The π-Inductive Effect. Application to π-Electron Distributions in Monosubstituted Benzenes

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Two important time-independent electronic effects have been recognized by organic chemists in describing the changes in electron distribution brought about by a substituent, the inductive and mesomeric effects.[1] The former effect may be subdivided into the σ- and π-inductive effects. The importance of the π-inductive effect in the case of the halogenobenzenes has been pointed out[2] and Burdon[3] has used the concept of a π-inductive effect to rationalize, in a qualitative fashion, nucleophilic aromatic substitution in polyhalogenobenzenes. However there has been no attempt to investigate the importance of the π-inductive effects of other substituents (NO_2, NH_2, CN, etc.), on the ground-state electron distribution of substituted benzenes.

The change in potential at the substituted carbon atom due to the π-inductive effect of the substituent in a monosubstituted benzene can be derived from spectroscopic data. This involves an analysis of the second-order inductive shift of the benzene 2600 Å band[4] in substituted benzenes and the first-order inductive shift of the azulene visible band. The interesting feature is that the values for the change in potential obtained by these two methods are for the most part in good agreement with one another. The frequency shifts in the substituted azulenes were obtained by neglecting the mesomeric effect of the substituent, and the agreement between the two methods, suggests that this is a reasonable approximation. The first-order inductive shift in the azulene visible band depends on the *change* in electron density at the position of substitution on excitation, and hence it seems a reasonable assumption that the electron distribution in the ground state will be determined by the π-inductive effect. The question then arises as to the possibility that the ground-state electron densities in substituted benzenes are also largely determined by the π-inductive effect of the substituent. Taking $\beta = -2{\cdot}6$ ev (spectroscopic data),[5] together with the spectroscopic data for the first-order inductive shift of the azulene band, the differential changes in coulomb integrals at the substituted carbon atom are as shown in the Table. (In the case of F and OMe, where data were not available, the inductive parameters were derived from the second-order inductive shift of the benzene 2600 Å band.)

The change in coulomb integral associated with replacing the CH group in benzene by nitrogen to form pyridine is shown in the last line of the Table. It is interesting to note that the value for this parameter derived solely from spectroscopic data agrees well with that suggested on other grounds.[6–8]

TABLE

Substituent	Differential change in coulomb integral in units of β
NH_2	$-0{\cdot}656$
OMe	$-0{\cdot}565$
F	$-0{\cdot}419$
Cl	$-0{\cdot}169$
Me	$-0{\cdot}157$
Br	$-0{\cdot}141$
CN	$0{\cdot}158$
CO·Me	$0{\cdot}258$
NO_2	$0{\cdot}416$
(N)	$0{\cdot}894$

Within the framework of Hückel theory the ground-state π-electron distributions of some monosubstituted benzenes have been calculated, taking into account only the π-inductive effect of the substituent. Recently Spiesecke and Schneider[9] have suggested that ^{13}C chemical shifts might be employed to obtain information about π-electron density distributions in aromatic systems and this method has been used in the case of azulene.[10] In the case of monosubstituted benzene derivatives, the contribution to the shielding constants from the anisotropy of the substituent at the *para*-position may be neglected as may the σ-inductive effect, so that the major contribution will arise from the change in π-electron density.[9] The Figure shows a plot of ^{13}C chemical shift against the change in π-electron density at the *para*-carbon atom. The correlation is surprisingly good and lends considerable support to the hypothesis that *ground-state* π-electron distributions are determined largely by the π-inductive effect of the substituent. In the case of the *meta* ^{13}C chemical shifts, contributions arising from the magnetic anisotropy and σ-inductive effects of the substituent may be expected to be small, and the calculated π-electron densities would then suggest that the shifts should be uniformly small as is found experimentally.[9]

Most of the common substituents have π-inductive and mesomeric effects of the same sign, and it has been pointed out[11] that these will lead qualitatively to similar electron distribution in monosubstituted benzenes, except for a small difference at the *meta*-position. In general therefore it will be difficult to assess the relative importance of the two effects. In the case of aniline however a distinction can be made. The π-inductive repulsion is greatest when the NH_2 group is planar. The mesomeric effect is also greatest when the NH_2 group is planar. Recent evidence[12] shows quite clearly that aniline is non-planar in the *ground state* and this would seem to be good evidence for the dominance of the π-inductive effect. For the nitroso-group the π-inductive and mesomeric effects might be expected to be opposite in sign.[13] Depending on the electron distribution, electron affinity, and ionization potential of the attached π-system, either effect may become dominant and give rise to opposite effects.

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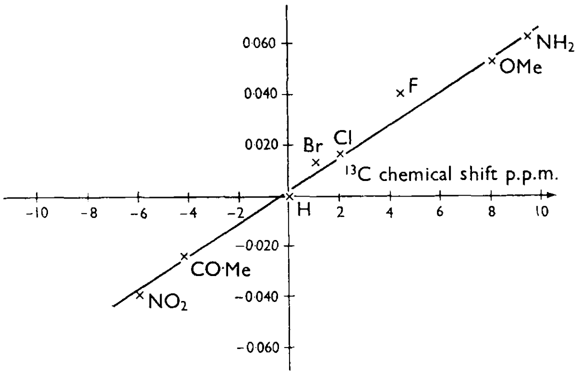

FIGURE

Difference in π-electron density calculated by "π-inductive model" versus ^{13}C *chemical shift at the* para-*position in monosubstituted benzenes.*

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