

# Unusual Conjugation Effects in Aromatic Anion Radicals and their Importance in Modern Synthetic Methodology\*

Zoriy V. Todres

Institute of Organo-Element Compounds, USSR Academy of Sciences, V-334 Moscow 117813 GSP-1, USSR

Todres, Z. V., 1990. Unusual Conjugation Effects in Aromatic Anion Radicals and their Importance in Modern Synthetic Methodology. – Acta Chem. Scand. 44: 535–541.

Experimental facts connected with the peculiarities of conjugation in aromatic anion radicals are described. Synthetic applications of observed effects are discussed. The reactivities of thioalkyl- and nitro-aromatics are significantly changed after single-electron capture: the thioalkyl group becomes an acceptor instead of a donor, and the nitro group, usually an acceptor, becomes a donor. *o*-Dinitrobenzene anion radical acquires the capability of coupling with arenediazonium ions. An unusual effect is observed in *p*- or *o*-styryl substituted nitrobenzene, namely that the main part of the electron density is not localized in the nitro group bond, but on the C=C bridge i.e. that a transfer of the reaction centre is apparent.

Nitrostilbenes and cyanoferrocenylethylenes give anion radicals that instantly isomerize from the *cis* to the *trans* forms. Although the anion radical of  $\beta$ -cyanoferrocenylethylene is stable as a monomer, that of  $\beta$ -nitroferrocenylethylene is dimerized immediately after its formation. Thus, the cyano group competes less strongly than the ferrocenyl group for the unpaired electron, whereas the nitro group is a much better electron acceptor than the ferrocenyl group. Anion radicals of nitrobenzenes with SCl and SCN substituents are different in terms of spin distribution: the SCl group absorbs an unpaired electron in spite of the presence of the nitro group, whereas the SCN group cannot overcome the high electron affinity of the nitro group.

All of the effects mentioned can be interpreted by means of quantum-chemical models.

The chemistry of organic ion-radicals is well documented, and up-to-date data have been accumulated in several surveys.<sup>1-4</sup> However, research into certain areas of the initial ideological design remain unfinished, and many important problems still need to be addressed. One such problem concerns the peculiarities of conjugation in aromatic anion radicals.

This is the main topic for discussion in this review. In addition, the connection between special substitution effects in aromatic anion radicals and the potential for the extension of modern synthetic methodology will be explored. For brevity, the review will concentrate on the more unusual substitution effects; some typical examples will be examined, and the validity of the approach will be shown in which calculation and experiment are combined to describe the changes in reactivity produced by activation of the substrate with an excess of electron density.

In the anion radicals of nitro compounds an unpaired electron is localized on the nitro group and this localization depends on the nature of the nitro compound. The value of the hyperfine splitting constant in the ESR spectrum reflects the extent of localization of the unpaired electron;  $a(N)$  values of a number of nitro compounds are given in Table 1.

\* In part presented as a main section lecture at the 32nd IUPAC Congress in Stockholm, Sweden, August 2–7, 1989.

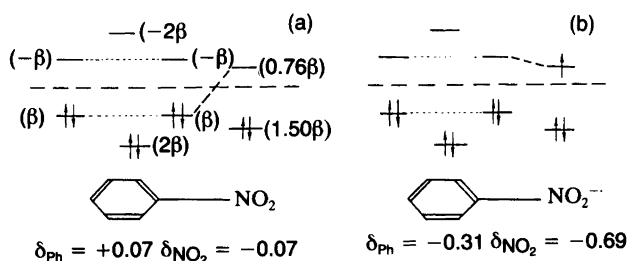
As shown in Table 1, aliphatic nitro compounds produce anion radicals in which the spin density is localized entirely on the nitro group. In contrast, the spin density of the nitrobenzene anion radical is spread over the aromatic ring due to conjugation. However, according to calculations<sup>5</sup> the nitro group retains about 65–70 % of the spin density.

Table 1. Nitrogen hyperfine splitting constants  $a(N)$  from experimental ESR spectra of nitro compounds.

Compounds	Constant $a(N)$ /mT	Reference
Nitroalkanes	0.24–0.25	5,6
Nitrobenzene	0.10	7
3-Nitro- <i>o</i> -xylene	0.18	8
Nitrodurene	0.20	8

Table 2. Effective charges on the R and SX groups in anion radicals of  $p$ -RC<sub>6</sub>H<sub>4</sub>SX<sup>-</sup> type (the rest of the charge, up to unity, is in the nucleus).

R	SX	$-q_R$	$-q_{SX}$
H	SCl	0.05	0.78
NO <sub>2</sub>	SCl	0.20	0.76
H	SCN	0.06	0.54
NO <sub>2</sub>	SCN	0.48	0.27

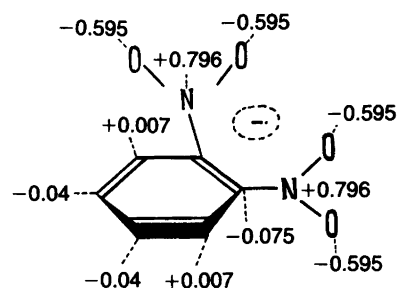


Scheme 1.

