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Stereochemical Results of Electron Transfer

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Data characterising the contribution of electron transfer processes to the stereochemistry of reactions of organic compounds are discussed and the stereochemical changes accompanying electron transfer are analysed. It is shown that the decrease of the barrier to rotation in electron transfer facilitates the *cis–trans* isomerisation of ethylenes and an increase of the difference between the energies of the rotational isomers of certain radical-ions relative to neutral molecules decreases the rate of mutual rotation. The influence of the formation of ion pairs by the anionic and cationic components of the radical-ion salts on the stabilisation of unusual geometrical forms of the molecule is discussed. The conversion of cyclopolyenes into ionic forms with a ring current of delocalised electrons, which fixes the ring atom in a single plane, is considered as a special case of electron transfer. The chemical and physical properties of cyclo-octatetraene, azocine, and their ionic forms are compared. The bibliography includes 143 references.

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I. INTRODUCTION

Electron transfer processes occupy an increasingly important position in modern ideas about reaction mechanisms[1,2]. It is assumed that the migration of atoms or atomic groups in a chemical reaction is preceded by electron transfer from one of the reacting molecules to the other[3]. Thus, by taking into account the role of electron transfer processes, it is possible to extend significantly the available information about the mechanism of the given reaction and facilitate thereby the selection of the optimal conditions for its occurrence. Naturally, the study of electron transfer processes has become possible only when new instrumental research techniques, particularly ESR, NMR, and microwave spectroscopy of chemically polarised nuclei, have been introduced into chemical practice.

Electron transfer results in products with new interesting properties. We may note that one-electron transfer gives rise to products corresponding to the transfer of a unit charge from the donor (D) to the acceptor (A). Products of incomplete transfer (donor–acceptor complexes) have been adequately investigated. Since the studies of Izmail'skii[4,5] and then Brackman[6] and Mulliken[7], considerable advances have been made in the elucidation of the structure of charge-transfer complexes and their thermodynamic and spectroscopic characteristics[8,9]. Much attention is devoted at present to the determination of the role of these complexes in reaction mechanisms[10,11]. Molecular complexes are formed when the interaction between D and A is insufficient for complete charge transfer; in complete charge transfer the products are radical-ion salts or even free radical-ions:

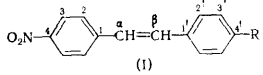
$$D + A \rightarrow [D^{\delta+}, A^{\delta-}] \rightarrow [D^{\cdot}, A^{\cdot-}] \rightarrow D^{\cdot} + A^{\cdot-}.$$

Naturally, molecules involved in charge transfer undergo changes in their electronic structure to a greater extent the stronger the donor–acceptor interaction. There is also then a possibility of a qualitatively new result when the change in electronic structure leads to a change in molecular geometry. However, due attention has not so far been paid to the geometrical consequences of electron transfer. In considering the properties of charge-transfer complexes it has usually been assumed that on formation of the complex neither the donor nor the acceptor undergoes a change in its geometry (see, for example, Hanstein et al.[12]). This was based on the conclusion reached by Orgel and Mulliken[13] that the geometry of charge-transfer complexes (or the steric effect) does not in general influence the position of the spectral charge-transfer bands.

On the other hand, X-ray diffraction studies have shown that the formation of the radical-ion salt $[D^{\cdot}, A^{\cdot-}]$ entails a serious distortion of the geometry of the initial molecule. For example, the conversion of the neutral molecule of 7,7,8,8-tetracyanoquinodimethane into the radical-anion is accompanied by an increase in the length of the multiple bonds and a shortening of the single bonds. This effect has been observed for the rubidium[14], morpholinium[15], and *N*-ethyl-1-methylbenzimidazolium[16] salts.

II. GEOMETRICAL ISOMERISATION AS A RESULT OF ELECTRON TRANSFER

The addition of a further electron to the 7,7,8,8-tetracyanoquinodimethane molecule leads to a change in its electronic structure: the multiple bond orders are reduced and those of single bonds are increased[14]. A similar change in bond orders is revealed also by quantum-mechanical calculations by the Hückel molecular orbital method for electron transfer to *p*-nitrostilbene and its substituted derivatives with the general formula (I).[17] In the radical-ion the order of the $\alpha-\beta$ bond is reduced and those of the $1-\alpha$ and $\beta-1'$ bonds are increased. The orders of the $2-3$ and $2'-3'$ bonds in the ring are also increased, while those of the $1-2$ ($1'-2'$) and $3-4$ ($3'-4'$) are diminished.



(I)

Similar results were obtained in calculations on the radical-ions of *p*-nitrobiphenyls [18]. Thus calculations have shown that electron transfer to nitrostilbenes (I) can lead to changes in the electronic structure which verge on the formation of a quinonoid structure or the ethylenic $\alpha-\beta$ bond approaches a single bond. In the ground state of the stilbene molecule the rotation of the benzene rings around the ethylenic bond is forbidden. However, the partial decrease of the double-bond character of the link between the atoms α and β as a result of electron transfer should probably lead to some decrease of the energy barrier to rotation. The presence of the nitro-group in stilbenes naturally promotes this conversion into the quinonoid form. Therefore, recent calculations on the ionic forms of unsubstituted stilbene, carried out by a combination of the Coulson–Hay and LCAO-MO methods [19] are extremely interesting. These calculations have shown that the conversion of stilbene into a radical-cation or a radical-anion lowers the barrier to *cis–trans* isomerisation almost by a factor of 2. The results of the calculations are presented in Fig. 1. In order to assess their validity, it is important to note that the calculated energy of the *cis–trans* isomerisation of the neutral stilbene molecule agrees well with thermochemical measurements [19]. The calculated geometrical parameters of stilbene and the results of X-ray diffraction analysis are also satisfactorily consistent [19]. The calculated barrier to the *cis–trans* isomerisation of stilbene (35.4 kcal mole^{-1}) agrees well with the experimental value (36.7 kcal mole^{-1}) and the predicted value for the first excited state is extremely low, as has in fact been assumed in the familiar models for the photoisomerisation of stilbene [19].

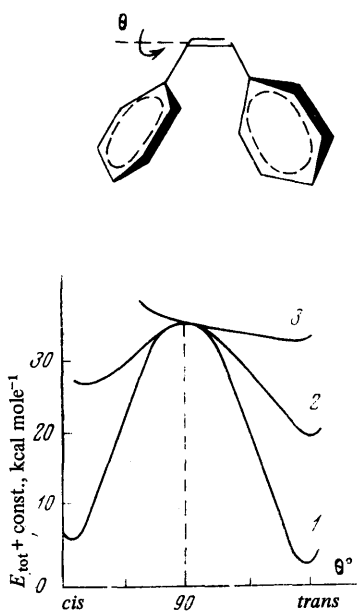
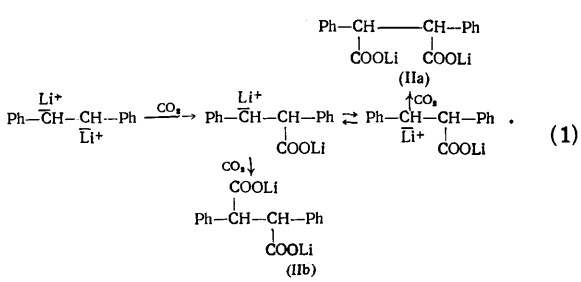


Figure 1. Changes in the energy E_{tot} of the stilbene molecule and radical-ion as a function of the angle of rotation of the ring θ about the central ethylenic bond ($\theta = 0°$ for the *cis*-configuration): 1) neutral molecule; 2) radical-anion or radical-cation; 3) molecule in the first excited state.

From the standpoint of the results of these calculations, it is interesting to consider the experimental data concerning the behaviour of olefins in reactions where electron transfer may be an intermediate stage. Schlenk and Bergmann [20,21] established that, when ethylenic compounds are treated with alkali metals in ethers, the products are adducts which react with carbon dioxide to from dicarboxylic acids. The steric structures of these acids were found to be determined by the nature of the metal employed and not by the configuration of the initial ethylene. It was discovered that the reaction of vicinal and organodimetallic derivatives with methyl iodide gives rise to the initial ethylenes and not to methylation products. Under these conditions, only the *trans*-isomer is obtained from both *trans*- and *cis*-stilbenes after treatment with metals and then with methyl iodide. An admixture of *trans*-stilbene appeared in certain experiments on the carboxylation of the products obtained by the treatment of *cis*-stilbene with alkali metals.

