Anion Radicals of a Series of [2.2]Paracyclophanes and α,ω-Diarylalkanes. II. An Electron Spin Resonance Investigation

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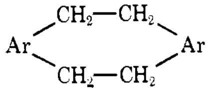
Abstract: Esr and electrochemical data have been obtained for the anion radicals of a series of [2.2]paracyclophanes (I) and α,ω-diarylalkanes ($Ar(CH_2)_nAr$), where Ar is equivalent to benzene (B), naphthalene (N), anthracene (A), and pyrene (π), and for Ar = naphthalene (n = 2, 3, 4). These molecules contain two aromatic ring systems where the degree of interaction between the rings is a function of the size of the ring and the conformational freedom of the molecule. The paracyclophanes exhibit strong interaction between the π systems and the electron transfers between the rings rapidly on a time scale characteristic of esr hyperfine splittings, *i.e.*, $>10^8$ sec^{-1}. Upper and/or lower limits for the electron exchange rate (ν_e') in the diarylalkanes were established. Values of ν_e' for $BCH_2CH_2B\cdot^-$, $NCH_2CH_2N\cdot^-$, $N(CH_2)_3N\cdot^-$, $N(CH_2)_4N\cdot^-$, $ACH_2CH_2A\cdot^-$, and $\pi\text{-}CH_2CH_2\text{-}\pi\cdot^-$ are $<10^6$, 10^6–10^8, 10^6–10^8, 10^6–10^8, $> 10^8$, and 10^6–10^8 sec^{-1}, respectively. The exchange rates were found to be consistent with the existing theory for intramolecular electron exchange. Semiquantitative estimates of the solvation energy of the anion radical and the electron vibration interaction were made. Polarographic data showed that the rings in the two classes of compounds behave as separate but weakly interacting π systems and the strength of this interaction is related to the separation between the first and second one-electron waves. These data were used to estimate the tendency for the anion radicals to disproportionate.

The [*m.n*]paracyclophanes and α,ω-diarylalkanes offer unique systems for studying the effects of interring interactions on the properties of ion radicals of molecules possessing two similar aromatic rings. The esr spectra of the anion radicals of several [*m.n*]paracyclophanes and diphenylalkanes were first reported by Weissman.[1] He found that the rate of intramolecular electron transfer between the rings was related to the number of carbon atoms in the bridging unit and was manifested in the observed hyperfine patterns. A theoretical interpretation of the optical and esr spectra of [2.2]paracyclophane was given by Ishitani and Nakagura.[2] Gerson and Martin,[3] with the aid of improved resolution from modern esr spectrometers, offered a more complete interpretation of the esr spectrum of several paracyclophanes and diphenylalkanes. They noted the existence of unsymmetrical ion pairs for [2.2]paracyclophane with K^+ as the counterion. Their results are in qualitative agreement with Weissman's. A theory of the factors controlling intramolecular electron transfer rates in the radical anion of bibenzyl was proposed by McConnell.[4] He considered the electron to be trapped on one of the rings by the electron vibrational interaction and by polarization of the surrounding solvent molecules by the charge. When the molecule receives sufficient energy through random thermal processes an electron jump to an adjacent ring may take place.

In order to determine the effects of various aromatic ring and bridge groups on the properties of these molecules we have conducted an esr and electrochemical investigation of a series of [*m.n*]paracyclophanes and α,ω-diarylalkanes. The properties of these anion radicals were discussed in the preceding paper.[5] The compounds which were investigated are the [2.2]paracyclophanes (I) with Ar = benzene (BPC), 1,4-naphthyl (NPC), and 9,10-anthryl (APC), and the α,ω-diarylalkanes $Ar(CH_2)_nAr$ with Ar = benzene ($B(CH_2)_nB$), 1-naphthyl ($N(CH_2)_nN$), 9-anthryl ($A(CH_2)_nA$), and 1-pyrenyl ($\pi\text{-}(CH_2)\text{-}_n\pi$).


I

From the line widths and hyperfine patterns of the esr spectrum it is possible to estimate upper and/or lower limits for the rate of intramolecular electron exchange in these compounds. The polarographic reduction potentials of these species provide information on the ease of reduction of the molecules as a whole compared to the isolated individual rings and also help to characterize their chemical behavior. A knowledge of electron transfer rates should also provide a test of the predictions of the McConnell theory[4] and provide a criterion for predicting the effects of chemical modification of these systems on intramolecular electron transfer rates.

Experimental Section

The anion radical solutions for the esr studies were prepared in glass vessels under high vacuum (10^{-5} mm) using anhydrous solvents. Solvents were prepared and transferred to alkali metal mirrors or alloys *via* breakseals. The actual reductions were carried out at −78° in order to prevent decomposition of the primary anion radical species. The complications involved in the generation and handling of the anion radicals were described in the previous paper[5] and the absence of any spurious paramagnetic species formed in the decomposition was established.

The esr spectra were recorded on a Jeolco 3 BSX esr spectrometer operating at 100 kHz modulation. In order to ensure that the broadened lines observed in some of the spectra were not instrumental in origin, the spectra of some known aromatic radical anions were reproduced. Using modulation amplitudes, power levels, time constants, and sweep rates similar to those required to resolve the approximately 80-mG splittings of the *tert*-butyl protons in

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[1] S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 6462 (1958).

[2] A. Ishitani and S. Nagakura, *Mol. Phys.*, 12, 1 (1967).

