Electrochemical study of some bromo-substituted [2.2]paracyclophanes

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The potentials of electrochemical oxidation ($E_{1/2}{}^{Ox}$) and reduction ($E_{1/2}{}^{Red}$) of monobromo- and isomeric di- and tribromo[2.2]paracyclophanes as well as $E_{1/2}{}^{Ox}$ of mono-, di-, and tribromobenzenes were measured in acetonitrile. The similarity between the properties of *pseudo-para*-disubstituted cyclophanes and *meta*-disubstituted benzenes, on the one hand, and *pseudo-meta*-disubstituted cyclophanes and *para*-disubstituted benzenes, on the other hand, was confirmed by the existence of a linear relationship between $E_{1/2}{}^{Red}$ of bromo-substituted [2.2]paracyclophanes and $E_{1/2}{}^{Red}$ of the corresponding bromo-substituted benzenes. The results were explained in terms of the qualitative theory of molecular orbitals, taking into account a "through space" interaction between the π-systems of the benzene rings.

Key words: electrochemistry, oxidation, reduction; molecular orbitals; [2.2]paracyclophane, bromo-subsituted [2.2]paracyclophanes; polybromobenzenes.

Para- and metacyclophanes have been analyzed electrochemically in a number of studies.[1–6] The main purposes of these studies included the generation of radical cations and anions, studying the ESR spectra of these species, and elucidation of the strength of the donor-acceptor interaction between the parallel benzene moieties "through space" and through side σ-C—C bonds. The redox behavior of halo-substituted cyclophanes has not yet been studied. In the present work, the electrochemical properties of some mono-, di-, and tribromo-substituted [2.2]paracyclophanes were studied in order to elucidate the mutual effect of the Br atoms located at the same or at different rings of the cyclophane system and to compare it with the mutual effect of the Br atoms in polybromo-substituted benzenes, whose polarographic behavior we have studied before.[7]

Experimental

Bromobenzenes and isomeric tribromo[2.2]paracyclophanes were previously synthesized and characterized for the first time in our works.[7,9] Mono- and isomeric dibromo[2.2]paracyclophanes were obtained according to the Cram method.[8]

The electrochemical oxidation of bromo-substituted [2.2]paracyclophanes and bromobenzenes was carried out on a platinum rotating electrode (υ = 2800 rpm) and on a stationary disc electrode (S = 11.8 mm^2, r = 2.57 mm) using a setup based on a RA-2 polarograph. The potentials were measured against a silver chloride electrode. A 0.05 M solution of Bu_4NBF_4 in dry MeCN at 20 °C was used as the reference solution (the concentration of compounds was $2 \cdot 10^{-3}$ mol L^{-1}). A platinum plate (5×12 mm) was used as the auxiliary electrode. The working solutions were placed in a stationary cell (volume 20 mL) equipped with an auxiliary electrode, a reference electrode, and a system for passing a stream of argon.

The electrochemical reduction of [2.2]paracyclophanes was performed on a mercury layer electrodeposited on a platinum electrode. The electrolysis was carried out for 5 min at −1 V in a 0.01 M solution of mercury(II) acetate in MeCN. The mercury surface obtained was washed with water and acetone and dried. The other experimental conditions were the same as in the oxidation experiments.

Results and Discussion

Electrochemical measurements were carried out by cyclic voltammetric and polarographic methods on a rotating disc electrode. Oxidation processes were studied on a platinum electrode with a mercury layer obtained by electrolyzing mercury(II) acetate. The use of a mercury film electrode enabled measurements at cathodic potentials up to −2.8 V.

The formulas of the [2.2]paracyclophanes studied are presented below. The numbering of the carbon atoms used in this work is also given.

The electrochemical parameters of the oxidation and reduction of compounds **1—7**, as well as those for benzene (**8**) and some bromo-substituted benzenes (**9—15**) are presented in Table 1.

