ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 7, pp. 1291–1295. © Pleiades Publishing, Ltd., 2010.
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Mechanism of Influence of *para*-Substituents on the Carbon Atoms in the Side Chain of Aromatic Compounds

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Received May 9, 2009

Abstract—Mechanism of conductivity of the effect of *para*-substituents on the side chain of aromatic compounds based on the induction and the resonance effects and the effect of "positive charge" is considered.

DOI: 10.1134/S1070363210070133

In the work presented the mechanism of conductivity of electronic effects of *para*-substituents (Y) through the benzene ring and the side chain containing multiple bonds in the compounds of the type Y–C_6H_4–CH=CH–CN and Y–C_6H_4–O–CH=CH_2, Y = $N(Me)_2$, OMe, F, H, NO_2 is considered.

The mechanism of conductivity in such compounds is often described on the basis of model of π-polarization according to which the effect of the substituent Y on the side chain ZX is determined by spatial polarization of π-electronic system Z–X by the dipole of substituent Y [1, 2]. The known fault of this model is its inapplicability to substituents ZX not containing π-bonds. Ability of the substituent Y to influence the highly polar Z–X bonds and some other statements (see below) are also doubtful.

For the explanation of interaction of *para*-substituents Y and ZX in the benzene derivative YC_6H_4ZX a model was suggested based on the inductive and the resonance effects of substituent Y and the effect of "positive charge" [3]. We plan to use this model for the above-mentioned compounds.

Effect of "positive charge" may be described as follows. If in the narrow series of structurally similar molecules built from non-transition elements of the general formula ABC where the electronegativity (χ) of A and C is higher than the electronegativity of B, and therefore B is a positively charged atom, χ(A) increases, and the negative charge on C increases in spite of the inductive effect of A.

Let us assume, that in the benzene derivative the substituent ZX (for example, ZX = CF_3, CN, NO_2, COOH, $CONH_2$, etc.) creates positive charge on C^1 atom in the place of its bonding. In this case the effect of substituent Y on the electron density of Z is determined by the degree of alteration of positive charge on C^1 under the action of this substituent. The increase in the positive charge (in the case of electron-acceptor substituent Y) is accompanied by the increase in the negative charge on Z and vice versa, the decrease in the positive charge (in the case of electron-donor substituent Y) causes the decrease in this charge. The change in the charge on C^1 may be caused by the direct influence of Y on this atom as well as by its influence on the electronegativity of C^2 and C^6 carbon atoms of the benzene ring. The charge transfer from the C^1 to Z atom increases with the increase in the electron-accepting ability of Y as well as the transfer of charge from Z to C^1 atom at the increase in the donor ability of Y.

Substituents Y are characterized by the inductive (σ_I) and mesomeric (σ_R) parameters. The major part of the electron-accepting substituents (CF_3, CN, NO_2, etc.) has the parameters of the same sign. For example, for NO_2 $\sigma_R = 0.15$, $\sigma_I = 0.63$ [4]. This means that they have the same direction. The majority of the electron-donor substituents [NH_2, $N(Me)_2$, etc.] is characterized by the parameters of different signs, e.g., for NH_2 $\sigma_R = -0.76$, $\sigma_I = 0.10$ [4]. This means that these effects are opposite to one another, and in this case the resonance effects prevail over the inductive ones. Special group

is formed by OMe and halogens.Their parameters are close in value but have different signs. For example for F: $\sigma_R = -0.44$, $\sigma_I = 0.50$ [4].

The effect of substituent Y on the atoms of the side chain is usually described by the equation containing σ_I and σ_R parameters characterizing the substituent Y:

$$\Delta P = P - P^0 = \rho_I\sigma_I + \rho_R\sigma_R. \quad (1)$$

Here some property P in the substituted compound is compared with the property P^0 in the unsubstituted one (Y = H) [5], and ρ_I and ρ_R are constants determining the degree of influence of the inductive and the resonance effects of substituent Y respectively.

For description of the resonance effect (σ_R) one of four resonance scales is chosen (σ_R, σ_R^{BA}, σ_R^+, σ_R^-), and in some cases the nonlinear resonance scale is used [6].