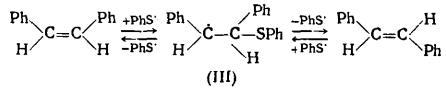
The results of Schlenk and Bergmann were tested by Wright and coworkers [22,23] and by Doran and Waack [24]. It was found that olefins give rise very readily to products resulting from the addition of two alkali metal atoms (dianions) with a change in colour. The electronic spectra of the stilbene dianion and radical-anion differ little [24] and the ESR spectra have not been recorded. On treatment with dimethyl sulphate, the stilbene metallation product gives rise to 2,3-diphenylbutane, while the reaction with methyl iodide, methyl alcohol and benzoyl chloride regenerates the stilbene, which always has the *trans*-structure. Since alkali metals, which can cause exhaustive reduction of the ethylenic double bond, were used in the reaction, it may be that these observations are due to the characteristics of the structure of the stilbene dianion. Szwarc and coworkers [25] believe that the *cis*-stilbene radical-anion is stable and that the product of the two-electron transfer (the dianion) actually undergoes isomerisation. According to Suzuki et al. [26], the stilbene dianion is almost planar and its alkali metal salts in ethereal solvents are ionic aggregates in which cations are located close to the carbon atoms of the central ethylenic bond above and below the plane of the molecule. The substitution of one of the ethylenic carbon atoms results in mutual rotation [27]. This is why the same mixture of the dilithium salts of *meso*- and (±)-diphenylsuccinic acids, (IIa) and (IIb), in proportions of 2 : 1 [reaction (1)] was obtained by Wright [22] in the carboxylation of the dilithium adducts of both *cis*- and *trans*-stilbenes.



(1)

cis-Stilbene is converted similarly into the *trans*-form on heating in the presence of traces of thiophenol. It was established that [28] the isomerisation is due to the addition

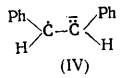
(and subsequent elimination) of the phenylthiyl radical to stilbene [reaction (2)]:



(2)

(III)

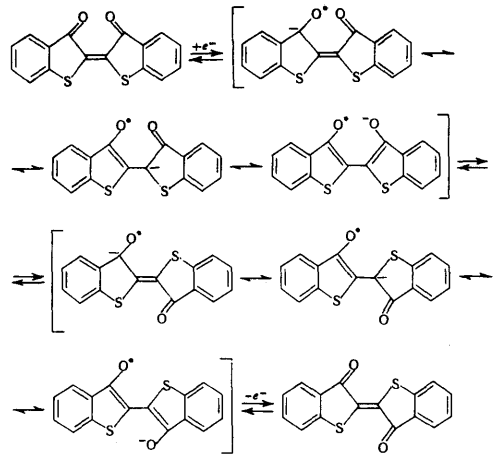
In contrast to the transfer of two electrons, the capture of one electron does not by itself convert stilbene into the almost "hydrogenated" product. However, the state of the central ethylenic bond in this radical-anion (IV) approaches that of the radical (III).



(IV)

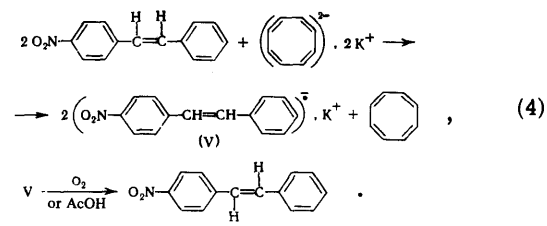
Johnson and Chang [29,30] attempted to compare the ESR spectra of the radical-anions of *cis*- and *trans*-stilbenes and to compare the rates of electron transfer from these radical-anions to the corresponding neutral molecules. They assumed that the ESR spectra should differ at least slightly and that the rate of electron transfer to *cis*-stilbene should differ from the rate of simple electron exchange between *trans*-stilbene and its radical-anion if the process is associated with a change in configuration. Electron exchange between species with similar configurations should be faster [31]. It was found that the ESR spectra of the potassium or tetra-alkylammonium salts of the radical-anions of *cis*- or *trans*-stilbene do not differ significantly. However, Johnson and Chang emphasise that the absence of differences between the ESR spectra does not alone indicate that *cis*- and *trans*-stilbenes give rise to radical-anions with the same structure. It was not possible to discover differences between the rates of electron transfer from the radical-anion to the neutral molecule either. In the formation of the stilbene radical-anion in the presence of a large amount of the *cis*-isomer, it was impossible to measure the broadening of the ESR line during the exchange and hence calculate the electron transfer rate constant. Having modified the method for the formation of the radical-anions, Chang and Markgraf [32] were able to detect by ESR a difference between the kinetics of electron transfer reactions involving *cis*- and *trans*-stilbenes. For this purpose, it was necessary to employ ultraviolet irradiation. However, irradiation sharply reduces the activation barrier to isomerisation (cf. Fig. 1). Clearly, under such conditions one observes only the rates of complex processes and the values obtained cannot be attributed to electron transfer alone. The reaction rate constants for *trans*- and *cis*-stilbenes are 10^9 and 10^3 litre mole^{-1} s^{-1} respectively. If the electron transfer rate constants differed by this amount, the implication would be that the stilbene radical-anions have the *trans*-configuration. However, it has been noted in a number of studies that irradiation of the radical-anions with ultraviolet light entails their *cis*–*trans* isomerisation and not *trans*–*cis* isomerisation, as for the corresponding neutral compounds [33,34].

Chang et al. [35] used a combination of the ESR and ultraviolet irradiation methods also in the investigation of the radical-anions formed in the reduction of thioindigo with metallic potassium. No difference was observed in the rates of electron exchange between the thioindigo radical-anion and the *cis*- and *trans*-isomers of thioindigo. However, the authors nevertheless suggest that the paramagnetic species formed from thioindigo has the *trans*-structure. They believe that the mutual repulsion of the carbonyl groups, which is sharply enhanced after electron transfer [reaction (3)], is the driving force of the isomerisation.



(3)

Direct evidence for *cis*–*trans* isomerisation as a result of electron transfer was obtained [36] in a study of the reaction of the dipotassium derivative of cyclo-octatetraene with nitro-derivatives of stilbene of type (I, R = H or NO_2) in tetrahydrofuran (THF). The reaction is homogeneous in THF. Dipotassiocyclo-octatetraene is a fairly weak reducing agent. After giving up its electrons, it is converted into neutral cyclo-octatetraene, whose yield can be readily determined. All these factors make it possible to specify exactly the amount of donor, to estimate the extent of electron transfer, to determine the nature of the products, and to elucidate their reactivities. It was established that under these conditions 4-nitro-*cis*-stilbene (I, R = H) gives rise to the potassium salt of a radical-anion, whose ESR spectrum was obtained and analysed. After treatment of the products of reaction (4) with oxygen, 4-nitrostilbene was isolated as a mixture of the *cis*- and *trans*-isomers in proportions of 1.5 : 1 in an overall yield of 80%. The electron transfer reaction went to completion under these conditions (there was a quantitative formation of cyclo-octatetraene). When equimolar amounts of the donor and acceptor were used, i.e. under the conditions of two-electron reduction of 4-nitro-*cis*-stilbene, only partial *cis*–*trans* isomerisation was again observed. Oxygen abstracts an electron from the radical-anion, for example the reaction of the potassium salt of nitrobenzene with oxygen in THF results in the formation of nitrobenzene in 80% yield. The neutral compound is formed also on treatment of the potassium salt of nitrobenzene in THF with water [37]. When the products of the electron transfer to 4-nitro-*cis*-stilbene are treated with water or acetic acid, the same mixture of the *cis*- and *trans*-isomers of 4-nitrostilbene is formed in an overall yield of 90%. [36] Since neither oxygen nor the resulting potassium acetate gives rise to any chemical changes in the 4-nitro-*cis*-stilbene solution in THF, it was concluded that the reaction proceeds in accordance with reaction (4).



