[2.2]Paracyclophane-4,7,12,15-tetrone, [2.2](1,4)Naphthalenophane-4,7,14,17-tetrone, and 1,4,8,11-Pentacenetetrone Radical Anions − A Comparative ESR Study

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Received September 29, 1997

Keywords: 1,4-Benzoquinones / [2.2]Paracyclophanes / 1,4,8,11-Pentacenetetrones / Cyclic voltammetry / Radical anions / ESR/ENDOR spectroscopy / Intramolecular electron transfer

Three types of tetrone radical anions in which two 1,4-benzoquinone units are connected by ethano ($\mathbf{1}^{\bullet-}$, $\mathbf{2}^{\bullet-}$), [2.2]paracyclophane ($\mathbf{3}^{\bullet-}$, $\mathbf{4}^{\bullet-}$), and anthracene bridges ($\mathbf{5}^{\bullet-}$, $\mathbf{6}^{\bullet-}$) have been studied by ESR and ENDOR spectroscopy. The displacement of the unpaired electron over the two π moieties in the [2.2]cyclophane radical anions $\mathbf{1}^{\bullet-}$−$\mathbf{4}^{\bullet-}$ and the marked difference between the first and second reduction potentials, $\Delta E = |E_2^0 - E_1^0| \geq 0.20$ V, are evidence for a substantial intramolecular electronic interaction between the two electrophores. Similar ΔE data for the *syn*- (**3**) and *anti*-naphthalenophanes (**4**) indicate that most of the intramolecular electronic interaction takes place through the [2.2]paracyclophane bridge. When ion pairing is inhibited by complexation of the cation, the unpaired electron in $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$ is also delocalized over the whole pentacenetetrone system at temperatures as low as 160 K.

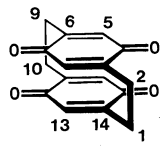
The intramolecular electron exchange between 1,4-benzoquinone units in rigid bis(1,4-quinone) radical anions is of interest in the study of intramolecular electron-transfer systems[1]. In the literature there are various systems with fixed arrangements of 1,4-benzoquinone units. As a basis for our studies we chose the *pseudogeminal*- (**1**) and *pseudoortho*-[2.2]paracyclophane-4,7,12,15-tetrone (**2**)[2], in which the 1,4-benzoquinone units lie on top of each other with a separation of approximately 3.1 Å between the ring centres. As a result of this close contact, the unpaired electron in the corresponding radical anions $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ should be delocalized over the whole molecule[3][4]. Similar behaviour is expected for the radical anion derived from the *syn*-[2.2](1,4)naphthalenophane-4,7,14,17-tetrone (**3**)[5]. In the *anti* arrangement **4**[5], however, the quinone units are further apart; it is therefore open to question whether the intramolecular electron transfer in the corresponding radical anion $\mathbf{4}^{\bullet-}$ is fast or slow on the ESR time scale (about 10^7 s^{-1}). Recently, in a thorough ESR study of conjugated quinone and imide radical anions, Miller et al.[6] generated electrochemically the alkyl substituted 1,4,8,11-pentacenetetrone radical anions $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$ in dimethylformamide and dichloromethane solutions containing 0.1 M tetrabutylammonium tetrafluoroborate. They found that at room temperature the unpaired electron in $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$ is equally displaced over both quinone units (electrophores), a(H) = 1.34 G (12 H, CH_3). At low temperature (approximately 190 K), however, the ESR spectra clearly indicated a localization of the unpaired electron on one quinone unit of the planar conjugated pentacene skeleton, a(H) = 2.89 G (6 H, CH_3). As a result of this and other findings the question of whether these radical anions might be thought of as mixed-valence species was considered[6].

Cyclic voltammetry provides further information on the intramolecular interaction. For compounds with two identical arene electrophores linked by varied alkano bridges, for example, the limit of the fast intramolecular electron transfer in the corresponding radical anions was found to correspond to a difference of about 0.1 V between the first and second reduction potentials, $|E_2^0 - E_1^0| \cong 0.1$ V[7]. A comparable value was determined for the 1,4,8,11-pentacenetetrone **6** ($|E_2^0 - E_1^0| \cong 0.15$ V)[6]. In corresponding molecular systems, therefore, a potential difference of larger than 0.2 V between the first and second reduction potentials points to a fast ($\geq 10^7$ s^{-1}) intramolecular electron transfer in the radical ion. We therefore measured the reduction potentials of **1**−**4** and **6** by cyclic voltammetry in order to characterize the intramolecular electronic interaction in these compounds.

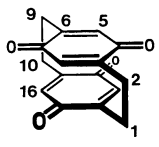
The reduction potentials of **1**−**4** and **6**, measured with a glassy carbon electrode versus Ag/AgCl in 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) acetonitrile or dichloromethane solution, are given in Table 1 together with those of the reference compounds **7**-**10**. All data are referred to ferrocene; the oxidation potential $FeCp_2^{-/0}$ was set to 0.00 V.