As the property P the value of the ^{13}C chemical shift is frequently used. Values of ^{13}C chemical shifts have sufficiently complex nature, nevertheless, the importance of the paramagnetic member $\sigma^P = -\text{const}\Delta E^{-1}r^{-3}\Sigma Q$ is evident. Here ΔE^{-1} is the reciprocal value of the (averaged) electronic exciting energy, r^{-3} is the reciprocal radius cube of the 2*p*-orbital of the atom under measurement, ΣQ is the bond order, charge density matrix. Two last values are associated by some researchers with the electron density on the carbon atom.

For the structurally similar aromatic compounds linear correlations of different type connecting δ_C and the electron densities on carbon atoms calculated by means of the quantum-chemical methods are described [7], and theoretical basis of such correlations is published in [8]. The consideration of variations in δ_C permits conclusions on the trends in alteration of charge on the carbon atom in this series.

Measurements of δ_Z at low concentrations of organic substance in the inert solvent showed that electron-acceptor substituents cause the upfield shift of δ_Z [9]. The observed shift is opposite to the expected one ("reverse" shift) because such substituents might cause the decrease in electron density on Z, and hence, cause the downfield shift. Electron-donor substituents (Y) also cause the reverse effect, but with the opposite sign. In this case the downfield δ_Z is observed. But the majority of electron-donor substituents are differently directed, that is why C^α carbon atom, the first atom in the side chain of substituent, is deshielded at the introduction of the electron–donor substituent Y. In some cases such atom is shielded what is connected with the competition of the inductive and the resonance effects of these substituents. The term "reversive" shows that Bromilow et al. assume the dependence of δ_C on the electron density on carbon atom, that is, on ΣQ.

When the charge on the atom Z is positive the change in the electron density on X is also deter-mined by the effect of "positive charge." When Y is the electron-acceptor substituent the electron density decreases, and if Y is the electron-donor substituent, it increases.

The ability of the two-parametric Eq. (1) to reproduce with high accuracy experimental data was checked on the large number of examples, that is, on *para*- and *meta*-substituted styrenes, phenylacetylenes, benzonitriles, carbonyl compounds [10], and in the inves-tigation of conductivity of the effects produced by the substituents Y, for example in $Y–C_6H_4–C\equiv C–C(O)OEt$ [11], etc.

In this work the experimental data on chemical shifts ^{13}C for the C^1, C^α, C^β, C(CN) atoms in *para*-substituted β-arylacrylonitriles $Y–C_6H_4–C^\alpha H=C^\beta H–C\equiv N$ [12] are used. To explain the character of changes in δ_C for this compound we suggest that C^1 atom and C^α, C^β, and CN atoms of the side chain are charged positively. It is doubtless that C^1 atom in this compound is charged positively since the electronegativity of $–CH=CH_2$ group (χ 2.9–3.0) is higher than the electronegativity of phenyl (χ 2.6–2.8) [13,14]. Besides, χ of this group increases at the substitution of hydrogen atom with the electronegative –CN group. Let us compare the character of variation in ^{13}C chemical shifts on C^α and C^β carbon atoms in *trans*-$Y–C_6H_4–C^\alpha H=C^\beta H–CN$ (**I**) and $Y–C_6H_4–C^\alpha(OMe)=C^\beta H_2$ **II**. In the second compound the hydrogen atom on C^α is substituted with the electronegative methoxy group, that is, C^α is the positively charged carbon atom. Let us assume that $Y = NO_2$. Here and below δ_C values are presented in ppm with respect to Y = H. Negative δ_C values mean that the shielding takes place. From the above it follows that for compound **I** $\delta(C^\alpha) = -2.52$, $\delta(C^\beta) = 4.86$ [12], and for compound **II** $\delta(C^\alpha) = -2.20$, $\delta(C^\beta) = 3.40$ [15].

As seen, the character of variation in δ_C of C^α and C^β carbon atoms in these compounds is similar.The introduction of electron-acceptor substituent $Y=NO_2$ in both cases leads to the shielding of C^α and deshielding of C^β. According to the "positive charge" effect it becomes possible if the charge of C^α in compound **I** is

positive. The charges on C^{β} atom in compounds **I** and $Y–C_6H_4–C^{\alpha}H=C^{\beta}(CN)_2$ (**III**) is probably also positive. Let us compare the character of δ_C variations in these compounds at the assumption that Y = CN. For substance **I** $\delta(C^{\alpha})$ = –2.04, $\delta(C^{\beta})$ = 4.08, $\delta_C(CN)$ = –0.88 [12], while for compound **III** $\delta(C^{\alpha})$ = –3.35, $\delta(C^{\beta})$ = 5.57, $\delta_C(CN)(\gamma E)$ = –0.65 [15].

