Three Paramagnetic Reduction Stages of Phenyl-Substituted
1,2,9,10-Dibenzo[2.2]paracyclophane-1,9-dienes. Radical
Anions, Triplet Dianions, and Radical Trianions As Studied by
ESR and ENDOR Spectroscopy

Armin de Meijere, Fabian Gerson, Burkhard König, Oliver Reiser, and
Thomas Wellauer

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Reaction of 2 with potassium or cesium mirror in an ethereal solvent yielded a fairly persistent radical anion 2−, which has been studied in detail by ESR, ENDOR, and TRIPLE-resonance spectroscopy. The unpaired electron in 2− is accommodated in the ethano bridging groups in [2.2]paracyclophane (1) by o-phenylene leads to the dibenzo derivative 2. The D2h symmetry of 1 is preserved in 2, as the planes of the lateral benzene rings are perpendicular to the mean planes of the benzene decks in the central phane unit. The first synthesis of 2 was reported a few years ago. More recently, not only 2 but also its derivatives 3, 4, and 5, bearing phenyl substituents at the lateral rings, have become readily available via a simple preparative route.

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mainly in the central phane unit, in accord with the reduction potential, $E_{1/2}$, of 1 (-3.00 V vs SCE)$^5$, being substantially less negative than that of benzene (-3.42 V)$^4$. Actually, the $E_{1/2}$ value of 2 is -2.68 V.$^6$ as the uptake of an electron by the central phane unit becomes easier by the enlargement of the molecular framework on passing from 1 to 2. Also, due to the presence of several mutually orthogonal $r$-systems, 2 can accept more than one electron,$^6$ but its dianion proved not persistent enough to allow detection by ESR or NMR spectroscopy. Prolonged reduction of 2 with an alkali metal in ethereal solvents at low temperatures resulted in the formation of secondary products, which arose from the cleavage of a bond between benzene rings.$^{10}$

The propensity of a molecule to take up electrons and the persistence of multiply charged anions are usually enhanced by greater delocalization of the negative charges. In the case of 2, such an enhancement should thus be brought about through phenyl substitution of the lateral benzene rings by which the $r$-systems of these rings in 2 are extended to those of biphenyl in 3 and 4 and of o-terphenyl in 5. One may, therefore, expect that further reduction of the radical anions 3$^-$-5$^-$ will yield multiply charged species that are sufficiently persistent to be characterized by ESR or NMR spectroscopy. As is shown in the present paper, this expectation has been fully borne out by experiment, which also resulted in the formation of secondary products, which arose from the cleavage of a bond between benzene rings.$^{10}$

Results and Discussion

Radical Anions. Reaction of the phenyl-substituted dibenzo-[2.2]paracyclophanes 3, 3-$d_2$, 4, 5, and 5-$rBu_4$ with potassium mirror generated the corresponding radical anions. 1,2-Dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF) served as solvents; in several samples tetrahydrofuran (MTHF) was added to DME. 1,2-Di-$r$Bu$_4$- with potassium methoxyethane (DME), tetrahydrofuran (THF), and 2-methyl-

The ESR spectra of the radical anions thus obtained were taken in the temperature range 193-263 K; they had a rather small total width (1.4-1.5 mT for 3$^-$-5$^-$, 1.1-1.2 mT for 3-$d_2^-$ and 5-$rBu_4^-$). Their poor resolution was caused by a large number of protons having small coupling constants and, presumably, by electron exchange with simultaneously formed dianions. Analyses of these spectra were carried out by the ENDOR technique,$^{11}$ as illustrated for 5$^-$ in Figure 1. The proton coupling constants for 3$^-$, 4$^-$, and 5$^-$ are given in Figure 2. Their signs were determined by general TRIPLE resonance,$^{13}$ assuming that the largest values are negative. The coupling constants for 3$^-$ and 4$^-$ are almost half as large as those of the protons in the corresponding positions of the radical anion of biphenyl (6),$^{12}$ and they belong to sets of twice as many nuclei. Analogous relations hold for the proton coupling constants of 5$^-$ with respect to those of the radical anion of o-terphenyl (7).$^{13}$ Assignments to protons in the individual positions of 3$^-$-5$^-$ have thus been based on comparison with the hyperfine data for 6$^-$ and 7$^-$ (Figure 2). These assignments were confirmed by ESR and ENDOR studies of 3-$d_2^-$ and 5-$rBu_4^-$.