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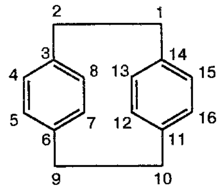

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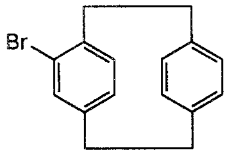

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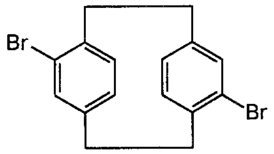

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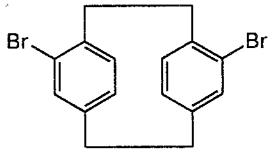

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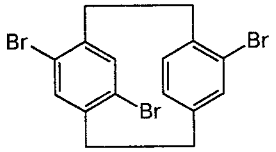

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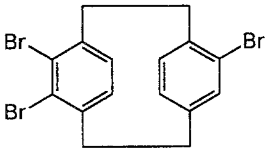

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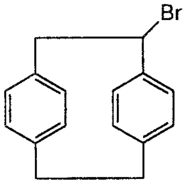

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Oxidation. All of the compounds studied undergo one-step irreversible electrochemical oxidation, in which two or four electrons are transferred. Diffusion limiting currents are observed in all cases, since the peak currents on the cyclic voltammograms depend linearly on the potential sweep rate (which was varied from 50 to 500 mV s^{-1}). The bromo-substituted paracyclophanes undergo oxidation more easily than bromo-substituted benzenes having the same number of Br atoms at the ring. This may be due to the electron-donating effect of bridging alkyl groups. Like in the case of bromobenzenes, the oxidation potentials are shifted in the anodic direction as the number of Br atoms in a molecule increases; this is due to the electron-withdrawing effect of the halogen atoms.

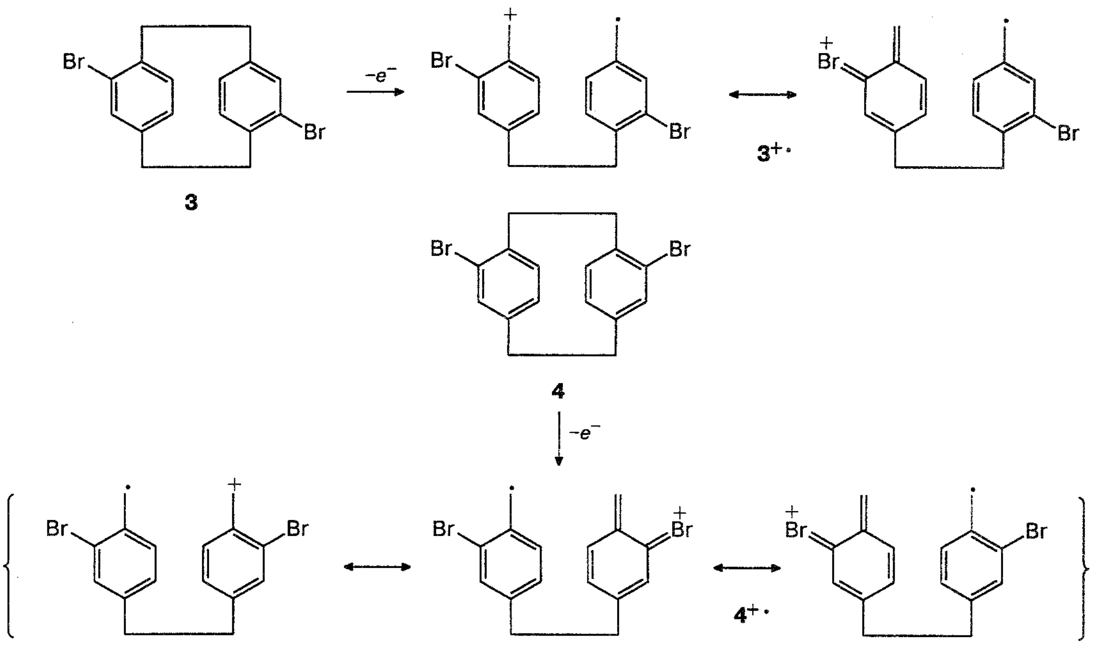
Table 1. Parameters of the electrochemical oxidation and reduction of bromo-substituted [2.2]paracyclophanes and benzenes (MeCN, 0.05 $M\,Bu_4NBF_4$, 20 °C; an Ag/AgCl/KCl(sat.) reference electrode)