[3] F. Gerson and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, **91**, 1883 (1969).

[4] H. M. McConnell, *J. Chem. Phys.*, **35**, 508 (1961).

[5] J. M. Pearson, D. J. Williams, and M. Levy, *J. Amer. Chem. Soc.*, **93**, 5478 (1971).

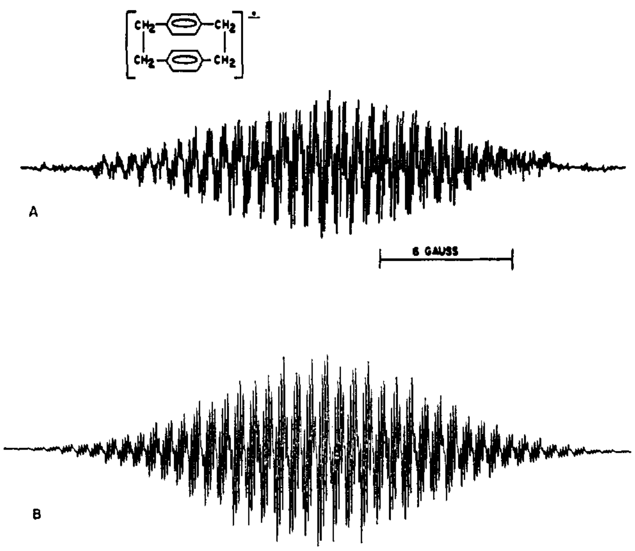

Figure 1. Esr spectrum of (A) BPC·⁻, K⁺, in THF at −95° and (B) the computer simulation of this spectrum using the coupling constants given in the text.

tri-*tert*-butylphenoxy radical it was not possible to increase the resolution over the spectra reported here.

The THF and DME were fractionated and distilled from calcium hydride into glass vessels and stored over sodium–anthracene. The HMPA was distilled twice *in vacuo* over calcium hydride and thoroughly outgassed and stored in glass breakseals.

Esr spectral simulations were accomplished with a computer program supplied by Dr. J. Jagur-Grodzinski (State University of New York–College of Forestry) and modified by Mr. Andrew Wilson (Xerox Corp.) for use with the UNIVAC 1108 computer and CalComp plotter.

The preparation of the parent compounds with the exception of the ring-deuterated compounds $ACH_2CH_2A\text{-}d_{18}$ and APC-d_{16} are given in ref 5. The ring-deuterated anthracene paracyclophane ($C_{32}H_8D_{16}$) was synthesized from anthracene-d_{10}. Anthracene-d_{10} was converted into 9,10-bischloromethylanthracene-d_8 using formaldehyde and HCl and the paracyclophane was prepared as described in ref 5. The yield was 50% (based on anthracene-d_{10}). The fully ring-deuterated dianthrylethane, $C_{30}H_4D_{18}$, was prepared from anthracene-d_{10} by conversion to 9-anthraldehyde-d_9 using dimethylformamide and phosphorous oxychloride. The aldehyde was reduced to the ethane as described in ref 5. Mass spectral analysis confirmed the structures.

Electrochemical data were recorded on a Beckman Electroscan 30 Electroanalytical system. Polarographic results were obtained with a 25-ml cell employing a dropping mercury electrode (dme) as working electrode, an isolated platinum wire auxiliary electrode, and an aqueous saturated calomel electrode (sce) in a separate Luggin capillary compartment filled with test solution, as the reference electrode. Purification of solvent, *N,N*-dimethylformamide (Burdick and Jackson), and general procedures described in the literature[6] were followed. Solutions were 0.1 *M* in supporting electrolyte, tetra-*n*-butylammonium iodide or tetraethylammonium perchlorate, and 10^{-3}–10^{-4} *M* in electroactive species. The uncertainty in $E_{1/2}$ was estimated at ±5 mV. Cyclic voltammetric experiments were carried out at a platinum disc electrode (~0.03 cm²) with scan rates in the range of 100–500 mV/sec.

Results

Esr Spectra. BPC·⁻. The esr spectrum of BPC·⁻ prepared with K in THF is shown in Figure 1. The spectrum can be simulated with four sets of four equivalent protons with coupling constants of 3.78, 1.96, 1.27, and 0.68 G and one $^{39}K^+$ splitting of 0.12 G. The resolution compares well with that obtained by Gerson and Martin[3] and is greatly improved over that reported earlier by Ishitani and Nakagura.[2] This result establishes a high level of confidence in our ability to generate these very unstable species and also in the resolution of the esr spectrometer.

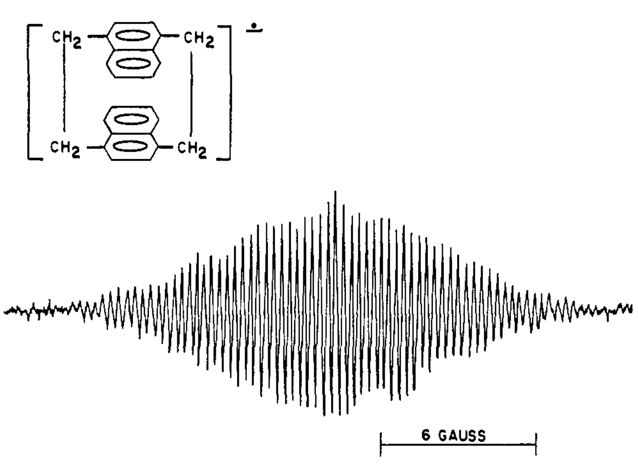

Figure 2. Esr spectrum of NPC·⁻, K⁺, in DME at −70°.