The changes observed on passing from 3$^-$ to 3-$d_2^-$ and from 5$^-$ to 5-$rBu_4^-$ were those expected for the replacement of the ring protons having the largest coupling constants [3$^-$: 0.212 mT (2 H), 5$^-$, 0.126 mT (4 H)] by deuterons and tert-butyl groups, respectively. Thus, a striking decrease (0.3-0.4 mT) in the total width of the ESR spectra occurred, along with the disappearance of the hyperfine splitting.
of the outermost proton ENDOR signals associated with the pertinent coupling constants. For the protons other than those in deuteriated or substituted positions, the coupling constants remained practically unchanged, as deduced from the ENDOR spectra. The hyperfine splitting from the two deuterons in 3-d$_2$ was determined to be 0.031 mT from the deuteron ENDOR signals; that from the 36 protons of the four tert-butyl substituents in 5-tBu$_4^-$ could not be exactly measured by either ESR or ENDOR spectroscopy (it was estimated to be smaller than 0.005 mT).

The coupling constants for 3''-5'' (Figure 2) depended only slightly on the solvent (DME, THF, MTHF, or DME/HMPT) and temperature (193-263 K). They clearly point out that, in contrast to 2'', the unpaired electron in 3''-5'' is taken up by one of the lateral π-systems and not by the central phenyl unit. The first reduction potentials, $E_{1/2}(1)$, of 6 ($-26.8$ V) and 7 ($-2.62$ V) are considerably less negative than that of the parent cyclophane 1 ($-3.00$ V). Moreover, these potentials are equal to the first reduction potential of the constituent systems in these molecules.

The hyperfine data for 3''-5'' also indicate that, with some exceptions (see below), electron transfer between the two equivalent lateral π-systems is fast on the hyperfine time scale (ca. 10$^7$ Hz), and the unpaired electron appears to be delocalized over both systems. As the frequency of such an electron transfer is determined by the rate of synchronous migration of the counterion between its sites at the two moieties, the cation K$^+$ must move relatively fast from one lateral π-system to another, i.e., it's association with the radical anion is rather weak (loose ion pairs).

The association becomes stronger when the cation solvating power of the solvent decreases, which is the case in the sequence DME/HMPT > DME > THF > MTHF and also upon raising the temperature. Accordingly, proton ENDOR spectra of 5'' in THF and MTHF above 243 K exhibited additional weak signals corresponding to coupling constants exactly twice as large as those given in Figure 2. These signals are diagnostic of the electron transfer and the K$^+$ migration being slow on the hyperfine time scale and that arise from radical anions more strongly associated with the counterion (tight ion pairs). Thus, in THF or MTHF above 243 K, loose and tight ion pairs of 5'' with K$^+$ coexist in the same solution. Ample evidence of such a coexistence has accumulated in the last decade, particularly for the radical anions of cyclophanes.5,16

It is noteworthy that the protons in the "inner" and "outer" positions of the phenyl substituents in 5'' appeared to be equivalent even when, in this special case, the temperature was lowered from 193 to 158 K (solvated THF). From the width of the ENDOR signals (Figure 1), one estimates that the differences in the coupling constants of the "inner" and "outer" protons can be at most 0.012 and 0.005 mT for the ortho and meta positions, respectively (Figure 2). Since the coalescence temperature must be lower than 158 K, the upper limit to the free activation energy, $\Delta G^*$, for the rotation of the phenyl substituent was estimated as 21 kJ mol$^{-1}$.17 For the radical anion of o-terphenyl 7, the corresponding differences in the coupling constants are 0.045 and 0.017 mT (Figure 2) and the pertinent energy is 29 kJ mol$^{-1}$.14

The lower $\Delta G^*$ value for 5'' compared to that for 7'' is consistent with the π-bond order of the relevant inter-ring linkages; on going from 7 to 7'', this order increases by 0.084, but the analogous enhancement is only half as large on passing from 5 to 5'' (de-localization of the unpaired electron over two lateral o-terphenyl π-systems).

**Table 1. Zero-Field Splittings, $D_z$ and Mean Separation, $r$, of the Two Unpaired Electrons in the Triplet Dianions 3''-5''-8'8'' and 5-Br$_4^-$**

<table>
<thead>
<tr>
<th>Dianion</th>
<th>solvent temp. K</th>
<th>$D_z$ mT</th>
<th>$r$, pm</th>
<th>$r_{opt}$ pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3''-8''</td>
<td>THF 150</td>
<td>3.45</td>
<td>930</td>
<td>1160</td>
</tr>
<tr>
<td>MTHF 115</td>
<td>3.65</td>
<td>915</td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF 120</td>
<td>2.70</td>
<td>1010</td>
<td>1180</td>
<td></td>
</tr>
<tr>
<td>MTHF 115</td>
<td>3.05</td>
<td>970</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-Br$_4^-$</td>
<td>THF 130</td>
<td>2.85</td>
<td>990</td>
<td>1270</td>
</tr>
<tr>
<td>MTHF 115</td>
<td>3.35</td>
<td>940</td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF 150</td>
<td>3.35</td>
<td>940</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MTHF 115</td>
<td>3.75</td>
<td>905</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5aExperimental error, ±0.005 mT. 5bDistance between the centers of the two lateral π-systems as derived from molecular models.


