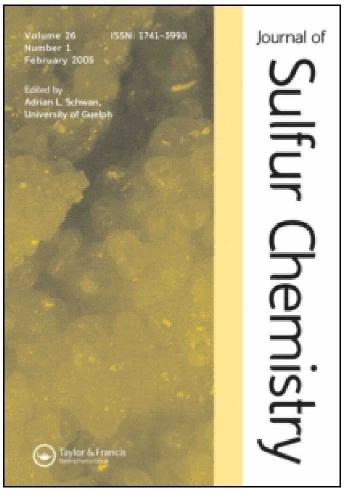

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Problems Involved in the Elucidation of the Donor-Acceptor Nature of Substituents in Aromatic Sulfur-Containing Radical Anions

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Problems Involved in the Elucidation of the Donor-Acceptor Nature of Substituents in Aromatic Sulfur-Containing Radical Anions

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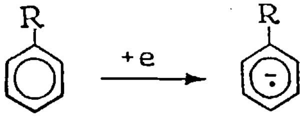
A review of data in the literature indicates that the subdivision of substituents into donors and acceptors is of value for uncharged sulfur-containing aromatic compounds but appears somewhat useless for radical anions of the same molecules. A novel general approach is suggested for the characterization of the substituent effects in radical anions. The method employs correlation diagrams to evaluate the difference between the orbital energies of the aromatic moiety and the substituent. The approach is combined with a variety of experimental data and presented here.

Sulfur-containing aromatic radical anions are growing in importance for organic synthesis. Because of this, the elucidation of the donor-acceptor nature of substituents in radical anions is becoming an urgent problem.

Aromatic radical anions are of special interest. Radical anions with aromatic nuclei exhibit rather high stability. These radical anions are formed when aromatic molecules acquire one electron without subsequent bond destruction. Radical anions have all the bonds which were present initially; radical anions differ from initial molecules by an unpaired electron (Scheme 1).



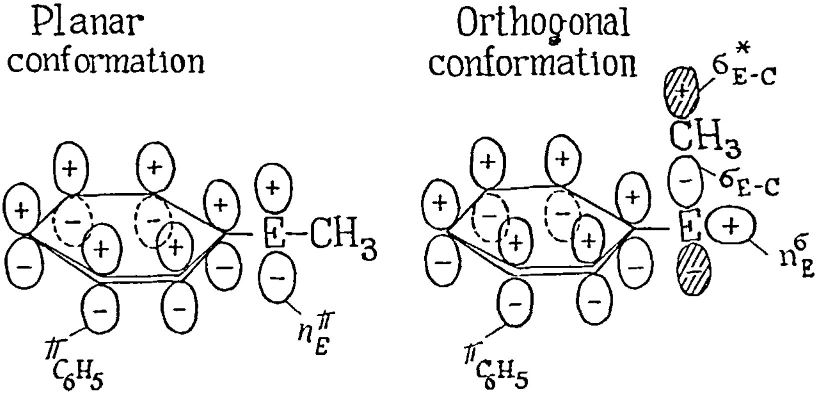
Scheme 1

Thus, a one electron transfer changes the total number of electrons in an aromatic molecule by one unit. What does such a change imply?

Organic molecules contain dozens of conjugated electrons. At first sight it seems that the change of these dozens by only one electron is not a significant effect.

The analysis of our own and literature data shows, however, that one electron transfers give rise to pronounced changes in effects of substituents on molecular properties.

Conjugative interactions between aromatic rings and ER (E = O, S) substituents are usually assumed to occur through the p-type lone pair of the sulfur (oxygen) atom, being important only when the ER group is coplanar with the aromatic system. This kind of interaction is responsible for the planarity of phenol[1] and thiophenol[2] because the planar structure is stabilized by delocalization of the sulfur or oxygen lone pair (Scheme 2).



