

CHEMICAL SHIFTS AND ELECTRON DENSITIES IN SUBSTITUTED BENZENES

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ABSTRACT

Calculation of electron densities at various positions of nitro-benzene, benzaldehyde and benzoic acid have been made using conventional MO method, taking for coulomb and resonance integral values given by Orgel *et al.* for nitrogen and oxygen. It has been established that, although the calculated electron density values agree fairly well with the chemical reactivity of these compounds, electron density at ortho, meta or para position was not directly proportional to the chemical shift in proton resonance spectra of these compounds. It has been established that the proton resonance spectra is affected by the magnetic dipole of the aromatic molecule which gives rise to diamagnetic anisotropy. Thus Corio and Dailey's suggestion that the magnitude of chemical shift may be utilized in evaluating the electron densities at various positions of a substituted benzene cannot be substantiated.

It is now a well established fact that the chemical shifts observed in the proton resonance spectra indicate the difference in electron densities at chemically non-equivalent protons (Gutowsky and Hoffmann, 1951; Ramsey, 1950, 1952). The shift arises from the small magnetic field set up by the electrons, which opposes the applied field and is directly proportional to it. This is commonly called the diamagnetic shielding of the proton by the electrons. The result of this shielding effect is a set of absorption lines which correspond to the number of non-equivalent protons present in the molecule. Ethyl alcohol, for example, shows three principal groups of absorption lines which correspond to the non-equivalent CH_3 , CH_2 and OH protons.

Of late Corio and Dailey (1956) have suggested that the relative chemical shifts observed in the substituted benzenes compared to the parent compound may be utilized in the evaluation of the relative electron densities at ortho, meta and para positions of the substituted compound. The published data of Corio and Dailey is, however, at variance with the relative chemical reactivities of the various positions and with the theory of induced alternating polarity (Wheland and Pauling, 1935) for most of the compounds recorded by them. The sign convention adopted by Corio and Dailey for the chemical shift is such that a positive shift for a proton indicates that it is less diamagnetically shielded than the proton in benzene (that is, the density of electron cloud in the neighbourhood of the proton is smaller than that about a proton in benzene), and a negative shift corresponds to a proton which is more diamagnetically shielded than the protons in benzene. The signs of chemical shift from Corio and Dailey's work suggest that the electron densities are lowered at all the three positions—ortho, meta and para—in some of the substituted benzenes, although theoretically it is predicted that the substituent should induce an alternation of polarity, increasing the electron densities at ortho and para positions while lowering them at the meta position and vice versa, depending on the electronegativities of the substituents.

However, in Corio and Dailey's estimation the electron density at ortho, meta and para positions of the substituted benzene is expressed relative to that in benzene, while the chemical reactivity expresses the electron density at ortho, meta and

para positions relative to one another. Hence in order to make a logical correlation between the two sets of values a complete electron density calculation should be made on some of the substituted benzenes for which the proton resonance and the chemical reactivity data are available. With this end in view electron density calculations by LCAO MO method have been made on nitro-benzene, benzaldehyde and benzoic acid, the results of which are reported in the present paper.

METHOD OF CALCULATION AND RESULTS

The conventional MO calculation is too well known to be described here (cf. Basu, 1954). The perturbation calculations (Basu and Bhattacharya, 1957) that may be used in the case of heterocyclic compounds are rather drastic approximations in the present case, since the compounds contain more than one hetero atom in different state of hybridization. The uncertainty in this type of calculation arises from the selection of parameters for the coulomb and the exchange integrals for the hetero atoms. Wheland and Pauling (*loc. cit.*) and Longuet-Higgins and Coulson (1949) have used certain values for these parameters in the case of a number of hetero aromatic compounds in order to get electron densities consistent with the chemical reactivity. Orgel *et al.* (1951) have shown that these parameters put too much weight on formal charge and give wrong values for the dipole moments of these hetero aromatic compounds. A suggestion made by Wheland and Mann (1949) to get around this difficulty has also been shown by Orgel *et al.* to be invalid for hetero compounds. They have suggested certain values for these parameters for oxygen, nitrogen and carbon in different state of hybridization from the considerations of experimental and theoretical resonance moment of the compounds containing these hetero atoms. These values have been found to give the electron densities consistent with the chemical reactivity in addition to the right value for the dipole moment.