In this case δ_C variations have the same character, while the sign of charge on the C^{β} atom bound with two CN groups is evidently positive. Hence, the sign of charge on C^{β} atom in the compound **III** is also positive. It is explained by the fact that the electronegativity of CN group (χ = 3.3) is sufficiently high, and also by the presence of multiple bonds in the side chains of compounds under study.

For such bonds high concentration of electron density on bonds and the extension of the π-bond peaks in the direction perpendicular to the bond line in the distribution of the deformational electron density [16] are characteristic. Due to that C^{α} and C^{β} atoms of multiple bond despite the presence of neighboring hydrogen atoms show the deficiency of electron density, namely they are involved in the "positive charge" effect as the positively charged atoms.

Experimental data on the variations in δ_C of the C^1, C^{α}, C^{β}, C(N) in the compounds $Y–C_6H_4–C^{\alpha}H=C^{\beta}H–C\equiv N$ [12] in relation to the same compound with Y = H, and also the frequencies of C≡N bond vibrations (ν, cm^{-1}) and the integral intensities of absorption of vibrations of this bond A ($l\ mol^{-1}\ cm^{-2}$) are presented below.

Y	$\delta(C^1)$	$\delta(C^{\alpha})$	$\delta(C^{\beta})$	δ(CN)	ν	A
NMe_2	–11.69	0.20	–6.99	1.74	2211.1	4943
OMe	–7.08	–0.19	–2.81	0.77	2217.1	3583
F	–3.80	–1.16	–0.09	0.00	2221.1	2952
H	0.00	0.00	0.00	0.00	2220.5	2451
NO_2	5.83	–2.52	4.86	–0.98	2225.1	1542

Electron-donor subsituent Y = NMe_2 causes the decrease in the positive charge on C^1 (shielding). According to the "positive charge" effect it leads to the increase in the positive charge on C^{α} (deshielding) and negative charge on C^{β} (shielding). As we suggest that C^{β} atom is charged positively, according to the same effect the shielding of C^{β} must cause deshielding of the carbon atom from the CN group and an increase in the negative charge on nitrogen. This means that the increase in polarity of the nitrile bond takes place. If the electron-acceptor substituent Y, for example, NO_2 group, is introduced, it must lead to deshielding of C^1, shielding of C^{α}, deshielding of C^{β}, and shielding of the nitrile carbon atom (decrease in positive charge of carbon) and decrease in the negative charge on nitrogen (decrease in the polarity of nitrile bond).

At the assumption that the charges on C and N atoms are constant in the course of vibration, integral intensity of absorption of the band of C≡N bond vibration A in the IR spectrum must be proportional to the square of bond polarity. According to the above-presented analysis electron-donor substituents Y must increase its intensity, and the electron-acceptor ones must decrease it in relation to the compound with Y = H. Note here that form of the C≡N bond vibration is not characteristic because it mixes significantly with the vibration of the adjacent C–C bond. That is why the fact of variation in the intensity of the absorption band observed in the spectrum cannot be a reliable sign of variation in the character of chemical bond caused by intramolecular interactions. But correlation of the observed tendency of variation in the intensity of absorption depending on the nature of substituent Y with the tendency of variation in the polarity of nitrile bond also depending on the nature of substituent and evaluated on the basis of the "positive charge" effect improves this reliability.

The effect of mainly electron–donor or electron-acceptor substituents Y on the ZX side group we considered above. These substituents exhibit opposite effect on the electron density of Z and X atoms. Halogens and methoxy group reveal the properties of donors as well as of acceptors. In *para*-position halogens must exhibit mainly +*M*-effect and increase the electron density on C^1. At the same time halogens have significant strong inductive effect influencing the C^2 and C^6 atoms and hence competing with +*M*-effect. Mesomeric effect of methoxy group appears on the background of noticeable inductive effect of this group. Note that in the first approximation effect of halogens and the methoxy group on the atoms of ZX-group is the result of addition of the effect of "positive charge" caused by the inductive and the resonance effects of these substituents. Just this addition explains δ_C values close to zero (see for example δ_C value for Y = F).

