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THE NON-ADDITIVITY OF ^{13}C-^{19}F AND ^{13}C-H COUPLING CONSTANTS

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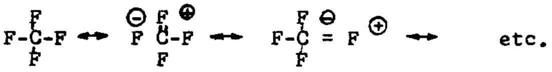
The proposal that the largest contribution to electron coupled nuclear spin-spin interactions is due to so-called Fermi contact was first advanced by Ramsey.(1) An important step in the process which has lead to the acceptance of this view is the calculation of Karplus and Grant(2) who applied Ramsey's operator to polyatomic molecules. Using valence-bond functions, involving hybrid orbitals, excellent numerical values of the coupling constants for the splitting of boron, carbon and nitrogen with protons were obtained. A recent review,(3) while recording the general agreement that the contact mechanism is most important in proton-proton interactions, has pointed out that data for couplings between other nuclei, especially ^{13}C-^{19}F splittings, have been interpreted as indicating that the contact mechanism is not an adequate explanation. For example, the studies of Harris(4) and Muller and Carr(5) clearly show that instead of the expected monotonic increase of $J_{13}C-_{19}F$ with increasing fluorination of methane, the value of CF_4 (257 c.p.s.) is less than that for CHF_3 (272 c.p.s.).

In their calculation of coupling constants Karplus and Grant(2) dealt only with hydrogen bonded to another element; that is to say σ bonds. However, Pauling(6) has pointed out that the carbon-fluorine bonds of organic polyfluorides have double bond character. He postulated that resonance forms such as II and III make a significant contribution to the stabilization of molecules with two or more fluorine atoms on a single carbon:



$$\overset{F}{\underset{F}{F-C-F}} \longleftrightarrow \overset{\ominus}{F}\ \overset{F\ \oplus}{\underset{F}{C-F}} \longleftrightarrow \overset{F\ \ominus}{\underset{F}{F-C}} = F^{\oplus} \longleftrightarrow \quad \text{etc.}$$

I II III

Since Pauling's explanation of the short carbon-fluorine bond distance by this double-bond-no-bond resonance other unusual properties of organic polyfluorides have been similarly interpreted.(7)

It is unreasonable to expect a theory developed for pure σ bonding to apply to a bond with considerable π character. Therefore the fact that splittings between atoms for which double-bond-no-bond resonance is important are not in strict analogy with the data derived from uncomplicated cases and should not be interpreted as an inadequacy of the contact mechanism.

Furthermore, it is of interest to note that those cases where Malinowski's additivity relation(8) for J_{13}-C-H in substituted methanes has been shown(9) to fail are just those which *double-bond-no-bond resonance* is important.(7) This is readily understandable in terms of Karplus' and Grant's work. The valence-bond functions they used(2) involve hybrid orbitals and $J_{^{13}C-H}$ must necessarily be a function of the *s*-character of the orbital carbon used to bond hydrogen. If the carbon atom is involved in a bonding situation which is inadequately described by the hybrid orbitals used in the calculation, then deviations from an additivity relation based on a generalization of such calculations must be expected.

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