These calculations are based upon hfs constants  $a(\text{N})$  and  $a(\text{H})$  taken from the nitrobenzene anion radical ESR spectrum. The same result arises from the calculation of the spin distribution between the phenyl nucleus and the nitro group by use the MO Hückel approximation<sup>4</sup> [cf.  $\delta(\text{Ph})$  and  $\delta(\text{NO}_2)$  values given in Scheme 1]. Reduction of the  $\pi$ -conjugation in the  $\text{PhNO}_2$  system as a result of steric hindrance intensifies the localization of the unpaired electron (see Table 1).

Consideration of the quantum chemical values of the nitrobenzene anion radical is of particular interest. The model for the calculation includes a combination of fragment orbitals for Ph and  $\text{NO}_2$ , and the results are represented in Scheme 1 [part (a) refers to neutral  $\text{PhNO}_2$ , part (b) to the anion radical,  $\text{PhNO}_2^{\bullet-}$ ]. The nitro group in neutral nitrobenzene evidently acts as a  $\pi$ -acceptor which pulls the electron density out of the aromatic ring. An unpaired electron will obviously occupy the first vacant  $\pi$ -orbital of the nitro group (i.e., the orbital of lowest energy). Scheme 1 shows that the nitro group in the nitrobenzene anion radical can, in fact, act as a  $\pi$ -donor. Such a prediction is of great significance, since the nitro group in neutral aromatic nitro compounds is recognised as a strong  $\pi$ -acceptor and a reservoir of 4–6 additional electrons. When the  $\text{NO}_2$  group is transformed into the  $\text{NO}_2^{\bullet-}$  group, a change in both the sign and value of the correlation constant is observed.<sup>9</sup> A formal comparison of the Hammett constants for  $\text{NO}_2$ ,  $\text{NO}_2^{\bullet-}$  and  $\text{NH}_2$  groups shows  $\text{NO}_2^{\bullet-}$  to be close to  $\text{NH}_2$  in terms of donating ability:  $\sigma_m(\text{NO}_2) = +0.71$ ,  $\sigma_m(\text{NO}_2^{\bullet-}) = -0.17$ ,  $\sigma_m(\text{NH}_2) = -0.16$ .

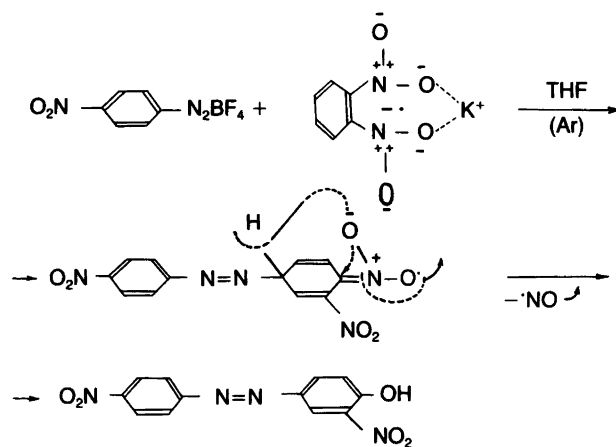
Having captured the single electron, the nitro group then acts as a negatively charged substituent. Similarly, the stable anion radical resulting from aryldiazocyanides [ $(\text{N}=\text{NCN})^{\bullet-}$ ] interacts with the rest of the molecule as a donor.<sup>10</sup> Using other nitro derivatives of an aromatic heterocyclic series, the generality and statistical relevance of the observed  $\sigma_m(\text{NO}_2^{\bullet-})$  constants can be confirmed.<sup>11,12</sup> The sign and absolute magnitude of the Hammett constant are invariant whatever the cation (K, Na or  $\text{Alk}_4\text{N}$ ) in the anion radical salts of nitro compounds studied. Such invariance is caused by the linear dependence between (i) electrochemical reduction potentials of substituted nitrobenzenes and (ii) the contribution of vacant  $\pi^*$  orbitals of the nitro group to  $\pi$  orbitals of anion radicals which are occupied by the single electron.<sup>13</sup>



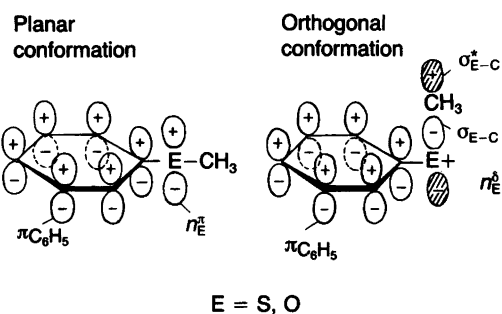
Scheme 2.

Similar Hückel calculations on the *o*-dinitrobenzene anion radical lead to the unpaired electron distribution diagram depicted in Scheme 2. If the spin density of this anion radical is considered as unity, each nitro group carries  $-0.394$ , and each *para*-position  $-0.04$ . It is important that the charge resting in the *ortho*-position is low but positive. In other words, the attack of cation-type electrophiles is predicted to take place at the negatively charged positions, i.e. the *para*-positions. *ortho*-Substitution seems to be of low probability.

