceeded to calculate the ionicities of C–X bonds required to match the *eQq* values [*1*]. Subsequently, DAILEY used molecular dipole moments to estimate the ionic content of C–X bonds [2]. For the halomethanes, these studies yielded halogen hybridization values of 0 to 15% and C–X bond ionicities of 10 to 20%.

GORDY also evaluated ionic content from electronegativity differences, but assigned a relatively minor role to hybridization changes at the X atoms [3]. WHITEHEAD and JAFFÉ elaborated this approach by using orbital electronegativities [4]. In a further extension of these ideas, GILSON employed variable carbon orbital hybridization [5], as determined from the formula of MULLER and PRITCHARD relating $J(^{13}C\text{–}H)$ values to *s*-character [6]. MULLER [7] and DREESKAMP and SACKMANN [8] have examined this approach and agree that $J(^{13}C\text{–}H)$ depends for most compounds only on C hybridization. They concluded that the substituent affects J through the dependence of hybridization on substituent electronegativity. The interdependence of hybridization and electronegativity has been discussed in detail by BENT [9].

SHOOLERY has suggested that J should exhibit a cubic dependence on the effective nuclear charge (Z_{eff}) experienced by the *s*-electron [10]. On this basis, electronegative substituents would be expected to augment J, and GRANT and LITCHMAN have proposed that changes in Z_{eff} produced by charge withdrawal are adequate to account for the changes observed in J without involving large variations in hybridization [11]. These workers calculated Z_{eff} from bond charge transfer estimated from bond moments. (The latter were obtained by resolving dipole moments vectorially, ignoring contributions from hybridization of the halogen lone pairs.) CONSIDINE has correlated a number of diverse molecular properties with JAFFÉ's group electronegativities, calculated with C hybridization restricted to tetrahedral [12]. He has concluded that it is possible to account for the observed variations in molecular properties with substitution without invoking corresponding changes in hybridization of the C atom.

ROBINSON has found the calculated dipole moment of HCl to be quite dependent on halogen hybridization [13]. The use of pure *p*-orbitals for Cl in these computations led to ionic character inconsistent with energy considerations and with the value of $\partial\mu/\partial d$. KASTLER, using antisymmetrized functions for all seven outer halogen electrons, was able to calculate dipole moments for HF, HCl and HBr (but not HI) using only *p*-orbitals for the halogens [14]. However, SCHATZ has pointed out that KASTLER's approach leads to an unreasonably large value of eQq in HCl [15].

The above review, while not exhaustive, is representative of both the interest in these problems and the diversity of opinions associated with them. In this communication we describe yet another effort to interpret the structure of chemical bonds by relating their descriptive parameters to selected experimental quantities. For this purpose we have elected to use dipole moments (μ), $^{13}C\text{–}H$ couplings (J) and nuclear quadrupole couplings (eQq). The methods employed for calculating these quantities involve only two adjustable parameters, which are the hybridization of the halogen atom and ionicity of the C–X bond. (All other required quantities are either experimentally determined or are fixed by the method of calculation.) Thus, any pair of the three experimental quantities (μ, J and eQq) can be used to fix the two parameters, and the third observed value will then be available to evaluate the results.

Calculations

To calculate J and μ for the series $CH_{4-M}X_M$, the following functions were used:

$$\Psi_{CH} = N_{CH}\,[(1 - M\lambda^2)^{1/2}\,\psi_{CH} + M^{1/2}\,\lambda\psi_{+CH}] \tag{1}$$

$$\Psi_{CX} = N_{CX}\,[(1 - M\lambda^2)^{1/2}\,\psi_{CX} + (M - 1)^{1/2}\,\lambda\psi_{+CX} + \lambda\psi_{X-}] \tag{2}$$

$$\Psi_{X} = N_{X}\,[(1 - \lambda^2)^{1/2}\,\psi_{X} + \lambda\psi_{X-}]\,. \tag{3}$$

The ψ are normalized two electron valence bond functions, i.e.,

$$\psi_{CH} = \frac{\varphi_C(1)\,\varphi_H(2) + \varphi_H(1)\,\varphi_C(2)}{(2 + 2S^2_{CH})^{1/2}}\;;\; \psi_{X-} = \varphi_X(1)\,\varphi_X(2)$$

etc., and λ is the ionic parameter for the CX bond. Using a function of the type $\varphi_C(1)\,\varphi_H(2) + \varphi_H(1)\,\varphi_C(2) + \lambda_C\,\varphi_C(1)\,\varphi_C(2)$, COULSON [*16*] found it necessary to use $\lambda_C \approx 1$ to predict a bond moment of 0.4 D for methane with Slater orbitals. KARPLUS and GRANT [*17*] found a λ_C^2 of 0.14 necessary to match the experimental value of $J(^{13}C\text{–}H)$ in methane based on the particular choice of 9 eV for the average excitation energy. The value of J for methane may be calculated in agreement with experiment using a λ_C^2 of 0 for $\Delta E = 10.6$ eV, employing DUNCANSON and COULSON's [*18*] atomic orbitals or for $\Delta E = 10.25$ eV with TUBIS' orbitals [*19*]. Reasonable values of ΔE have been assumed to be in the range of 9—12 eV [*20*]. Considering this and the fact that replacing a H atom with a CH_3 group in methane only changes J by 1 cps (from 125 to 126 cps), no ionic character of the type $\varphi_C(1)\,\varphi_C(2)$ has been included in the CH bond description.