Figure 3. ESR spectra of the triplet dianions $S'^{-2}$ (top and center) and $S^{-1}C'^{-2}$ (bottom). Solvent and temperature as indicated. Counterions, $K^{+}$.

where $\tau$ is in picometers and $D'$ in milliteslas. Table I gives the $2D'$ and $\tau$ values for all triplet dianions, both in viscous THF and glassy MTHF. These values compare well with the distances, $r_{c}$, between the centers of the two lateral biphenyl or $o$-terphenyl $\pi$-systems in $3-5$. Thus, each of these lateral $\pi$-systems in $3'^{-2}-5'^{-2}$ must accommodate one unpaired electron.

The relatively large separation (ca. 1 nm) of the two electrons must here be responsible for the failure to observe the "forbidden" $\Delta M_{S} = 2$ transitions at the half-field. For the same reason, the interaction between the two electrons should be slight, as should be the difference in the energies of the dianion singlet and triplet states (singlet–triplet splitting $2J$). In fact, exhaustive reduction of 3 and 5 with Li, Na, or K in THF-$d_{4}$ at 195 K yielded $^{1}H$ and $^{13}C$ NMR spectra that were ascribed to the singlet dianions $3'^{-}$ and $5'^{-}$, as spin relaxation of the solutions regenerated the corresponding neutral compounds with an intact carbon framework. Reliable analyses of these spectra were, however, impaired by the low intensities of the signals and their large width caused by the presence of paramagnetic species. Studies of the temperature dependence performed on the ESR spectra of $5'^{-2}$ in glassy MTHF suggest that the ground state of the dianions is triplet ($J < 0$). The intensities of these spectra increased steadily by lowering the temperature in the range 150–100 K, relative to those of the corresponding radical anions taken at the same temperature prior to the formation of the dianions. The $J$ value estimated from these studies by applying the relation

$$\ln \left[ \frac{I(t)}{I(m)} \right] = -\ln \left[ 3 + \exp(J/kT) \right] + \text{const}$$

is $-2$ kJ mol$^{-1}$ where $I(t)$ stands for the spectral intensity of the triplet dianion and $I(m)$ for that of the radical monoanion.

Observation of singlet and triplet dianions for the same hydrocarbon is not unprecedented. It has been reported$^{21}$ that such diamagnetic and paramagnetic species were produced by reaction of 1,2-di(9-anthryl)ethane with alkali metals in an ethereal solvent and that they have been characterized by their NMR and ESR spectra, respectively. The $^{1}H$ and $^{13}C$ NMR spectra of the singlet dianions pointed to an even distribution of the two negative charges over both anthracene $\pi$-systems of the hydrocarbon.$^{23}$

Radical Trianions. In all triplet ESR spectra, strong central absorption was observed. Its intensity increased on further contact with the potassium mirror at the expense of the triplet-state signals. In fluid solutions, this absorption gave rise to well-defined ESR and ENDOR spectra, which drastically differed from those of the corresponding radical anions. Their total width was ca. 2.5 mT, i.e., almost twice as much as that observed for $3^{-}-5^{-}$. The new paramagnetic species were identified as the radical trianions $3'^{-3}$, $3^{-}d_{2}$, $3'^{-}c$, $5'^{-3}$, and $5^{-}d_{2}$, formed from the dianions by the uptake of a third additional electron. This attribution was corroborated by the finding that photooxidation of the solutions with a high-pressure Hg lamp ($\lambda > 330$ nm, cut off by a Pyrex filter) led to a partial reappearance of the ESR spectra of the respective radical anions.$^{22}$

The ESR and ENDOR spectra of the radical trianions, taken at 193–263 K with DME, THF, and MTHF as solvents, are illustrated in Figure 4 by those of $5^{-3}$. Since the ESR resolution

was incomplete, the proton coupling constants again had to be
derived from the ENDOR spectra. They are given for 3*-5, 4*-
and 5*- in Figure 5, along with the analogous values for the
radical anions of the cyclophanes 1 and 2. Assignments of the by far
largest coupling constant to the eight protons in the central phane
unit. Relevant constants to be negative, the signs of the remaining ones were
determined by general TRIPLE resonance. The hardly no-

coupling constants of the protons throughout appeared to be equivalent
for 3*-5*- which are significantly more

which is flanked by two lateral

This preference is less straightforward in the case of

Figure 5. Coupling constants (in mT) of the protons in the radical
trianions 3*-5*, 4*- and 5*- and the corresponding values for the radical
anions 1* and 2*. In the case of 5*- the upper numbers refer to DME,
and the lower ones to THF and MTHF as solvent. Experimental error,
±0.002 and ±0.001 for the coupling constants (absolutely) larger and
smaller than 0.1 mT, respectively. g factor of 3*-5*; 2.0026 ± 0.0001.

