Intramolecular Electron Transfer between Terminal 1,4-Dimethoxybenzene Units in Radical Cations with a [2.2](1,4)Naphthalenophane, [2.2](1,4)Anthracenophane, and Pentacene Skeleton

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Various radical cations, in which two terminal 1,4-dimethoxybenzene units are anellated to [2.2]paracyclophane (**2b**$^{\bullet+}$, **3b**$^{\bullet+}$), [2.2](1,4)naphthalenophane (**4d**$^{\bullet+}$), and anthracene bridges (**5**$^{\bullet+}$), have been studied by ESR and ENDOR spectroscopy. In the *syn*- and *anti*-naphthalenophane radical cations **2b**$^{\bullet+}$ and **3b**$^{\bullet+}$ the delocalization of the unpaired electron over both π-moieties and the distinct difference between the first and second oxidation potentials, $\Delta E = E_2^0 - E_1^0$, are evidence for a substantial intramolecular electronic interaction between the two electrophores. Extension of the bridge in **4d**$^{\bullet+}$ and **5** by benzo anellation results in a localized radical cation. Strong intramolecular electronic interaction between the two electrophores is found in the 1,4,8,11-tetramethoxy-pentacene radical cation (**5**$^{\bullet+}$). The syntheses of **4d** are described.

The rate of intramolecular electron transfer in biselectrophoric radical ions is influenced by various factors[1]. Most important are the relative spatial arrangement of the electrophores modified by the length and conformation of the linking group, the nature of the electrophores, and the reorganization energy, which is composed of the conformational changes of the molecule upon electron transfer, the arrangement of the counterion, and the solvent reorganization. In [2.2](1,4)arenophanes, e. g. **1**−**4**, the spatial arrangement of the identical π-subunits is fixed. The electrophores are rigidly held in an almost parallel orientation at a distance of approximately 3.1 Å similar to the arrangement of the benzene rings in the skeleton of the parent [2.2]paracyclophane (**1a**)[2]. Because of this defined molecular geometry, [2.2](1,4)arenophane radical ions are attractive model compounds for studying specific modes affecting the intramolecular electron transfer. Fundamental ESR studies of radical anions derived from [2.2]paracyclophane (**1a**)[3], *syn*- (**2a**) and *anti*-[2.2](1,4)naphthalenophane (**3a**)[4][5][6], and *anti*-[2.2](1,4)anthracenophane (**4a**)[7] showed that the unpaired electron in these species is delocalized over both π-subunits within the time scale of the ESR experiment (ca. 10^7 s^{-1}).

Recently, we studied the intramolecular electron transfer of a range of [*n.n*]paracyclophane radical cations, in which two 2,5-dimethoxy-1,4-phenylene units were connected by alkano bridges of varying lengths[8]. Radical cations of this type are persistent over a wide temperature range and have the advantage that ion pairing is less significant. In the *pseudogeminal* (**1b**$^{\bullet+}$) and the *pseudoortho* 4,7,12,15-tetramethoxy[2.2]paracyclophane radical cations the unpaired electron was found to be delocalized over both π-moieties and the distinct difference between the first and second oxidation potentials, $\Delta E = E_2^0 - E_1^0$ proved a strong intramolecular electronic interaction between the two electrophores[8]. This, however, must not be valid for the benzo-anellated derivatives **2b**$^{\bullet+}$, **3b**$^{\bullet+}$, and **4b**$^{\bullet+}$, since the terminal 1,4-dimethoxybenzene units change considerably the spin-population distribution and hence reduce the spin population within the [2.2]paracyclophane bridge. It is therefore open to question whether the intramolecular electron transfer in **3b**$^{\bullet+}$ and in **4b**$^{\bullet+}$ is fast or slow on the ESR time-scale, in contrast to the radical anions **2a**$^{\bullet-}$, **3a**$^{\bullet-}$, and **4a**$^{\bullet-}$ which all show a fast intramolecular electron transfer. In this context, the fully conjugated 1,4,8,11-tetramethoxypentacene radical cation (**5**$^{\bullet+}$) is also of interest, since the rate of the intramolecular electron transfer in the related 1,4,8,11-pentacenetetrone radical anion depends decisively on the experimental conditions[9][10].