The method used for calculating J is based on the Fermi contact contribution to the coupling and involves the same assumptions used by MULLER and PRITCHARD [*6*]. This contribution may be written

$$J_{NN'} = \frac{\gamma_N\,\gamma_{N'}}{h\,\Delta E}\,(8\beta h/3)^2\,\langle\Psi\,|\,\delta(r_{1N})\,\delta(r_{2N})\,\Psi\rangle \tag{4}$$

where all terms have their usual meaning. When (1) is substituted in (4) we obtain the following (were $N = N_{CH}$).

$$\begin{aligned} J_{HC} = \frac{64\,\beta^2\,h\,\gamma_H\,\gamma_C}{9\,\Delta E}\,N^2\,[\varphi^2_H(0)\,\{C_0^2\,\varphi^2_C(0) + 2\,C_0\,C_i\,\varphi_C(0)\,\varphi_{C^+}(0) + C_i^2\varphi^2_{C^+}(0)\} +\\ + \varphi_H(0)\,\varphi_H(R)\,\{C_0^2\,\varphi_C(0)\,\varphi_C(R) + C_0\,C_i\,\varphi_C(0)\,\varphi_{C^+}(R) +\\ + C_0\,C_i\,\varphi_C(R)\,\varphi_{C^+}(0) + C_i^2\,\varphi_{C^+}(0)\,\varphi_{C^+}(R)\} +\\ + \varphi^2_H(R)\,\{C_0^2\varphi^2_C(R) + 2\,C_0\,C_i\,\varphi_C(R)\varphi_{C^+}(R) + C_i^2\varphi^2_{C^+}(R)\}] \end{aligned} \tag{5}$$

where $C_0 = \left(\frac{1 - M\,\lambda^2}{2 + 2\,S^2_{CH}}\right)^{1/2}$ and $C_i = \left(\frac{M\,\lambda^2}{2 + 2\,S^2_{+CH}}\right)^{1/2}$. For methane $\lambda = 0$. Using TUBIS' orbitals [*19*] the three terms in the expression are 0.0650, −0.0033, and 0.0001, respectively. Since the first term contributes 95% of the effect, the latter two are dropped. Making the substitution, $Z = \left(\frac{\varphi_{C^+}(0)}{\varphi_C(0)}\right)\left(\frac{2 + 2\,S^2}{2 + 2\,S^2_+}\right)^{1/2}$ with

$$\varphi_C = \alpha s_C + (1 - \alpha^2)^{1/2}\,p_C \text{ and } \varphi_{C^+} = \alpha_+ s_{C^+} + (1 - \alpha_+^2)^{1/2}\,p_{C^+}\,,$$

$$\begin{aligned} J_{HC} = \left[\frac{64\,\beta^2\,h\,\gamma_H\,\gamma_C}{h\,\Delta E}\,\varphi^2_H(0)\,\varphi^2_C(0)\right](N^2)\,[(1 - M\,\lambda^2)\,\alpha^2 + 2\,(M - M^2\,\lambda^2)^{1/2}\\ Z\alpha\alpha_+ + M\,\lambda^2\,Z^2\,\alpha_+^2]\,. \end{aligned} \tag{6}$$

To match the experimental value of J for methane requires that the first bracket equal 500 and

$$J_{\mathrm{HC}} = 500\, N^2 \alpha^2 \{(1 - M\lambda^2) + 2\lambda(M - M^2\lambda^2)^{1/2} Z + M\lambda^2 Z^2\}\,. \tag{7}$$

The hybridization of the covalent molecule and ionic fragments have been assumed equal for simplicity. The above expression is similar to that of MULLER and PRITCHARD [*6*] except that it includes the effect of charge induced on carbon by ionic character in the bonds not under consideration and changes due to the difference in overlap of neutral or positive carbon with the hydrogen atom in question. The above expression is also very similar to that previously derived by use of the J operator on the atomic wave function of carbon in CHXYZ molecules [*21*], except for the inclusion of the CH and $_+$CH bond overlaps and the use of normalized wave functions. The values of α for the compounds studied were determined by the method of maximum overlap [*8, 21, 22, 23*]. The discussion given in Ref. [*24*] regarding the lack of constraints on hybridization by lone pairs are equally applicable to unoccupied orbitals. For this reason, the hybridization of the ionic fragments was maintained at the value determined for the covalent molecular structures.