The cyclic voltammograms of the paracyclophanes **8** and **9** containing one quinone unit show one reversible one-electron reduction step similar to the reference compound 2,5-dimethyl-1,4-benzoquinone (**7**). The higher reduction po-

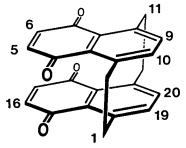
  1434−193X/98/0202−0221 $ 17.50+.50/0



1



2
2a: 1,1,2,2,9,9,10,10-D_8



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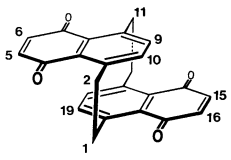

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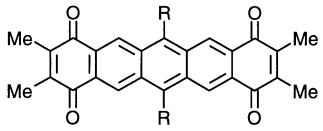
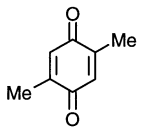
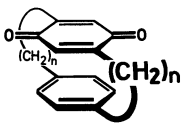


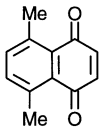
5: R = H
6: R = hexyl



7



8: n = 2
8a: n = 2; 1,1,10,10,12,13,15,16-D_8
9: n = 4



10

Table 1. Reduction potentials and potential differences $\Delta E = |E_2^0 - E_1^0|$ of the quinones **1**, **2**, **7**, **8**, and **9** in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile and **3**, **4**, **6**, and **10** in 0.1 M tetrabutylammonium hexafluorophosphate dichloromethane solution[a]. The reduction potentials E^0 are given versus ferrocene $FeCp_2^{-/0}$

	E_1^0(±0.01) [V]	E_2^0(±0.01) [V]	$\Delta E = E_2^0 - E_1^0$ [V]
1[8]	−0.77	−1.19	0.42
2[8]	−0.90	−1.22	0.32
3	−1.07	−1.30	0.23
4[b]	−1.13	−1.33	0.20
6	−1.37	−1.53	0.16
7[8]	−1.04		
8[8]	−1.23		
9	−1.15		
10	−1.32		

[a] Glassy carbon electrode versus Ag/AgCl − [b] A third reversible reduction step is observed at $E_3^0 = -1.77$ V.

tential of **8** ($E_1^0 = -1.23$ V) and **9** ($E_1^0 = -1.15$ V) compared to that of the reference compound **7** ($E_1^0 = -1.04$ V) indicates that the linked 1,4-phenylene moiety in **8** and even in **9** ($n = 4$) acts as an additional donor electrophore.

For the [2.2] paracyclophane-4,7,12,15-tetrones **1** and **2** the cyclic voltammograms display two distinctly separate and reversible one-electron reduction steps. The strong intramolecular interaction between both electrophores, particularly in the *pseudogeminal* orientation (**1**), lowers the first reduction potential significantly. Studies of charge-transfer interactions in the corresponding quinhydrones have already provided evidence[2] that the *pseudogeminal* arrangement with better suited π overlap favours the intramolecular interaction between the electrophores. The large potential differences $\Delta E = |E_2^0 - E_1^0|$ of **1** (0.42 V) and **2** (0.32 V) clearly indicate that the unpaired electron of the corresponding radical anions should be delocalized over the whole molecule.

The cyclic voltammograms of the [2.2](1,4)naphthalenophane-4,7,14,17-tetrones (**3**, **4**) also yield two, in the case of **4** even three, distinctly separate and reversible one-electron reduction steps. Surprisingly, the reduction potentials of the *syn* **3** and *anti* **4** are very similar (Table 1), although the quinone units in the *anti* arrangement **4** are significantly further apart than in the *syn* orientation **3**. Charge-transfer electron spectra of the corresponding quinhydrones also showed only small differences[5]. These observations indicate that most of the intramolecular electronic interaction in **3** and **4** takes place through the [2.2]bridged arene units. A direct through-space interaction of the benzoquinone units in the *syn* arrangement **3** is apparently of minor importance. This view is supported by the crystal structure of the parent *syn*-[2.2](1,4)naphthalenophane[9], which shows that the bridged arene rings are distorted into a boat shape. The non-parallel disposition of the naphthalenes causes the inter-ring separation to increase with distance from the bridged C atoms. The non-bonded distances between corresponding atoms on the opposite outer rings range from 3.15 to 3.90 Å yielding a mean value of about 3.5 Å which is significantly larger than that of **1** (about 3.1 Å)[10]. The potential differences $\Delta E = |E_2^0 - E_1^0|$ of **3** (0.23 V) and **4** (0.20 V) suggest that the unpaired electron of the corresponding radical anions should be displaced over the whole molecule, but their values are only slightly larger than that of the 1,4,8,11-pentacenetetrone **6** (0.16 V). Therefore, the cyclic voltammogram of **6** was recorded again for direct comparison.

The reduction of the cyclophane-quinones and of the reference compounds with potassium to the corresponding radical anions was carried out in the presence of 2.2.2-cryptand (Kryptofix® 222)[11] to inhibit any possible ion pairing. The radical anions were readily generated by this procedure and were sufficiently long lived at low temperature to perform detailed ESR and ENDOR studies. The results obtained, i.e. the isotropic hyperfine coupling constants, are collected in Table 2.