The hyperfine data point unequivocally at the accommodation
of the unpaired electron in 3*-5* by the central phane unit.
Thus, these radical trianions can be regarded as the radical anion
of [2,2]paracyclophane (1), which is flanked by two lateral \( \pi \)-

systems orthogonal to it, each bearing one negative charge.

Starting with the di-anions, an additional electron may, in
principle, be accepted either by one of these singly charged \( \pi \)-
systems or by the formally uncharged central phane unit. Relevant
in this respect are the second reduction potentials, \( E_{1/2}^{(2)} \), of the
lateral \( \pi \)-systems, biphenyl (6) or \( \pi \)-terphenyl (7), as compared with the first reduction potentials, \( E_{1/2}^{(1)} \), of the cyclophanes 1 and 2. In the case of 3* and 4*,- the preference of the unpaired
electron for the central phane unit can readily be accounted for by the \( E_{1/2}^{(2)} \) value of -3.18 V for 6, which is significantly more
negative than the potentials \( E_{1/2}^{(1)} \) of both 1 (-3.00 V) and 2
(-2.68 V). This preference is less straightforward in the case of

Figure 6. Schematic representation of the mono-, di-, and trianions
obtained upon the consecutive uptake of three electrons by 3*-5*.
The (incomplete) circles stand for the lateral biphenyl or \( \pi \)-terphenyl \( \pi \)-syst-
ems. Paired and unpaired electrons are symbolized by a minus sign (\( \cdot \))
and a minus sign above a dot (\( \cdot \)), respectively. 27

5*-2, as the \( E_{1/2}^{(2)} \) value of 7 is -2.72 V and thus only slightly
more negative than -2.68 V. Nevertheless, the hyperfine data for
4* indicate no doubt that in this radical trianion the unpaired
electron is also mainly located in the central phane unit and not in
a lateral \( \pi \)-terphenyl \( \pi \)-system. Association of the radical
trianion with three K* counterions can play an important role
in this case. It manifests itself for 5*- by the striking dependence
of the coupling constants on the solvent (Figure 5), a behavior
contrasting that of 3* and 4*.

Under the experimental conditions used in these studies (solvent,
DME, THF, or MTHF; temperature, 193-263 K), the eight

cyclopane protons throughout appeared to be equivalent (5*)
practically equivalent (3* and 4*) of this case. It manifests itself for 5*- by the striking dependence
of the coupling constants on the solvent (Figure 5), a behavior
contrasting that of 3* and 4*.

Formation of the trianions by 3-5 might also lead to a quartet
state in which three electrons are unpaired. A number of reports
on paramagnetic molecules in a quartet ground state exist in the
literature. 23-26 All these species are neutral triradicals containing
three identical monoradical moieties such as triaryl[methyl, 23
verdazyl, 24 hydrazyl, 25 and aroxyl 26 (in particular, galvinoxyl 26-5).
To our knowledge, quartet trianions of \( \pi \)-systems, like those in
3-5, have not yet been studied. For a quartet molecule in a glassy
solution, one expects that the ESR spectrum should consist of five
signals when \( x \) and \( y \) features coincide. 27-29,32,35,36. A Charac-
teristic of this spectrum is the appearance of a strong absorption

23 (a) Schmauss, G.; Baumg"{a}rtel, H.; Zimmermann, H. Angew. Chem.
Brickmann, J. Chem. Phys. Lett. 1972, 17, 86. (d) Kothe, G.; Brickmann,
(b) Kothe, G.; Wasmann, K. H.; Nauck, A.; Oehmes, E.; Rieser, J.; Wallenfelds
Chem. 1974, 78, 265. (b) Harres, W.; Kurreck, H.; Reusch, J.; Gierke, W.
M"{o}bius, K.; Plati, M.; Biehl, R. J. Am. Chem. Soc. 1978, 100, 7505. (d)
The subsequent reduction steps leading to paramagnetic mono-
di-, and trianions are schematically depicted for 3-5 in Figure 6. These species have been characterized as follows:

(i) Radical (doublet) anions, 3*-5*, with one unpaired
electron in a lateral σ-system. Electron exchange with the second equivalent system is fast on the hyperfine time scale, except under conditions of tight ion pairing.

