PERTURBATION THEORY OF SUBSTITUENT EFFECT. QUANTUM CHEMICAL STUDY OF THE POSITIVE BRIDGING EFFECT

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Mechanism of the so-called "positive bridging effect" was studied on the basis of an equation which can be viewed as a quantum chemical analogue of the Hammett equation. From this study it follows that the effect is presumably due to solvation effects of the reaction medium.

One of the classical tools of the physical organic chemistry for studying the transmission of substituent effect is the use of linear-free energy relationships (LFER). A great amount of experimental material accumulated so far made it possible to formulate simple empirical rules allowing the Hammet ϱ constants to be systematised and qualitatively interpreted for reactions in a series of structurally similar skeletons. For instance, the "transmission factors" for simple structural groups such as $-CH_2-$, $-N=N-$, $-CH=CH-$ *etc.* were thus determined by means of the so-called $\varrho - \varrho$ technique[1]; these factors were shown to be remarkably constant regardless of the reaction type. This phenomenon was discussed in detail from the point of view of the correlation analysis[1,2]. In an absolute majority of cases, these "transmission factors" are smaller than 1, in accordance with an intuitive idea that the sensitivity of a given reaction to the transmission of substituent effect should decrease with increasing distance of the substituent from the reaction center. However, in recent years several sets of reactions were found for which these intuitive ideas do not hold. Thus, Litvinenko and coworkers[3-5] have found that in the reaction of 4'-substituted 4-aminodiphenyls (DP), 4-aminodiphenyl ethers (DPE), 4-aminodiphenyl sulphides (DPS) and 4-aminodiphenylamines (DPA) with picryl chloride the Hammett constants increase in the order $\varrho_{DP} < \varrho_{DPE} < \varrho_{DPS} < \varrho_{DPA}$, *i.e.* they are larger for compounds bearing a bridging heteroatom rather than for 4-aminodiphenyl. The finding of this so-called positive bridging effect stimulated immediately a wide discussion, because of discrepancy with the generally accepted views and also with results of some experimental studies, in which a small to zero transmission factor was found for —O—, —S— and —NH— bridges in substituted diphenyl ethers, diphenyl sulphides and diphenylamines[6-8]. However, the ensuing experimental studies did not disprove, but on the contrary corroborated the existence of the positive bridging effect[9-15]. A more complete survey of experimental results can be found in the review by Litvinenko[2]. However, the mechanism of this effect remained unclear. On the basis of a correlation analysis it has been suggested that the existence of the positive bridging effect necessarily requires strengthening of the resonance interactions to occur between the bridging atom M and both the benzene nuclei, but this qualitative explanation did not specify in detail the manner in which this strengthening should take place. Moreover, it is clear that a correlation analysis alone cannot provide a more profound elucidation of this effect. For this reason, it is necessary to turn to the quantum theory which describes the molecular properties at a microscopic level.

Based on the second-order perturbation theory, we recently derived an equation[16,17] which can be regarded as a quantum chemical analogue of the Hammett equation. This relationship made it possible to interpret theoretically the laws for the transmission of substituent effect in a great number of reactions on various structural skeletons[17,18]. One of the results of this approach is the possibility of theoretically calculating the transmission factors for various structural groups, such as —CH=CH—, —N=N— *etc.*. The aim of this work is to elucidate at a microscopic level the reasons for strengthening of the resonance interactions between the bridging groups —O—, —S— or —NH— and the benzene nuclei in the diphenyl system and to contribute thus to a better understanding of the mechanism of the positive bridging effect.

THEORETICAL

As the Hammett equation can be applied only to reactions in conjugated systems, one can suppose that the transmission of substituent effect characterised by the ϱ constant is determined first of all by the π-electronic structure of a given skeleton. Therefore, it can be expected that for a theoretical description of the transmission of substituent effect it will be sufficient to turn to the quantum chemical methods working only with the so-called π-electron approximation. As shown earlier[17], a satisfactory interpretation of the Hammett ϱ constants can be achieved using even the simple HMO method. However, a generalisation covering cases which require electronic repulsion to be included has also been possible and was already done[18–20]. The substituent effect was modelled only by the change $\Delta\alpha_\mu$ in the Coulombic integral for an atom bearing a substituent and an equilibrium or a rate process was then described by the change $\Delta\alpha_\nu$ in the Coulombic integral at the reaction center. Using the second-order perturbation theory leads to Eq. (*1*) which can be regarded as a quantum chemical analogue of the Hammett equation:

$$\log (k_{\mu\nu}/k_{0\nu}) = -\pi_{\mu\nu}\,\Delta\alpha_\mu\,\Delta\alpha_\nu/2{\cdot}3RT\,. \qquad (1)$$