E = S, O

Scheme 2

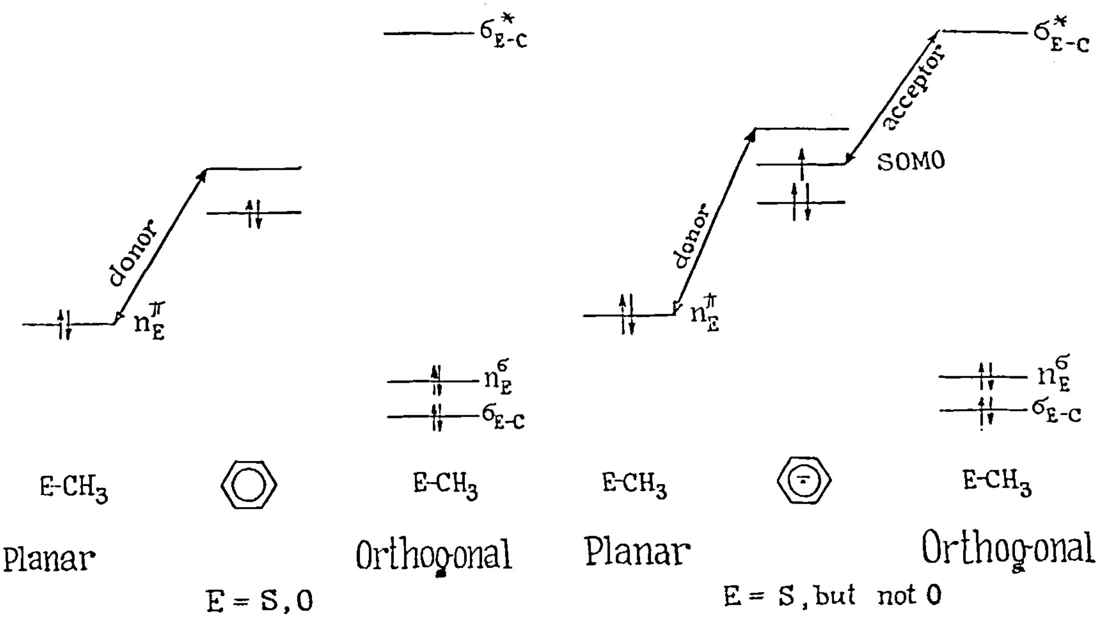
However, even when the ER group adopts an orthogonal conformation, conjugative interaction can, in principle, occur[3] between the π-system of the aromatic ring and the substituent through the doubly occupied σ and σ^* molecular orbitals of the ER bond (Scheme 2).

In practice, such interactions are small when the molecule is uncharged because of the large energy gap between the π-type orbitals of the aromatic ring and σ (σ^*) orbitals of the ER group (Scheme 3).

Such a $\pi - \sigma^*$ interaction may become significant for radical anions.[4] A one-electron transfer affects the highest π-orbital, which in the neutral molecule is unoccupied; the energy gap between the one-electron occupied π-orbital and the σ^*-orbital of the substituent is reduced (Scheme 3).

From the chemistry of phenol and thiophenol it is known that in substituted benzenes SR or OR groups are π-donors in the most common planar conformation. But the same groups can also act as π-acceptors in an orthogonal conformation. In this case, the requirements for interaction between the orbitals of ring and substituent to be significant are satisfied. The electron acceptor capability of a substituent such as SR is favored in the radical anion state, since the energy gap between the singly occupied π-orbital and the vacant σ^* orbital is lower than in the uncharged initial state.

In the planar conformation the important interactions are those occurring between the sulfur lone pair of the π-type (n_E^{π}) and the lowest unoccupied molecular orbital (LUMO) of a negative benzene fragment. In the orthogonal conformation interactions occur between the singly occupied molecular orbital (SOMO) of a benzene anion and the vacant low-lying σ^* orbital associated with the SR bond (Scheme 3). Both interactions are stabilizing, but the results in each case are quite different: while