(ii) Triplet anions, 3**2--5**2, with two unpaired electrons, one in each of the two lateral σ-systems. Experimental evidence suggests a simultaneous presence of singlet diatoms in which the two electrons are paired.

(iii) Radical (doubled) trianions, 3**3--5**3, with two paired electrons, in each of the lateral π-systems and one unpaired electron in the central phenyl unit. Simultaneous occurrence of quartet trianions, with three unpaired electrons, could not be confirmed experimentally.

This interpretation is in full accord with the cyclic voltamogram of 5-Bu4. The first two reversible reduction waves of this compound appear at E1/2(1) = -2.54 V (neutral σ-monoanion) and E1/2(2) = -2.61 V (monoanionic σ-dianion), i.e., close to the potential E1/2(1) of the terphenyl 7(-2.62 V), whereas a third, likewise reversible, wave is observed at E1/2(3) = -2.80 V (dianionic σ-trianion). The finding that this E1/2(3) value of 5-Bu4 is somewhat more negative than the potential E1/2(1) of the dibenzoylephane 2(-2.68 V) can readily be rationalized in terms of the two negative charges that are present in the lateral π-systems of 5-Bu4 at the uptake of an additional electron by the central phenyl unit (Figure 6).

(27) Due to an excessive line broadening, the NMR spectra of the singlet diatoms could not be reliably analyzed (see above), so that the charge distribution in these diamagnetic species has not been established unequivocally. As indicated in Figure 6, it is assumed that each of the two lateral π-systems accommodates one negative charge. Such a structure is considered to be favored by electrostatic repulsion and it also complies with the spin distributions in the corresponding radical anions and, particularly, in the radical cations. However, an alternative structure with both electrons occupying, at least temporarily, only one of the lateral π-systems cannot be completely ruled out in default of direct experimental evidence.

Conclusions

The synthesis of 3*,-4*,-5*, and 5*-Bu4* have been reported; a detailed description will be given in a forthcoming paper. 3-d2 was prepared by a procedure analogous to that used for 3*,-4* with the reagent styrene being replaced by its p-deuterium derivative.

Experimental Section

The tandem flowing afterglow-selected ion flow tube has been employed to measure rate coefficients for a series of 12 bimolecular isotope-exchange reactions of methoxido–methylene clusters. From these kinetic measurements the dissociation energies of several hydrogen-bonded dimers were determined: CH3OH-DOCH3 (28.3 ± 0.1 kcal/mol), CH3O-HOCDO (28.5 ± 0.1 kcal/mol), CH3O-DOCD3 (28.1 ± 0.1 kcal/mol) CD3O-HOCDO (28.9 ± 0.1 kcal/mol), and CD3O-DOCD3 (28.5 ± 0.1 kcal/mol). Differences in the bond strengths of these cluster ions can be understood in terms of the acidity of the neutral molecule and the basicity of the anion involved in the cluster: a given ion makes a stronger bond with a stronger acid while a given neutral molecule makes a stronger bond with a stronger base. By use of literature values of the electron affinity of the methoxy radicals along with the known RO-H and RO-D bond strengths, the gas-phase acidities (AH°acid) of CD3OD (383.9 ± 0.7 kcal/mol), CH3OD (383.5 ± 0.7 kcal/mol), and CD2OH (382.0 ± 0.7 kcal/mol) were calculated. A simple model is employed to predict reaction efficiencies and branching ratios for these isotope-exchange reactions.

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We are greatly obliged to Prof. M. Rabinovitz, The Hebrew University of Jerusalem, Israel, and K. Müllen, Johannes Gutenberg—Universität Mainz, F.R.G., in whose laboratories the NMR studies of the reduction products of 2, 3, and 5 were carried out. Our thanks are also due to Prof. J. Heinze, University of Freiburg, F.R.G. for communicating his cyclic voltammetric data to us prior to publication. Financial support by the Swiss National Science Foundation and the German Fonds der Chemischen Industrie is gratefully acknowledged. B.K. and O.R. are indebted to the Studienstiftung des Deutschen Volkes for graduate fellowships.

Hydrogen–Deuterium-Exchange Reactions of Methoxido–Methanol Clusters

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I. Introduction

One of the goals of gas-phase ion chemistry is to determine intrinsic reactivities and thermochemistry in order to provide a fuller understanding of solution chemistry. A particularly powerful tool toward this end is to employ cluster ions and investigate the effects of solvation as solvent is added to a reaction, one molecule

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