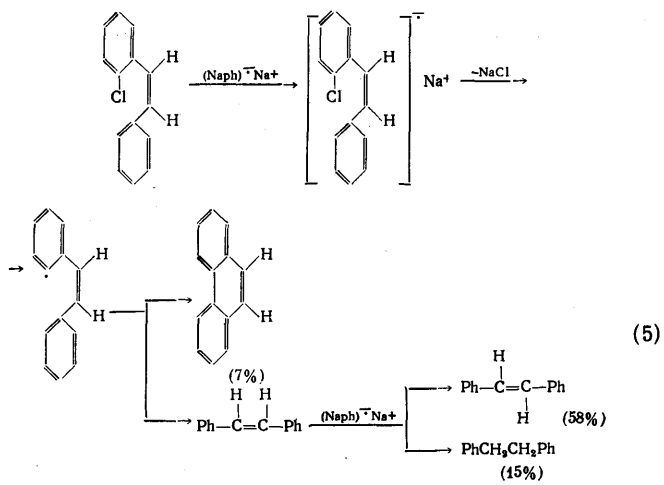
(4)

(V)

The one-electron transfer to 4-nitro-*trans*-stilbene under these conditions leads to the recovery of the initial

trans-isomer and the quantitative formation of cyclo-octatetraene. The absence of the isomerisation of 4-nitro-*trans*-stilbene is probably due to the fact that, under the reaction conditions, the energy barrier to the rearrangements of the radical-anion of this compound to the *cis*-isomer is much higher than for the *trans*-trans-formation of the radical-anion of 4-nitro-*cis*-stilbene. Thus, according to Golebiewski and Parczewski [19], the conversion of the *cis*-stilbene radical-anion into the *trans*-isomer requires approximately 10 kcal mole^{-1}, while the conversion of the *trans*-form into the *cis*-form of the radical-anion requires about 18 kcal mole^{-1} (Fig. 1). The symmetrical 4,4'-dinitro-*cis*-stilbene is completely converted into the *trans*-isomer on treatment with dipotassio-cyclo-octatetraene and then with oxygen or acetic acid [38]. It is interesting that protonation of the radical-anions or dianions of *p*-nitrostilbenes does not lead to the formation of *p*-nitrobibenzyls, i.e. the ethylenic bond is not hydrogenated. This finding is unexpected, since electron-transfer from sodionaphthalene to stilbene in THF leads to bibenzyl after protonation [see reaction (5)]. [39] The introduction of the nitro-group into stilbene should, of course, promote reduction. In nitrostilbene the additional electron is probably effectively held by the nitro-group, which prevents the addition of protons to the carbon atoms of the ethylenic bond. In other words, the degree of electron saturation of the central ethylenic bond in the products under consideration is sufficient for isomerisation but not for the addition of protons.

The conclusions reached in the study of the stereochemical results of electron transfer are consistent with the literature data concerning the behaviour of the corresponding neutral compounds under conditions where electron exchange is possible. Thus selective reduction of 4,4'-dinitrostilbene with tin in hydrochloric acid leads to 4,4'-diamino-*trans*-stilbene regardless of whether the initial dinitro-compound has the *cis*- or *trans*-configuration [40]. On treatment with potassium methoxide, 4-nitro-*cis*-stilbene is converted into a mixture of the *cis*- and *trans*-isomers [41]. On treatment with lithium in ether and then with carbon dioxide, 4-chloro-*cis*-stilbene gives rise to a mixture of products consisting of 4-chloro-*trans*-stilbene, 4-chloro-*cis*-stilbene, and *trans*-stilbene-4-carboxylic acid [42]. The reaction of 2-chloro-*cis*-stilbene with an excess of sodionaphthalene [(Naph)$^-$Na$^+$] in THF leads to phenanthrene, bibenzyl, and *trans*-stilbene. Singh and Kumar [39] explain the observed reactions in terms of reaction (5).



(5)

The addition of an electron to the double bond evidently lowers the barrier to rotation about the bond. The one-electron reduction of ethylenic compounds can be regarded in a certain sense as a stage in the conversion into ethane derivatives. From this point of view, it is important, in principle, to know the stereochemical results of the abstraction of an electron from the double bond. Calculations have shown [19] that the enhanced stability of the *trans*-form is also characteristic of the stilbene radical-cation, i.e. the one-electron oxidation product. The experimental confirmation of this finding is still inadequate. It is known [43] that fuming nitric acid induces the *trans*-isomerisation of *cis*-stilbene. The conversion of *cis*-stilbene into *trans*-stilbene under the influence of iodine [43] may proceed via the formation of the stilbene radical-cation and the iodide anion, which then give rise to neutral stilbene (*trans*-form) and iodine. In this case complete charge transfer may not, of course, necessarily occur. The isomerisation takes place in a complex where the donor and acceptor orbitals strongly overlap. Indeed, *cis*- and *trans*-stilbenes form in hexane solution different complexes with iodine, which give rise to charge-transfer bands at 354 and 365 nm respectively [44]. It is not clear from the literature whether the bands merge after a time and microwave spectroscopic studies have not been made on the system. Furthermore, it would be interesting to show whether the interaction leads to the appearance of paramagnetic species, i.e. whether the ^{1}H NMR signal of the olefinic protons of *cis*-stilbene shifts as a result of the mixing of the reactants. For example, in the presence of the stable 2,2,6,6-tetramethylpiperidin-1-oxy-radical the signal of the $\overset{|}{=}C-H$ protons in dimethyl maleate shifts towards a high field [45]. The signals of the methyl protons of dimethyl maleate remain in the same position. Hence it follows that a complex is formed in which the orbitals of the unpaired electron of the radical overlap with the π orbitals of the dimethyl maleate double bond. In the presence of nitroxy-radicals there is a sharp increase in the rate of isomerisation of dimethyl maleate to dimethyl fumarate and the radicals are not consumed. The probability of the isomerisation of maleate in a complex with the radical exceeds by seven orders of magnitude the probability of the isomerisation of its free molecule [45].

According to Il'ina [46], the oxidation of *cis*-stilbene by the salts $Mn(OAc)_3$ and $Co(OAc)_3$ in acetic acid or by the salt $Tl(OCOCF_3)_3$ in trifluoroacetic acid leads to a mixture of acetates (or trifluoroacetates) of hydrobenzoin (*meso*-type) and isohydrobenzoin [(±)-type]. As in the synthesis of diphenylsuccinic acids according to Scheme 1, the amount of *meso*-derivatives obtained is approximately twice as large as that of the (±)-derivatives. This ratio of stereoisomers holds for *trans*-stilbene, but the oxidation is faster. When $Mn(OAc)_3$ in acetic acid is used, *trans*-stilbene is oxidised seven times faster than *cis*-stilbene. Part of the olefin remains unchanged at the end of the process and an appreciable amount of the *trans*-isomer is produced from *cis*-stilbene. Bivalent metal salts, for example $Mn(OAc)_2$, formed as a result of the reaction cannot induce the *trans*-isomerisation of *cis*-stilbene. Such isomerisation is not caused by trifluoroacetic acid either. When $Tl(OCOCF_3)_3$ in CF_3COOH was used as the oxidant, stilbene radical-cations were detected, their amount decreasing in the course of the reaction. Il'ina [46] proposed reactions (6) and (7), according to which one-electron oxidation of stilbene involves the intermediate formation of the radical-cation, possibly in the form of the complex (VI). This stage is reversible. If the

starting compound in reaction (6) is *cis*-stilbene, then the organic part of the complex (VI) is capable of at least partial *cis–trans* isomerisation. The conversion of (VI) into an acetoxy-derivative and oxidation of the resulting radical (VII) lead to the complex (VIII), which decomposes with formation of the final products (IXa) (*meso*-type) and (IXb) [(±)-type], as in reaction (7).

$$\underset{(cis\text{- or }trans\text{-})}{PhCH{=}CHPh} + Tl(OCOCF_3)_3 \underset{}{\overset{CF_3COOH}{\rightleftharpoons}} \underset{(VI)}{[PhCH\dot{C}HPh][Tl(OCOCF_3)_3]^-} \xrightarrow{CF_3COOH}$$

$$\rightarrow \underset{(VII)}{[PhCH(OCOCF_3)CHPh]} + Tl(OCOCF_3)_2;$$

$$2Tl(OCOCF_3)_2 \xrightarrow{fast} Tl(OCOCF_3)_3 + TlOCOCF_3\ , \qquad (6)$$

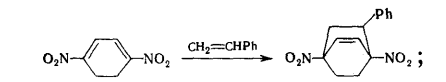
$$VII + Tl(OCOCF_3)_3 \xrightarrow{CF_3COOH} \underset{(VIII)}{[PhCH(OCOCF_3)CHPh][Tl(OCOCF_3)_3]^-} \xrightarrow{CF_3COOH}$$

$$\rightarrow \underset{(IX)\ \ [a)meso\text{-};\ b)\ (\pm)\text{-}]}{PhCH(OCOCF_3)CH(OCOCF_3)Ph} + Tl(OCOCF_3)_2;$$

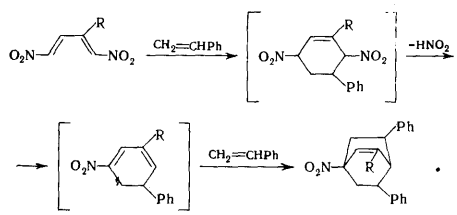
$$2Tl(OCOCF_3)_2 \xrightarrow{fast} Tl(OCOCF_3)_3 + TlOCOCF_3\ . \qquad (7)$$

The salt $Tl(OCOCF_3)_2$, which should be paramagnetic disproportionates very rapidly[47] [see reactions (6) and (7)]. This leads to the formation of the diamagnetic thallium(III) and thallium(I) trifluoroacetates and the ESR spectrum reveals the presence of the stilbene radical-cations only. Owing to its high acidity, in trifluoroacetic acid the addition of the acetoxy-group to the double bond proceeds via the one-electron oxidation to the radical-cation and not via the addition of Tl^{3+} to one of the olefinic atoms (as in acetic acid[48]).