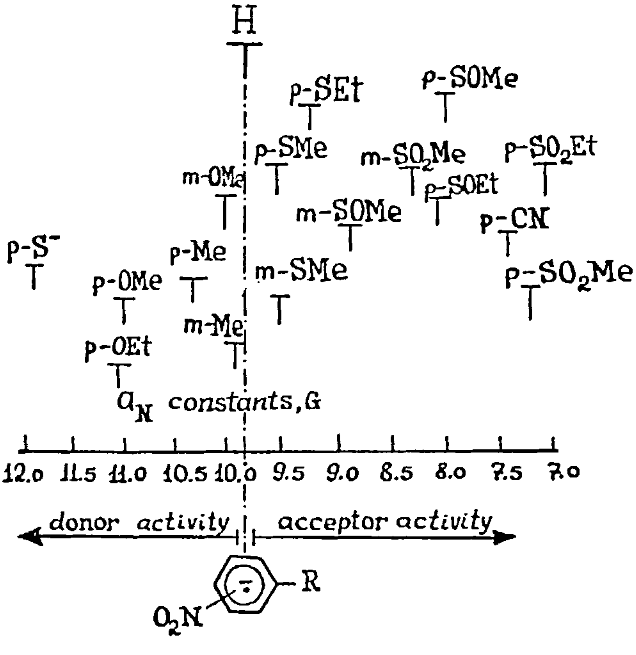
Scheme 3

the n_E^π-LUMO causes a charge transfer from the substituent to the $C_6H_5^{\cdot-}$ fragment, the SOMO-σ_{S-C} causes a charge transfer from the $C_6H_5^{\cdot-}$ fragment to the substituent.

What have experiments shown? Consider the ESR spectra of radical anions of nitrobenzene derivatives. Push off the radical anion of the unsubstituted nitrobenzene and compare the hyperfine coupling constants for the nitrogen of the nitro groups, a_N. A comparison of the a_N values for the substituted and unsubstituted nitrobenzene radical anions provides information about the electronic effect of the substituent. An increase in the nitrogen splitting after substitution suggests that the entering group has an electron-releasing character, while a decrease of the same constant is indicative of the electron acceptor character of the substituent. Values of a_N show clearly[5-7] the donor character of S^-, OEt, OMe, and Me substituents and the acceptor character of SMe, SEt, SOMe, SOEt, SO_2Me, SO_2Et, and CN (Scheme 4).

Thus, the transformation of thioanisol into a radical anion has two results: (i) the interaction of new orbitals which is energetically advantageous; (ii) the stabilization of the orthogonal conformation (Scheme 3). The combined influence causes a change in the SCH_3 effect. Although this substituent acts as donor in uncharged aromatic molecules, in radical anions it acts as an acceptor.

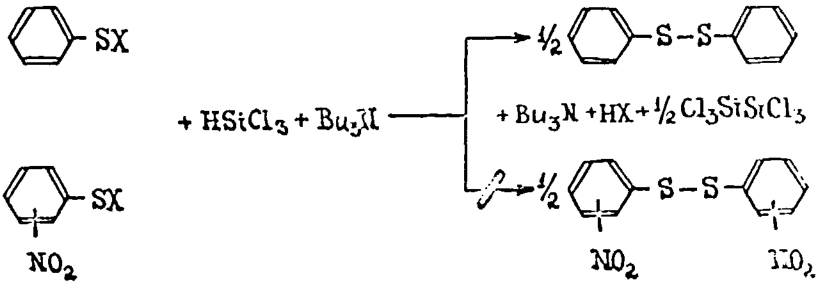
In connection with Scheme 4, it is interesting to take notice of the nitroarenesulfenate radical anions $(O_2NC_6H_4SOR)^{\cdot-}$. In these radical anions, as shown above, there appear two acceptor fragments, *i.e.* a nitro group and a SOR group. Such a peculiarity needs to take into account in chemical practice, for example, the use of nitroarenesulfenate protection. The proper choice of conditions needed for removing nitrosulfenate protection can be ascertained from the properties of nitroarenesulfenate radical anions. The introduction of nitroarenesulfenate protection is used in various conversions of complicated (especially bioorganic) molecules containing the amino or oxy group. To recover activity of the amino or oxy group after these conversions the nitroarenesulfenate protection must be removed.



Scheme 4

The competition of acceptor fragments should be taken into account when a sulfur-containing group rather than a nitro group is to be reduced.