The observed behavior of the spectrum was attributed by Gerson and Martin[3] to an unsymmetrical ion pair where the electron is rapidly (but not necessarily equally) delocalized over both rings and the ion pair interconverts between its mirror image slowly on a time scale compared with the hyperfine interaction. In DME the spectrum simplifies to two sets of eight equivalent protons with no metal splitting, corresponding to the free ion with equal delocalization over both rings.

NPC·⁻. The spectrum of the species derived from reduction of NPC with K in DME at −70° is shown in Figure 2. It contains a large number of overlapped lines and it was not possible to resolve them sufficiently to measure any reliable coupling constants. Attempts to computer simulate this spectrum with values of the coupling constants roughly one-half the value of those for the 1,4-dimethylnaphthalene radical anion with three sets of four and one set of eight equivalent protons and a 70-mG line width gave spectra resembling the experimental one. However, a completely satisfactory set of constants could not be obtained. This spectrum is consistent with what would be expected for an overlapped 1125-line spectrum from complete delocalization of the electron over both rings and is totally different from the relatively simple 135-line spectrum that would be expected if the electron was associated with one ring.

APC·⁻. The esr spectrum of APC·⁻ was recorded in DME at −70°. Complete delocalization of the electron over both rings was demonstrated with the ring-deuterated analog APC-d_{16}·⁻. The spectra of these two species are shown in Figure 3. The spectrum of APC-d_{16}·⁻ shows the expected nine lines resulting from the eight equivalent bridge protons. The ratio of intensities of lines for eight equivalent protons is 1:8:28:56:70:28:8:1. The separation between peaks is approximately 1.6 G which is roughly one-half of the methyl splitting of 3.88 G reported for the 9,10-dimethylanthracene radical anion.[7]

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(6) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **88**, 2669 (1966).

(7) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, 5, 31 (1962).

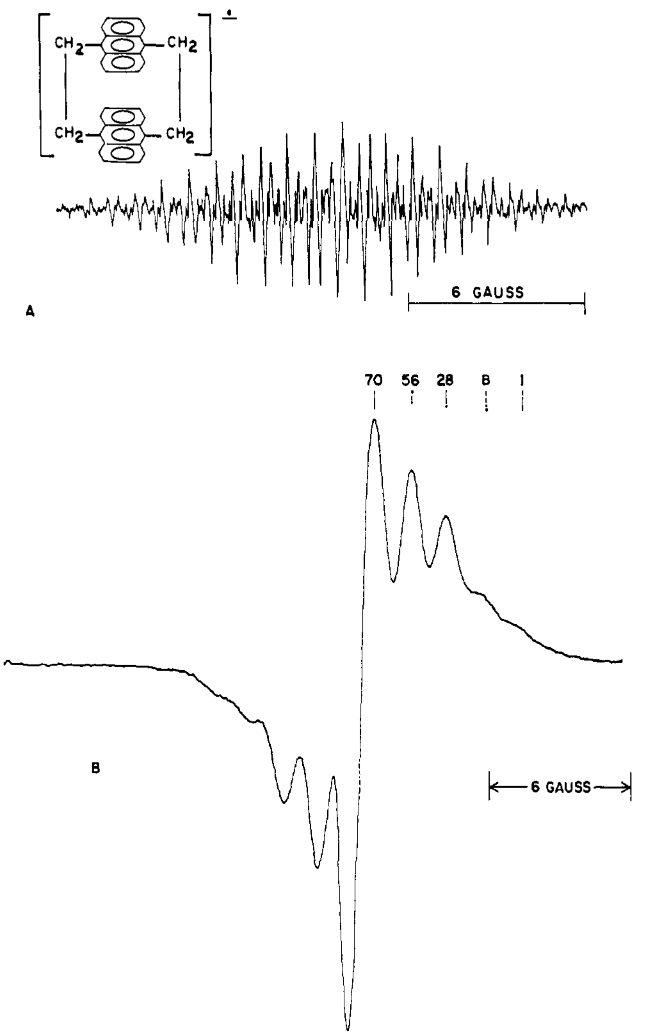
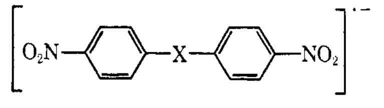


Figure 3. Esr spectrum of (A) APC·$^-$, K$^+$, and (B) APC-d_{16}^-, K$^+$, in DME at −70°.

BCH$_2$CH$_2$B·$^-$. The spectrum of BCH$_2$CH$_2$B·$^-$ in DME at low temperature was reported by Gerson and Martin.[4] The spectrum corresponds to one set each of four and three equivalent (or nearly equivalent) protons and is characteristic of localization of the electron on one of the rings.