The [2.2]paracyclophan-4,7-dione radical anion ($\mathbf{8}^{\bullet-}$) has already been observed when **8** in aqueous alcoholic solution was reduced with dithionite followed by the addition of alkali. The complex ESR spectrum of $\mathbf{8}^{\bullet-}$ obtained was tenta-

Table 2. Isotropic hyperfine coupling constants of the radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{6}^{\bullet-}$ and $\mathbf{8}^{\bullet-}$–$\mathbf{10}^{\bullet-}$ in dimethoxyethane (kryptofix® 222, potassium) unless otherwise stated and *g* values

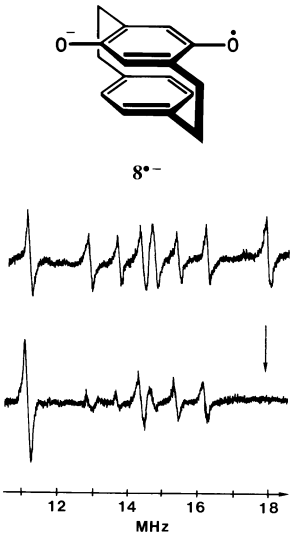
	Method	*T* [K]	$a(H_{aromatic})$ [G]	$a(H_{aromatic})$[G]	*a*(H)[G]	*a*(H)/G	*g*
$\mathbf{1}^{\bullet-}$	ESR	220	0.98 (5,8,12,16-H)		1.57 (1,2,9,10-H)	0.93 (1′,2′,9′,10′-H)	2.0055
	ENDOR	220	−0.98		+1.58	+0.94	
$\mathbf{2}^{\bullet-}$	ESR[a]	300	0.74 (5,8,12,16-H) [b]		0.44 (1,2,9,10-H)	0.09 (1′,2′,9′,10′-H)	
	ESR	220	0.70 (5,8,12,16-H)		0.43 (1,2,9,10-H)		2.0050
	ENDOR	220	−0.71		+0.44		
$\mathbf{3}^{\bullet-}$	ESR	220	1.38 (5,6,15,16-H)	0.49 (9,10,19,20-H)	0.58 (1,2,11,12-H)	0.13 (1′,2′,11′,12′-H)	2.0055
	ENDOR	220	−1.40	−0.46	+0.60	+0.12	
$\mathbf{4}^{\bullet-}$	ESR	300	1.14 (5,6,15,16-H)	0.65 (9,10,19,20-H)			2.0049
	ENDOR	220	−1.14	−0.65	0.08		
$\mathbf{5}^{\bullet-}$	ESR[c]	300			1.17 (H-CH_3, 12H)		
	ESR[c]	160			1.24 (H-CH_3, 12H)		
	ESR	220			1.26 (H-CH_3, 12H)		2.0046
	ENDOR	220	−0.12 (5,7,12,14-H)		+1.26		
$\mathbf{6}^{\bullet-}$	ESR[c]	300			1.21 (H-CH_3, 12H)		
	ESR[c]	200			1.23 (H-CH_3, 12H)		
	ESR	300			1.22 (H-CH_3, 12H)		2.0046
	ENDOR	220	−0.11 (5,7,12,14-H)		+1.27		
$\mathbf{8}^{\bullet-}$	ESR	220	2.39 (5,8-H)		1.19 (2,9-H)	0.60 (2′,9′-H) 0.12 (6H)[d]	2.0048
	ENDOR	220	−2.40		+1.19	+0.59 0.13[d]	
$\mathbf{8a}^{\bullet-}$	ESR	220	2.39 (5,8-H)		1.18 (2,9-H)	0.62 (2′,9′-H)	
	ENDOR	220	−2.40		+1.19	+0.61	
$\mathbf{9}^{\bullet-}$	ESR	220	2.13 (7,10-H)		1.57 (4,11-H) 0.47 (2H)	0.68 (2H)	2.0050
	ENDOR	220	−2.11		+1.58 +0.47	+0.68 +0.09	
$\mathbf{10}^{\bullet-}$	ESR	220	3.08 (2,3-H)	0.87 (6,7-H)	0.52 (H-CH_3, 6H)		2.0050
	ENDOR	220	−3.10	−0.87	+0.52		

[a] DMSO, propiophenone, potassium *tert*-butoxide. – [b] Unaffected in $\mathbf{2a}^{\bullet-}$. – [c] MTHF. – [d] Based on the simulation of the ESR spectrum, this *a*(H) = (−)0.13 G splitting originates apparently from six hydrogens representing three sets of two equivalent hydrogens.

tively interpreted as arising from the coupling constants *a*(H) = 2.19 (2 H), *a*(H) = 1.25 (2 H), *a*(H) = 0.71 (2 H), and *a*(H) = 0.15 G (2 H)[12]. When $\mathbf{8}^{\bullet-}$ was generated by reduction with potassium in DME, the ^{1}H-ENDOR spectrum showed four line-pairs (Figure 1) with the splittings *a*(H) = 2.40, *a*(H) = 1.19, *a*(H) = 0.59, and *a*(H) = 0.13 G which are close to those reported[12]. In order to elucidate the assignment the selectively deuterated [1,1,10,10,12,13,15,16-D_8][2.2]paracyclophan-4,7-dione radical anion ($\mathbf{8a}^{\bullet-}$) was studied. In the ^{1}H-ENDOR spectrum of $\mathbf{8a}^{\bullet-}$ only the central line-pair is absent. The remaining three line-pairs correspond to three different hydrogen sets in the quinone unit, i.e. the four methylene hydrogens in the positions 2 and 9 of $\mathbf{8a}^{\bullet-}$ give rise to two different coupling constants which represent the *syn*- and *anti*-hydrogens with regard to the carbonyl function. Accordingly, the simulation of the resolved ESR spectrum of $\mathbf{8a}^{\bullet-}$ agreed well with experiment for *a*(H) = −2.39 (5,8-H), *a*(H) = +1.18 (2,9-H), *a*(H) = +0.62 (2′,9′-H). The assignment given is based on the relative signs of the coupling constants provided by general triple resonance[13] (Figure 1). Simulations of the ESR spectrum of $\mathbf{8}^{\bullet-}$ suggest that the small *a*(H) = (−) 0.13 G splitting originates probably from six hydrogens representing three sets of two equivalent hydrogens in the attached 1,4-phenylene unit. Although the negative sign observed for these similar splittings may not be valid for all of them, it is expected for the 12,15- and 13,16-hydrogen sets.