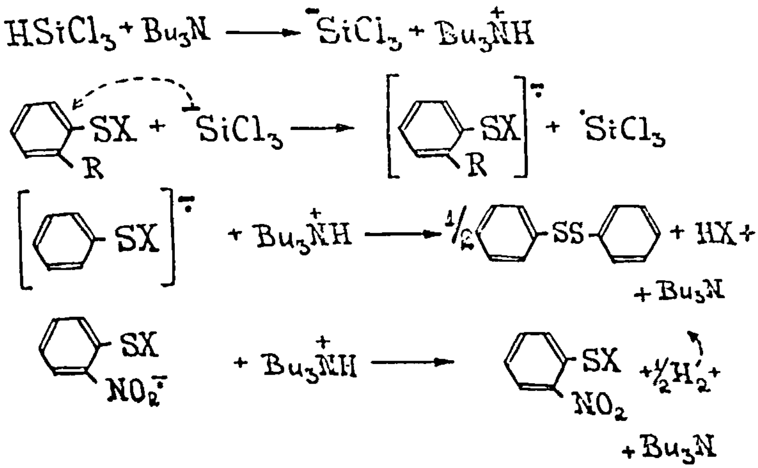
Among a number of reductive systems the trichlorosilane-tributylamine system has been investigated.[8] It has been found that by using trichlorosilane and tributylamine, only those arenesulfinic derivatives can be reduced which contain no nitro groups. Nitroarenesulfenate analogues remain unchanged in these conditions (Scheme 5).



$X = CN, OCH_3,$ N◯O

Introduction of nitrosulfenic acid derivatives into a mixture of trichlorosilane and tributylamine results in hydrogen evolution.

Trichlorosilane with tributylamine yields the trichlorosilyl anion and tributylammonium cation (Scheme 6).



Scheme 6

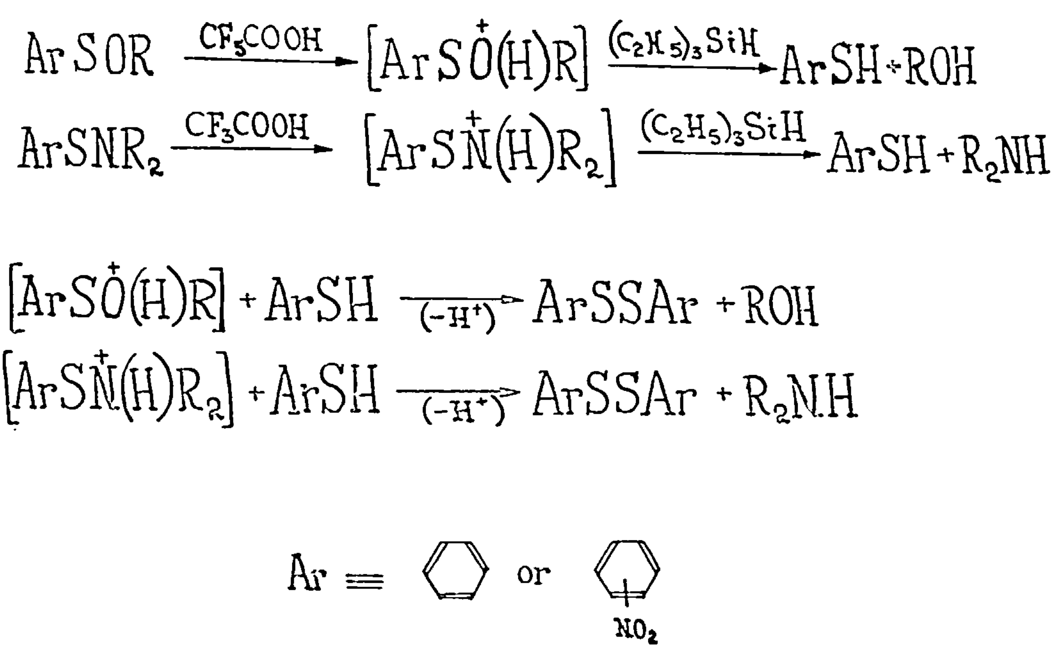
From this stage, a chain of conversions begins, involving one-electron transfer from the trichlorosilyl anion to the sulfenic acid derivative. Nitrobenzenesulfenate compounds produce stable radical anions which give off one electron to the proton present in the counter-ion, *i.e.*, the tributylammonium cation (Scheme 6).

The sulfur-containing group in nitrobenzenesulfenates is not cleaved. In this they are markedly different from the benzenesulfenic acid derivatives not containing a nitro group. Due to the presence of a nitro group in the nucleus, a one-electron oxidation of the radical anion with a proton, followed by hydrogen evolution, occurs instead of cleavage of the sulfur-containing fragment.