Experimental data are set out below. The ability of nitrobenzene anion radicals to undergo azo-coupling has been studied.<sup>14</sup> This reaction is known to proceed for aromatic rings of substituted donor-type groups such as amino and hydroxy; aromatic compounds containing only the nitro groups do not participate in this reaction. It is also worth noting that benzenediazo cations are strong electron acceptors. For instance, the reaction between aryldiazonium fluoroborates and the sodium salt of the naphthalene anion radical proceeds by electron transfer which converts the aryldiazonium cations into benzene and its derivatives, and sodium naphthalene anion radical into uncharged naphthalene; products of azo-coupling were not found.<sup>15</sup> In a reaction in which potassium salts of anion radicals of nitrobenzene and *o*-dinitrobenzene were allowed to react with benzenediazo cations (in THF),<sup>14</sup> potassium nitrobenzene anion radical appears to react with diazonium cations ac-



Scheme 3.



Scheme 4.

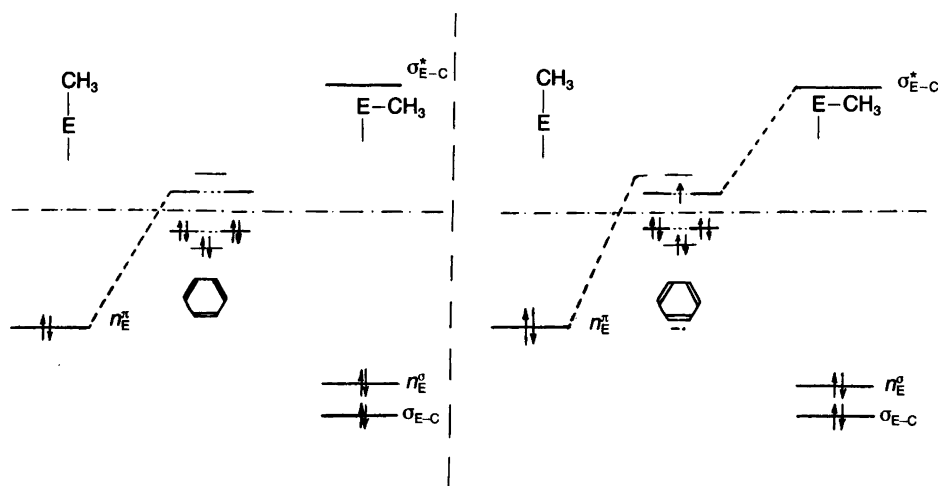
cording to the electron transfer scheme (as does the naphthalene anion radical), whereas *o*-dinitrobenzene potassium yields an azo-coupled product according to Scheme 3. The reaction leads to a *para*-substituted product, entirely in accordance with Scheme 2. It was established, by means of labelled-atom experiments and gas-phase analysis, that azo-coupling is accompanied by the conversion of one of the nitro groups into a hydroxy group, the radical product being made stable by elimination of the nitrogen monoxide radical. This last was identified as one of reaction products.

This change of substituent effect, on changing the uncharged molecule to the corresponding anion radical, appears to be possible not only for the nitro group, but also for other substituents. An exciting example of this is provided by comparison of RO and RS (R = alkyl) substituent electron effects in aromatic molecules.<sup>16</sup> Both groups are known to be electron donors, however, in the anion radical form, the RO and the RS groups exert different effects. The MeO-substituted compound keeps its donor properties, but the MeS counterpart becomes an acceptor. This is particularly apparent from a comparison of the ESR spectra of the nitrobenzene anion radical and its derivatives, in particular the MeO- and MeS-substituted ones. The introduction of substituents into nitrobenzene, in general, affects the value of  $a(N)$  arising from the splitting of the

unpaired electron resonance by the nitrogen atom in the anion radical. If the group introduced is a donor, the  $a(N)$  value increases; if it is an acceptor, the  $a(N)$  value is reduced. As follows from a comparison of  $a(N)$  constants, the MeO and EtO groups act similarly to Me and S<sup>-</sup> groups (donors); the MeS and EtS groups act similarly to CN, SO<sub>2</sub>Me and SO<sub>2</sub>Et groups (acceptors).<sup>17-20</sup>

The sharp contrast between the electronic effects exerted by oxyalkyl and the thioalkyl groups in anion radicals can be explained by means of group orbital-energy diagrams. The usual mechanism involving  $n, \pi$ -conjugation requires the MeO or MeS group to be situated in the same plane as the aromatic ring. However, these groups are also able to position themselves orthogonally to the aromatic ring, (Scheme 4). As can be seen from Scheme 4, the planar conformation is stabilized by  $n, \pi$ -conjugation between the oxygen or sulfur atom with the ring. This  $n, \pi$ -conjugation is impossible in the orthogonal arrangement, and only the  $\sigma$  electrons of the sulfur or oxygen appear to be involved. Only the  $\sigma$  orbitals of these atoms are symmetrically available for aromatic  $\pi$  orbital overlap (when fragments of the molecule are oriented perpendicularly). However, an interaction between  $\pi$ -electrons of the nucleus with the vacant  $\sigma^*$  orbitals of the substituent is also possible, such an interaction being symmetrically allowed. In practice,  $\sigma, \pi$  and  $\sigma^*, \pi$  interactions are not too important in the case of uncharged molecules, since the gap between the aromatic  $\pi$  orbitals and  $\sigma(\sigma^*)$  orbitals of the substituents is too wide (Scheme 5).