Extension of the bridges leads to some changes. The ^{1}H-ENDOR spectrum of the [4.4]paracyclophan-6,9-dione

Figure 1. ^{1}H-ENDOR spectrum of the radical anion $\mathbf{8}^{\bullet-}$ in DME/kryptofix® 222 at 220 K together with a general triple resonance spectrum, pump frequency 17.87 MHz



$\mathbf{8}^{\bullet-}$

radical anion ($\mathbf{9}^{\bullet-}$) shows five line-pairs corresponding to *a*(H) = −2.11, *a*(H) = +1.58, *a*(H) = +0.68, *a*(H) = +0.47, and *a*(H) = +0.09 G. Based on these results the ESR spectrum of $\mathbf{9}^{\bullet-}$ was simulated with good agreement between the observed and calculated spectra for *a*(H) = 2.13 (2 H), *a*(H) = 1.57 (2 H), *a*(H) = 0.68 (2 H), and *a*(H) = 0.47 G (2 H). Similar to $\mathbf{8}^{\bullet-}$, the −2.11 G coupling constant of $\mathbf{9}^{\bullet-}$ is assigned to the 7,10 hydrogens and the

+1.58 G constant to the 4,11 hydrogens. The additional positive splittings obviously represent further β- and γ-hydrogen sets of the bridges.

In the *pseudogeminal*- (**1**$^{\bullet-}$) and *pseudoortho*-[2.2]paracyclophan-4,7,12,15-bisquinone radical anion (**2**$^{\bullet-}$), the unpaired electron is expected to be delocalized over the whole molecule. This is predicted by the large potential differences $\Delta E = |E_2^0 - E_1^0| = 0.42$ (**1**) and 0.32 V (**2**), and results from the close spatial contact of the quinone units. Consequently, three sets of four equivalent hydrogens should show up in the ESR and ^{1}H-ENDOR spectra of **1**$^{\bullet-}$ and **2**$^{\bullet-}$. Accordingly, the special triple resonance spectrum of **1**$^{\bullet-}$ (Figure 2b) shows three separate lines and the simulation of the ESR spectrum (Figure 2a) using the data a(H) = −0.98 (5,8,13,16-H), a(H) = +1.57 (1,2,9,10-H), and a(H) = +0.93 G (1′,2′,9′,10′-H) is consistent with the observed spectrum. General triple resonance provided the relative signs which led directly to the given assignment. The results of the *pseudoortho* radical anion **2**$^{\bullet-}$ are different. Its ^{1}H-ENDOR spectrum shows two line-pairs, the signs of the corresponding coupling constants are opposite, and the ESR spectrum (Figure 3) was simulated with the data a(H) = 0.70 (4 H) and a(H) = 0.43 G (4 H). Under the experimental conditions used (DME, potassium, kryptofix® 222) the expected third splitting was not observed. Fortunately, these radical anions can also be readily generated by other procedures, e.g. when the compounds **1** or **2** are dissolved in DMSO containing traces of potassium *tert*-butoxide or by use of the enolate anion of propiophenone as a one-electron reducing agent[14]. The highly resolved ESR spectrum of **2**$^{\bullet-}$ generated in DMSO reveals, besides a(H) = 0.74 (4 H) and a(H) = 0.44 G (4 H), a further small splitting of a(H) = 0.09 G (4 H). The ESR spectrum of **2a**$^{\bullet-}$ with complete deuteration of the bridges shows a quintet of broad lines separated by about 0.74 G (5,8,13,16-H). Hence, the smaller splittings of 0.44 and 0.09 G represent the methylene hydrogens arranged *syn* and *anti* with regard to the carbonyl functions. As expected the coupling constants of the quinone hydrogens in **1**$^{\bullet-}$ and **2**$^{\bullet-}$ have about half the magnitude of those in **8**$^{\bullet-}$ and **9**$^{\bullet-}$. However, when the splittings of the *syn* and *anti* methylene hydrogens are compared in this series, no relation can be detected. The marked differences probably arise from particular through-space interactions and slight variations of the molecular conformation which change the dihedral angle in the methylene bridges. Further information may become available by specific labelling of the *syn* or *anti* methylene hydrogens, although this cannot, as yet, be achieved.

5,8-Dimethyl-1,4-naphthalenedione (**10**) is the basic electrophore of the [2.2](1,4)naphthalene-4,7,14,17-tetrones **3** and **4**. ^{1}H ENDOR and general triple resonance of the radical anion **10**$^{\bullet-}$ yielded at 220 K the HFC coupling constants a(H) = −3.10 (2,3-H), a(H) = +0.87 (6,7-H), and a(H) = +0.52 G (6 H, 5,8-CH_3) which agree well with the simulation of the highly resolved ESR spectrum. Their assignment was derived from ESR results of the 1,4-naphthalenedione and 2,3-dimethyl-1,4-naphthalenedione radical anions[15].