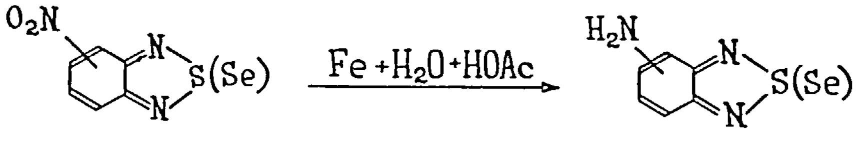
The predisposition of groups such as SOR or SNR_2 to reductive cleavage sharply increases after their protonation. For the trifluoroacetic acid-triethylsilane system the reduction has been found to proceed selectively to afford dinitrodiaryl disulfides in high yields. The reactions described in Scheme 7 are applicable to compounds with and without nitro groups.[8]

From the foregoing, it is clear that for the reactions beginning from the radical anion formation stage, the deciding factor is the change in distribution of the unpaired electron caused by the nitro group. The latter is a powerful acceptor substituent. The nitro group captures the unpaired electron thus preventing the reductive cleavage of the SOR and SNR_2 groups (Scheme 6).

This particularity is important also for the nitro derivatives of thiaheteroaromatic compounds such as piazthiol (Scheme 8). A molecule of nitropiazthiol has two electrophilic centers like the previously examined nitroarenesulfenic acid derivatives. For nitropiazthiol these centers are the electronegative nitro group and the electrophilic heteroring. By means of a weak reductive system such as mordanted iron chips in water selective reduction of the nitro group has been achieved[9] without cleavage of

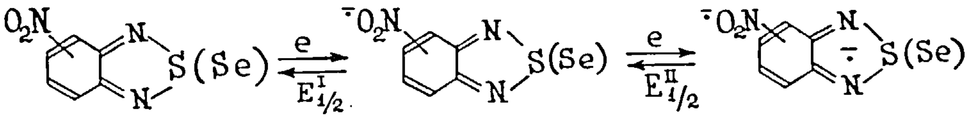


Scheme 7



Scheme 8

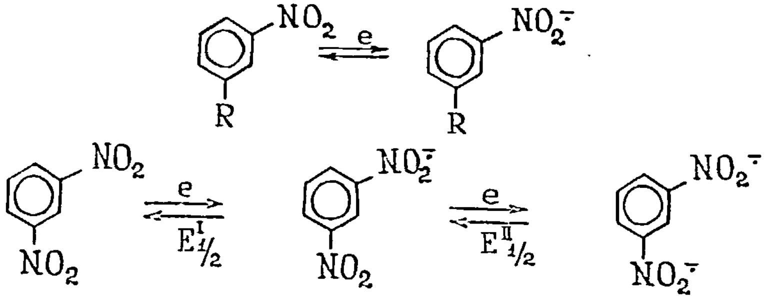
For nitropiazthiol and nitropiaselenol the two first stages of polarographic electron transfer were proved[9-11] as depicted in (Scheme 9). Both waves are one-electron and reversible (solvent—DMF, the supporting electrolyte—Et_4NBr).



Scheme 9

Piazthiols and piaselenols with polarographically inactive substituents yield only one reversible, single-electron wave;[11] for the waves $E_{1/2}$ values are correlated with suitable σ-constants.[11]

Under the conditions used for piazthiol and piaselenol (DMF, Alk_4N^+ salt), the polarographic reduction of substituted nitrobenzenes was investigated.[12] In each case the process had a first one-electron reversible wave. For m-dinitrobenzene both the first and the second waves were one-electron and reversible, as revealed by direct-current and cyclic voltammetry (Scheme 10).



Scheme 10

The one-electron reduction of all aromatic nitro compounds yields radical anions, characterized by effective electron localization on the nitro group. The nitro group is known to be a strong electron-accepting substituent. Since many important reactions of aromatic nitro compounds proceed through the stage of radical anion formation, it is essential to know whether the nitro group retains its acceptor properties after capture of one electron.