Conversion of a neutral molecule into an anion radical leads to the occupation of the lowest energy vacant orbital; this is the  $\pi$  orbital of the benzene ring in both anisole and thioanisole. Charge transfer is possible only by means of an interaction of vacant and occupied orbitals, when the energy gap between them is not too wide. As the  $\sigma^*$  orbitals of the anisole MeO group are too far away from the ring  $\pi$ -orbital occupied by the single electron, conjugation conditions in the anion radical compared with the neutral molecule remain unchanged. The thioanisole MeS group

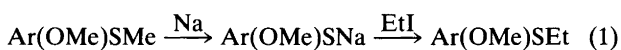


Scheme 5.

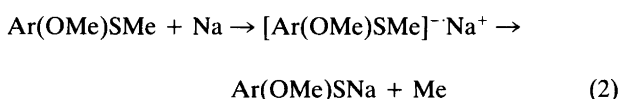
differs from the anisole MeO group in that the  $\sigma^*$  orbital is at a lower energy level. In this case, population of the lowest vacant aromatic  $\pi$ -orbital by the single electron changes the conjugation conditions, and  $\sigma^*,\pi$ -interaction becomes more favourable than  $n,\pi$  interaction, because the energy gap between the  $\sigma^*$  and  $\pi$  orbitals is narrower. In other words, conditions created in the anion radical promote charge transfer from the ring to the substituent rather than from the substituent to the ring, as is the case in the neutral molecule. It is these conditions that most likely stabilize the orthogonal conformation rather than the planar one which thus explains why the conversion of thioanisole into the anion radical causes a change in the orientation of the MeS group relative to the aromatic ring plane.

Such a situation may, intuitively, be expected in methoxy-polyacenes. INDO calculations, performed on the free anion radicals of 9-methoxyanthracene and 9,10-dimethoxyanthracene based on the standard geometry of anthracene, estimate that the orthogonal conformation is more stable than the planar one.<sup>21</sup> The calculated differences in bonding energies for the two conformations are about 192.4 kJ (9-methoxyanthracene anion radical) and 562.8 kJ (9,10-dimethoxyanthracene anion radical with both the MeO groups orthogonally disposed). The calculated and experimental hyperfine splitting constants  $a(\text{H})$  in the ESR spectra of anion radicals mentioned are in closest agreement for the orthogonal rather than the planar conformer. The electron spin densities of methyl carbons increase because of the  $\sigma,\pi$  interaction of the aromatic (polyacenic) system with the MeO bonds. In contrast, this weakens the MeO-C bond and results in MeO-C bond scission, an event which was observed through emergence of ESR signals of demethoxylated anthracene anion radicals  $\text{ArH}^-$ .<sup>21</sup>

Bearing the above discussion in mind, an interesting example would be an aromatic compound in which both MeO and MeS substituents were present. Anion radicals of methoxy(thiomethyl)anthracenes are not yet documented in the literature, but anion radicals of methoxy(thiomethyl)benzenes are known. Methoxythioanisoles contain both groups - MeO and MeS - in the same molecule. The reaction of methoxythioanisoles with sodium leads to cleavage of the carbon-sulfur bond [eqn (1)].<sup>22</sup> The interaction



of the aromatic compound with sodium involves electron transfer from which the anion radicals of the substrate are formed; these reactive intermediates then undergo dissociation to sodium arenethiolate and methyl radical



[eqn. (2)]. This behaviour probably reflects the fact that the unpaired electron is accepted by the sulfur atom, since this element can expand its valence shell by using d-orbitals.<sup>22</sup>

Reduction of sulfonium salts with potassium in graphite in THF gives sulfide and radicals [eqn. (3)].<sup>23</sup> Thus the

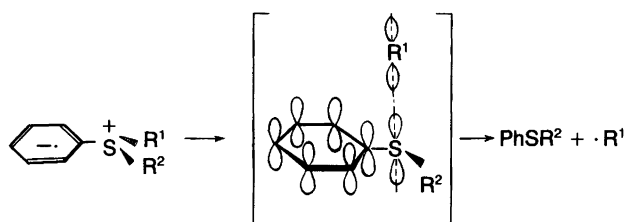


reaction, on the face of it, consists of an electron transfer to the positive centre of the ion, the subsequent transformation of the sulfur-centred radical, through radical abstraction, and formation of the sulfide.

Such a simple picture cannot, however, explain many unusual characteristics of the reaction. Trialkylsulfonium salts do not react under these conditions; phenyl(dialkyl)sulfonium salts expel alkyl groups, preferably bulkier alkyl groups. In spite of the positive charge on the sulfur atom, an electron is delocalized into the phenyl ring with the formation of the novel ' $\pi$ -ligand radical anion sulfonium cation'.<sup>23</sup> This phenomenon is illustrated by Scheme 6.