NCH$_2$CH$_2$N·$^-$. The esr spectrum of NCH$_2$CH$_2$N·$^-$ was recorded in a number of solvents and at various temperatures. Novel line-width effects can be seen that are associated with intramolecular electron transfer at frequencies in the range of the electron–nuclear hyperfine interactions. The existence of such effects was first recognized by Harriman and Maki[8] for radical anions of the type



where X = CH$_2$, S, O, and CH$_2$CH$_2$, and where X is absent. They found that in cases where the electron spin has a net isotropic interaction with only one ring and the charge is localized on one ring, the change in energy of the $\Delta M_s = \pm 1$ transition expressed as a frequency is given by

$$\Delta\nu = \Sigma_{\mathrm{A.B}} a_{\mathrm{N}}(M_\mu'' - M_\mu') \qquad (1)$$

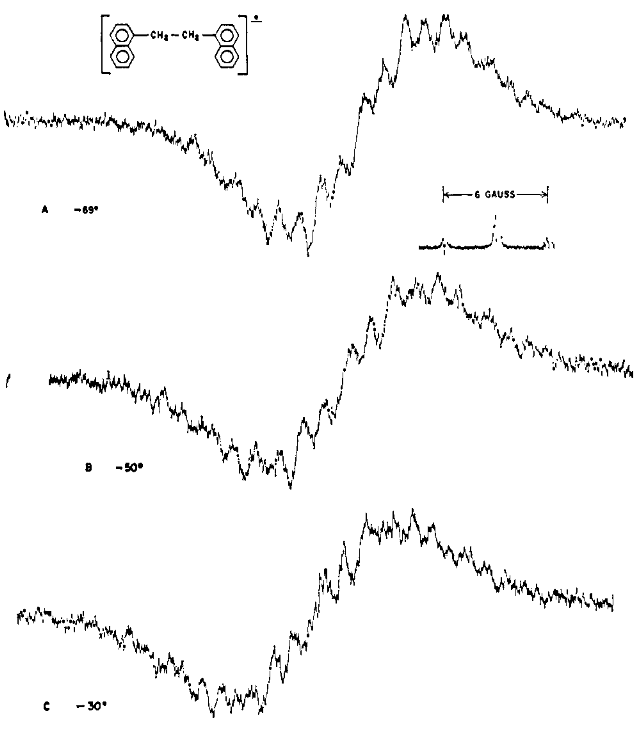


Figure 4. Esr spectrum of NCH$_2$CH$_2$N·$^-$, K$^+$, in DME at (A) −69°, (B) −50°, and (C) −30°.

where a_{N} is the hyperfine coupling constant (sec^{-1}) and M_μ'' and M_μ' are the z components of the nuclear spin angular momentum of nucleus μ in the two rings A and B, respectively. When M_μ'' is identical with M_μ', $\Delta\nu$ will be zero and the line width of that $\Delta M_s = \pm 1$ transition will be unaffected by the rate of electron transfer. In cases where the electron exchange rate ν_e is less than $\Delta\nu$, separate $\Delta M_s = \pm 1$ transitions will be observed. For $\nu_e \simeq \Delta\nu$ the two transitions will broaden and eventually collapse and when $\nu_e \gg \Delta\nu$ a single sharp line at $\bar{\nu} = {}^1/_2\Sigma_{\mathrm{A.B}}(M_\mu' + M_\mu'')$ will be observed. The conditions of validity for this approach are that the jump process must be Markoffian (the value of M_μ on ring A does not depend on the value of M_μ in ring B and *vice versa*) and the nuclear spin relaxation time must be long compared with the electron exchange frequency ν_e.

The spectrum of NCH$_2$CH$_2$N· in DME at −69, −50, and −30° is shown in Figure 4. Spectra were also recorded in THF and THF + 2% HMPA but are not shown here. The spectra in all of the solvents are complex and consist of sharp components superimposed on broader ones. Careful examination of the central line in the spectra shown in Figure 4 shows the presence of sharp components on the broadened background. The sharp lines become more prominent as the temperature is raised to −30°. The signal-to-noise ratio in the spectra is rather low but this was necessary in order that the spectra be scanned as rapidly as possible to avoid serious decomposition. Other lines in the spectra when examined carefully exhibit sharp components that vary with temperature. The overriding S shape of these curves can be understood if the number of values of $\Delta\nu$ in eq 1 are calculated. In the case of the bis(p-nitrophenylphenyl) anions reported by Harriman and Maki[8] there are n^2 possible values of $\Delta\nu$ where n is the number of distinct hyperfine frequencies for a localized state. For example, in bis(p-nitrophenyl) sulfide n = 9 and

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(8) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).

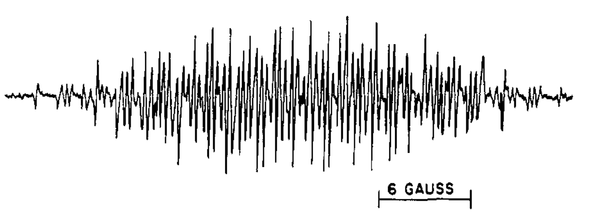


Figure 5. Esr spectrum of the paramagnetic species formed in the reduction of NCH_2CH_2N over potassium in HMPA at 20°.

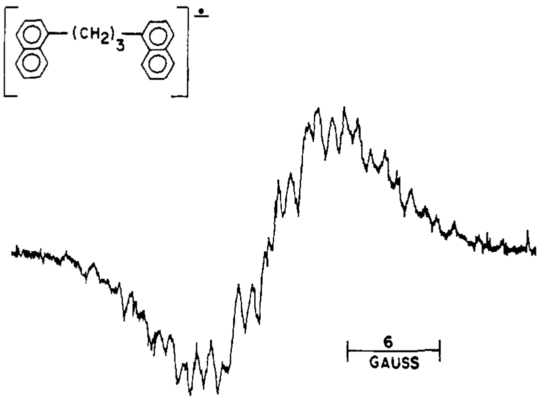


Figure 6. Esr spectrum of $N(CH_2)_3N\cdot^-$, K^+, in DME at $-70°$.