In Eq. (*1*), $\pi_{\mu\nu}$ denotes the atom-atom polarisability. The Eq. (*1*) makes it possible to interpret the reaction constants ϱ for a given reaction on a series of various structural skeletons. However, it has already been stressed[17] that Eq. (*1*) can be used for calculating the ϱ constants only relative to a chosen standard. Starting from Eq. (*1*), the ratio of constants for the given and the standard skeleton can be expressed by Eq. (*2*):

$$\varrho_i/\varrho_0 = \pi^i_{\mu\nu}\,\Delta\alpha^i_\nu/\pi^0_{\mu\nu}\,\Delta\alpha^0_\nu\,. \qquad (2)$$

If the perturbation $\Delta\alpha^i_\nu$ for a given reaction within a given series can be considered as roughly constant and independent on the kind of the skeleton, the Eq. (*2*) then

reduces to Eq. (3) indicating that there exists a linear relationship between the magnitude of the ϱ constant and the atom–atom polarisabilities.

$$\varrho_i/\varrho_0 = \pi^i_{\mu\nu}/\pi^0_{\mu\nu} . \qquad (3)$$

The regression line which describes this relationship should pass through the origin and its slope is equal to $\varrho_0/\pi^0_{\mu\nu}$. This simple functional dependence has really been found in a number of cases[17]. The ϱ_i/ϱ_0 ratio can also be interpreted in terms of the Palm's $\varrho - \varrho$ technique[1] as a transmission factor for skeleton i. The Eq. (3) then offers a possibility of theoretically calculating this transmission factor on the basis of quantum chemical quantities. A comparison of ϱ constants for the protonation of 4-substituted anilines, 4'-substituted 4-aminodiphenyls and 4-aminostilbenes as well as 4-aminoazobenzenes[2] may serve as an example substantiating the validity of Eq. (3) and illustrating the calculation of the transmission factors. The dependence of the experimental values of ϱ constants upon the calculated values of the atom–atom polarisabilities is given in Fig. 1. The unsubstituted molecules of aniline (*1*), 4-amino-

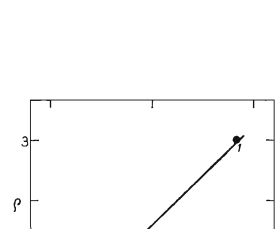


FIG. 1

Dependence of Experimental Values of ϱ Constants for Protonation of Amines (50% C_2H_5OH/H_2O, 20°C) upon Calculated Values of Polarisabilities $\pi_{\mu\nu}$

1 Substituted anilines, *2* substituted aminodiphenyls, *3* substituted aminostilbenes, *4* substituted aminoazobenzenes. Experimental data were taken from ref.[2].

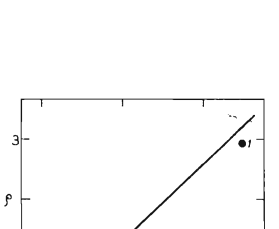


FIG. 2

Dependence of Experimental Values of ϱ Constants for Dissociation of Phenols (60% C_2H_5OH/H_2O, 20°C) upon Calculated Values of Polarisabilities $\pi_{\mu\nu}$

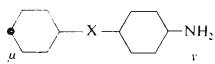
1 Substituted phenols, *2* substituted hydroxyazobenzenes. Experimental data were taken from ref.[2].

diphenyl (*II*), 4-aminostilbene (*III*) and 4-aminoazobenzene (*IV*) were used as the quantum chemical models for the polarisability calculations. By choosing the substituted anilines as the standard, the transmission factors for groups —C_6H_4—, —CH=CH— and —N=N— are given by the ratios ϱ_{II}/ϱ_I, ϱ_{III}/ϱ_I and ϱ_{IV}/ϱ_I, respectively. From the very good fit noted in Fig. 1 it is clear that the theoretical transmission factors $(\pi^i_{\mu\nu}/\pi^0_{\mu\nu})$ will be close to the experimental values.

The dissociation of substituted phenols and 4-hydroxyazobenzene (Fig. 2) may serve as another example illustrating the relationship (*3*). The experimental values of ϱ constants were taken again from the literature[2,10,11]. Although in this case a somewhat greater scattering is observed, it is still clear that the simple expression (*3*) correctly reflects the most principal features of the transmission of substituent effect.