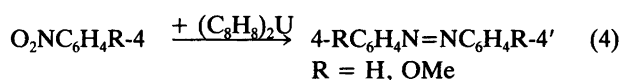
In fact, the electron that passes from the donor to the acceptor enters the lowest unoccupied molecular orbital (LUMO). The LUMO must not only be vacant but also of low energy. Trialkylsulfonium cations are resistant to reduction, i.e. they cannot supply the required low-lying vacant orbitals, despite the fact that they have positive charges on the sulfur atoms. Phenyl(dialkyl)sulfonium cations, on the other hand, do have low-lying orbitals, and these are essentially benzene ring orbitals. The anion radical of a phenyl-containing sulfonium cation, ' $\pi$ -ligand anion-radical cation',<sup>23</sup> disintegrates as shown in Scheme 6. The transition state for cleavage may be envisaged<sup>23</sup> to involve overlap of the singly occupied molecular orbital of the aromatic ring with the  $\sigma^*$  orbital of the bond undergoing homolytic cleavage, as shown in Scheme 6. Thus the selectivity of the bond breakage is determined primarily by the relative energies of incipient radicals. Relief of steric strain appears to play a role, with the bulkier group being preferentially cleaved. Naturally, a group of greater size will be eliminated more easily since the bond between that group and the sulfur atom becomes longer and therefore weaker. Moreover, a group of a greater size tends to arrange itself perpendicularly to the plane of an aromatic ring. Steric strain is lower, so  $\pi,\sigma^*$  conjugation is more favourable. This is why conjugation of this type occurs so easily.

The delocalization of the unpaired electron in the 4-nitrostilbene anion radical seems to be similar in nature to

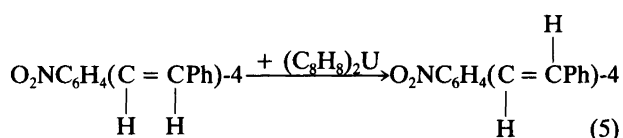


Scheme 6.

that in the nitrobenzene anion radical. The consensus of opinion is that the LUMO of neutral aromatic nitro derivatives (which accommodates the electron) is essentially an orbital of the 'free' nitro group. The styryl group of neutral 4-nitrostilbene is conjugated with the nitro group and acts as a weak donor, as indicated by values of the Hammett constants:  $\sigma_p(\text{NO}_2) = +0.78$ ,  $\sigma_p(-\text{CH}=\text{CHPh}) = -0.07$ . If the styryl substituent retained its donor nature in anion radicals, an increase and not a decrease in the value of  $a(\text{N})$  would be observed. Experiments show that  $a(\text{N})$  values for anion radicals of nitrostilbenes decrease (not increase) in comparison with the  $a(\text{N})$  value for the anion radical of nitrobenzene. This is true both for coordination complexes of nitroanion radicals, in which the counter-ion is potassium, and for 'naked' nitroanion radicals. For potassium complexes (with THF as the solvent)  $a(\text{N}) = 0.980$  mT, for  $\text{PhNO}_2^- \text{K}^+$  and for  $4\text{-PhCH}=\text{CHC}_6\text{H}_4\text{NO}_2^- \text{K}^+$ ,  $a(\text{N}) = 0.890$  mT.<sup>24</sup> For the 'naked' anion radicals (with THF as the solvent and 18-crown-6-ether as a decomplexer)  $a(\text{N}) = 0.848$  mT for  $\text{PhNO}_2^-$  and for  $2\text{-PhCH}=\text{CHC}_6\text{H}_4\text{NO}_2^-$ ,  $a(\text{N}) = 0.680$  mT.<sup>25</sup> Reduction of nitrobenzene<sup>26,27</sup> and 4-methoxynitrobenzene<sup>26</sup> by uranium-, thorium- and lanthanum-di(cyclooctatetraene) complexes leads to azoxy



compounds [eqn. (4)]. Under the same conditions 4-styrylnitrobenzene (4-nitrostilbene) undergoes only *Z/E*-isomerization with no nitro-group reduction [eqn. (5)].<sup>26,28</sup> An



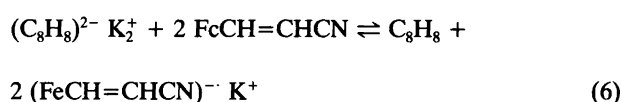
important conclusion from this is that transference of the reaction centre takes place. Substitution of nitrobenzene by a styryl (not methoxy) group protects the nitro group from reduction and at the same time causes a shift of excess electron density to the olefinic bond.