$n^2 = 81$ possible values for $\Delta\nu$. In NCH_2CH_2N, $n = 3 \times 2^7$ for seven nonequivalent ring protons and two equivalent methylene bridge protons and $n^2 = (3 \times 2^7)^2$ It can easily be seen that this will result in a much more complex spectrum with a great deal of additional overlap of broadened lines.

Since DME is known to yield esr spectra characteristic of the free anion[3] it is assumed that these selective line-width effects result from intramolecular electron exchange in the frequency range of the hyperfine interactions.

The spectrum of the reduction product of NCH_2CH_2N was also recorded in pure HMPA at ambient temperature. Initial contact of the HMPA solution with K at low temperature gave a solution with a single sharp intense line corresponding to solvated electrons. As this line disappeared, the spectrum shown in Figure 5 appeared. This spectrum is identical with that of the 1-methylnaphthalene radical anion prepared by K reduction in HMPA at room temperature. This finding can be rationalized on the basis of the mechanism of decomposition of the anion radical of NCH_2CH_2N proposed in the preceding paper. The anion radical which is formed initially decomposes instantaneously at ambient temperatures to form the benzylic anion NCH_2^-. This anion can abstract a proton from solvent and reduction will generate the anion radical of 1-methylnaphthalene, the observed species.

$N(CH_2)_nN\cdot^-$. The esr spectrum of $N(CH_2)_3N\cdot^-$ and in DME at $-70°$ is shown in Figure 6. It is apparent that this species exhibits a spectrum characteristic of the intermediate exchange region. A similar spectrum is observed for $N(CH_2)_4N\cdot^-$ in DME at $-70°$ indicating that this molecule also exhibits an intermediate range spectrum.

$\mathbf{ACH_2CH_2A\cdot^-}$. The spectrum of $ACH_2CH_2A\cdot^-$ in DME at $-70°$ is shown in Figure 7A. The lines are considerably sharper than for $NCH_2CH_2N\cdot^-$ indicating that the exchange is rapid, *i.e.*, $\sim 10^8$ or greater. The spectrum of the completely ring-deuterated analog is also shown in Figure 7B. The spectrum was overmodulated so that the larger proton splitting could be distinguished from the deuterium splitting. The splitting between the peaks is about 1.8 G. The coupling constant for the methyl group in 9-methyl anthracene has been reported as 4.26 G.[6] The coupling constant for the methylene bridge protons should be roughly half this value if exchange is rapid. The observed value of 1.8 G should be less than the true coupling constant because of overlap of the lines. Although the five lines cannot be completely distinguished, the splitting that is observed argues for rapid exchange of the electron between the rings.

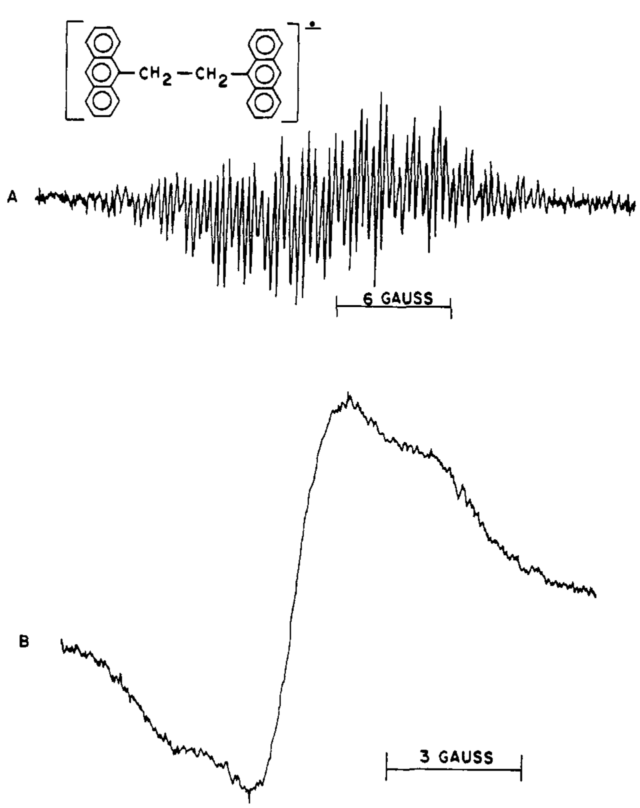


Figure 7. Esr spectrum of $ACH_2CH_2A\cdot^-$, K^+(A), and ACH_2CH_2A-$d_{18}\cdot^-$, K^+ (B), in DME at $-70°$.

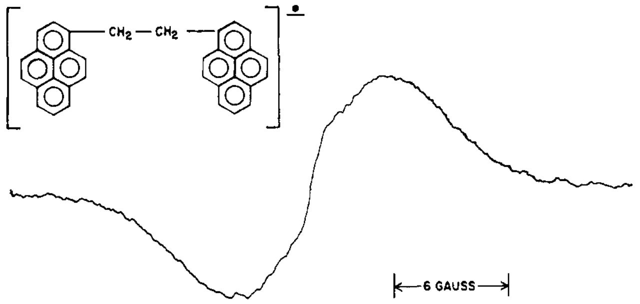


Figure 8. Esr spectrum of π-CH_2CH_2-$\pi\cdot^-$, K^+, in DME at $-70°$.