We report herein the syntheses of **4d** and **5** and the preparation of required reference compounds. The oxidation potentials of **2b**, **3b**, **4d**, and **5** were determined by cyclic voltammetry, which together with the ESR/ENDOR results of the corresponding radical cations characterize the intramolecular electron transfer in these biselectrophoric species.

Syntheses

In the series **1b**−**4b**, the 5,5′,8,8′-tetramethoxy-*anti*-[2.2](1,4)anthracenophane radical cation (**4b**$^{\bullet+}$), a possible borderline case with regard to the rate of the intramolecular electron transfer, is of particular interest. However, our synthetic efforts to build up this anthracenophane have, as yet, been unsuccessful. One problem involved is the oxidation sensitivity in the 9,10-positions of the anthracene subunits. Therefore, we tried to protect these positions by phenyl substitution. In analogy to the synthesis of 9,9′,10,10′-tetra-

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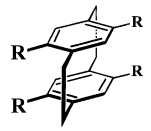
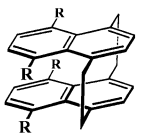
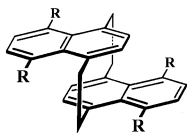
Scheme 1



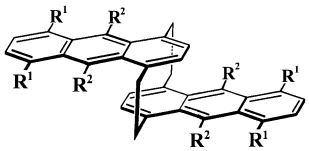
	R
1a	H
1b	OMe



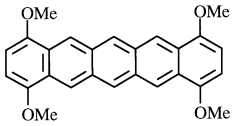
	R
2a	H
2b	OMe



	R
3a	H
3b	OMe



	R^1	R^2
4a	H	H
4b	OMe	H
4c	H	Ph
4d	OMe	Ph

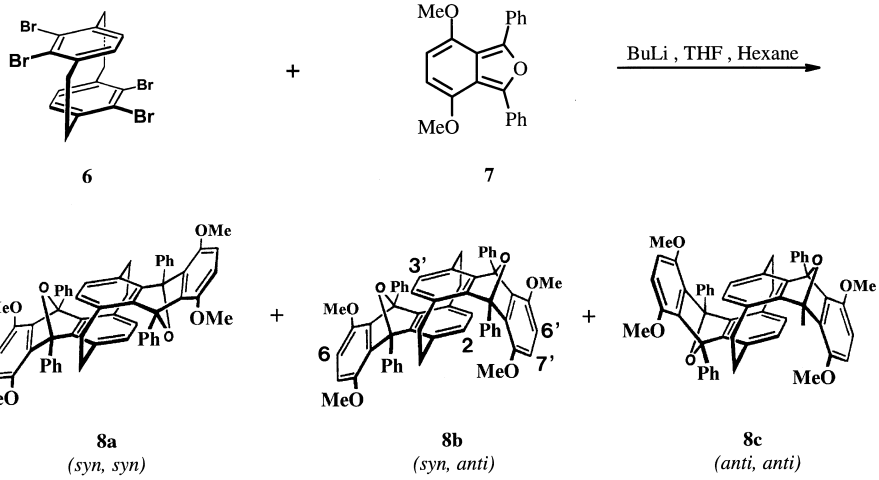


5

phenyl-*anti*-[2.2](1,4)anthracenophane (**4c**) by de Meijere et al.[11], the aryne intermediates derived from 4,5,12,13-tetrabromo[2.2]paracyclophane (**6**)[12] were trapped by 4,7-dimethoxy-1,3-diphenylisobenzofuran (**7**)[13] to give a mixture of the expected three diastereomeric bis-cycloadducts (overall yield 74%): *syn*,*syn*-**8a**, *syn*,*anti*-**8b**, and *anti*,*anti*-**8c**, which were separated by flash chromatography (Scheme 2). The stereochemical terms *syn* and *anti* refer to the orientation of the bicyclic oxygen bridge with regard to the [2.2]paracyclophane skeleton. Our structural assignments are based on the ^{1}H-NMR results. The unsymmetric **8b** shows