Compound	Oxidation,[a] $E_{1/2}^{Ox}$/V (n)	Reduction,[b] $-E_{1/2}^{Red}$/V (n)
1	1.52 (2)	3.00^5
2	1.75 (2)	2.70 (2)
3	1.83 (–)[c]	2.47 (2); 2.68 (2)
4	1.88 (2)	2.54 (2); 2.74 (2)
5	2.03 (2 or 3)	2.29 (2); 2.58 (2); 2.75 (<2)
6	2.00 (4)	2.14 (4); 2.68 (2)
7	1.75 (4)	2.07 (2)
C_6H_6 (**8**)	2.30 (1)	$3.37\ (1)^{10}$
C_6H_5Br (**9**)	2.22 (2)	$2.62\ (2)^7$
1,4-$Br_2C_6H_4$ (**10**)	2.38 (>2)	$2.31(2);\ 2.60\ (2)^7$
1,3-$Br_2C_6H_4$ (**11**)	2.41 (>2)	$2.08\ (2);\ 2.58\ (2)^7$
1,2-$Br_2C_6H_4$ (**12**)	2.43 (>2)	$2.02\ (4)^7$
1,2,4-$Br_3C_6H_3$ (**13**)	2.52 (4)	$1.66\ (2);\ 2.31\ (2);\ 2.61\ (2)^7$
1,2,3-$Br_3C_6H_3$ (**14**)	2.45 (4)	$1.53\ (2);\ 2.06\ (2);\ 2.59\ (2)^7$
$C_6H_5CH_2Br$ (**15**)	2.00 (2)	$1.22\ (2)^{11}$

[a] On a Pt electrode; n is the number of electrodes participating in the redox process. [b] On a mercury film electrode. [c] The compound is very poorly soluble even in boiling MeCN.

The number of electrons (n) involved in the oxidation increases as the number of Br atoms in a molecule increases. This is observed both with polybromo-substituted [2.2]paracyclophanes and with polybromobenzenes. For example, the experimentally determined values are $n = 4$ for tribromobenzenes **13** and **14**, $n = 6$ to 8 for isomeric tetrabromobenzenes, and $n = 10$ for C_6HBr_5 and C_6Br_6. Probably, the explanation is that the product formed at the first, *e.g.*, two-electron step undergoes oxidation more easily than the starting compound; the product formed at the second step oxidates even more easily, *etc.* According to the data available in the literature,[5] the electrochemical oxidation of [2.2]paracyclophane in media possessing a decreased proton-donating ability (MeOH, EtOH) involves the cleavage of a C—C exocyclic bond, whereas acyloxylation of an aromatic ring in media with high proton-donating ability (CF_3COOH) does not involve the cleavage of the C—C bridging bond. Since we used acetonitrile as the solvent, it can be assumed that the first mechanism is operative in the case studied.

Scheme 1



In view of this, it is interesting to compare the oxidation potentials of *pseudo-para* (**3**) and *pseudo-meta* (**4**) dibromo-derivatives of [2.2]paracyclophane. It is evident from the data in Table 1 that compound **3** undergoes oxidation somewhat more easily (by 50 mV) than compound **4**. If we assume that the first electron in the oxidation process leaves the bonding σ-orbital of a C—C bond, then the calculation of the number of resonance structures for cation radicals of the *pseudo-meta* ($\mathbf{4}^{+\cdot}$) and *pseudo-para* ($\mathbf{3}^{+\cdot}$) isomers indicates that the cation radical $\mathbf{4}^{+\cdot}$ can be more stable than $\mathbf{3}^{+\cdot}$, since a greater number of structures can be written for the former radical (some of these are presented in Scheme 1). Hence, the use of the resonance theory leads us to the conclusion that the oxidation at the C—C σ-bond should occur more easily in the case of compound **4** than in the case of compound **3**, which contradicts the experimental data.