$\boldsymbol{\pi}$-$\mathbf{CH_2CH_2\pi\cdot^-}$. The esr spectrum of π-CH_2CH_2-$\pi\cdot^-$ in DME at $-70°$ is shown in Figure 8. The spectrum is broad and there is very little discernible hyperfine structure. The value of n^2 is $(3 \times 2^9)^2$ for π-CH_2CH_2-π compared with $(3 \times 2^7)^2$ for NCH_2CH_2N and hence a more broadened spectrum with less discernible hyper-

Table I. Half-Wave Reduction Potentials[a] of Diarylalkanes, Paracyclophanes, and Related Compounds

Compound	E_1	E_2	$E_{1/4}$	$E_{3/4}$	$(E_{1/4} - E_{3/4})$	K^c
9-Methylanthracene[b]	−1.95	−2.50				
9,10-Dimethylanthracene[b]	−1.96	−2.52				
ACH_2CH_2A			−1.82	−1.97	0.15	2.9×10^{-3}
APC			−1.7	−2.0	0.30	8.5×10^{-4}
1-Methylnaphthalene[b]	−2.50					
1,4-Dimethylnaphthalene[b]	−2.50					
NPC (anti)			−2.38	−2.50	0.12	1.1×10^{-2}
NPC (syn)			−2.35	−2.46	0.11	1.5×10^{-2}
NCH_2CH_2N			−2.42	−2.58	0.14	5.6×10^{-3}
$N(CH_2)_3N$			−2.47	−2.55	0.08	2.3×10^{-2}
$N(CH_2)_4N$			−2.48	−2.54	0.06	6.3×10^{-2}
1-Methylpyrene[b]	−2.07	−2.60				
π-CH_2CH_2-π			−1.88	−2.00	0.12	1.1×10^{-2}

[a] E values are in volts *vs.* sce. [b] For these molecules E_1 and E_2 refer to the first and second half-wave reduction potentials, *i.e.*, formation of the radical anion and dianion, respectively. [c] Values of K were obtained using values of $E_{1/4}$ and $E_{3/4}$ and eq 2, ref 8.

fine structure is observed. These observations are consistent with an exchange frequency in the intermediate region for this molecule.

Electrochemistry

The half-wave reduction potentials for the series of [2.2]paracyclophanes and diarylalkanes (excluding the phenyl derivatives which do not undergo reduction in an accessible voltage range) and their simple aromatic analogs are shown in Table I. The values obtained for the simple aromatic molecules were in very good agreement with published data.[9,10] Polarographic reduction traces of the diarylalkanes and [2.2]paracyclophanes revealed the presence of two waves of equal height and slope with, in certain cases, a well-defined shoulder separating them. Values of i_d/c, where i_d is the diffusion-controlled limiting current and c is the concentration of electroactive material, were similar for all these compounds so that the same number of electrons is indicated for each overall process. Reduction, therefore, appears to take place *via* two one-electron steps at very nearly the same potential which is reasonable for molecules possessing two almost independent but interacting π systems. The difference in potential at which the reduction occurs will be related to the strength of the interring interaction.

The mechanism of the reduction can be formulated

$$S + e \rightleftharpoons S\cdot^- \qquad E_1$$

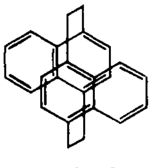
$$S\cdot^- + e \rightleftharpoons S^{2-} \qquad E_2$$

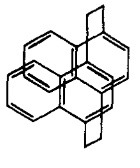
where $S\cdot^-$ is the anion radical and S^{2-} the two-electron reduced species. The shape of the polarographic wave corresponding to this two-step reduction will be related to the degree of interaction of the two rings in the molecule and also to the equilibrium constant K for the disproportionation. This treatment is valid provided that

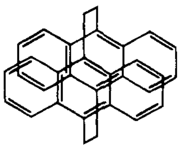
$$2S\cdot^- \rightleftharpoons S^{2-} + S \qquad K$$

both electrode reactions are reversible and this was confirmed for DMF as solvent using cyclic voltammetric techniques. The values of E_1, E_2, and K were calculated according to the procedure of Harriman and Maki[8] using the potentials $E_{1/4}$ and $E_{3/4}$ where E_n is the potential at ni_d and i_d is the diffusion current for the overall two-step reduction. The results are presented in Table I.

The values of $E_{1/4} - E_{3/4}$ provide a measure of the degree of interaction between the two π-ring systems and the results indicate the greatest interaction in APC. The low values for both the syn and anti isomers of NPC can be accounted for by molecular distortion. In these molecules the ring interactions can be minimized by rotation about the bridge to ring C–C bond resulting in an 11° distortion angle in the bridged rings.[11]


anti-NPC


syn-NPC


APC

Such a molecular distortion is not possible in APC and the two π systems are more closely parallel and more strongly interacting. The degree of interaction in the diarylethanes is similar for naphthalene, anthracene, and pyrene. In the naphthalene series, increasing the number of $-CH_2-$ groups in the bridge results in a decreased interaction. The reason for this will become apparent in the discussion of the esr data. The equilibrium constants, K, for the disproportionation reaction follow a similar pattern.

Direct comparison of the results for the paracyclophanes and diarylalkanes may not be strictly valid because of the possibility that differences in molecular orientation at the electrode surface may affect the mechanism of the reduction. As shown in Figure 9, the two rings in the diarylalkanes can approach the electrode surface simultaneously, whereas in the rigid paracyclophane molecule this is not possible. Too little is known about the actual reduction mechanism to comment any further.