The dipole moments were calculated as sums of contributions from bond electrons, lone-pair electrons and positive nuclei:

$$\mu = \sum \mu_b \cos\theta_b + \sum \mu_{lp} \cos\theta_{lp} \tag{8}$$

where θ_b and θ_{lp} are the angles between the bond and lone pair, respectively, and the molecular symmetry axis, and

$$\mu_{\mathrm{bond}} = eR - e \sum r_i \tag{9}$$

$$\mu_{lp} = -\, e \sum r_k\,. \tag{10}$$

The R are bond lengths; r_i and r_k are distances to the corresponding electrons from C and X, respectively, averaged over the functions used in the maximum overlap calculations.

Nuclear quadrupole couplings were calculated from DAILEY's formula:

$$eQq_{\mathrm{mol}} = (1 - i)\,(1 - \alpha^2) eQq_{\mathrm{atom}}\,.$$

In order to compare the results of the eQq calculations with those obtained from the J and dipole moment calculations, a relationship between λ and i is necessary. The following relation was used:

$$i = \frac{\lambda^2 + \sqrt{M-1}\,\lambda^2 S_1 + \lambda(1 - M\lambda^2)^{1/2} S_2}{N_x}$$

where S_1 is the overlap between the valence bond functions $\Psi_{+\mathrm{CX}}$ and $\Psi_{+\mathrm{CX}-}$ and S_2 is the overlap between the functions for Ψ_{CX} and $\Psi_{+\mathrm{CX}-}$.

All calculations were carried out by determining the CX ionic character necessary to match the experimental values of eQq, J, and μ for increments of 0.05 from 0 to 100% in the s-character of the halogen bonding orbital. The calculations of J and μ were performed using Slater atomic orbitals. Experimental values of eQq for the molecules as gases were taken from DAILEY's tabulation [*2*]. Gas values for the dipole moments were taken from "Tables of Experimental Dipole Moments"

Table 1. *Intersection Values for the Halogen s-Character and* CX *Ionicity*

	$J - eQq$ intersection %		$J - \mu$ intersection %		
	s	i	s	i	α[a]
CH_3Cl	21.8	13.0	14.7	12.4	.529
CH_3Br	9.7	16.4	7.3	17.0	.527
CH_3I	2.5	13.5	4.3	14.7	.528
CH_2Cl_2	14.1	16.8	7.0	15.0	.568
CH_2Br_2	2.8	18.5	4.0	19.7	.559
CH_2I_2	0.1	9.6	3.1	13.5	.564
$CHCl_3$	8.2	17.5	4.8	16.0	.607
$CHBr_3$	1.3	14.3	3.8	17.2	.601

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[a] The carbon hybrid orbital pointing toward hydrogen is formulated $\varphi_C = \alpha\, s_C + (1 - \alpha^2)^{1/2}\, p_C$.

by McClellan [*25*]. Values of $J(^{13}CH)$ are available in the literature. However we used values obtained here for 25 mole % solutions in cyclohexane, since these couplings show a sizeable solvent dependence [*26*, *27*]. Infinite dilution values in an inert solvent would have been preferable but were not available.

Tab. 1 shows the bond parameters for the halomethanes which simultaneously match either the nuclear quadrupole coupling and ^{13}CH coupling constant or the dipole moment and ^{13}CH coupling constant. The last column of Tab. 1 shows the value used for the s-character of the carbon orbital directed toward hydrogen in these molecules. These values were determined by the maximum overlap procedure. Tab. 2 shows the values calculated for μ and eqQ using the s and i obtained from the intersection of the J with eQq and J with μ curves, respectively. Also given are the values obtained using the average of s and i from these intersections and for comparison, the experimental values of μ and eqQ. Fig. 1 shows the combinations of s and i which result in agreement between the observed and calculated values of $J(^{13}CH)$, eqQ, and μ for the monohalomethanes. The curves obtained for the di- and trihalomethanes are very similar, therefore not shown.