The alternative assumption is that the first electron leaves the aromatic π-system formed due to the "through space" interaction of two benzene rings. As a result of this interaction, the possibility for the mutual influence of two Br atoms bonded to different benzene rings appears. It has been shown previously that the direct conjugation between (−*M*) and (+*M*) substituents (*e.g.*, NO_2 and NH_2) bonded to different rings of [2.2]paracyclophane is possible in *pseudo-meta*[12] isomers but not in *pseudo-para* isomers. Therefore, *pseudo-para*-disubstituted paracyclophanes should "resemble" *meta*-disubstituted benzenes, and *pseudo-meta*-disubstituted paracyclophanes should "resemble" *para*-disubstituted benzenes,[11,12] which has been confirmed to some extent in a study of the bromination of [2.2]paracyclophane.[13] This behavior is explained by charge transfer between the rings. However, it is evident from Table 1 that this rule is invalid in the case of electrochemical oxidation: *para*-dibromobenzene **10** more readily undergoes oxidation than the *meta* isomer **11**; however, *pseudo-meta*-dibromo[2.2]paracyclophane, which should "resemble" *para*-dibromobenzene, undergoes oxidation less readily than the *pseudo-para* isomer.

However, the *pseudo-para* and *pseudo-meta* isomers of dibromo[2.2]paracyclophane behave "normally" in the electrochemical reduction: the former compound more easily undergoes reduction than the latter, in agreement with the fact that *para*-dibromobenzene is reduced less easily than *meta*-dibromobenzene. A qualitative explanation of these effects based on a consideration of the molecular-orbital interactions between the rings is given below.

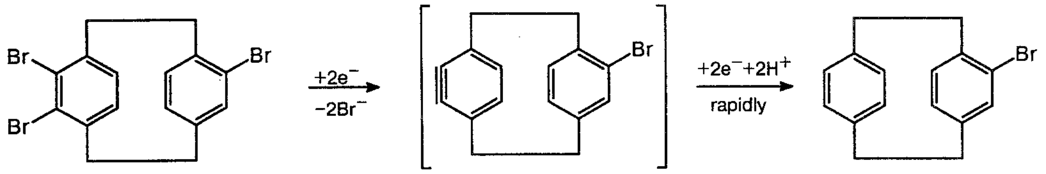
Reduction. The reduction of polybromo[2.2]paracyclophanes, like that of polybromobenzenes,[7] gives rise to as many waves as there are Br atoms present in a molecule; furthermore, all of these are two-electron waves. This implies that each step corresponds to the reductive elimination of one Br atom (Scheme 2).

Scheme 2

$$\mathrm{RBr}_n \xrightarrow[-\mathrm{Br}^-]{+2e^- + \mathrm{H}^+} \mathrm{RHBr}_{n-1} \xrightarrow[-\mathrm{Br}^-]{+2e^- + \mathrm{H}^+} \mathrm{RH_2Br}_{n-2} \longrightarrow \textit{etc.}$$

The only exception is compound **6**. In this case the first wave corresponds to the transfer of four electrons. The four-electron transfer, like that in the case of 1,2-dibromobenzene,[7] is explained by the synchronous elimination of two bromide ions (Scheme 3) *via* an intermediate easily reducible aryne.

Scheme 3



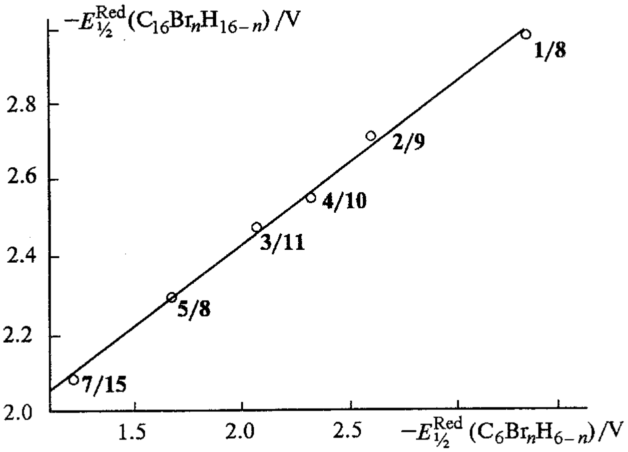


Fig. 1. Relationship between the reduction potentials of bromo-substituted [2.2]paracyclophanes and benzenes (MeCN, 0.05 *M* Bu_4NBF_4, 20 °C).