two signal sets each for the *syn*- and *anti*-OCH_3 groups, the [2.2]paracyclophane 2,3- and 2′,3′-hydrogen atoms, and the 6,7- and 6′,7′-hydrogen atoms, which were specifically assigned by NOE experiments. Irradiation of the *syn*-OCH_3 signal at $\delta = 3.50$ gave a positive NOE response for the *syn*-6,7-H at $\delta = 6.47$ and irradiation of the *anti*-OCH_3 signal at $\delta = 3.76$ yielded a positive NOE response for the 2,3-H at $\delta = 4.63$ and for the *anti*-6′,7′-H at $\delta = 6.77$. Correspondingly, the structures of **8a** and **8c** were assigned. The yields of the individual isomers depend on the reaction conditions. Preferentially formed is the *anti*,*anti*-**8c** (about 35%), whereas the *syn*,*syn*-**8a** is produced in only very low yield. Treatment of these isomers with trimethylsilyl iodide[11][14] removes not only the bridging oxygen atoms, but also cleaves the methoxy groups. Therefore, we confined the further experimental studies to the *anti*,*anti*-**8c**. Deoxygenation of this isomer with trimethylsilyl iodide afforded the target anthracenophane **4d** in 20% yield.

A feasible synthesis of the 1,4,8,11-tetramethoxypentacene skeleton is a double Diels–Alder cycloaddition of 3,6-dimethoxybenzocyclobuten-1-ol (**10**) with 1,4-benzoquinone. Miller et al.[15] prepared 5,8-dimethoxy-1,4-anthraquinone (**9**) by cycloaddition of **10** with 1,4-benzoquinone. Their attempts to achieve a further cycloaddition were unsuccessful. Under enforced conditions (reaction temperature 200°C), however, it is possible to carry out a double cycloaddition to give the required 1,4,8,11-tetramethoxypentacene-6,13-dione (**11**), which was reduced by treatment with lithium aluminium hydride followed by trimethylsilane to afford 6,13-dihydro-1,4,8,11-tetramethoxypentacene (**12**). Preliminary dehydrogenation tests of **12** in solu-

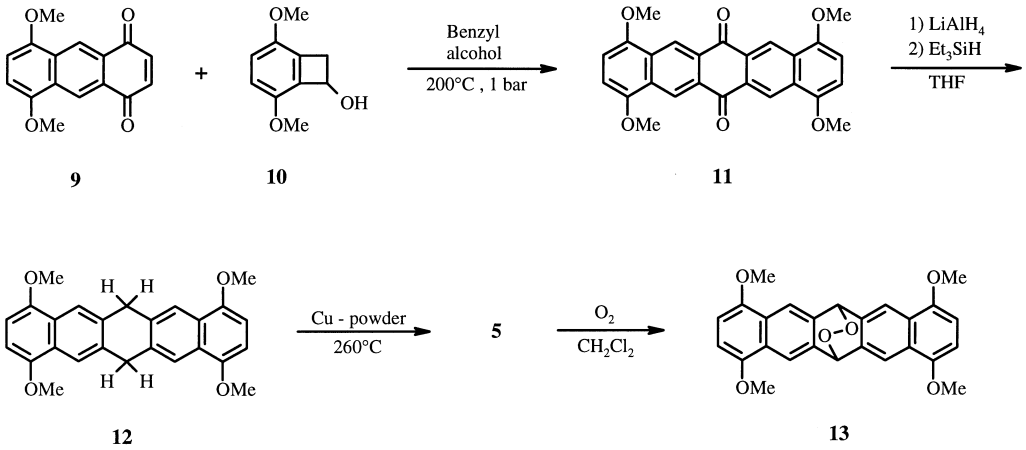
Scheme 2



6 **7**

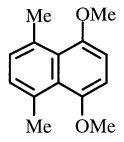
8a *(syn, syn)* **8b** *(syn, anti)* **8c** *(anti, anti)*