One of the specific features of the experimental data for *cis*- and *trans*-compounds $Y–C_6H_4–C^{\alpha}H=C^{\beta}H–C\equiv N$ (^{13}C NMR data) which is not explained by

the polarization model is that the results of effect of substituent Y on C≡N group are close despite the different location of these groups in relation to Y [12].

trans-Compound	*cis*-Compound
C^{α} $-3.3\sigma_I - 1.3\sigma_R^0$	$-3.5\sigma_I - 0.6\sigma_R^-$
C^{β} $6.0\sigma_I + 8.1\sigma_R^{BA}$	$5.5\sigma_I + 8.5\sigma_R^{BA}$
CN $-1.2\sigma_I - 1.1\sigma_R^+$	$-1.5\sigma_I - 1.0\sigma_R^+$

In our model of interaction of Y and ZX such similarity of data seems evident.

Note that the proposed mechanism of conduction of the effect of substituents into the side systems satisfactorily describes the variations in ^{13}C chemical shift of the side chain carbon atoms in following compounds: Y–C_6H_4–CH=CHC(O)–C_6H_5 [17], Y–C_6H_4–CH=CH–C(O)OEt, Y–C_6H_4–C≡C–C(O)OEt [11]. But with the help of this mechanism it is impossible to explain the variations in ^{13}C chemical shift in the compound C_6H_5–CH=CH–CO–C_6H_4Y [16] which is connected evidently with the conformational lability of such compounds [18].

Let us also consider the mechanism of conduction of the effect of the substituent Y in *para*-substituted phenylvinyl ethers Y–C_6H_4–O–CH=CH_2.

Data on δ_C [19], vibration frequencies, ν (cm^{-1}), and the integral intensities of the absorption bands A (l mol^{-1} cm^{-2}) of the double bond CH=CH in the IR spectra of these compounds [20] are listed below.

Y	$\delta(C^1)$	$\delta(C^{\alpha})$	$\delta(C^{\beta})$	ν	A
NH_2	–7.69	1.79	–2.24	–	–
NEt_2	–	–	–	1641	3750
H	0.00	0.00	0.00	1646	2490
NO_2	4.29	–2 .13	3.95	1647	1790

For the compounds of such type the mechanism of interaction of Y and ZX is also based on the above-described effects. Introduction of the electron-acceptor substituent, for example, NO_2, causes the decrease in the electron density on C^1 (deshielding) resulting in the increase in electron density on the oxygen atom, the decrease in its electronegativity, and the increase in the negative charge on C^{α} (shielding). The latter factor according to the "positive charge" effect favors the decrease in electron density on C^{β} (deshielding of this atom). The introduction of the electron-donor substituent Y leads to opposite results, that is, to the increase in the electron density on C^1 leading to the decrease in the electron density on the oxygen atom, the increase in χ(O), the decrease in the electron density on C^{α} (deshielding of this atom), and its increase on C^{β} (shielding). Hence, at the introduction of electron-acceptor substituent the polarity of the double bond increases, and in the presence of the electron-donor one, it decreases.

IR spectral data show [20] that in vinyl aryl ethers having strong electron-acceptor and electron-donor *para*-substituents two conformers A and B exist.

In the latter most stable one the planes of the vinyl and aryl fragments are oriented close to the plane of C–O–C fragment. For this conformer Chuvashev et al. [20] have calculated the charges on C^{α} and C^{β} carbon atoms of the vinyl bond and the polarity of this bond in relation to the nature of *para*-substituent by means of the PPDP/C method. It was shown that the polarity of the bond increases at the introduction of the electron-donor substituent and decreases in the case of the electron-acceptor one. Variations in A value of the CH=CH_2 double bond in the IR spectra of this compound (see above) agree with the analyses of variation in electronic densities on C^{α} and C^{β} atoms calculated in [20] and by us on the basis of ^{13}C NMR data.

Hence, the model we suggested describes the mechanism of conduction of the effect of substituent Y to the side chain atoms in these compounds as the electron density perturbation created by the substituent on C^1 atom of benzene ring by means of its resonance and inductive effects transferred along the side chain due to the operation of the "positive charge" effect. Such perturbation is transferred along the σ- as well as π-bonds of the compounds under study. The model permits to describe correctly the tendency in variation of ^{13}C chemical shift along the side chain. The suggested model apparently gives a definite physical sense to two-parametric Eq. (1).

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