Discussion

From the esr data it has been possible to obtain experimental estimates of electron exchange rates in the anion radicals of a series of paracyclophanes and diarylalkanes. The data can be summarized by stating the observed limits for exchange rates in these systems. The paracyclophanes $BPC\cdot^-$, $NPC\cdot^-$, and $APC\cdot^-$ have exchange rates greater than 10^8 sec^{-1}. Because of the strong spatial overlap in the paracyclophanes the electron may be considered to be simultaneously delocalized

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(9) L. H. Klemm, A. J. Kohlik, and K. G. Desai, *J. Org. Chem.*, **28**, 625 (1963).

(10) L. H. Klemm and A. J. Kohlik, *ibid.*, **28**, 2044 (1963).

(11) J. R. Froines and P. J. Hagerman *Chem. Phys. Lett.*, **4**, 135 (1969).

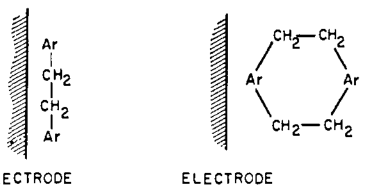

Figure 9. Schematic drawing of the approach of the α,ω-diarylalkane and [2.2]paracyclophane molecule to the electrode surface.

over both rings. This is clearly demonstrated in the case of BPC·⁻ and APC·⁻. Although it was not possible to obtain hyperfine coupling constants for NPC·⁻, it is qualitatively consistent with the fast exchange case. The radical anion of bibenzyl has an exchange rate of less than $\sim 10^6$ sec^{-1} while $NCH_2CH_2N\cdot^-$, $N(CH)_3N\cdot^-$, $N(CH)_4N\cdot^-$, and $\pi\text{-}CH_2CH_2\text{-}\pi\cdot^-$ appear to have exchange rates in the 10^6–10^8 sec^{-1} region and $ACH_2CH_2A\cdot^-$ is greater than $\sim 10^8$ sec^{-1}. Supporting evidence for the existence of the proposed anion radicals and their decomposition pathways were obtained by uv-visible and nmr spectroscopy and chemical quenching techniques and were reported in the preceding paper.[5]

A model was proposed by McConnell[4] for explaining the factors that control electron transfer rates in diarylalkane molecules. He considered explicitly the case of BCH_2CH_2B but the considerations of the model are general. Since the data that we have obtained comprise systematic variations of ring and bridge sizes it is instructive to discuss these results in terms of that model and to determine if the predicted and experimental results are consistent.

In the McConnell model the degenerate lowest unoccupied molecular orbitals on the left and right rings, ϕ_l and ϕ_r, are combined linearly to form two new states

$$\psi_s = \frac{1}{\sqrt{2}}(\phi_l + \phi_r) \tag{2}$$

and

$$\psi_a = \frac{1}{\sqrt{2}}(\phi_l - \phi_r) \tag{3}$$

It is assumed that the spatial overlap between the rings is negligible and, therefore, all direct matrix elements between the rings are zero, *i.e.*

$$\langle \phi_l | \mathrm{H} | \phi_r \rangle = 0 \tag{4}$$

The two states ψ_s and ψ_a will, however, interact differently with excited configurations involving the bridge and their degeneracy will be removed giving rise to an energy gap estimated from second-order perturbation theory

$$g = -(2T^2/D)(t/D)^{N-1} \tag{5}$$

where $t = \langle \mathrm{d_q} | \mathrm{H} | \mathrm{d}_{q+1} \rangle$ gives the resonance interaction between the lowest excited carbon d orbital backbone configuration with appropriate symmetry. $T = \langle \phi_l | \mathrm{H} | \mathrm{d_l} \rangle$ represents the interaction between the LEMO and the d orbital on the carbon to which the bridge is attached. D is the energy required to remove the odd electron from ϕ_l or ϕ_r and place it in a noninteracting 3d orbital and $N = n + 2$ where n is the number of carbon atoms in the bridge. If the effects of solvent and nuclear framework are neglected then

$$\nu_e = h^{-1}g \tag{6}$$

where ν_e is the electron transfer frequency.

The effects of solvent and nuclear configuration will tend to trap the charge on the ring in ϕ_l or ϕ_r and drastically reduce the value of ν_e given in eq 6. The energy of interaction between electron and the ring is given by

$$E_0 = S_0 + S_0' \tag{7}$$

where S_0 is the interaction of the trapped electron with the solvent dipoles and S_0' is the energy involved in distorting the nuclear configuration when the electron is trapped. Through a variational treatment of the potential energy asociated with the solvent and nuclear configuration, McConnell showed that the potential energy was a minimum when the electron was trapped on one ring or the other.

In order to estimate the effect of the self-trapping energy E_0 on the electron exchange rate McConnell obtained the following expression for the exchange frequency

$$\nu_e' = \frac{\pi}{2}\Upsilon_c^{-1}g(\Gamma kT)^{-1}\exp\left(\frac{E_0}{kT}\right) \tag{8}$$

where

$$\Gamma = 1 + 1/\Upsilon_c^2 g^2 h^{-2} \tag{9}$$

and Υ_c is the lifetime of a thermally activated state where the transfer of the electron is most likely to take place and is referred to as the "charge resonance region" and is assumed to have a value of approximately 10^{-11} sec.