From the standpoint of the changes in geometry induced by electron transfer, it is interesting to consider again the mechanism of the 1,4-addition of dienes to the ethylenic bond (the Diels–Alder reaction). An early charge transfer stage[49], associated with a change in the geometry of the initial reactants, is also possible in this process. Naturally, this effect can appear most clearly when there is a difference between the polarities of the diene and dienophile. The reaction of styrene with 1,4-dinitrobuta-1,3-diene constitutes an example with a very large difference of this kind. Clearly the dinitro-derivative must be regarded as an electron acceptor in relation to styrene. Dienes of this type are inactive in the classical diene synthesis reaction[50], but they do react with nucleophilic dienophiles of the styrene type[51]. The reaction is therefore of "inverse" electronic type. 1,4-Dinitrocyclohexa-1,3-diene reacts with styrene under comparatively mild conditions (100°C, 10 h, in xylene) with formation of a 1 : 1 adduct [reaction (8)].[51] The fixed *S-cis*-configuration of this diene remains unchanged also in the intermediate stages, which ensures that the familiar rules of Alder and Stein[49] hold. Since the configuration of the open-chain 1,4-dinitro-1,3-dienes may change in the initial stage of the reaction, more severe conditions are required for the formation of adducts. The reaction proceeds only on heating at 140°C for 40 h in the absence of solvent and is accompanied by the elimination of the nitro-group and a second interaction with the dienophile [reaction (9)].[51] Presumably, more severe conditions are needed to impart to the diene component of the transition complex the configuration required for the formation of the ring†.



(8)



(9)

The occurrence of *cis–trans* isomerisation in the chemical reaction involving an electron transfer stage was confirmed by Fraser and Taube[53], who investigated the reaction of Cr^{2+} or V^{2+} ions with complex salts containing the (methyl maleato)pentamminecobalt(III) cation. In an acid medium an oxidation–reduction reaction takes place, as a result of which there is not only a decrease of the charge of the complex cation by unity but the cation also exchanges the methyl maleate ligand for water [reaction (10)]:

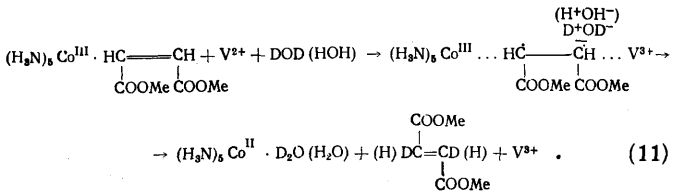
$$[Co(NH_3)_5 \cdot (CHCOOMe)_2]^{2+} + Cr^{2+}\ \ (or\ V^{2+}) + H_2O \xrightarrow{HClO_4}$$

$$\rightarrow [Co(NH_3)_5 \cdot H_2O]^{2+} + Cr^{3+}\ \ (or\ V^{3+}) + (CHCOOMe)_2\ . \qquad (10)$$

The liberated ligand is hydrolysed in an acid medium to ethylene-1,2-dicarboxylic acid. Under these conditions, not all the acid formed has the *cis*-configuration corresponding to the ligand in the initial complex. Fumaric acid (*trans*) is formed together with maleic acid (*cis*); the amount of the latter is greater the higher the concentration of perchloric acid in the reaction mixture. A mixture of isomeric acids is formed in the presence of D_2O and the C–D bond is present only in fumaric acid but not in maleic acid. When the (methylfumarato) pentamminecobalt(III) cation is reduced in D_2O [reaction (10)], only fumaric acid without an admixture of maleic acid is formed and which does not contain C–D bonds. Probably electron transfer from Cr^{2+} or V^{2+} to the complex ion proceeds via the mechanism of the socalled "double exchange"[54]. The reducing agent (Cr^{2+} or V^{2+}) transfers an electron to the bridging group (maleate) and the latter transfers it further to the oxidising agent [cobalt(III)]. Thus the bridging $(CHCOOMe)_2$ group is alternately reduced and oxidised with isomerisation of maleic acid to fumaric acid. When the electron is localised at the ethylenic bond, the addition of a proton (deuteron) takes place. After the abstraction of an electron from the ethylenic bond, the H^+ ion (in H_2O) or H^+ and D^+ ions in (D_2O) are split off. Hydrogen isotope exchange involving the –C=C– bond is observed. The conversion of cobalt(III) into the bivalent form proceeds simultaneously with the substitution of the ethylenedicarboxylic acid diester in

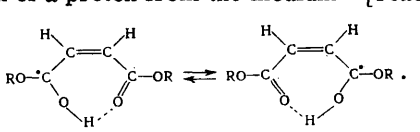
† A somewhat similar situation arises in the dehydration of fumaric acid to maleic anhydride on heating. Eliel believes[52] that at a high temperature the dehydration is preceded by the migration of the double bond. Thermal isomerisation has been observed for many olefins; in all such compounds there is a barrier to rotation about the double bond of about 40 kcal $mole^{-1}$.[52]

the inner sphere of the complex by a water molecule [reaction (11)].



(11)

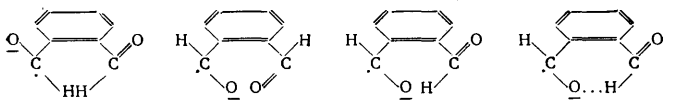
The absence of hydrogen isotope exchange involving the ethylenic bond in the dimethyl fumarate ligand can be explained by the fact that in this case the bridge is not directly involved in the electron transfer. The role of this ligand is more likely to be to bring closer together the two positively charged ions for "direct electron exchange" [54] between their overlapping orbitals. Fraser and Taube's study [53] contributed much to the elucidation of the mechanism of the inner-sphere electron transfer. At the same time an explicit relation between electron transfer and geometrical transformations was first noted. A few more studies were then made in which the properties of the products resulting from electron transfer to dialkyl fumarates or dialkyl maleates were compared [55-59]. It was shown that in pyridine, dimethyl sulphoxide (DMSO), and dimethylformamide (DMF) these compounds are reduced in stages [55-57]. Radical-anions capable of undergoing one-electron oxidation are formed in the first stage. The half-wave potentials for the reduction of maleate and fumarate differ but the one-electron oxidation of the resulting radical-anions is characterised by the same half-wave potentials. The above relations between the $E_{1/2}$ for the cathodic and anodic waves hold also at a very high alternating frequency, up to 500 Hz. [57] This implies that the radical-anions formed from maleate and fumarate have similar energies. The ESR spectra of the products of the electrochemical reduction of dimethyl fumarate and maleate are identical at the potential of the limiting currents of the first waves regardless of the temperature at which they are recorded [58]. According to the authors, it is unlikely that the ESR spectra of the *cis*- and *trans*-radical-anions are completely identical. Thus, if it is assumed that the ESR spectra of the *cis*- and *trans*-radical-anions should differ, the above observation indicates a rapid and almost complete *trans*-isomerisation of the *cis*-radical-anions. At the same time, if the radical-anions are obtained in a proton-donating medium, the *cis*- and *trans*-isomers give rise to different ESR [60] and electronic [59] spectra. Under these conditions, maleates evidently give rise to unusually stable radical-anions, whose structure is fixed by the formation of a ring with participation of a proton from the medium [59] [reaction (12)].