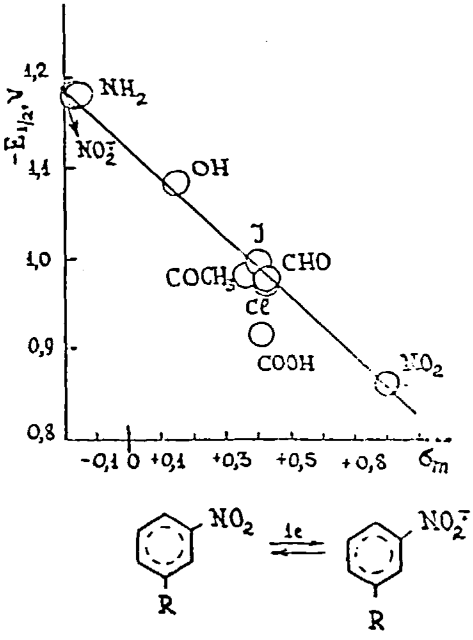
The effect of the m-$NO_2^{\cdot-}$ substituent is, of course, the most informative for our problem. This group, in the meta position, cannot be in conjugation with the reaction center so that the conditions are favorable for the manifestation of any possible acceptor effect. Thus, 'the methoxy group which acts as donor in the ortho and para positions of the benzene ring acts as an acceptor in the meta position.[13] Regrettably, there are no reported values of $\sigma_{m\text{-}NO_2^{\cdot-}}$. In order to evaluate these constants one plots the points for the second half-wave potentials of nitropiazthiol, nitropiaselenol, and m-dinitrobenzene on the corresponding correlation lines. Thus it was found[12] that the σ value for the m-$NO_2^{\cdot-}$ substituent was -0.17 with confidence interval -0.02 to -0.32. Hence $\sigma_{m\text{-}NO_2^{\cdot-}}$ is negative over the entire interval of confidence. It should be recalled that for the nitro group $\sigma_{m\text{-}NO_2} = +0.71$ (*cf. ref.* 13). The change in the sign of σ means that the nitro group, which is a strong electron-accepting substituent, becomes an electron donor after the capture of one electron.

The question arises whether the found constant works in the case of alkali salts of nitroaromatic radical anions.

Alkali salts, but not Alk_4N^+ salts, are formed in most substitution reactions.[14] In the case of the sodium (but not tetraalkylammonium) salt of m-dinitrobenzene radical anion there is a strongly non-equivalent distribution of the captured electron between the two nitro groups. In fact, ESR data have shown[15,16] that for this sodium salt the coupling constant a_N is 9.0 G for one nitrogen atom and only 0.2 G for the other.

In order to shed light on this question, the polarographic reduction of a series of substituted nitrobenzenes in DMF with $NaClO_4$ as a supporting electrolyte was studied.[12] The reduction mechanism was as cited above; on the correlation graph the points of the $NO_2^{\cdot-}$ and NH_2 groups appeared almost together (see Section 11).

Thus, the constant for the $NO_2^{\cdot-}$ group is negative in the whole reaction series considered. Consequently, this constant is most probably of a general nature and should



Scheme 11

be applicable to widely differing nitroaromatic radical anions. This constant reflects the electronic properties of the substituent and is evidently independent of medium effects (ion aggregations). It is important that the constant found has a numerical value which is the same for the naked radical anion and its ion pair with a sodium cation.

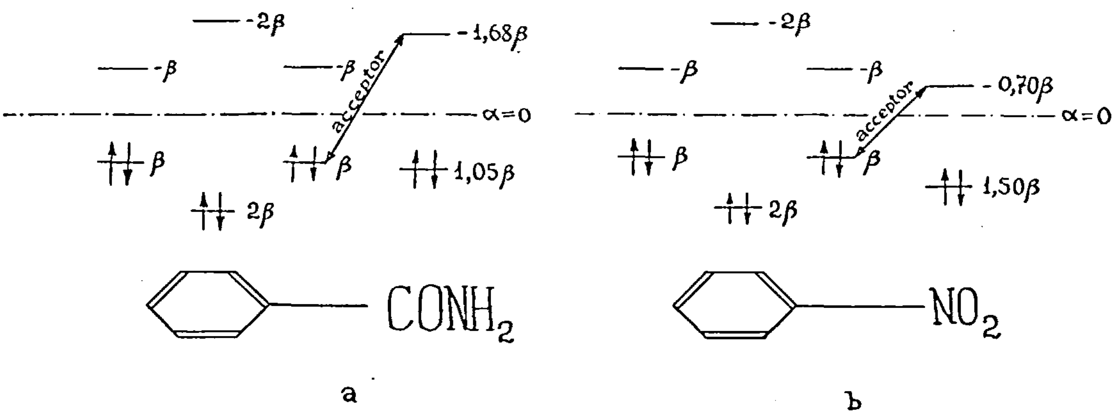
In the area of uncharged aromatic compounds the nitro group is a much more powerful negative substituent than the carboxamide group. Nevertheless, after one-electron capture, the nitro group becomes a donor; meanwhile, the carboxamide group in radical anion molecules retains accepting properties: $\sigma_{p\text{-CONH}_2^{\cdot-}}$ is found[17] to be +0.14, whereas $\sigma_{p\text{-CONH}_2}$ is determined[18] to be +0.43. According to *ref.* 11 $\sigma_{p\text{-NO}_2^{\cdot-}} = -0.29$.