Figure 2. (a) ESR spectrum of the radical anion **1**$^{\bullet-}$ in DME/kryptofix® 222 at 220 K together with a simulation using the data in Table 2; (b) ^{1}H special triple resonance spectrum of **1**$^{\bullet-}$ in DME/kryptofix® 222 at 220 K

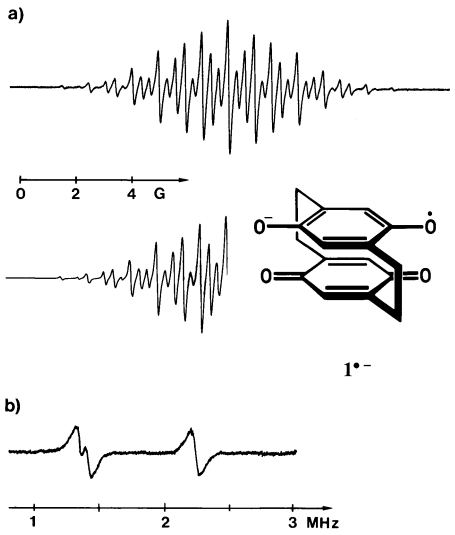
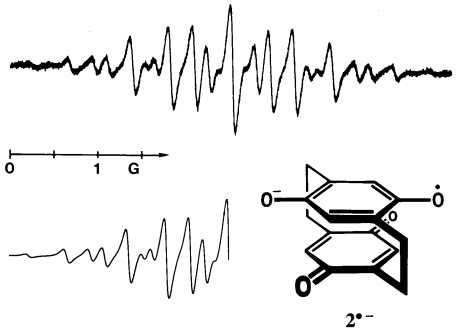


Figure 3. ESR spectrum of the radical anion **2**$^{\bullet-}$ in DME/kryptofix® 222 at 220 K together with a simulation using the data in Table 2



The four line-pairs in the ^{1}H-ENDOR spectrum of the *syn*-[2.2](1,4)naphthalene-4,7,14,17-tetrone radical anion (**3**$^{\bullet-}$), corresponding to a(H) = −1.40 (5,6,15,16-H), a(H) = +0.60 (1,2,11,12-H), a(H) = −0.46 (9,10,19,20-H), and a(H) = +0.12 G (1′,2′,11′,12′-H), confirm that all sets of four equivalent hydrogens lead to observable splittings. Simulations performed using very similar data (Table 2) were in good agreement with the satisfactorily resolved ESR spectrum of **3**$^{\bullet-}$ (Figure 4). The individual splittings were assigned based on the results of the radical anion **10**$^{\bullet-}$. ESR and ENDOR results of **3**$^{\bullet-}$ clearly prove that the unpaired electron is displaced over the whole molecule on the ESR time scale, although the potential difference, $\Delta E = |E_2^0 - E_1^0| = 0.23$ V, is rather small. In the *anti* isomer **4** the potential difference decreases to 0.20 V. The ^{1}H-ENDOR spectrum of **4**$^{\bullet-}$ shows two line-pairs corresponding to a(H) = −1.14 (5,6,15,16-H) and a(H) = −0.65 G (9,10,19,20-H), and satisfactory simulations of the ESR spectrum of **4**$^{\bullet-}$ were performed using these data (Figure 5). Again the assignments were made in relation to the results of the reference radical anion **10**$^{\bullet-}$. In the centre of

the ^{1}H-ENDOR spectrum an additional weakly indicated line-pair can be observed, a(H) ≈ 0.08 G, which probably originates from bridge hydrogens. The ESR data of **4**$^{\bullet-}$ clearly show that in the *anti* radical anion too, the unpaired electron is displaced over the whole molecule.

Figure 4. ESR spectrum of the radical anion **3**$^{\bullet-}$ in DME/kryptofix® 222 at 300 K together with a simulation using the data in Table 2

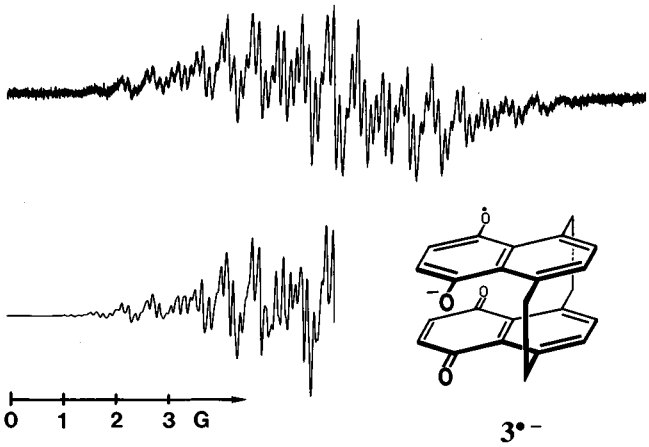
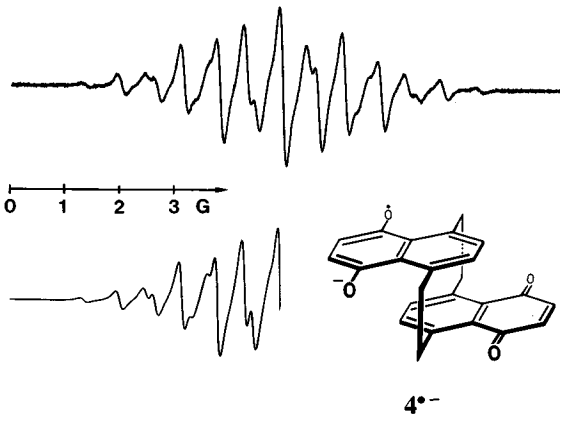