Such subtle differences between anion radicals of nitrobenzene and nitrostilbene, observed experimentally, are well reproduced by quantum-chemical calculations (MO LCAO method in a CNDO/2 approximation).<sup>26</sup> As shown by single-electron wave-function analysis of vacant orbitals in both molecules, one-electron transfer to (*Z*)-4-nitrostilbene should be followed by the predominant localization of the single electron in the region of the ethylenic bond. The influence of the nitro-group atomic orbitals is insignificant in nitrostilbene. The nitro-group atomic coefficients  $C_i$  of the molecular wave function  $\Psi_b$  are for (*Z*)-4-nitrostilbene half those for nitrobenzene. The excess electron population of the first vacant orbital for the compounds under consideration increases for the nitro group of nitrobenzene ( $q = 0.3832$ ) in comparison with the nitro group of nitrostil-

bene ( $q = 0.0764$ ). The unpaired electron in the latter case [with (*Z*)-4-nitrostilbene], is largely localized on the olefinic bond ( $q = 0.2629$ ). It is noteworthy that the first vacant level of (*Z*)-4-nitrostilbene is of lower energy than that of nitrobenzene: energy levels are 38 and 135 kJ, respectively. This means that 4-nitrostilbene acceptor properties should be greater than those of nitrobenzene. This theoretical conclusion was checked experimentally by comparing the stability constants of nitrobenzene- or (*Z*)-4-nitrostilbene-*N,N*-dimethylaniline electron donor-acceptor complexes.<sup>26</sup> The EDA complex with (*Z*)-4-nitrostilbene is about four times more stable than the nitrobenzene-EDA complex. Entirely in accordance with theoretical prediction, the formation of the 4-nitrostilbene-*N,N*-dimethylaniline complex is found to cause a *Z/E*-conversion of the stilbene component.<sup>26</sup>

The above-mentioned isomerization in a donor-acceptor complex proceeds slowly, but electron transfer to nitrostilbene from cyclooctatetraenedipotassium or other suitable donors causes a rapid, practically immediate, *Z/E*-conversion.<sup>29</sup> It is worth noting that the observed phenomenon of immediate *Z/E*-isomerization initiated by electron transfer could be used for the realization of 'electronic memory' at individual molecular levels.

The situation in which the spin density is enriched around the ethylenic bond is typical for anion radicals of indigoids as well as for the anion radical of 4,4'-dinitrostilbene.<sup>29,30</sup> The example of thioindigo is representative. A mixture of (*Z*)- and (*E*)-thioindigo, if treated with a small amount of potassium (with dimethoxyethane as the solvent), undergoes complete conversion into the (*E*)-isomer.<sup>31</sup> Obviously, a number of the thioindigo molecules undergo initial one-electron reduction and then one-electron exchange with the remaining neutral molecules. Thus, all the molecules of (*Z*)-isomer at some time acquire excess electron density, the duration of which appears to be enough for a *Z/E*-conversion. Naturally, it is not only a metal that can act as a donor, but also an organic compound, if the ionization potential is sufficiently low. A metal is better replaced by the cyclooctatetraene dianion, since its dipotassium salt is soluble in ethers and thus it can be used as a 'dissolved electrode,' and the degree of electron transfer can be estimated according to the extent of neutral cyclooctatetraene liberated.<sup>32</sup> An example is shown in eqn. (6), where  $\beta$ -ferrocenyl- $\alpha$ -cyanoethylene acts as the

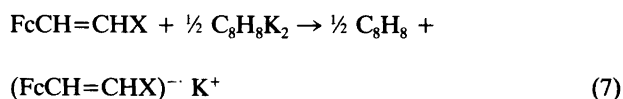


$\text{C}_8\text{H}_8$  = cyclooctatetraene; Fc = ferrocenyl

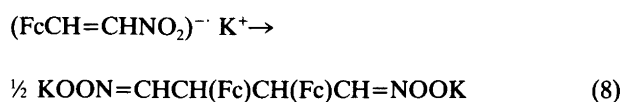
acceptor.<sup>33,34</sup> The reaction is reversible, and all the four components have been proved to be present in the mixture. A peculiarity of the equilibrium state in eqn. (6) is that electron transfer proceeds only to an extent of 20%. Calculation of equilibrium constants in terms of donor and ac-

ceptor redox potentials predicts the same value for the extent of reaction. The primary anion radicals of (*Z*)- $\beta$ -ferrocenyl- $\alpha$ -cyanoethylene isomerize into the (*E*)-form, with a conversion yield of 65%. The exchange of one hydrogen atom at the ethylenic bond by deuterium decreases the extent of conversion by 50%,<sup>35</sup> by the 'stercoisotopic effect.' No other changes (such as dimerization, double-bond saturation, proton abstraction, splitting) occur with the substrate. The (*E*)-isomer (taken as an acceptor) is transformed into the anion radical with a yield close to that mentioned above, with retention of geometry. Two conclusions may be drawn. (a) The energy level of the anion radical produced from (*E*)-ferrocenyl(cyano)ethylene is situated significantly lower than that of anion radical produced from the (*Z*)-isomer (only *Z/E* and not *E/Z* isomerization is observed). (b) Anion-radicals of the substrate are formed not only by eqn. (6), but also by an electron exchange between these anion radicals and uncharged ferrocenyl(cyano)ethylene molecules also present in solution. The extent of *Z/E* isomerization is more than three times greater than that of electron transfer from the cyclooctatetraene dianion. Thus, a situation supposed in the thioindigo case is proved directly for ferrocenyl(cyano)ethylene, namely, that electron exchange leads to a considerable increase in the effective concentration of anion radicals and in the extent of *Z/E* isomerization.