Bromo-substituted paracyclophanes are reduced less easily than bromobenzenes containing the same number of Br atoms. A satisfactory correlation exists between the reduction potentials of bromo-substituted paracyclophanes and those of some bromo-substituted benzenes selected in an appropriate way. The pair [2.2]paracyclophane/benzene also lies on the correlation straight line (Fig. 1).

The correlation equation has the form

$$E_{1/2}^{\mathrm{Red}}(C_{16}Br_nH_{16-n}) = 0.43\,E_{1/2}^{\mathrm{Red}}(C_6Br_nH_{6-n}) - 1.54,$$

$n = 0 \div 3$.

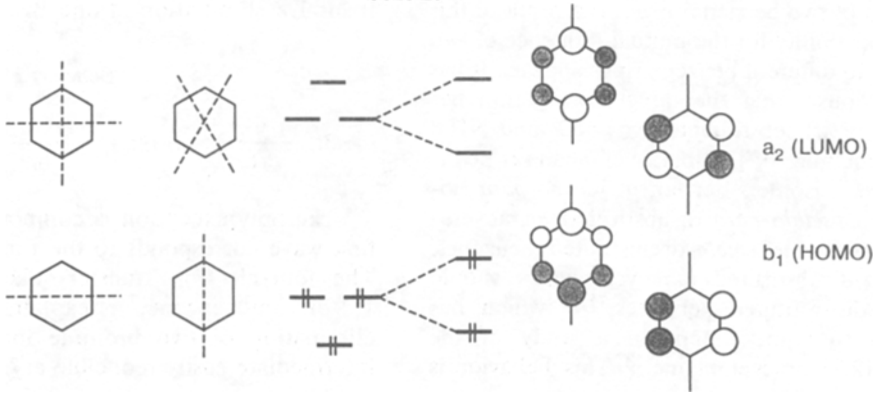
One can see in Fig. 1 that the reduction potential of compound **2** correlates with the reduction potential of C_6H_5Br, while the $E_{1/2}^{\mathrm{Red}}$ of compound **7** correlates with $E_{1/2}^{\mathrm{Red}}$ of $C_6H_5CH_2Br$ (**15**). It seems quite natural to compare these pairs since their structures are alike. However, the $E_{1/2}^{\mathrm{Red}}$ of *pseudo-para*-dibromo[2.2]paracyclophane **3** correlates with $E_{1/2}^{\mathrm{Red}}$ of *meta*-dibromobenzene rather than with that of *para*-dibromobenzene; the $E_{1/2}^{\mathrm{Red}}$ of the *pseudo-meta* isomer **4** correlates with $E_{1/2}^{\mathrm{Red}}$ of *para*-dibromobenzene, while the $E_{1/2}^{\mathrm{Red}}$ of compound **5** correlates with that of 1,2,4-tribromobenzene (**8**). This correlation shows that the rule of the similarity in the behavior of *pseudo-para/meta* and *pseudo-meta/para* isomers for substituted paracyclophanes and benzenes is indeed valid in the case of electrochemical reduction.

Redox orbitals of dibromo[2.2]paracyclophanes. To explain the similarity between the *pseudo-para/meta* and *pseudo-meta/para* dibromo-substituted [2.2]paracyclophanes and benzenes during electrochemical reduction and between *pseudo-para/para* and *pseudo-meta/meta* compounds during electrochemical oxidation, we proposed to use the qualitative theory of molecular orbitals (MO) based on the following assumptions.

1. The redox orbitals whose energies determine $E_{1/2}^{\mathrm{Ox}}$ and $E_{1/2}^{\mathrm{Red}}$ are the π-levels formed due to the interaction of the π-HOMOs and π-LUMOs of the two π-systems of substituted benzene rings located in parallel planes.

2. An unsubstituted benzene molecule contains two degenerate π-HOMOs and two degenerate π*-LUMOs. However, the degeneration is eliminated in substituted benzenes: in the case of *para*-dialkylbenzenes an orbital of symmetry b_1 becomes the highest occupied orbital, while an orbital of symmetry a_2 becomes the lowest unoccupied orbital (Scheme 4).