Figure 5. ESR spectrum of the radical anion **4**$^{\bullet-}$ in DME/kryptofix® 222 at 220 K together with a simulation using the data in Table 2



The low temperature ESR spectra of **5**$^{\bullet-}$ and **6**$^{\bullet-}$, electrochemically generated in the polar solvent dimethylformamide, demonstrated a localization of the unpaired electron on one quinone unit[6]. Thus, the results for the radical anion **4**$^{\bullet-}$ with $\Delta E = |E_2^0 - E_1^0| = 0.20$ V raise the question of why the planar conjugated 1,4,8,11-pentacenetetrone radical anions **5**$^{\bullet-}$ and **6**$^{\bullet-}$, which have a very close $\Delta E = |E_2^0 - E_1^0| = 0.16$ V, are different. Although under the experimental conditions[6] ion pairing is not expected, we checked this point by generating **5**$^{\bullet-}$ and **6**$^{\bullet-}$ in the presence of kryptofix® 222. The ESR spectrum of **5**$^{\bullet-}$ in 2-methyltetrahydrofuran (MTHF) at 300 K is adequately simulated with a(H) = 1.17 G (12 H, CH_3) and remains almost unchanged down to 160 K (Figure 6). A further small splitting of −0.12 G, representing the 5,7,12,14 hydrogens, is found in the ^{1}H-ENDOR spectrum of **5**$^{\bullet-}$.

Figure 6. ESR spectra of the radical anion **5**$^{\bullet-}$ in MTHF/kryptofix® 222 at 300 and at 160 K

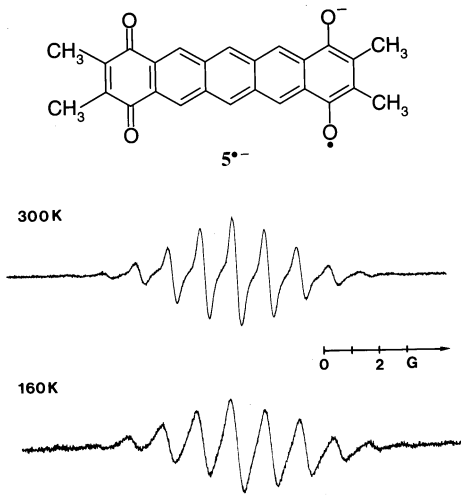
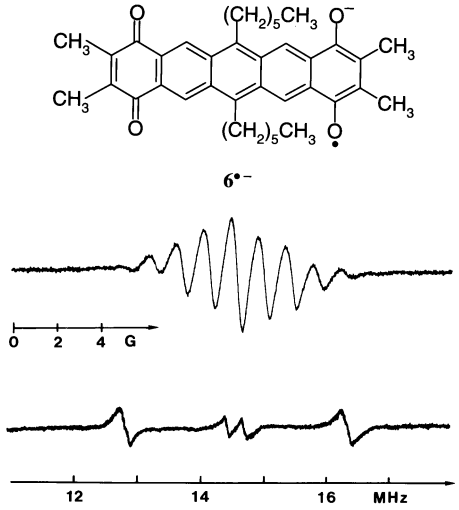


Figure 7. ESR spectrum of the radical anion **6**$^{\bullet-}$ in MTHF/kryptofix® 222 at 200 K and ^{1}H-ENDOR spectrum of **6**$^{\bullet-}$ in DME/kryptofix® 222 at 220 K



Similar ESR (300−200 K) and ^{1}H-ENDOR (220 K) spectra were also obtained for the radical anion **6**$^{\bullet-}$ (Table 2, Figure 7). The results for **5**$^{\bullet-}$ and **6**$^{\bullet-}$ in the temperature range 300−160 K provide clear evidence that the unpaired electron is delocalized over the whole pentacenetetrone system when ion pairing is inhibited by complexation of the cation.

In all three groups of tetrones studied there is a marked intramolecular interaction between both quinone electrophores. This is substantiated by the difference between the first and second reduction potentials with $\Delta E = |E_2^0 - E_1^0| \geq 0.10$ V and by the delocalization (ESR time scale) of the unpaired electron on the two electrophores in the corresponding radical anions as demonstrated by ESR.