(12)

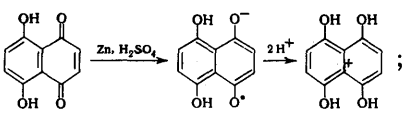
III. INFLUENCE OF COORDINATION INTERACTIONS ON THE STEREOCHEMISTRY OF ELECTRON TRANSFER PRODUCTS

Carbonyl compounds capture an electron and are converted into ketyls, which contain a negatively charged oxygen atom. This atom is a particularly powerful proton acceptor. Reaction (12) shows how the formation of a hydrogen bond prevents the *cis*–*trans* isomerisation of the maleate ester, which can occur on electron transfer. The enhancement of the affinity of the negatively charged carbonyl oxygen for a proton ensures the formation of stable hydrogen bonds with molecular fragments which are otherwise incapable of it. An example is provided by the C–H fragment of the aldehyde group. The radical-anion of phthalaldehyde is planar [61] and therefore might exist in three forms: *exo*- (X), *enao*- (XI), and *meso*- (XII):



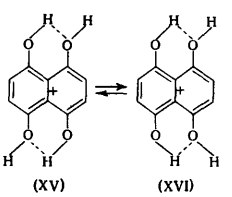
(X) (XI) (XII) (XIII)

Only the *meso*-conformer, in which the mutual orientation of the functional groups ensures the formation of a hydrogen bond involving the proton of one aldehyde group and the negatively charged oxygen atom of the other [structure (XIII)], can be detected by ESR. The influence of hydrogen bonds of this type on the conformation of electron transfer products is shown also when the negative charge of the oxygen atom is neutralised by protons from the medium. Thus the reduction of naphthazarin (XIV) with zinc dust in sulphuric acid leads to the radical-cation of naphthazarin semiquinone [reaction (13)], whose ESR spectrum changes with temperature [62]. This variation has been attributed to mutual interconversions of the *cis*- and *trans*-forms (XV) and (XVI) respectively. The equilibrium position (and hence the form of the ESR spectrum) can be represented at a specified temperature with satisfactory accuracy if it is assumed that the isomerisation mechanism includes the dissociation of the intramolecular hydrogen bond via mechanism (14). The exchange of the hydroxyl protons of the radical-cation with the medium is then much slower than isomerisation. The height of the potential barrier to isomerisation is 3–5 kcal and is comparable to the energy of the hydrogen bond in systems of type (XV) (3–7 kcal). [62]



(13)

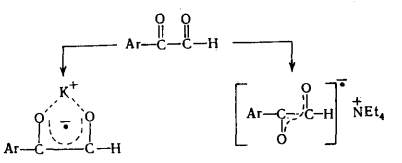
(XIV)



(14)

(XV) (XVI)

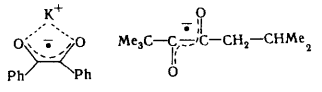
The conformation of the semidione is fixed even more rigidly when an alkali metal cation is coordinated to the two carbonyl groups. Thus the one-electron reduction of 3,4,5-trimethoxyphenylglyoxal with potassium t-butoxide in DMSO gives rise mainly to the *cis*-semidiones (XVII), while in the electrolysis in DMF, in the presence of tetraethylammonium perchlorate as the carrier electrolyte, the main product is the *trans*-isomer (XVIII) [63] [reaction (15)].



(15)

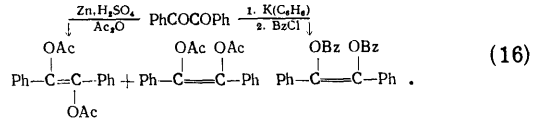
(XVII) (XVIII)

The ESR spectrum of the sodium salt of the benzil ketyl in THF shows splitting due to Na^+ (0.6 G), while in the ESR spectrum of the sodium salt of the ketyl of 2,2,6,6-tetramethylhexane-3,4-dione in THF there is no splitting whatever due to Na^+.[64] While the benzil ketyl can give rise to the contact ion pair (XIX), the formation of a species of type (XX) from the 3,4-dione is difficult owing to steric hindrance. This semidione exists in the form of a free ion or an ion pair separated by solvent molecules.



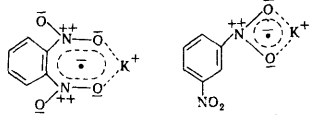
(XIX) (XX)

If the benzil ketyl ion does not form part of an ion pair, it exists in the *trans*-form, but in the case of the potassium salts the *cis*-form, in which both charged oxygen atoms are in the vicinity of the metal cation, [as in compound (XIX)] is more stable[65]. On benzoylation, such a radical-ion pair gives rise mainly to *cis*-dibenzoylethylene[65], while the reduction of benzil under conditions which do not stabilise the contact ion pair is not stereospecific[65,66] [reaction (16)].



(16)

The coordination of the potassium cation to two oxygen atoms in the radical-anion of *o*-dinitrobenzene leads to the stabilisation of the unusual configuration in which the nitro-groups are spread out in a single plane. In neutral *o*-dinitrobenzene the coplanarity of the two nitro-groups is ruled out both by calculation[67] and experiment[68,69]. In the potassio-derivative of *o*-dinitrobenzene (XXI) the coordination of the metal cation to both nitro-groups leads to the formation of a condensed "ring" in which there is a possibility of additional delocalisation of the unpaired electron. Indeed, the ESR spectra in dimethoxyethane (DME) or in THF show that the unpaired electron in (XXI) is equally delocalised over the two nitro-groups (the constants for the splitting by the nitrogen atoms $a_N^1 = a_N^2 = 3.2$ G),[70] while in the potassium salt of the radical-anion of *m*-dinitrobenzene (XXII) the delocalisation is essentially over only one of the two groups ($a_N^1 = 9.3$ G, $a_N^2 \leq 0.2$ G).[71,72] This contrasts sharply with ESR spectroscopic data for the radical-anions obtained by electrolysis in acetonitrile in the presence of tetra-n-propylammonium perchlorate as the supporting electrolyte: $a_N^1 = a_N^2 = 3.16$ G for *o*-dinitrobenzene and $a_N^1 = a_N^2 = 4.68$ G for *m*-dinitrobenzene[73]. The difference can be understood if account is taken of the nature of the counterion. When the counterion is a small cation (potassium), the formation of a closely knit ion pair is possible. The K^+ ion can than make its vacant *d* and *p* orbitals available for the π electrons of the radical-anion system[54]. When a tetraalkylammonium cation is used as the counterion, the mutual approach of species with different charges is hindered by the alkyl groups. Ion pairs with the potassium cation are stable, i.e. exist longer than is required for the detection of the ESR signal. This follows from a comparison of the polarographic behaviour of the three isomeric dinitrobenzenes in the same solvent (DMF) using tetraethylammonium or potassium perchlorate as the carrier electrolyte[74]. The half-wave potentials corresponding to the conversion of *p*- and *m*-dinitrobenzenes into radical-anions are independent of whether tetraethylammonium or potassium counterions are employed. The radical-anion is formed from *o*-dinitrobenzene at a potential more positive almost by 100 mV when tetraethylammonium perchlorate is replaced by potassium or sodium perchlorate. Changes in the composition and structure of the electrical double layer do not influence under these conditions the reduction mechanism, which has been shown by a special study[75] to consist of the reversible transfer of one electron. Since the transfer of one electron to *o*-dinitrobenzene in the presence of potassium perchlorate as the carrier electrolyte proceeds at a less negative potential than in the presence of tetraethylammonium perchlorate, it is clear that the potassium salt does indeed have the minimum energy, i.e. is characterised by the highest degree of delocalisation of spin density.

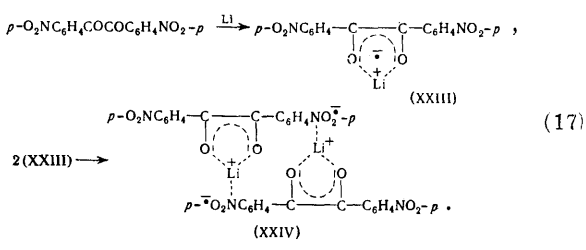


(XXI) (XXII)

The structure (XXI) favours greater delocalisation of the unpaired electron, but the anionic component of the salt is then forced to assume an unusual conformation. These properties of *o*-dinitrobenzene should be manifested also in chemical reactions, where, as can be seen from reaction (12), the role of the ring-closing species may be played by the proton. Indeed, the reduction of both nitro-groups at once is observed in the electrolysis of *o*-dinitrobenzene in the presence of water[76], while in the *para*-[76] or *meta*-isomer[77] only one nitro-group is reduced.