Table 2. *Calculated Values of the Dipole Moments and Nuclear Quadrupole Couplings in the Halomethanes*

	μ_{exp}	μ_{calc}[a]	μ_{calc}[b]	eQq_{exp}	eQq_{calc}[c]	eQq_{calc}[b]
CH_3Cl	−1.94	−2.37	−2.17	.6813	.7506	.7162
CH_3Br	−1.79	−2.07	−1.93	.7501	.7758	.7633
CH_3I	−1.64	−1.28	−1.51	.8424	.8159	.8282
CH_2Cl_2	−1.54	−2.28	−1.92	.7147	.7909	.7556
CH_2Br_2	−1.43	−1.14	−1.30	.7921	.7719	.7814
CH_2I_2	−1.10	+0.20	−0.65	.9043	.8348	.8670
$CHCl_3$	−1.07	−1.49	−1.30	.7557	.7985	.7773
$CHBr_3$	−1.00	−0.35	−0.71	.8456	.7955	.8183

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[a] Calculated using the values for s and i given in columns 1 and 2 of Tab. 1.

[b] Calculated using the average of columns 1 and 3 for s and the average of columns 2 and 4 for i from Tab. 1.

[c] Calculated using the values s and i given in columns 3 and 4 of Tab. 1.

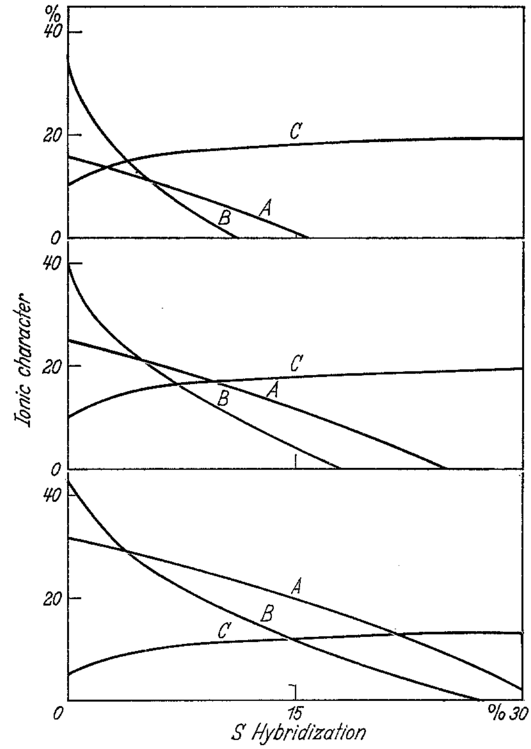

Fig. 1. Plot of Ionic character versus s-hybridization for methyl iodide (top), methyl bromide (middle) and methyl chloride (bottom). The curves are the loci of values of these two parameters which reproduce the experimental values of the nuclear quadrupole coupling (A), electric dipole moment (B), and ^{13}CH coupling (C)

Discussion

To examine the necessity of invoking variable hybridization of carbon, the first calculation of J, eQq, and μ was carried out restraining carbon to an sp^3 state. Under this condition it was necessary to allow valence bond forms with two bonds simultaneously in an ionic state in order to match the experimental value of J for $CHCl_3$ and $CHBr_3$. Also, of the eight molecules studied, only CH_3Cl exhibited an intersection of J and μ under this condition.

There has been considerable argument over whether or not interorbital and interatomic angles coincide. The next calculation was therefore carried out with hybridization coefficients determined from the experimental angles. It is interesting that under this condition it was possible to match the experimental value of J for only two molecules (CH_3Cl and CH_3Br) without including doubly ionized structures in the formulation. This result appears to support the contention that bent bonds are the rule except where excluded by symmetry [*6*].

In the third phase of this study, the hybridization of the carbon orbitals was determined by the condition of maximum total orbital overlap in the molecule. The results for the methyl halides are depicted in Fig. 1. Similar results were obtained for the di- and trihalomethanes. Due to the rather parallel nature of the curves for μ and eQq a small shift of either along the abscissa produces a large change in the ordinate. For this reason, the $eQq - \mu$ intersections are probably not very reliable. The values of CX ionicity and halogen hybridization at which the J curve intersects the eQq and μ curves are given in Tab. 1. Considering the approximations involved and rather crude wave functions used, the correlation is excellent. The transferability of the bond parameters determined in this way is shown in Tab. 2. Due to the rapid change in slope of the curve for μ in the vicinity of zero, values of μ calculated using the hybridization and ionicity from the $J - eQq$ intersections are not quantitative. However, they are the correct order of magnitude and the series members are correctly related to each other. Parameters determined by the $\mu - J$ intersections produce eQq values which agree to within 10% of experiment for all cases. Columns 4 and 7 of Tab. 2 give the values of μ and eQq calculated using the average values of s and i from the $eQq - J$ and $\mu - J$ intersections. The calculated values of J, of course, are equal to the experimental values.

These results provide an indication of the internal consistency of the bond characterizations derived from the experimental data and methods described here. The degree of consistency achieved, as indicated, e.g., in Tab. 1, is reasonably good, particularly when viewed against the various interpretations recorded in the literature. The results also provide some support for the idea that neither charge transfer nor changes in hybridization is alone adequate to account for the effects of substituents on the properties considered.

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