Scheme 3

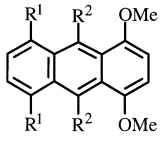


tion showed that the generated violet 1,4,8,11-tetramethoxypentacene (**5**) decomposes rapidly. Therefore, in analogy to the dehydrogenation of 6,13-dihydropentacene to pentacene by Clar and John[16], a mixture of compound **12** in copper powder was heated to 260°C, and the generated pentacene was sublimed out of the reaction mixture at reduced pressure to yield **5** as violet lustrous crystals (57%). Violet solutions of **5** on air bleach within 1 h to give the yellow 6,13-dihydro-6,13-epidioxy-1,4,8,11-tetramethoxypentacene (**13**).

Scheme 4



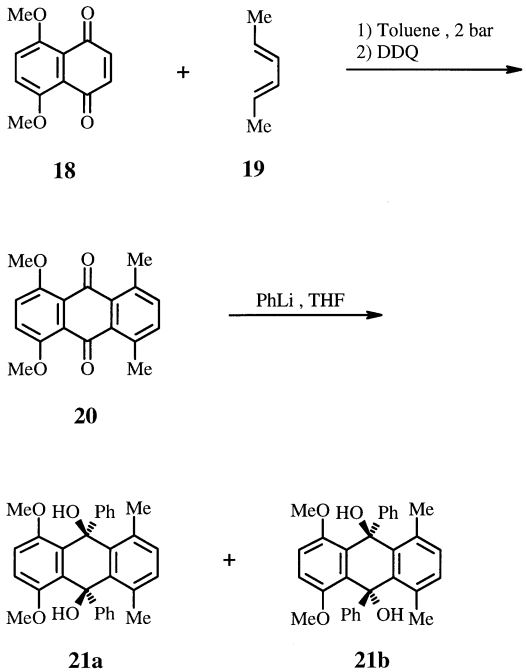
14



	R^1	R^2
15	H	H
16	Me	H
17	Me	Ph

Besides 1,4-dimethoxy-5,8-dimethylnaphthalene (**14**) also the anthracene derivatives **15**–**17** were required as reference compounds. 1,4-Dimethoxyanthracene (**15**) was obtained by reduction of 1,4-anthraquinone with sodium dithionite[17] and subsequent methylation of the formed 1,4-dihydroxyanthracene. Diels–Alder addition of *E,E*-2,4-hexadiene (**19**) to 5,8-dimethoxy-1,4-naphthoquinone (**18**) and subsequent dehydrogenation of the cycloadduct with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) provided 1,4-dimethoxy-5,8-dimethyl-9,10-anthraquinone (**20**, Scheme 5), which can be readily transformed into **16** and **17**. Reduction of **20** with lithium aluminium hydride led to a mixture of *cis*- and *trans*-9,10-dihydroxy derivatives, which was directly further reduced with phenylhydrazine[18] to yield 1,4-dimethoxy-5,8-dimethylanthracene (**16**) with an overall yield of 66%. Addition of phenyllithium to **20** afforded 9,10-dihydro-*cis*-9,10-dihydroxy-1,4-dimethoxy-5,8-dimethyl-9,10-diphenylanthracene (**21a**) and the corresponding *trans* isomer **21b**. A crystal structure determination of **21a**[19] confirmed unambiguously the structural assignment of the isomers. Owing to the buttressing effect of the methoxy and methyl groups in the *peri*-1,4,5,8-positions on the 9,10-substituents, the 9,10-dihydroanthracene framework of **21a** is forced to adopt a planar arrangement and, furthermore, the *cis*-9,10-phenyl groups assume a perpendicular conformation with regard to this plane. Reduction of this *cis* isomer with phenylhydrazine[18] provided readily the reference compound 1,4-dimethoxy-5,8-dimethyl-9,10-diphenylanthracene (**17**).