In our calculations we have used the following coulomb (E) and exchange (β) integrals as suggested by Orgel *et al.*

$$\begin{aligned}
 (C \text{ attached to N or O}) \quad E_N &= E_C + \beta & \beta_{CC} &= \beta \\
 & E_O = E_C + 2\beta & \beta_{CO} &= 1.4\beta \\
 & E_C = E_C + 0.1\beta & \beta_{CN} &= 1.2\beta \\
 & & \beta_{NO} &= 0.6\beta
 \end{aligned}$$

With these values the calculated electron densities at various positions of nitro-benzene, benzaldehyde and benzoic acid are given in Fig. 1 (*a, b, c*). In benzene the electron densities at various positions are all equal to unity. In Table I are given the change (dq) in electron densities at ortho, meta and para positions of the various compounds studied relative to benzene.

TABLE I
Electron densities at ortho, meta and para positions in some substituted benzenes

Compound	dq		
	ortho	meta	para
Nitro-benzene	-0.1894 (+0.97)	-0.0098 (+0.30)	-0.2282 (+0.42)
Benzaldehyde	-0.0776 (+0.73)	+0.0026 (+0.23)	-0.0646 (+0.37)
Benzoic acid	-0.0524 (+0.63)	+0.0006 (+0.10)	-0.0436 (+0.17)

Within parentheses are given the values of chemical shift as reported by Corio and Dailey for these compounds.

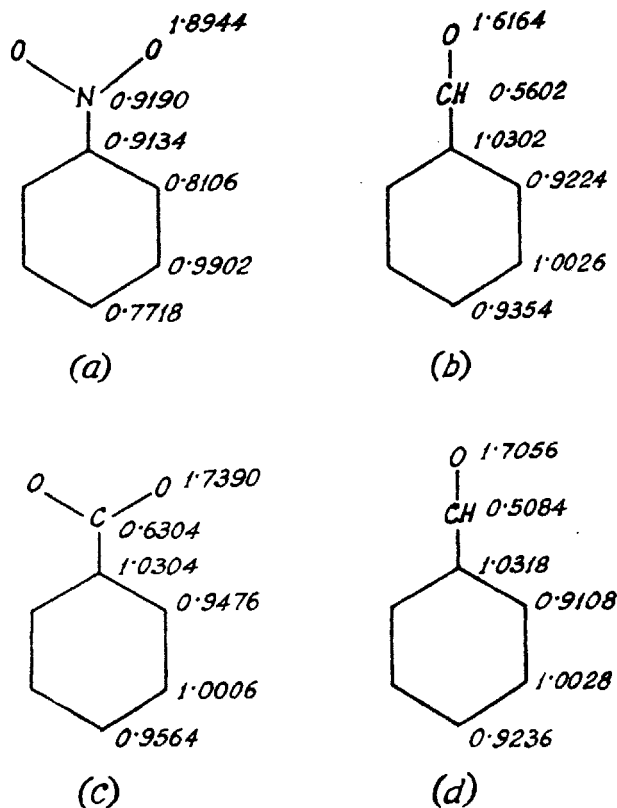


Fig. 1: Electron densities in nitro-benzene, benzaldehyde and benzoic acid.

DISCUSSION

From Table I it is evident that the electron density is lowered, compared to benzene, at all the positions in nitro-benzene, which is also in qualitative agreement with the positive chemical shift, indicating less diamagnetic shielding of protons at these positions. The lowering of electron density is more at para position with higher chemical shift, than that at meta position with lesser chemical shift. For ortho position, however, there is no agreement between the magnitude of the chemical shift and the electron density at all. In fact no such agreement is expected for the ortho position as it is well established from chemical considerations that this position behaves rather abnormally in many substitution reactions. This has been explained as due to steric effect (commonly known as ortho effect) and/or hydrogen bonding effect. The ortho position in nitro-benzene shows a large chemical shift, i.e. less diamagnetic shielding, which is consistent with the assumption of hydrogen bonding. Hence the chemical shift at the ortho position does not depend on the electron density alone. Even for the meta and para positions the magnitude of chemical shift is not directly proportional to the electron density. There must be some other factor or factors operative in these systems which is/are bringing about a chemical shift in the same direction as the lowering of electron density.