It should be noted that for both series of nitrobenzenes and benzamides ρ constants are similar.

The above discrepancy in the effects of the substituents NO_2 and $CONH_2$ in aromatic radical anions is, at first sight, unexplainable. However, this difference becomes quite clear when one takes into account the electronic structure of these radical anions. The results of our Hückel MO calculations are reproduced in Schemes 12 and 13; the parameters used are from *ref.* 19, 20.

In the benzamide radical anion the unpaired electron stays in the ring most of the time. In the nitrobenzene radical anion spin density localizes within the nitro group. As mentioned in the literature,[19] the lowest unoccupied orbital of nitrobenzene is essentially connected to the orbital of the "free" nitro group. This is the same orbital which contains the unpaired electron in the radical anion.

As seen from the Scheme 13a the passage of the unpaired electron to the lowest unoccupied molecular orbital of benzamide decreases the energy gap for the interaction



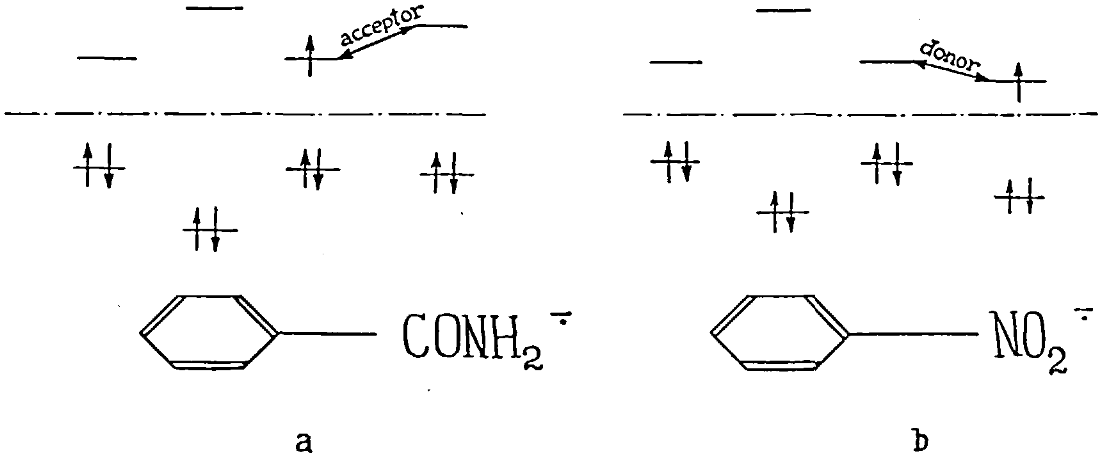
Scheme 12

of the carboxamide group with the nucleus. But such an interaction does not change the acceptor nature of the carboxamide group.

At the same time, conversion of nitrobenzene to the radical anion results (*cf.* Scheme 13b) in the population of the nitro group orbital without any appreciable changes in the energy level of the lowest vacant orbital of the nucleus. For this reason a donor rather than acceptor effect is observed.

Thus, the subdivision of the substituents in question (SR,SOR,SNR_2,SSR,SCN, NO_2,$CONH_2$) into donors and acceptors, which is usual when one discusses neutral aromatic compounds, is not so simple in the case of radical anions. By combining experimental data with quantum mechanical calculations, success can be achieved in explaining the apparent discord in the donor-acceptor behavior of a substituent toward the π-electron system of an aromatic radical anion.

An unpaired electron floating in an aromatic molecule gives to it new perfection and elegance in the same manner as floating water lilies lend special beauty to a reticent forest lake.



Scheme 13

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