Scheme 5



Cyclic Voltammetric Measurements

Cyclic voltammetric measurements provide information on the intramolecular electron interaction, and hence on the intramolecular electron-transfer rate. For compounds

containing two identical arene electrophores with varying bridge, the limit of the fast intramolecular electron transfer in the derived radical ions (ESR time scale, ca. 10^7 s^{-1}) was found to correspond to a difference of about 0.1−0.2 V between the first and second redox potential[1][8][9][10]. In order to determine this potential separation, the oxidation potentials of the compounds **2b**[20], **3b**[20], **4d**, and **5** with two 1,4-dimethoxybenzene electrophores each were measured with a glassy carbon electrode versus Ag/AgCl in dichloromethane/0.1 M tetrabutylammonium hexafluorophosphate solution, and, in addition, also those of the corresponding reference compounds **12** and **14**−**17**. Table 1 gives the data, which are referred to ferrocene: $FeCp_2^{+/0}$ is set to 0.00 V. The results indicate that all compounds are distinct electron donors.

Table 1. Oxidation potentials and potential differences $\Delta E = E_2^0 - E_1^0$ of the compounds **2b**, **3b**, **4d**, **5**, **12**, and **14**-**17** in dichloromethane/0.1 M tetrabutylammonium hexafluorophosphate[a]; the oxidation potentials E^0 are given versus ferrocene $FeCp_2^{+/0}$

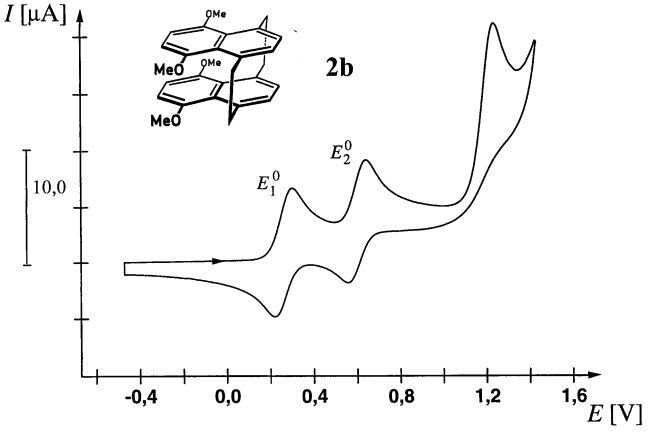
	E_1^0 (±0.01) [V]	E_2^0 (±0.01) [V]	$\Delta E = E_2^0 - E_1^0$ [V]
2b	+0.27	+0.66	0.39
3b	+0.39	+0.66	0.27
14	+0.42		
4d	+0.24	+0.34	0.10
15	+0.44		
16	+0.41		
17	+0.26		
5	+0.13	+0.54	0.41
12	+0.52	+0.61	0.09

[a] Glassy carbon electrode versus Ag/AgCl; reference ferrocene: $FeCp_2^{+/0}$ set to 0.00 V.

The cyclic voltammograms of the napthalenophanes **2b** (Figure 1) and **3b** show two distinctly separated and reversible one-electron oxidation steps. The first oxidation potential of the *anti* isomer **3b** (+0.39 V) is only slightly smaller than that of the reference compound **14** (+0.42 V). This indicates, that the electron-donor interaction through the [2.2]paracyclophane bridge in **3b** is very weak. The face-to-face orientation of the electrophores in **2b** , on the other hand, favours significantly the intramolecular electron-donor interaction and leads to a considerable decrease of the first oxidation potential (+0.27 V). For both compounds the potential differences $E_2^0 - E_1^0 \geq 0.27$ V predict a fast electron transfer in the corresponding radical cations. In the *anti*-anthracenophane **4d** the intramolecular electron interaction should be even weaker. Correspondingly, the first oxidation potential (+0.24 V) is very close to that of the reference compound **17** (+0.26 V) and the potential difference $E_2^0 - E_1^0$ goes down to 0.10 V. Therefore, the radical cation $\mathbf{4d}^{\bullet+}$ is a real borderline case, and the unpaired electron might be localized in one subunit with respect to the ESR time-scale.

