

2.6: delta and Hammett's sigma constants

Considerable work has been done over the last 30 years on chemical reactivities of aromatic compounds. Hammett⁸ has shown how much of the resulting data for reactivities of groups connected to benzene rings carrying substituents in the meta and para positions can be correlated with the aid of parameters δ (substituent) and ρ (reaction).

$$\log \frac{k_1}{k_0} = \sigma \rho$$

Each substituent can usually be assigned a σ constant the value of which depends on whether the substituent is located at a meta or para position. In turn, each reaction may be assigned a ρ parameter which measures the sensitivity of its rate to changes of substituents in the meta and para positions. The reaction parameter turns out to be a function of temperature, solvent, salt concentrations, and the character of the reagents employed. Hammett's relationship holds with very considerable precision for the ionization constants of meta- and para-substituted benzoic acids and the alkaline saponification rates of the corresponding ethyl esters. With its aid, one can compute many thousands of individual rates and equilibrium constants from rather small tables of substituent and reaction parameters. Hammett's σ constants are of particular interest to the present discussion and are taken normally to represent the difference in the logarithms of the ionization constants of the meta- or para-substituted benzoic acids and benzoic acid itself.

Numerous attempts have been made to correlate σ with various physical properties, such as polarographic reduction potentials, infrared vibration frequencies, and wavelengths of maximum absorption in electronic spectra. Gutowsky and coworkers have published data on the chemical shifts of a large number of meta- and para-substituted fluorobenzenes which are of considerable pertinence to the correlation of δ values with chemical reactivity parameters. Figure 2-4 shows the degree of correlation of fluorine δ values with Hammett's σ constants, and it is immediately clear that a different relationship holds from that customarily observed for chemical equilibrium and rate constants. In the first place, the points corresponding to substituents at meta positions fall along a line of substantially different slope from the best line drawn through the points for substituents located at para positions. This behavior has no exact parallel in chemical-reactivity studies.

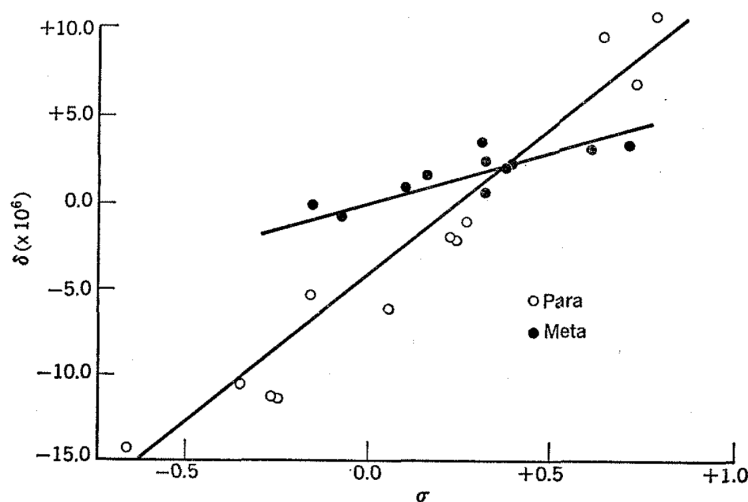


Fig. 2-4. δ values for ^{19}F resonance absorptions in meta- and para-substituted fluorobenzenes as a function of Hammett's substituent constant σ . (After Gutowsky and coworkers.)

Gutowsky interprets the data of Fig. 2-4 to mean that the resonance effects of substituent groups are more important in determining chemical shifts than are the other factors that make up the over-all electrical effect. The observed scatter of the points is expected on this basis, since the resonance contribution is already included for each substituent in the σ constants, at least to the extent that it influences chemical reactivity. Taft¹⁰ has evaluated the resonance contributions of substituents to their σ constants and has corroborated Gutowsky's suggestion that resonance effects are particularly important in determining the influence of substituents on fluorine δ values.

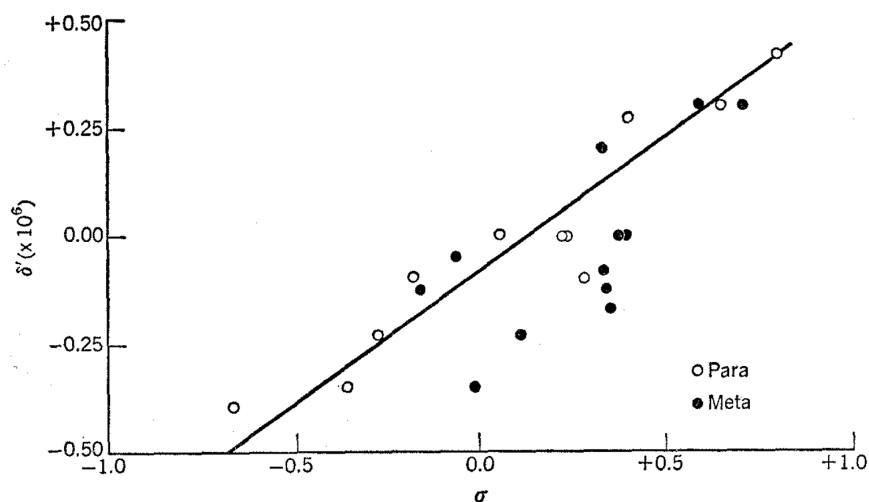


Fig. 2-5. Variation of proton δ' values (C_6H_{12} as standard) for substituted benzenes with Hammett's σ constants.

The situation for protons is not quite so simple. Dailey¹¹ and Bothner-By⁴ and coworkers have measured proton chemical shifts for a variety of benzenoid compounds. Some typical data are presented in Fig. 2-5, and it is seen that there is no simple relationship between σ and δ . Furthermore, no obvious tendency exists for the meta and para points to lie along lines with different slopes as is observed with substituted fluorobenzenes.

It is possible that some of the above anomalies may be due to abnormal diamagnetic shielding effects produced by the unsaturation electrons of the benzene ring, since when an aromatic compound is placed in a magnetic field, the π electrons circulate around the ring so as to produce a rather substantial local magnetic field directed normal to the ring which can influence the chemical shift. Waugh¹² has shown with 1,4-decamethylenebenzene that the position of each methylene group with respect to the circulating current of electrons above and below the ring is quite critical in determining the chemical shift of the methylene protons. The apparently abnormal chemical shift of acetylenic protons may be due to circulation of the unsaturation electrons around the axis of the triple bond in such a way as to set up a local field which opposes the applied field along the triple bond, thus causing more shielding than is normal for an unsaturated atom.

8 L. P. Hammett, "Physical Organic Chemistry," chap. 7, McGraw-Hill Book Company, Inc., New York, 1940.

9 H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, J. Am. Chem. Soc., 74, 4809 (1952).

10 R. W. Taft, Jr., J. Am. Chem. Soc., 79, 1045 (1957).

11 P. L. Corio and B. P. Dailey, J. Am. Chem. Soc., 78, 3043 (1957).

12 J. S. Waugh and R. W. Fessenden, J. Am. Chem. Soc., 79, 846 (1957).