This fact shows up much more prominently when we consider the sign and magnitude of chemical shift for ortho, meta and para positions of benzaldehyde and benzoic acid. It is evident from Table I that the chemical shift for all the positions in these two compounds is finite and positive, but the electron density at meta position is higher, compared to benzene, in the case of benzaldehyde and is about the same as benzene in the case of benzoic acid. From the consideration of electron density alone we expect a negative shift for the former and no shift for the latter.

An explanation for this may be found in the suggestion recently made by Bernstein *et al.* (1957) in order to explain the chemical shift in the proton resonance spectra of polynuclear hydrocarbons. In principle their model was the same as the one used by Pauling (1936) in order to explain the diamagnetic anisotropy of aromatic compounds. The principle may be explained considering the case of benzene. If we treat the electrons in benzene as free to move in a circular path, then on placing the molecule in a magnetic field of strength H perpendicular to the plane of the molecule, a current will be induced in the ring which will give rise to a magnetic moment of $3e^2a^2H/2mc^2$, where a is the radius of the ring. Bernstein *et al.* assumed that the phenyl ring in the magnetic field will behave as if a magnetic dipole of strength $3e^2a^2H/2mc^2$ has been placed at the centre of the ring with its axis parallel to the axis of hexagonal symmetry. This magnetic dipole will produce a field at the position of the ring proton and will thus reinforce the external field. The frequency shift due to this effect is given by

$$\lambda = (10^6 e^2 a^2 / 2mc^2) \cdot 1/r^3 \quad \dots \quad (1)$$

where r is the distance of the proton from the centre of the ring. In benzene, since r is the same for all protons, no difference is noted in the resonance frequency of the six phenyl protons, but this enhanced magnetic field is responsible for the difference in resonance frequencies of the phenyl and ethylenic protons. In the case of substituted benzenes considered in the present paper, it is evident that the nitro, carbonyl and carboxyl groups can undergo mesomeric interaction with the π -electrons of the phenyl ring. As a result the strength of the magnetic dipole will be changed and its axis will be displaced towards the substituent away from the centre of the ring. Consequently the protons at ortho, meta and para positions will each be at a different magnetic field due to molecular magnetic dipole and hence will show different chemical shift. The chemical shift will be determined by the electron density alone for those protons which are further away from the axis of the magnetic dipole, that is probably the protons at the para position. So it is evident that Corio and Dailey's suggestion that the chemical shift may be set proportional to the electron density cannot be justified either theoretically or experimentally.

That this disagreement is not due to any defect in the MO calculation itself is shown by the fact that the calculated electron densities are in complete agreement with the chemical reactivities of the various positions in the case of substituted benzenes considered here. Thus it is evident that relative to ortho and para positions the meta position has a higher electron density in all the compounds (Fig. 1). In the substitution reaction, therefore, the cationoid attack always takes place at the meta position (Wheland and Pauling, *loc. cit.*). This also confirms the classification of these substituents as meta-orientating by the organic chemists from a systematic study of a large number of substitution reactions. Since ortho and para positions are at lower electron densities they should be susceptible to anionoid attack. In fact under appropriate conditions such anionoid attack does take place, e.g. on fusion with solid sodium hydroxide nitrobenzene gives nitrophenol where OH group goes to ortho or para position.

Finally we must establish that our selection of parameters has been such as to make the calculation self-consistent. With this end in view we have recalculated the electron densities in benzaldehyde taking the coulomb integral for oxygen

equal to $E_c + 2.5\beta$ instead of $E_c + 2\beta$. The calculated values of electron densities are given in Fig. 1(d). It is evident that this change in coulomb integral changes the electron density for the various positions in the ring in the second decimal place. We may safely assume therefore that our parameters are self-consistent. As there is a second order variation in electron density with resonance integral no alteration in this quantity was made over that given by Orgel *et al.* from resonance moment consideration.

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