Having in hand the Eq. (*3*) as a means for the theoretical description of the Hammett ϱ constants, we can now turn attention to the problem of the positive bridging effect. In the course of studies on the transmission of substituent effect in reactions of 4′-substituted 4-aminodiphenyls, 4-aminoazobenzenes, 4-aminostilbenes and 4-aminobenzophenones with picryl chloride, Litvinenko and coworkers[3–5] have found that, according to expectation, the ϱ constants for these reactions are smaller than the ϱ constant for reactions of substituted anilines. Contrastingly, the values of ϱ constants found for 4′-substituted 4-aminodiphenyl ethers, 4-aminodiphenyl sulphides and 4-aminodiphenylamines show that the substituent effect is transmitted, despite of introduction of a bridging heteroatom, more effectively than in 4-aminodiphenyl chosen as the reference compound. Let us assume the values of ϱ constants for the former series of compounds (anilines, aminodiphenyls, aminostilbenes and aminobenzophenones), in a certain sense, as "normal" and let us try to determine as to whether the Eq. (*3*) is fulfilled in this series. As can be seen from Fig. 3, the linear dependence given by Eq. (*3*) holds very well for all members of the series. A somewhat larger deviation can be observed for substituted benzophenones; the reason for this deviation will be discussed below. However, an attempt to include in the same dependence the compounds exhibiting a positive bridging effect leads to unacceptably large deviations from linearity. A comparison of the polarisability values $\pi_{\mu\nu}$ for these compounds with the value for 4-aminodiphenyl as the reference compound reveals that the substituent effect should be transmitted in these compounds by about two orders of magnitude less effectively than in 4-aminodiphenyl. Such a fundamental discrepancy can be accounted for only by assuming that the quantum chemical model for calculating the polarisabilities presumably does not take into account an important structural factor which specifically operates just in 4-aminodiphenyl ether, 4-aminodiphenyl sulphide and 4-aminodiphenylamine. Our model for calculating the polarisabilities was based on idealised planar unsubstituted molecules of the general formula *V* (Scheme 1). In order to remove the above inconsistency let us try to modify the HMO model Hamiltonian for 4-aminodiphenyl

ether, 4-aminodiphenyl sulphide and 4-aminodiphenylamine so as to achieve an accordance of the polarisability values calculated on the basis of the modified model with the theoretical polarisability values "read" from the regression line (Fig. 3) for a normal set of skeletons. Inclusion of a bridging heteroatom is described in the HMO model by values of the Coulombic and resonance integrals α_X and β_{CX}, res-



V

X = —CH=CH—, —O—, —Se—,
—N=N—, —S—,
C=O, —NH—

SCHEME 1

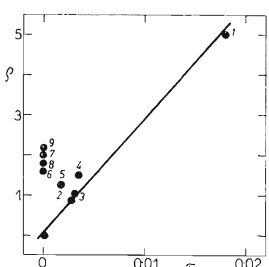


FIG. 3

Dependence of Experimental Values of ϱ Constants for Reactions of Amines with Picryl Chloride upon Calculated Values of Polarisabilities $\pi_{\mu\nu}$

1 Substituted anilines, *2* substituted aminostilbenes, *3* substituted aminoazobenzenes, *4* substituted aminodiphenyls, *5* substituted aminobenzophenones, *6* substituted aminodiphenyl ethers, *7* substituted aminodiphenyl sulphides, *8* substituted aminodiphenyl selenides, *9* substituted aminodiphenylamines. Experimental data were taken from ref.[2].

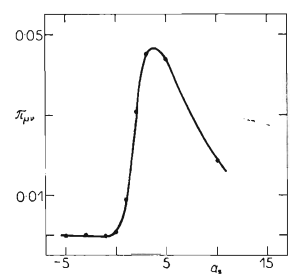
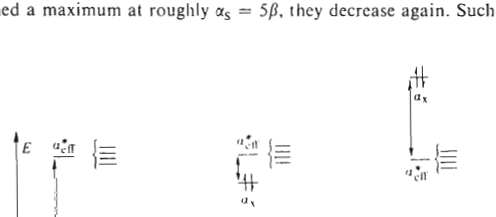


FIG. 4

Dependence of Calculated Values of Polarisabilities $\pi_{\mu\nu}$ upon Magnitude of the Coulombic Integral α_S in Aminodiphenyl Sulphide

pectively. As has been shown, the standard values of these parameters recommended by Stretwieser[21] for —O—, —S— and —N— lead to unexpectedly low polarisability values. In an example of modification of the model Hamiltonian, let us now follow the effect of changes in these parameters upon the atom–atom polarisability values. Fig. 4 shows the dependence of the value of $\pi_{\mu\nu}$ on the magnitude of the Coulombic integral α_S in 4-aminodiphenyl sulphide. It can be seen that the standard value of $\alpha_S = -1\beta$ corresponds to a nearly zero value of $\pi_{\mu\nu}$. The values of $\pi_{\mu\nu}$ increase by several orders of magnitude with increasing magnitude of α_S, which corresponds to a decrease in the effective electronegativity of the sulphur atom, and having attained a maximum at roughly $\alpha_S = 5\beta$, they decrease again. Such a depen-