Scheme 4



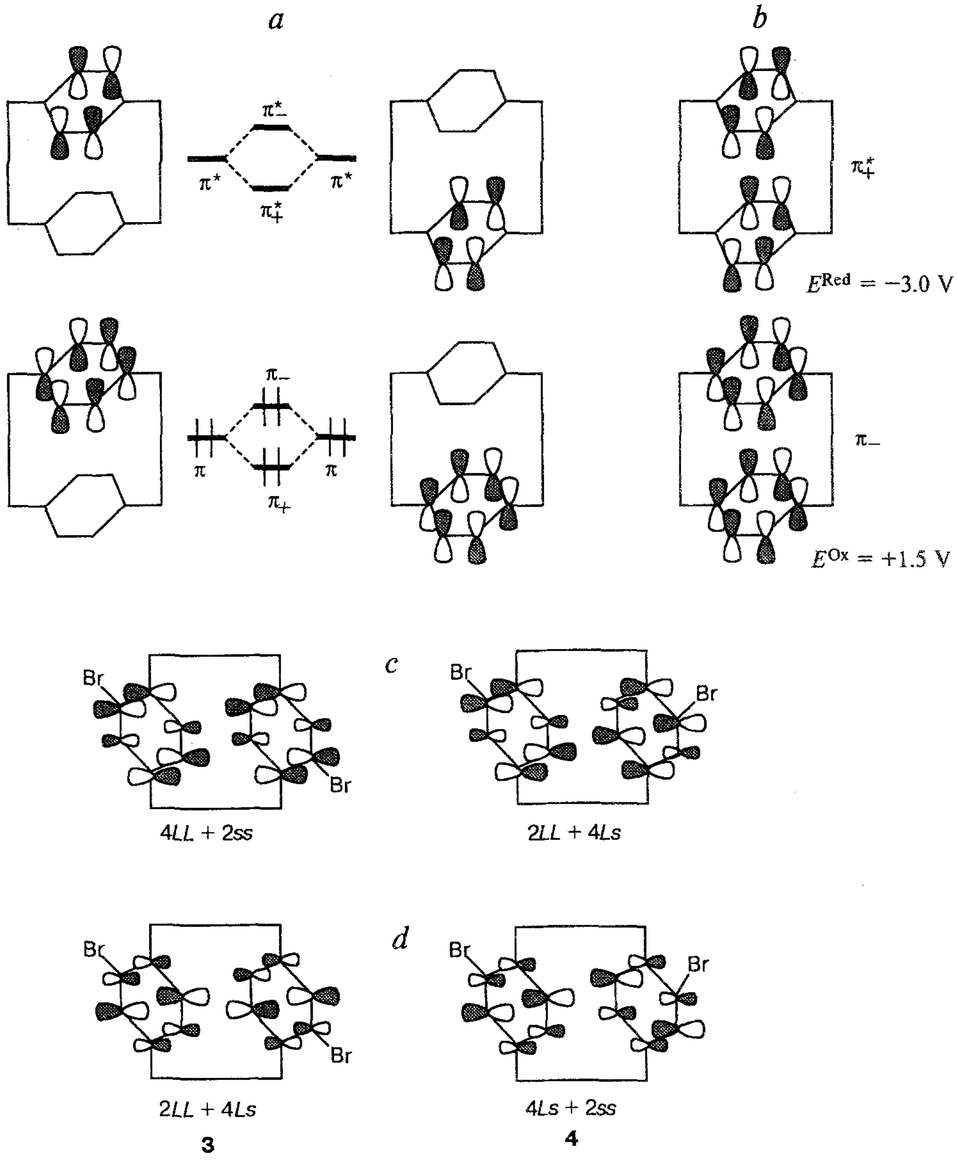


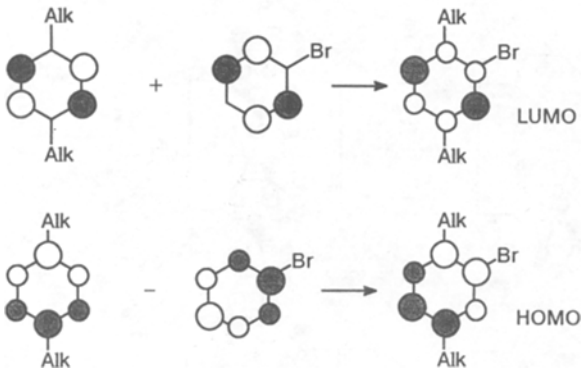
Fig. 2. Redox orbitals of [2.2]paracyclophane and its isomeric bromo-derivatives: *a*, splitting of levels upon the "through space" interaction of the π-systems of [2.2]paracyclophane; *b*, symmetry of π_- and π_+^*-orbitals; *c*, shape of π_--HOMO; *d*, shape of π_+^*-LUMO for *pseudo-para-* and *pseudo-meta* isomers of dibromo[2.2]paracyclophane (**3** and **4**, respectively).

Assuming that "half" of the paracyclophane has orbitals of a benzene ring analogous to orbitals of *para*-dialkylbenzene, one can state that the HOMO of [2.2]paracyclophane is an antibonding combination (π_-) of π-HOMOs of separate benzene rings (of symmetry b_1), whereas the LUMO of paracyclophane is a bonding combination (π_+^*) of π-LUMOs of the benzene rings (a_2).[14] The splitting of levels is sketched in Fig. 2, *a*. It follows from this figure that both the oxidation and reduction of unsubstituted [2.2]paracyclophane should occur more readily than those of benzene; this agrees with the experimental data (see Table 1). The symmetry of the π_--HOMO and π_+^*-LUMO of unsubstituted [2.2]paracyclophane is shown in Fig. 2, *b*; the participation of the antibonding σ*-orbitals of the bridging C—C bonds in the formation of the π_--orbital is not shown in the scheme.