The relation between the distribution of spin density in the products of electron transfer to organic molecules and the behaviour of these products in reactions is important but has so far been little investigated. It would be especially useful to know the reason for the particular sequence of chemical changes in the groups present simultaneously in the molecule.

From this standpoint, it is interesting to examine electron transfer to 4,4'-dinitrobenzil [reaction (17)]. Paramagnetic species whose ESR spectra depend on temperature and concentration, are then formed. It has been shown[78] that such electron transfer products can exist in the monomeric or dimeric forms [(XXIII) or (XXIV) respectively]. The former is present at high dilution and the latter at an increased concentration or at a low temperature.



(XXIII) (XXIV) (17)

In form (XXIII) the unpaired electron is delocalised mainly over the dicarbonyl group and in form (XXIV) over the nitro-groups. Under these conditions, 4,4'-dinitrobenzophenone gives rise to radical-anions in which the nitro-group and not the carbonyl group carries the maximum electron density[78]. These results of the analysis of the ESR spectra are consistent with chemical data; on

reduction with tin in hydrochloric acid, 4,4′-dinitrobenzophenone is converted into 4,4′-diaminobenzophenone [79] and 4,4′-dinitrobenzil is converted into 4,4′-diaminodeoxybenzoin (p-$H_2NC_6H_4CH_2COC_6H_4NH_2$-$p$). [80]

IV. CONFORMATIONAL INHOMOGENEITY OF THE ELECTRON TRANSFER PRODUCTS

The radical-anions obtained from aromatic nitro-compounds retain a twofold symmetry axis. It follows from the analysis of the hyperfine structure of the ESR spectrum of the nitrobenzene radical-anion that this species contains protons of three kinds only; *ortho*-, *meta*-, and *para*- [81,82] [structure (XXV)].

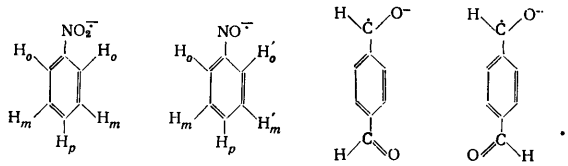
The situation is quite different in the conversion of nitrosobenzene into the corresponding radical-anion. According to ESR data [82,83], the nitroso-group is to some extent fixed in the plane of the ring after electron transfer. This leads to the appearance of five kinds of protons, since the two *meta*-positions (as well as the *ortho*-positions) become non-equivalent [structure (XXVI)].

The one-electron reduction of acetophenone leads to an ESR spectrum comprising 128 lines, corresponding to the three equivalent protons of the methyl group and the five non-equivalent ring protons [84].

The ESR spectrum of the products of the reversible one-electron reduction of benzaldehyde in DMF in the presence of tetra-alkylammonium supporting electrolytes contains 64 lines [84]. This form of the spectrum shows that the absence of a symmetry plane is characteristic of the benzaldehyde radical-anion. It was noted [85] that this unexpected result cannot be attributed solely to the interaction of the negatively charged carbonyl group with the nearest ring atoms. A more interesting phenomenon is probably involved—an unusual polarisation of the π-electron system of the radical-anion by the electric dipole of the charged carbonyl group.

The ESR spectra of the radical-anions of nitrobenzonitriles, obtained electrochemically in DMF, [86] show that the equivalence of the positions with respect to the nitrile group is maintained. This can be due either to the free rotation of the nitrile groups or to their linear disposition with respect to the symmetry axis of the molecule. The ESR spectra of the potassium salts of the radical-anions of terephthalonitrile in DME [87] demonstrate the equivalence of both the cyano-groups in the *para*-positions with respect to one another and of the benzene ring protons. It follows from the analysis of the hyperfine structure of the spectra that the constants for the splitting by the two nitrogen atoms are equal; also equal are the constants for the splitting by all the hydrogen atoms.

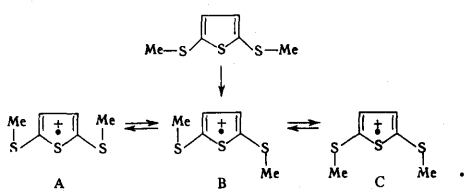
At the limiting current potential of the first reduction wave in DMSO in the presence of tetra-n-propylammonium perchlorate as the carrier electrolyte terephthalaldehyde gives rise to radical-anions, which exhibit two ESR spectra superimposed on one another. These spectra are characterised by the same g-factor, but have significantly different splitting constants [61,85]. If the rate (frequency) of rotation of the aldehyde groups were much higher than the frequency differences between the splitting constants of the rotational *cis*- and *trans*-isomers, the ESR spectrum of the radical-anions of terephthaldehyde would be averaged out. On the other hand, if the rate of mutual rotation of the groups were comparable to the frequency difference corresponding to the splitting in the spectra of the rotational *cis*- and *trans*-isomers, the ESR spectral lines would be broadened. Since a superposition of the spectra is observed, the implication is that the frequency of rotation is much smaller than the frequency difference corresponding to the splitting. It is unlikely that the observed superposition of the spectra could arise due to the presence of ion pairs with the same radical-anion but with different separations of the latter from the cation: a tetra-alkylammonium cation, which hardly forms ions pairs, was used in the above experiment [61,85]. Thus electron transfer to terephthalaldehyde leads to the formation of the two conformers (XXVIIa) and (XXVIIb).



(XXV) (XXVI) (XXVIIa) (XXVIIb)

The conformers (XXVIIa) and (XXVIIb) are physically distinguishable and the duration of their existence at any rate exceeds the ESR time constant, i.e. is greater than 1 ms. It follows from the analysis of the intensities of the corresponding signals that the rotational *cis*- and *trans*-isomers are formed in proportions of 1 : 1.4. [61,85] Conformationally inhomogeneous products were obtained also in electron transfer to 1,4-diacetylbenzene [88] and thianthrene-5,10-dioxide [89]. Durosemiquinone [90] and naphthazarin [62] are known to give rise to rotational *cis*- and *trans*-isomers of the radical-cations.

The oxidation of oximes leads to iminoxy-radicals having the general formula $R_2C{=}N{-}O^{\cdot}$. Under these conditions, *syn*-benzaldoxime yields both *syn*- and *anti*-isomers [91] and a similar result was obtained in the oxidation of benzophenone and fluorenone oximes [92]. Thiophen substituted in the 2- and 5-positions by methylthio-groups exists as one conformer only. One-electron oxidation with aluminium chloride in nitromethane results in the formation of conformationally inhomogeneous products, which may have structures A, B, or C. ESR showed the presence of the asymmetric conformer B and of one symmetrical conformer (A or B). [93]



A B C

The hindered rotation of the dimethylamino-groups about the bonds between the nitrogen atoms and the ethylenic carbon atoms is responsible for the presence of two types of methyl protons in the radical-cation of tetrakis(dimethylamino)ethylene [94]. Another instance of the restriction of the freedom of the mutual rotation of the groups was observed in Coppinger's cation, which is formed on oxidation of 3,3′,5,5′-tetra-t-butylbis-(4-hydroxyphenyl)methane [95].

The examples enumerated above are sufficient to illustrate the fact that the conjugation conditions in neutral molecules and in the corresponding one-electron transfer products are different. This entails a significant change in the mobility of the groups and ultimately a change in the energy relations of the rotational isomers. Thus calculations have shown [96] that the energies of the rotational *cis*- and *trans*-isomers of terephthalaldehyde differ by not more than 0.012 eV. On the other hand, in the series of

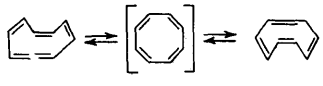
the corresponding radical-anions the *trans*-isomer (XXVIIb) is more stable than the *cis*-isomer (XXVIIa) by 0.083 eV, i.e. almost by 2 kcal. These calculations describe fairly completely the electronic structures of the molecules considered (the extended Hückel method with allowance for valence electrons by the Wolfsberg–Helmholtz method was used[97]). At the same time solvation and intermolecular electrostatic interaction effects would not of course be reflected when this approach is used. Therefore the observed quantitative difference between (XXVIIa) and (XXVIIb) can be far from the true values. Nevertheless, all the results show that electron transfer can significantly enhance the difference between the energy relations of the conformers.

Detailed study of the causes responsible for the conformational inhomogeneity of electron transfer products is one of the most attractive aspects of the present state of the investigations. There is a possibility of discovering general relations which are important and not self-evident.