SCHEME 2

dence of polarisabilites upon the effective Coulombic integral of the bridging heteroatom can be qualitatively explained by means of orbital interactions in the following manner: let us suppose that we have two isolated benzene nuclei characterised by a set of occupied and unoccupied molecular orbitals. The bridging heteroatom introducing two electrons into te conjugation is characterised by one doubly occupied orbital whose energy expresses the effective electronegativity of the bridge X. If we allow the initially isolated fragments to interact *via* inclusion of the resonance integral β_{CX}, the extent of conjugation is then given, at a constant value of β_{CX}, only by the Coulombic integral α_X of the bridging heteroatom. The interaction of the occupied orbital on the fragment X with the unoccupied orbitals on the benzene fragments is decisive for the magnitude of the resonance effects (whose increase raises the polarisability values). This interaction increases with decreasing magnitude of the difference $|\alpha_X - \alpha^*_{eff}|$ (Scheme 2). The extent of delocalisation is affected by an increase in the absolute value of the resonance integral (Fig. 5) similarly as by a decrease in the effective electronegativity of the atom X, except that in the former case the values of polarisabilities $\pi_{\mu\nu}$ increase monotonously with an increase in $|\beta|_{CX}$.

From these results it follows that an increase in the resonance interactions required by the correlation analysis[1,2] can be achieved at a microscopic level in two ways – by an increase in the absolute value of the resonance integral and by a decrease in the effective electronegativity of the bridging heteroatom X. In view of the fact that the real molecules of 4-aminodiphenyl ether, 4-aminodiphenyl sulphide and 4-aminodiphenylamine are non-planar and that therefore $|\beta|_{CX}^{real} < |\beta|_{CX}^{planar}$ ($|\beta|_{CX}^{real}$ thus lie still in the region for which the values of $\pi_{\mu\nu}$ are nearly zero – see Fig. 5), it is probable that the reason for the positive bridging effect can be sought first of all in a decrease in the effective electronegativity of the bridging atom X. What remains to be elucidated is the mechanism of this decrease in electronegativity.

In this context it is useful to turn back to the experimental results indicating that the magnitude of the positive bridging effect in the reaction of substituted amino derivatives Y-C_6H_4—X—C_6H_4—NH_2 with picryl chloride decreases for X in the order NH > S > O. The above reaction can be regarded as a nucleophilic substitution by the amino group lone pair at the electron-deficient C—Cl bond in picryl chloride. In the transition state of this reaction a partial charge transfer from the NH_2 group takes place, *i.e.* the electron density in the lone electron pair on the NH_2 group decreases. Now it is necessary to realise that a similar interaction, though unreactive, may utilise also the lone electron pairs on the bridging atom X; stated differently, some "solvation" of the lone electron pairs on the bridge X is taking place[16]. A partial decrease in the electron density in "solvated" lone electron pairs on the atom X can be described in the HMO model, which does not explicitly assume the solvating reagent, just by the required decrease in the effective electronegativity of the bridging atom X. The above mentioned deviation of the ϱ constant for the reaction of substituted aminobenzophenones with picryl chloride from the expected regression line can be explained in a similar way. In this case, however, obtaining a "correct" polarisability

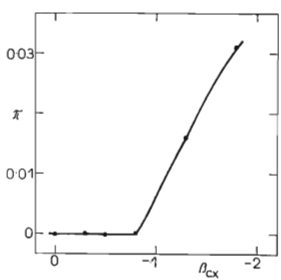


FIG. 5

Dependence of Calculated Values of Polarisabilities $\pi_{\mu\nu}$ upon Magnitude of the Resonance Integral β_{CX} in Aminodiphenylamine

value necessitates to raise the electronegativity of the carbonyl oxygen to a value of about $\alpha_0 = -2\beta$. This increase in electronegativity can be easily understood if one realises that in this case the lone σ electron pairs on the carbonyl oxygen are "solvated" by picryl chloride. A partial decrease in the electron density in these σ orbitals leads to formation of a partial positive charge at oxygen. Such a positively charged oxygen atom then exhibits an increased electronegativity to π electrons. This interpretation is supported by an increase in values of the transmission factors determined experimentally in cases where the carbonyl group is bonded directly in a complex with BF_3, BCl_3 *etc.*[2,22].

In some cases, a strengthening of the transmission factors may be due not only to intermolecular interactions of the type of "solvation by a reagent", but also to the presence of intramolecular factors. Thus, for instance, the ϱ constant for the dissociation of 4'-substituted 2,4-dihydroxyazobenzenes is significantly larger than that for the dissociation of 4'-substituted 4-hydroxyazobenzenes. An increase in the transmission factor for the —N=N— group is ascribed in this case to an intramolecular hydrogen bridge between the 2-hydroxy group and nitrogen of the azo group[2,22,23].

Based on this analysis, the existence of the positive bridging effect can be attributed to the specific solvation effect of the reaction medium. In some special cases this in principle intermolecular mechanism can be replaced by specific intramolecular interactions, for instance, of the hydrogen bond type.

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