Reactions of  $C_8H_8K_2$  and several ferrocenylethylene derivatives of general formula  $FcCH=CHX$  have been exam-



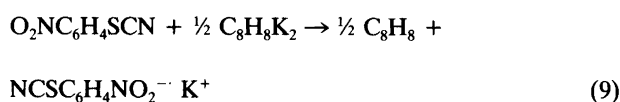
ined [eqn. (7)].<sup>34</sup> The reaction stops at the level of anion-radical salt formation only if  $X = CN$  (ESR method). If  $X = NO_2$ , an ESR signal is not detected and dimer formation



ensues at once [eqn. (8)]. THF was used as the solvent in all cases, the other experimental and isolation conditions also being comparable. The proton donor work-up yielded  $FcCH=CHCN$  and  $O_2NCH_2CH(Fc)CH(Fc)CH_2NO_2$ .

In the anion radical salts compared, the ferrocenyl group is a common substituent and its shielding effect cannot possibly be considered relevant, though its volume is great enough. Therefore, the effect of the Fc-substituent appears to depend on the nature of  $X$  [eqn. (7)]. In the competition for the unpaired electron the Fc fragment is comparable to CN and is much weaker than  $NO_2$ . Therefore, in the first case, the  $\pi$ -electron anion radical  $(FcCH=CHCN)^{\cdot-}$  can exist without undergoing dimerization. In the second case an unstable  $\sigma$ -electron (distonic) anion radical is formed that is immediately dimerized.

It is necessary to consider one further approach to the comparison of the activities of different acceptor groups present in the same molecule. This is the comparison of SCl with SCN as an acceptor in relation to the same reference group ( $NO_2$ ). The problem is important from the point of view of sulfenic biological activity. The compounds under study were subjected to two independent model reductive cleavage reactions: by treatment with (a)  $C_8H_8K_2$  in THF or (b) a mixture of  $HSiCl_3$  and  $R_3N$  ( $R = \text{alkyl}$ ) in benzene. As shown, aromatic sulfonyl chlorides under conditions (a) and (b) produce disulfides or thiols; the presence of the nitro group in the ring doesn't affect the reaction. Arylrhodanides without the nitro group behave in a similar way.<sup>36,37</sup> However, arylrhodanides containing the nitro group in the ring are converted into anion radicals with the SCN group remaining unchanged. This pathway is represented by eqn. (9).



Splitting of the SCN group is not observed, and, after single-electron oxidation, the  $NCSC_6H_4NO_2^{\cdot-}$  anion radical produces, initially,  $NCSC_6H_4NO_2$ . Yields are close to quantitative in the case of *ortho* and *para* derivatives, and disulfides and thiols are not observed. The rhodanide group thus competes less successfully than the sulfonyl chloride group with the nitro group for the extra electron.

The conclusion outlined above is entirely confirmed by quantum chemical LCAO MO CNDO/2 calculations, the results of which are shown on the Table 2.<sup>38</sup> It can be seen that a charge on the SCl group of the anion radical of sulfonyl chloride series depends little upon whether or not the nitro group is present in the aromatic ring. In the case of anion radicals of the rhodanide series, however, a charge on the SCN group is diminished by 50% if the nitro group is present in the molecule.

Thus, SCl and SCN have different electron-attraction properties. That conclusion is not self-evident, as the extent of polarization of the  $S^{\delta+}-X^{\delta-}$  bond in the SCl group has, until now, been considered to be comparable to that in the SCN group. For instance, Kharasch *et al.*<sup>39</sup> have pointed out that nitroarylrhodanides as well as nitroarene-sulfonyl chlorides, when dissolved in concentrated sulfuric acid, are converted equally into nitroarenesulfonium ions,  $O_2NArS^+$ .

As a general conclusion, it is evident that the population of aromatic molecules by a single electron changes the whole electronic structure of the resulting new species. An extra electron floating in an aromatic molecule gives to it new perfection and elegance in the same manner that floating water lilies lend peculiar beauty to a calm forest lake. As a practically significant result, new reactivities are evident, and new interesting substances, inaccessible in other ways, can be obtained.

Now new simple methods of preparing of anion radicals are continuously appearing. As an example,  $\text{Zn}/\text{OH}^-$  in DMSO can convert a wide variety of organic molecules with electron affinities up to  $-200 \text{ kJ mol}^{-1}$  into anion radicals.<sup>40</sup> A remarkable feature of this work is the ready formation of anion radicals even in the absence of inert conditions.

Recently, other authors<sup>41</sup> have reported the stabilization of such anion radicals as *p*-benzosemiquinone by inclusion-complex formation with cyclodextrin in aqueous environments.

These reductions offer novel, attractive alternatives to the existing methods of synthesis of anion radicals. The future perspectives of anion-radical organic chemistry are promising and varied.