3. The symmetry of the π-system of the bromo-substituted moiety in [2.2]paracyclophane can be qualitatively found from the symmetry of the π-orbitals of 1,4-dialkylbenzene and the π-orbitals of bromobenzene. For both compounds the π-LUMO has symmetry a_2 and the π-HOMO has symmetry b_1, since both alkyl- and bromo-substituents have π-donor properties. Building a linear combination of the π*-LUMOs and π-HOMOs of these molecules, we obtain a qualitative picture for dialkylbromobenzene (Scheme 5).

These shapes of the frontier orbitals generally agree

Scheme 5



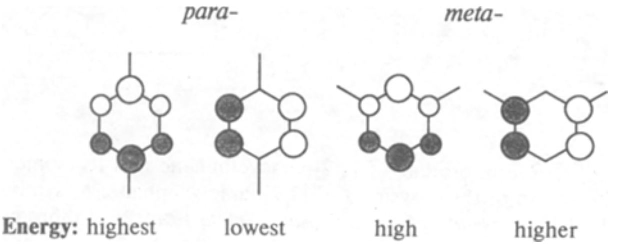
with the results of non-empirical calculations in the STO-3G and STO-21G(*) bases, as well as with the results of the PMX calculations recently performed by G. V. Vazhenin and R. Hoffmann[15] for 1-bromo-2,5-dimethylbenzene. The energy of the HOMO of this molecule is closer to that of the p_z-orbital of the bromine atom than to that of the π-type orbital of a methyl group, whereas the LUMOs are "more equidistant" with respect to the π-donor levels. This explains the fact that the HOMO of bromodimethylbenzene "resembles" that of bromobenzene, while the LUMO has a pseudo-symmetry axis passing through the C(3) and C(6) atoms, since the effects of the Br atoms and the CH_3 group on the LUMO are more alike than their effects on the HOMO. These orbitals can be used to estimate the degree of interaction between the π-systems of the benzene rings in *pseudo-para-* and *pseudo-meta-*[2.2]paracyclophanes **3** and **4**, respectively.