Experimental Section

General: Melting points were recorded on a Büchi 510 and are uncorrected. − Analytical TLC: DC Micro Cards Polygram SIL

G/UV_{254}, Macherey-Nagel. – ^{1}H NMR: Bruker Physik WP-80, AM 360 or AM 500 (internal reference tetramethylsilane, temperature 303 K). – MS: Finnigan MAT 212 or Jeol JMS-SX 102A (ionization potential 70 eV; only the most prominent peaks are listed, usually with $I_{rel} > 5\%$). – Cyclovoltammetry: All electrochemical studies were performed using an EG & G Princeton Applied Research 263 A potentiostat attached to an EG & G electrochemical microcell (K0264), which was equipped with a glassy carbon millielectrode (G0229, 2 mm diameter) as working electrode, a standard Ag/AgCl reference electrode (K0265), and a platinum wire counter-electrode (K0264). The measurements were carried out on degassed anhydrous acetonitrile or dichloromethane solutions containing the sample (0.5−1 mM) and tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte at 298 K. Cyclic voltammograms were scanned at a sweep rate of about 100 mV s^{-1}. Redox potentials are referred to ferrocene ($FeCp_2^{-/0}$, $E_1^0 = +0.352$ V) set to 0.00 V. – ESR and ENDOR: Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system; *g* values were determined using an NMR gaussmeter and a Hewlett-Packard 5342A microwave frequency counter; this was calibrated with the perylene radical cation. Hyperfine coupling constants measured in megahertz (ENDOR) were converted into gauss using 1 MHz = ($0.7145/g_{ex}$) G. The radical anions were generated by reduction of the parent compounds (about 1 mg) in dimethoxyethane (DME) or in methyltetrahydrofuran (MTHF) (1−2 ml) with potassium under high-vacuum conditions in the presence of kryptofix® 222 Merck (1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane; about 4 mg). The solvents were carefully dried (potassium) and deoxygenated. Potassium was purified by repeated vacuum distillation.

The compounds *pseudogeminal*- (**1**)[2b][2c] and *pseudoortho*-[2.2]paracyclophane-4,7,12,15-tetrone (**2**)[2a][2c], *syn*- (**3**)[5] and *anti*-[2.2](1,4)naphthalenophane-4,7,14,17-tetrone (**4**)[5], 2,3,9,10-tetramethyl-1,4,8,11-pentacenetetrone (**5**)[6], and 6,13-dihexyl-2,3,9,10-tetramethyl-1,4,8,11-pentacenetetrone (**6**)[6] were available in our laboratory or were prepared as described in the literature.

pseudoortho-4,7,13,16-Tetramethoxy[1,1,2,2,9,9,10,10-D_8][2.2]paracyclophane: Prepared from 1,4-bis(chloro[D_2]methyl)-2,5-dimethoxybenzene[4] and 1,4-bis(mercapto[D_2]methyl)-2,5-dimethoxybenzene[4] following the procedures as described in the literature for the undeuterated compound[2a][2c]: m.p. 121−122°C as found for the undeuterated compound[2a][2c]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.65 (s, 12 H, OCH_3), 6.10 (s, 4 H, 5,8,12,16-H). – EI-MS; *m/z* (%): 336 (100) [$M^{\bullet+}$]. – $C_{20}H_{16}D_8O_4$ (336.5): calcd. C 71.39, H + D 9.59; found C 71.41, H + D 9.80.

pseudoortho-[1,1,2,2,9,9,10,10-D_8][2.2]Paracyclophane-4,7,12,15-tetrone (**2a**): A mixture of *pseudoortho*-4,7,13,16-tetramethoxy[1,1,2,2,9,9,10,10-D_8][2.2]paracyclophane (1.51 g, 4.5 mmol) and pyridine hydrochloride (17.5 g, 0.15 mol) was heated to 200°C for 10 min. After cooling, the melt was dissolved in hot water (20 ml) and added to a solution of sodium metaperiodate (9.75 g, 45 mmol) in water (50 ml). After stirring for 1 h the precipitated product was filtered and washed with water and methanol. Flash chromatography of the residue on silica gel using trichloromethane as the eluent afforded compound **2a** (780 mg, 63%; $R_f = 0.45$, trichloromethane) as yellow crystals from methanol, m.p. 210°C (dec.) as found for the undeuterated compound[2a][2c]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 6.25 (s, 4 H, 5,8,12,16-H). – EI-MS; *m/z* (%): 277 (44), 276 (100) [$M^{\bullet+}$], 248 (34), 220 (56), 207 (70), 179 (29), 151(23), 82 (28), 69 (63), 41 (95). – $C_{16}H_4D_8O_4$ (276.3): calcd. C 69.54, H + D 7.30; found C 69.58, H + D 7.10.

[2.2]Paracyclophane-4,7-dione (**8**)[16]: A mixture of 4,7-dimethoxy[2.2]paracyclophane[17] (402 mg, 15 mmol) in pyridine hydrochloride (11.5 g, 0.1 mol) was heated under dry hydrogen chloride at 200°C for 20 min. After cooling the melt was dissolved in water (50 ml), and sodium metaperiodate (3.25 g, 15 mmol) was added with stirring. The bright brown solution was then extracted with dichloromethane (4 × 50 ml). The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the brown residue on silica gel using trichloromethane as eluent afforded compound **8** (168 mg, 47%; $R_f = 0.30$, trichloromethane) as yellow crystals from toluene/hexane, m.p. 180°C (dec.). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25−2.40 (m, 2 H, 2,9-*syn*-H with regard to 5,8-H), 3.00−3.20 (m, 4 H, 1,1,10,10-H), 3.20−3.30 (m, 2 H, 2,9-*anti*-H with regard to 5,8-H), 5.83 (s, 2 H, 5,8-H), 6.74 (dd, $^3J = 7.9$ Hz, $^4J = 1.9$ Hz, 2 H, 12,15- or 13,16-H), 6.86 (dd, $^3J = 7.9$ Hz, $^4J = 1.9$ Hz, 2 H, 13,16- or 12,15-H); irradiation of the 5,8-H signal at δ = 5.83 yielded a positive NOE response for 2,9-*syn*-H at δ = 2.25−2.40.