## References

1. *Photoinduced Electron Transfer. Part C.* Fox, M. A. and Channon, M., Eds., Elsevier, Amsterdam 1988.
2. Savéant, J. M. *Acc. Chem. Res.* 13 (1980) 323.
3. Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer, Heidelberg, FRG 1987.
4. Todres, Z. V. *Ion-radikaly v Organicheskom Sintezе, Khimia, Moskva SSSR* 1986.
5. Stone, T. M. and Maki, A. H. *J. Chem. Phys.* 37 (1962) 1326.
6. McKinney, T. M. and Geske, D. H. *J. Am. Chem. Soc.* 89 (1967) 2806.
7. Geske, D. H. and Maki, A. H. *J. Am. Chem. Soc.* 82 (1960) 2671.
8. Geske, D. H. and Ragle, J. L. *J. Am. Chem. Soc.* 83 (1961) 3532.
9. Todres, Z. V., Pozdeeva, A. A., Chernova, V. A. and Zhdanov, S. I. *Tetrahedron Lett.* (1972) 3835.
10. Kachukova, I. Ya., Ashkinadze, L. D., Shamsutdinova, M. H. and Kazitsyna, L. A. *Zh. Org. Khim.* 23 (1987) 1831.
11. Todres, Z. V., Zhdanov, S. I. and Tsveniashvili, V. Sh. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1968) 975.
12. Todres, Z. V., Pozdeeva, A. A., Chernova, V. A. and Zhdanov, S. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1972) 2454.
13. Koptuyug, V. A., Starichenko, V. F. and Breslav, I. I. *Zh. Org. Khim.* 24 (1988) 50.
14. Todres, Z. V., Hovsepyan, G. Ts. and Ionina, E. A. *Tetrahedron* 44 (1988) 5199.
15. Singh, P. R., Jayaraman, B. and Singh, H. K. *Chem. Ind. (London)* (1977) 311.
16. Bernardi, F., Mangini, A., Guerra, M. and Pedulli, G. F. *J. Phys. Chem.* 83 (1979) 640.
17. Alberti, A., Guerra, M., Martelli, G., Bernardi, F., Mangini, A. and Pedulli, G. F. *J. Am. Chem. Soc.* 101 (1979) 4627.
18. Alberti, A., Martelli, G. and Pedulli, G. F. *J. Chem. Soc. Perkin Trans. 2* (1977) 1252.
19. Ioffe, N. T., Kalinkin, M. I. and Todres, Z. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1970) 2409.
20. Bernardi, F., Mangini, A., Guerra, M. and Pedulli, G. F. *J. Phys. Chem.* 83 (1979) 640.
21. Lazana, M. C., Franco, M. L. and Herold, B. J. In: *Book Abstracts of the 32nd IUPAC Congress, Stockholm 1989*, p. 179, No. 6534; *J. Am. Chem. Soc.* 111 (1989) 8640.
22. Testaferri, L., Tiecco, M., Tingolli, M., Chianelli, D. and Maiolo, F. *Tetrahedron* 38 (1982) 2721.
23. Beak, P. and Sullivan, Th. A. *J. Am. Chem. Soc.* 104 (1982) 4450.
24. Todres, Z. V., Kursanov, D. N. and Starodubtseva, M. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1974) 230.
25. Todres, Z. V. *Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk* (1987) 78.
26. Todres, Z. V., Dyusengaliev, K. I., Tsvetkova, T. M. and Borisov, Yu. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 33 (1984) 351.
27. Grant, C. B. and Streitwieser, A. *J. Am. Chem. Soc.* 100 (1978) 2433.
28. Todres, Z. V., Dyusengaliev, K. I. and Sevast'yanov, V. G. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 34 (1985) 1297.
29. Todres, Z. V. *Russ. J. Phys. Chem.* 62 (1988) 1.
30. Bruni, P., Cardellini, L., Cardillo, B. and Tosi, G. *J. Heterocycl. Chem.* 19 (1982) 211.
31. Chang, R., Kehres, D. G. and Markgraf, J. H. *J. Org. Chem.* 38 (1973) 1608.
32. Todres, Z. V. *Russ. J. Phys. Chem.* 54 (1980) 631.
33. Todres, Z. V., Tsvetkova, T. M., Koridze, A. A., Denisovich, L. I. and Kursanov, D. N. *Dokl. Akad. Nauk SSSR* 254 (1980) 902.
34. Todres, Z. V. and Tsvetkova, T. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 36 (1987) 1433.
35. Todres, Z. V. and Ermekov, D. S. *J. Organomet. Chem.* 369 (1989) 371.
36. Todres, Z. V. and Avagyan, S. P. *Int. J. Sulfur Chem.* 8 (1973) 373.
37. Todres, Z. V. and Avagyan, S. P. *Phosphorus Sulfur* 4 (1978) 223.
38. Todres, Z. V., Tomilin, O. B. and Stankevich, I. V. *Zh. Org. Khim.* 18 (1982) 2132.
39. Kharasch, N., Buess, G. M. and King, W. *J. Am. Chem. Soc.* 75 (1953) 6035.
40. Handoo, K. L. and Gadru, K. *Tetrahedron Lett.* 27 (1986) 1371.
41. Kubozono, Y., Ata, M., Aoyagi, M. and Gondo, Y. *Chem. Phys. Lett.* 137 (1987) 467.

Received June 27, 1989.