2.5: Proton delta Values and Electronegativity

Chemical shifts are of considerable value in structural investigations involving nuclei in different locations. Several examples of such uses of proton chemical shifts will be described shortly, but first we shall consider possible correlations between δ and other structural parameters, since much effort has been expended in this direction. Most important are attempted correlations of δ with electronegativities and some parameters which have been shown to be useful in defining chemical reactivities. From the earlier discussions regarding the relation between chemical shift and electron density, one would expect electronegativity effects to be displayed by substituent groups, so placed as to influence the electron density around a given nucleus. Of course, the substituent or substituents can act also to change the chemical shift by effectively making a change in the solvent as well.

Dailey and Shoolery[7] have studied substituent effects in ethyl derivatives by determining differences in chemical shifts between the methylene and methyl protons as a function of X for CH_3CH_2X. The system is a particularly desirable one because the effect of X in altering the medium would be expected to be nearly the same at the two positions. An excellent correlation was noticed between the difference in resonance line positions for CH_3 and CH_2 protons of ethyl halides and the Huggins electronegativity values. The relationship was nicely linear (see Fig. 2-3) although there seems to be no real a priori reason for expecting this to be the case. With the aid of the linear relationship and chemical shifts for the protons of other ethyl derivatives, apparent electronegativities were assigned to a wide variety of substituent groups. The ultimate worth of the figures so obtained is yet to be demonstrated through correlation with other properties related to electronegativities.

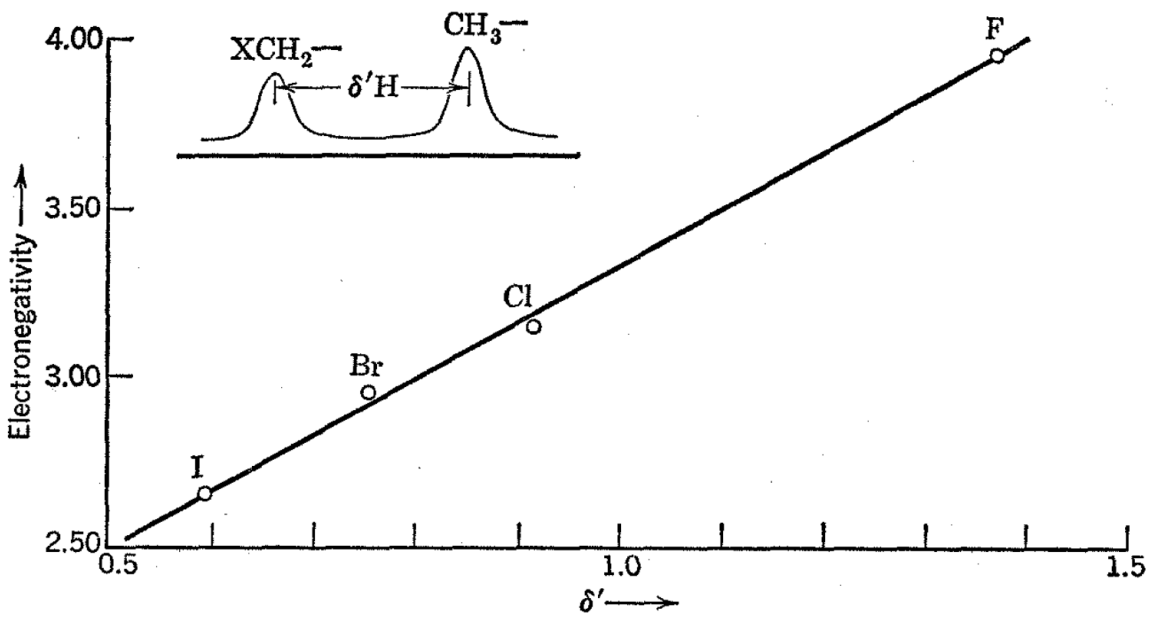

Fig. 2-3. Chemical shift between CH_2 and CH_3 protons of ethyl halides as a function of the Huggins electronegativity values. (*Courtesy of B. P. Dailey and the Journal of the American Chemical Society.*)

7 B. P. Dailey and J. N. Shoolery, J. Am. Chem. Soc., 77, 3977 (1955). Similar measurements have been made by Allred and Rochow.