The parameters in eq 7 are exponentially related to the electron transfer rate ν_e' by eq 8. Estimates of the parameters in this equation can be made. The solvation energy of a sphere of radius R is given by

$$S_0 = -\frac{1}{2}e^2(K - 1)/KR \tag{10}$$

where e is the electronic charge and K is the low-frequency dielectric constant. For a charge localized on a single ring, R should be approximately 2.5, 5.0, 7.5, and 7.5 Å for benzene, naphthalene, anthracene, and pyrene rings, respectively. For a dielectric constant of 10 (DME, −50°), the values of S_0 are given in Table II.

According to Siebrand[12] the electron–vibration interaction is conveniently described in terms of a potential well in which the electron has trapped itself. The well depth denoted by S_0' equals the energy difference between the distorted vibrational states of the ring on which the electron resides and the vibrational states of the unoccupied ring and is given by

$$S_0' = \langle \chi(\nu) | H_n | \chi(\nu) \rangle - \langle \chi^\circ(\nu) | H_n | \chi^\circ(\nu) \rangle \tag{11}$$

where $\chi(\nu)$ and $\chi^\circ(\nu)$ are nuclear wave functions corresponding to the distorted states, ν is the vibrational quantum number, and H_n is the vibrational part of the ionic Hamiltonian. In order to obtain an estimate of S_0', we will assume that the carbon bonds in the rings can be approximated as linear harmonic oscillators with an average force constant k for an aromatic C–C bond

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[12] W. Siebrand, *J. Chem. Phys.*, 40, 2223 (1964).

Table II

Molecule	gh^{-1}	$-S_0$, cm^{-1}	$\Sigma\Delta P_{r,s}$	$-S_0'$, cm^{-1}	ν_e', sec^{-1} Calcd	Found
BCH_2CH_2B	$\sim 10^{11}$	240	0.500	1501	$\sim 10^5$	$<10^6$
NCH_2CH_2N	$\sim 10^{11}$	120	0.409	1015	$\sim 10^6$	10^6–10^8
$N(CH_2)_3N$	$\sim 10^{10}$	120	0.409	1015	$\sim 10^5$	10^6–10^8
$N(CH_2)_4N$	$\sim 10^{9}$	120	0.409	1015	$\sim 10^4$	10^6–10^8
π-$(CH_2)_2$-π	$\sim 10^{11}$	80	0.223	317	$\sim 5 \times 10^7$	10^6–10^8
$A(CH_2)_2A$	$\sim 10^{11}$	80	0.216	310	$\sim 10^8$	$>10^8$

and eq 11 reduces to

$$S_0' = -\frac{1}{2}k\sum_{r,s}(\bar{q} - \bar{q}_0)_{r,s}^2 \tag{12}$$

where r,s signifies a summation over all adjacent carbon atoms and $\bar{q}$ and $\bar{q}_0$ are the distorted and undistorted bond distances. An approximate relationship exists between bond orders ($P_{r,s}$) and bond lengths and is given by[13]

$$\frac{\Sigma(\bar{q} - \bar{q}_0)_{r,s}}{\Sigma\Delta P_{r,s}} = -0.200 \tag{13}$$

Values of $\Sigma\Delta P_{r,s}$ were computed from the differences in bond orders for the anion radical and parent molecules from HMO theory and are listed in Table II with the values of S_0'. A value for k of 9×10^5 dyn/cm was used for estimating S_0'.

The value of g is very difficult to estimate. According to McConnell, a reasonable value of gh^{-1} is $\sim 10^{11}$ sec^{-1} for $BCH_2CH_2B\cdot^-$. We will assume it to be approximately the same for the other compounds containing two (CH_2) units in the bridge and that it is smaller by a factor of 10 for each additional CH_2 group. This latter assumption is based on the exponential dependence of g on the number of bridge carbons according to eq 5. The calculated values of ν_e' are compared with the experimental values in Table II.

The trends predicted by the theory agree reasonably well with experiment for molecules with $(CH_2)_2$ bridge units. The most notable discrepancy occurs in the series $(N(CH_2)_2N)\cdot^-$, $(N(CH_2)_3N)\cdot^-$, $(N(CH_2)_4N)\cdot^-$. The predicted order of magnitude decrease with each additional $(CH)_2$ group in the bridge does not appear to hold true. The reason for this is probably the neglect of conformations in which there is appreciable interaction between the rings. In spite of the crude approximations used in obtaining these numbers it is apparent that the effects of changes in solvent and molecular structure on intramolecular exchange rates in the diarylalkanes can be predicted in a semiquantitative manner.

Conclusions

Esr and electrochemical data have been presented for the anion radicals of a series of paracyclophanes and diarylalkanes. The strength of the interaction between the rings is reflected in the difference between the first and second half-wave reduction potentials and by the intramolecular electron transfer rates. The nature of the interaction between the rings appears to be different for the paracyclophanes and the diarylalkanes. In the former case complete delocalization of the electron between the two rings is observed and is attributed to strong spatial overlap between the rings. In the latter case where direct overlap between the rings is negligible (at least for the diarylethanes) the exchange rate is much slower and follows the predictions of McConnell's theory for charge transfer resulting from indirect interaction between the rings. It also appears that for $N(CH_2)_nN$ where $n = 3,4$ the dependence of exchange rate with chain length does not follow the prediction of McConnell's theory and this is probably due to the neglect of conformations where direct spatial overlap is appreciable. The influence of changes in solvent polarity and molecular structure on intramolecular exchange rates also appears to be predictable in a semiquantitative manner.

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(13) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966.