V. ELECTRON TRANSFER AND CONFORMATIONS OF CYCLOPOLYENES

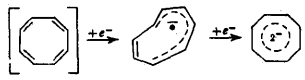
While in the instances discussed above electron transfer alters the conjugation conditions and hence the conformational mobility of the molecule, in cyclopolyenes electron transfer can lead to the formation of π-electron ring systems embracing all the ring atoms as a result of which the ring is maintained in one plane. We shall consider this phenomenon using cyclo-octatetraene and azocine as examples.

It is generally accepted that the structure of cyclo-octatetraene is best represented by the bent boat form (XXVIII) with L_{2d} molecular symmetry[98,99]. Single (1.462 Å) and double (1.334 Å) bonds, whose lengths do not differ significantly from the normal values for bonds of the C–C (sp^2–sp^2) (1.479 Å) and C=C (sp^2–sp^2) (1.338 Å) types respectively, alternate in the molecule[100]. The p_z orbitals located at the end of each single bond cannot overlap. This implies that there is no cyclic conjugation in cyclo-octatetraene and the bonds are localised. Cyclo-octatetraene, which is a vinylogue of benzene, behaves as a typical olefin. Some authors state[101,102] that it exhibits "blatant and unquestionable non-aromaticity". According to NMR data[102,103], there is a rapid and reversible migration of the double and single bonds in the cyclo-octatetraene molecule, leading to the conversion of the form (XXVIIIa) into (XXVIIIb) [reaction (18)].



(XXVIIIa) (XXIX) (XXVIIIb) (18)

It follows from the spectra that the activation energy for this transition is 14 kcal mole^{-1}, which is close to the 17 kcal mole^{-1} calculated by the LCAO-MO SCF method[104]. The planar conformation of cyclo-octatetraene (XXIX) is an intermediate form in equilibrium (18). It is believed[104] that the above inequality of bond lengths should persist in form (XXIX). The planar or almost planar form (XXIX) is involved in electron transfer. The unpaired electron in the resulting radical-anion (XXX) can probably be delocalised to some extent over the perimeter of the molecule[105]. In other words, one can imagine this radical-anion as a fairly planar cyclic system with nine π-electrons. This system should tend to capture yet another electron and become converted into the completely planar dianion (XXXI) with ten delocalised electrons, satisfying the familiar Hückel aromaticity rule ($4n + 2$; $n = 2$). Electron transfer thus prevents the bending of the planar form [see reactions (18) and (19)].



(XXIX) (XXX) (XXXI) (19)

The transfer of a second electron is of course associated with the expenditure of appreciable additional energy, since it requires the final flattening of the molecule and the overcoming of the mutual repulsion of the free electrons[106]. However, this results in the formation of the stable aromatic cyclo-octatetraene dianion. In THF solutions cyclo-octatetraene reacts fairly rapidly with two equivalents of metallic potassium and on extensive cooling well formed crystals of the dipotassium salt of the dianion (XXXI) may be precipitated. These crystals have not so far been investigated by X-ray diffraction. On drying or on contact with air, they explode. However, the solutions are stable. The vibrational spectrum of the dipotassium salt of the cyclo-octatetraene dianion resembles those of other planar aromatic systems[107]. The transition energy in the short-wavelength region of the electronic spectra of this dianion and benzene, calculated by the free electron method, are close[108]. The method of calculation used is said[109] to represent fairly well the qualitative features of the electronic spectra, including the transition energies. The protons of the dianion (XXXI) are represented in the NMR spectrum by a sharp singlet. The ^{1}H NMR spectrum of cyclo-octatetraene also consists of a singlet with a very similar chemical shift[110]. These characteristics of the spectrum can be in no way related to the previously proposed[111] structure of the dipotassio-compound (XXXII).



(XXXII)

The fact that the compound with a double negative charge does not exhibit a shift of the ^{1}H NMR signal to a high field is evidence for a ring current. The hypothesis of a π-electron ring current is described, for example, by London[112] and the problem is discussed by Peacock[109] and Musher[113]. The ^{7}Li NMR spectrum was used to demonstrate the presence of a π-electron ring current in the dilithium salt of the cyclo-octatetraene dianion (see Table and Fig. 2).

^{1}H NMR data[110,116] show that the dipotassium salt of the cyclo-octatetraene dianion exists preferentially in the form of a close ion pair. If a π-electron ring current is possible in the organic component of the dilithium salt (XXXI), the chemical shift of the ^{7}Li signal should differ from the usual value, for example, from the ^{7}Li shift in lithium alkyls. The ^{7}Li signal for the salt (XXXI) should be displaced towards both lower and higher fields, depending on whether the metal atom is in the deshielding or shielding zone (Fig. 2, zones A or B). The data in the Table show that, compared with n-butyl-lithium, dilithiocyclo-octatetraene resonates in a much higher field. The ^{7}Li shift for the salt (XXXI) is close in magnitude to the shift for cyclopentadienyl-lithium and the aromaticity of the cyclopentadienyl anion has already been reliably demonstrated (see, for example Rafiel'[101]). Since the ^{7}Li signal in the (XXXI) spectrum is significantly displaced towards a high

field, the following conclusions may be reached: (1) Li^+ is associated with the π-electron system of the dianion; (2) the π-electron system of the dianion can indeed induce a local magnetic field, i.e. ring currents; (3) the Li^+ cations are in the regions of increased shielding, i.e. below and above the plane of the dianion (Fig. 2).

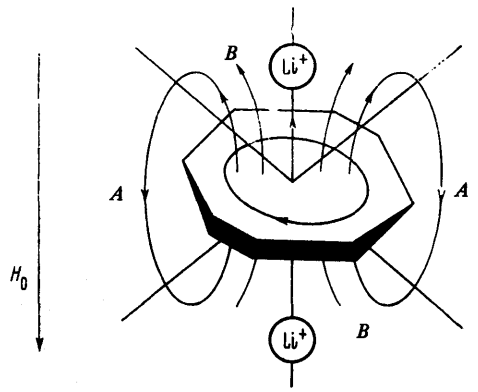


Figure 2. Graphical representation of the effect of the π-electron ring current in the dilithium salt of the cyclo-octatetraene dianion; A—deshielding zones; B—shielding zones.

It would be interesting to test these conclusions experimentally, particularly since, according to the results of recent studies [117,118], the possibility of the electrochemical synthesis of the ten-π-electron cyclo-octatetraene dianion is in fact ruled out. It was found that, after the formation of the radical-anions in THF, DMF, acetonitrile or pyridine ($E_{1/2} = -1.746$ V relative to the saturated calomel electrode), the addition of a second electron does not occur. The radical-anion is protonated by the hydrogen atom of the tetra-alkylammonium salt present in solution as the carrier electrolyte and this is followed by the one-electron reduction of the resulting radical $C_8H_9^{\cdot}$ [reaction (20)]. The anion $C_8H_9^-$ formed shows a smaller tendency than the radical-anion $[C_8H_8]^{\cdot-}$ to react with the supporting electrolyte cation and to be converted into cyclo-octatriene in the interaction with submillimolar (10^{-5} M) admixtures of water, which remain even in absolute solvents. Thus the electrochemical reduction of C_8H_8 consists of stages involving electron transfer and chemical reduction of the products; the process as a whole is irreversible:

$$C_8H_8 \xrightarrow{+\bar{e}} [C_8H_8]^{\cdot-} \xrightarrow{Bu_4N^+} C_8H_9^{\cdot} + Bu_3N + CH_3CH_2CH{=}CH_2;$$
$$C_8H_9^{\cdot} \xrightarrow{+\bar{e}} C_8H_9^- \xrightarrow{H_2O} C_8H_{10} \xrightarrow{+ne^-} \text{products.} \qquad (20)$$

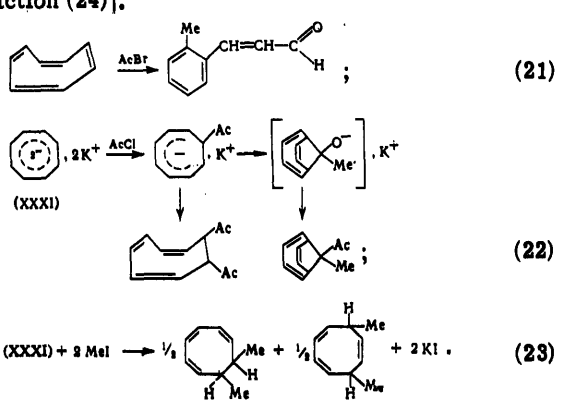
It has been noted [117] that, when no account is taken of the interactions between the dianion $C_8H_8^{2-}$ and the medium, leading to a specific organisation of the solvation shell, it is possible to estimate the difference between the potentials of the reduction of C_8H_8 to $[C_8H_8]^{\cdot-}$ and of the latter to $C_8H_8^{2-}$ as 3 V. Therefore, under the conditions of the electrochemical process, it is difficult to create potential differences such that the dianion $C_8H_8^{2-}$ can be formed.