Figure 2, *c* shows qualitative pictures of the (π_-)-HOMOs of *pseudo-para-* and *pseudo-meta* dibromo[2.2]paracyclophanes. Let us denote an atom with a large contribution of the atomic p-orbital to a particular π-orbital as L (large) and an atom with a small contribution as s (small). Then the orbital interaction can be represented *via* the sum of the products of atomic coefficients as $(4L^2 + 2s^2)$ for the *pseudo-para* isomer and as $(2L^2 + 4Ls)$ for the *pseudo-meta* isomer. It can be easily shown that $(4L^2 + 2s^2) > (2L^2 + 4Ls)$ (if this is the case, then $L^2 - 2Ls + s^2 > 0$, and hence $L > s$, which is true by definition). Hence, if we deal with interactions caused by overlapping and refer L and s to their absolute values, then the degree of interaction of two π-moieties expressed by their atomic coefficients will be greater in the *pseudo-para* isomer than in the *pseudo-meta* isomer, and the π_--level of the former isomer should be higher than that of the latter isomer. It is also important that there are some bonding interactions in the *pseudo-meta* isomer, whereas all of the six p-AOs of the *pseudo-para* isomer interact in an antibonding manner. This results in an additional decrease in the energy of the π_--orbital of the *pseudo-meta* isomer. Thus, compound **3** should undergo oxidation more easily than compound **4**, which is indeed observed experimentally (see Table 1).

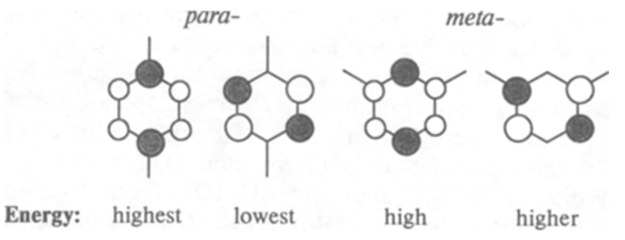
Similarly (Fig. 2, *d*), when we consider the products of the atomic coefficients for the interaction resulting in a π_+^*-LUMO, we obtain $(2L^2 + 4Ls)$ for the *pseudo-para* isomer **3** and $(4Ls + 2s^2)$ for the *pseudo-meta* isomer **4**. Obviously, $(2L^2 + 4Ls) > (4Ls + 2s^2)$, *i.e.*, the splitting of the π^*-levels in the *pseudo-para* isomer should be greater and the π_-^*-level should be lower than in the *pseudo-meta* isomer. Furthermore, some of the interactions in the *pseudo-meta* isomer turn out to be antibonding in nature (Fig. 2, *d*), which should additionally increase the energy of the π_+^*-orbital of the *pseudo-meta* isomer (compared to the energy of *pseudo-para*-dibromide). Thus, *pseudo-para*-dibromo[2.2]paracyclophane will be reduced more easily than the *pseudo-meta* isomer, which also agrees with the experimental data.

The results obtained imply that the application of the qualitative MO theory should allow us to explain the oxidation and reduction potentials of isomeric bromo-substituted [2.2]paracyclophanes. Although the electrochemical processes are completely irreversible, these potentials are, probably, primarily determined by the redox levels π_- and π_+^*. It can also be stated that the initial electronic changes, both during oxidation and during reduction, are localized at the cyclophane π-system.

It turned out that it was more difficult to use this qualitative approach to explain why oxidation is impeded and reduction is facilitated when changing from *para*-dibromobenzene to the *meta* isomer (see Table 1). The HOMOs of the benzene π-system, which are disturbed by the Br atoms (π-donor substituents), should have the following shapes and distribution of energies:



The assignment (high, low, *etc.*) was based on the coefficients at the substituted carbon atoms. Hence, it can be concluded that the *para* isomer should be oxidated more easily, which agrees with the experimental data. Now, let us consider the LUMOs of dibromobenzenes:



Obviously, the reduction of the *para* isomer should also occur more easily than that of the *meta* isomer. Thus, the qualitative conclusions agree with the experimental data in the case of oxidation but not in the case of reduction.

However, a semi-empirical calculation of the molecular orbitals by the CNDO/2 method[16] shows that, although the symmetry of the highest occupied and lowest unoccupied MOs is as shown above, the HOMO energy for the *para* isomer is 1.8 eV higher and the LUMO energy is 0.27 eV higher than those for the *meta* isomer. Hence, according to the calculations, the *para* isomer should be oxidated more easily and reduced less easily than the *meta* isomer.

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