[1,1,10,10,12,13,15,16-D_8][2.2]Paracyclophane-4,7-dione (**8a**): Prepared as described above using 4,7-dimethoxy[1,1,10,10,12,13,15,16-D_8][2.2]paracyclophane[4]: Yellow crystals, m.p. 180 (dec.). The ether cleavage led to a partial (approximately 50%) reexchange of the deuterons in the 12,13,15,16 positions. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.30 (d, $^2J = 12.7$ Hz, 2 H, 2,9-*syn*-H with regard to 5,8-H), 3.22 (d, 2 H, 2,9-*anti*-H with regard to 5,8-H), 5.82 (s, 2 H, 5,8-H), 6.7−6.8 (m, 1.3 H), 6.8−6.9 (m, 1.1 H).

[4.4]Paracyclophane-6,9-dione (**9**): To a solution of 6,9-dimethoxy[4.4]paracyclophane[4] (300 mg, 0.92 mmol) in anhydrous acetonitrile (35 ml) under argon, iodotrimethylsilane (0.9 ml, 6.3 mmol) was added with stirring, and the mixture was heated at 70°C for further 2 h. Iodotrimethylsilane (0.9 ml, 6.3 mmol) was again then added, and heating at 70°C was continued for a further 14 h. The mixture was hydrolized with water (20 ml) and extracted with diethyl ether (3 × 50 ml). The combined extracts were shaken with a saturated aqueous sodium sulphite solution, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was dissolved in acetone (200 ml), silver oxide (1.24 g, 50 mmol) was added, and the mixture was stirred for 1 h. After separation of the precipitated silver salts, the filtrate was evaporated under reduced pressure. Crystallization of the residue from acetone afforded compound **9** (226 mg, 83%; $R_f = 0.30$, dichloromethane) as yellow needles, m.p. 221−222°C (ref.[18]: m.p. 217−223°C). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.05−2.85 (m, 16 H, CH_2), 6.13 (s, 2 H, 7,10-H), 6.75−6.95 (m, 4 H, 16,17,19,20-H). – EI-MS; *m/z* (%): 295 (14), 294 (100) [$M^{\bullet+}$], 163 (16), 143 (11), 136 (17), 131 (15), 130 (15), 129 (20), 117 (20),115 (11), 104 (16), 91 (19). – $C_{20}H_{22}O_2$ (294.4): calcd. C 81.60, H 7.53; found C 81.53, H 7.80.

1,4-Dimethoxy-5,8-dimethylnaphthalene: To a stirred solution of 1,4-dimethoxy-5-hydroxymethyl-8-methylnaphthalene[5] (1.90 g, 8.2 mmol) in dichloromethane (60 ml) were added zinc iodide (4.12 g, 12.9 mmol) and sodium cyanoborohydride (4.05 g, 64.5 mmol) in small portions. Stirring at room temperature was continued for further 24 h. The mixture was then hydrolized with water (10 ml), and the separated organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The dark residue dissolved in dichloromethane, was filtered through a short silica gel column. After evaporation of the filtrate, the residue was distilled in a Büchi Kugelrohr distillation apparatus at 150°C /$2 \cdot 10^{-2}$ bar to yield the product (290 mg, 16%; $R_f = 0.69$, dichloromethane) as colourless crystals, m.p. 64−65°C. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.83 (s, 6 H, CH_3), 3.85 (s, 6 H, OCH_3), 6.73 (s, 2 H, 2,3-H), 7.07 (s, 2 H, 6,7-H). – EI-MS; *m/z* (%): 216 (93) [$M^{\bullet+}$], 201 (100) [$M^{\bullet+} - CH_3$], 173 (12), 115 (6), 108 (5). – $C_{14}H_{16}O_2$ (216.3): calcd. C 77.75, H 7.46; found C 77.69, H 7.74.

5,8-Dimethyl-1,4-naphthalenedione (**10**): To a stirred solution of 1,4-dimethoxy-5,8-dimethylnaphthalene (113 mg, 0.5 mmol) in acetonitrile (20 ml) and trichloromethane (10 ml) was added dropwise a solution of ammonium cerium(IV)nitrate (1.1 g, 2 mmol) in water (5 ml) over a period of 10 min. Stirring at room temperature was continued for further 2 h. Water (30 ml) was then added, and the mixture was extracted with dichloromethane (3 × 30 ml). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. Flash chromatography of the yellow residue on silica gel using dichloromethane as eluent afforded compound **10** (91 mg, 93%; R_f = 0.37, dichloromethane) as yellow crystals, m.p. 110−111°C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.71 (s, 6 H, CH_3), 6.84 (s, 2 H, 2,3-H), 7.40 (s, 2 H, 6,7-H). − EI-MS; *m/z* (%): 187 (19), 186 (100) [$M^{\bullet+}$], 185 (16), 158 (15), 157 (16), 141 (22), 132 (14), 130 (24), 129 (43), 128 (32), 127 (14), 115 (43), 104 (22), 103 (19), 78 (12), 77 (16). − $C_{12}H_{10}O_2$ (186.2): calcd. C 77.40, H 5.41; found C 77.44, H 5.60.

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