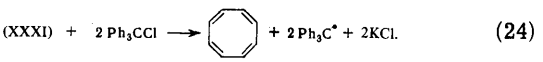
On the other hand, earlier investigators, for example Allendoerfer and Rieger [106], concluded on the basis of both classical and a.c. polarographic data that electrochemical electron transfer to the radical-anion $[C_8H_8]^{\cdot-}$ in DMF, DMSO, and acetonitrile is rapid, reversible, and takes place at a moderately negative potential. It is now necessary to either regard this conclusion as erroneous or to undertake a detailed test of the behaviour of cyclo-octatetraene in these systems. At the same time it would be necessary to compare the structures and properties of the two-electron reduction products obtained at the electrode and with the aid of alkali metals. A fairly high stability of alkali metal salts of the cyclo-octatetraene radical-anion and dianion in THF, DME, and even in liquid ammonia has been noted [119]; the dipotassium salt (XXXI) is capable of undergoing one-electron oxidation in THF solution with formation of $C_8H_8^{\cdot-}$, K^+. [120] The conversion of cyclo-octatetraene into an aromatic dianion is probably significantly facilitated by the formation of contact aggregates with the alkali metal cation. The latter increases the stability of the electron transfer products and at the same time itself interacts with the delocalised electron cloud.

The ^7Li chemical shifts for certain organolithium derivatives (relative to LiCl).

0.3 M soln. of compound in THF	σ (^7Li), p.p.m.	References
$Me(CH_2)_3CH_2Li$	1.5	114
	−8.55	114
	−8.37	115

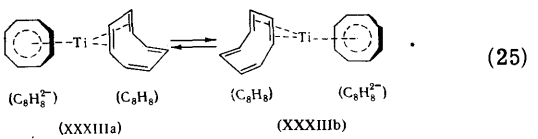
It is noteworthy that the chemical properties of the salts (XXXI) are determined primarily by the presence of the double negative charge. The chemical reactions cannot by themselves demonstrate whether this dianion has a planar or a non-planar structure. The results of the acylation of cyclo-octatetraene [121] and its dipotassio-derivatives [122] are presented in formulae (21) and (22). The alkylation of the salt (XXXI) by methyl iodide [reaction (23)] proceeds in the same way as reaction (22). [123] However, when triphenylmethyl chloride is used as the halide, disubstituted derivatives are not formed (cf. Azatyan [124]) and the reaction stops at the electron transfer stage [reaction (24)]. [125]





(24)

Electron transfer from (XXXI) to titanium tetrachloride leads to the reduction of the cation Ti^{4+} with simultaneous binding of two C_8H_8 rings into the complex $(C_8H_8)_2Ti$.[126] It follows from X-ray diffraction studies[127] that one eight-membered ring in this complex is bent, while the other is planar and that the rings are linked in different ways to the central metal atom. According to NMR data[128], at about 60°C there is intramolecular electron transfer via the metal, from one ligand to the other, so that form (XXXIIIa) is converted into (XXXIIIb) [reaction (25)].



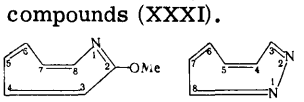
(25)

(XXXIIIa) (XXXIIIb)

Here one ring, which was previously planar, is bent, while the previously bent ring is converted into the planar form. The activation energy for this transition is 16–17 kcal mole^{-1}. It is extremely significant that the observed value is comparable to the one stated above for the inversion of cyclo-octatetraene[102,104] via reaction (18).

The abstraction of an electron from cyclo-octatetraene leads to a radical-cation whose ESR spectrum indicates a non-planar structure[129]. Calculations[106] also predict a non-planar form of this radical. The cyclo-octatetraene dication contains six π-electrons. If this dication had a planar structure, then, according to the Hückel rule, it would be aromatic and would exhibit an enhanced stability. So far such a dication has not been obtained, but it has been shown[130] that the ion $C_8H_8^{2+}$, formed under the influence of electron impact in a mass-spectrometer, is stable.

Azacyclo-octatetraene[102] has C=C vibration frequencies[131] and ultra-violet spectra[132] surprisingly similar to those of the nitrogen-free analogue (XXVIII). Hence one may conclude, according to Paquette and Kakihana[102], that the nitrogen-containing ring has, like cyclo-octatetraene, a strain-free boat form of type (XXXIV). According to the conditions of synthesis[102], all the azacyclo-octatetraene derivatives investigated contained a methoxy-group in the 2-position; in THF, DME, or liquid ammonia these compounds combine with two equivalents of potassium, forming dianions[133]. The NMR spectra show that the dianions are planar and contain delocalised ten-electron systems, i.e. have the structure (XXXV).[134] These are aza-analogues of compounds (XXXI).

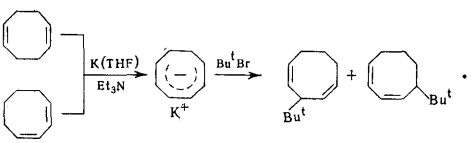


(XXXIV) (XXXVI)

The equalisation of the charge is also indicated by the formation of 3,4-, 3,6-, and 7,8-dihydro-derivatives on reaction of (XXXV) with proton donors and the interconversions of the dihydro-derivatives are impossible under the reaction conditions[133,134]. The electrochemical reduction of (XXXIV) at mercury or platinum electrodes in DMF or THF in the presence of tetra-n-butylammonium salts as carrier electrolytes[135–137] also leads to the dianion (XXXV). We may note that, according to data from the same laboratory[117], the electrochemical reduction of cyclo-octatetraene in an aprotic medium is arrested at the stage involving the formation of the radical-anion (XXX). This difference between (XXVIII) and (XXXIV) also follows from the calculation of the corresponding π-electron energy levels[138]. According to the authors, the transfer of the first electron to azacyclo-octatetraene is coupled with a change in its configuration (XXXIV) to an almost planar form, actually more planar than in the case of compound (XXX). This process requires such a high energy expenditure that the capture of a second electron, required to complete the decet ($4n + 2$; $n = 2$), proceeds without additional activation. This implies that the reduction of the radical-anion in a polarographic experiment should proceed more readily than that of the initial azacyclo-octatetraene and that, after the attainment of the potential corresponding to the transfer of the first electron, the second electron should also be transferred. It follows from the analysis of polarographic data[136] that the two-electron reduction of (XXXIV) to (XXXV) does indeed consists of two simultaneous one-electron stages.

Recently it proved possible to obtain also the diaza-analogue of cyclo-octatetraene for which the authors suggest the structure (XXXVI).[139] It would be interesting to show whether this compound is capable of undergoing a change in geometry in electron transfer reactions.

Electron transfer might also induce the isomerisation of non-conjugated cyclo-olefins to conjugated forms. Thus metallation of cyclo-octa-1,3-diene and cyclo-octa-1,5-diene leads [see reaction (26)] to the same anion, which on treatment with t-butyl iodide gives rise to a mixture of equal amounts of 3-t-butylcyclo-octa-1,4-diene and 5-t-butylcyclo-octa-1,3-diene[140].



(26)

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The data discussed in this review permit the conclusion that the geometry of organic compounds can change on electron transfer. The cause of such changes have been discussed. They may determine the stereochemical structure of the products obtained as a result of reactions involving an electron transfer stage. Consequently the detection of the stereochemical changes induced by electron transfer is important for the investigation of the mechanisms of many organic reactions. In particular, it is important to study the relation between the geometry of the repeat units in high-molecular-weight compounds and the method used to initiate polymerisation. On the other hand, it would be useful to take into account more fully the role of electron exchange processes in biochemical reactions. Indeed, many biomolecules with unsaturated bonds are involved in reactions associated with electron transfer. Here one may include the chemical changes arising, for example, in the processes involved in vision[141] or in the isomerisation of unsaturated aliphatic acids under the influence of enzymes[142,143]. The capacity to undergo a change in configuration on electron transfer might be used to select new biologically active substances; no doubt other no less important applications are also possible. The aim of the present review is to attract attention to the stereochemical results of electron transfer.

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