The cyclovoltammogram of **5** confirms that this compound is an extraordinary strong electron donor (E_1^0 = +0.13 V). The first oxidation potentials of related reference compounds are significantly larger; **12**: +0.52 V, **15**: +0.44 V. Furthermore, the large potential difference $E_2^0 - E_1^0$ = 0.41 V of **5** predicts unambiguously a delocalized π-electronic structure for its radical cation. In contrast to the weak electron interaction between the 1,4-benzoquinone subunits in 1,4,8,11-pentacenetetrone[9][10], the 1,4-dimethoxybenzene electrophores in **5** are strongly coupled.

Figure 1. Cyclic voltammogram of **2b** in dichloromethane/0.1 M tetrabutylammonium hexafluorophosphate, v = 100 mV s^{-1}



ESR and ENDOR Studies

Oxidation of the compounds **2b**, **3b**, **4d**, **5**, and **14**−**17** with lead tetraacetate or tris(4-bromophenyl)aminium hexachloroantimonate(V) generated readily the corresponding radical cations, which were sufficiently long-lived to perform detailed ESR and ENDOR studies. The determined isotropic hyperfine coupling (hfc) constants and g values are collected in Table 2.

The resolved ESR spectrum of the basic reference radical cation $\mathbf{14}^{\bullet+}$ shows four groups of equivalent hydrogen atoms and was well simulated with the values given in Table 2. In addition, general triple resonance[21] provided the relative signs of the ^{1}H-hfc constants. As one would expect, positive values were found for the hydrogen atoms of the CH_3 and OCH_3 groups and negative values for the two sets of ring hydrogen atoms. The assignment of the hfc constants to the specific molecular positions was made in analogy to the results of the 1,4-dimethylnaphtalene radical cation[22].

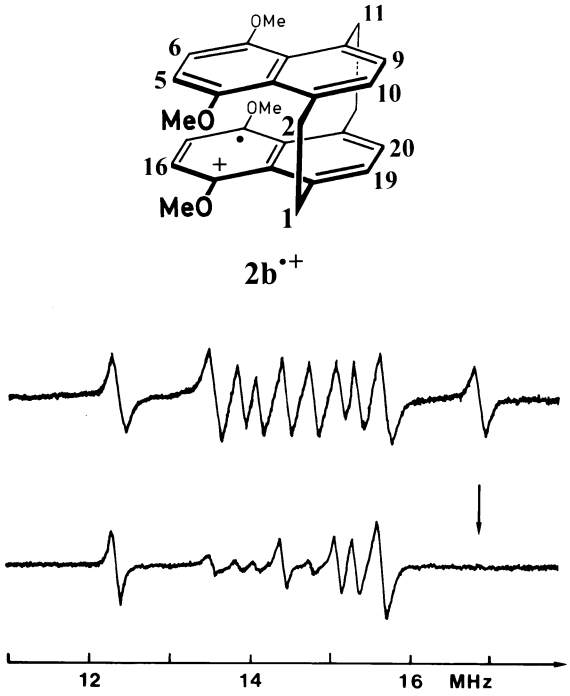
Due to the molecular symmetry of the *syn*- **2b** (C_{2v}) and *anti*-naphthalenophane **3b** (C_{2h}) a hfc splitting pattern of five sets of equivalent hydrogen atoms are expected for the corresponding radical cations. Correspondingly, the ENDOR spectrum of $\mathbf{2b}^{\bullet+}$ (Figure 2) shows five hydrogen-line pairs, and general triple resonance indicates the relative signs as additional information. Furthermore, special triple resonance[21] identified $a(H-OCH_3)$ = +0.76 G (12 H). Therefore, a(H) = +0.52 and a(H) = +0.36 G represent the *syn* and *anti* sets of the methylene hydrogen atoms, which cannot yet be specifically assigned by experiment. As expected, the $a(H-OCH_3)$ splitting of $\mathbf{2b}^{\bullet+}$ is about half the magnitude (+0.76 G) compared with $a(H-OCH_3)$ = +1.43 G of the reference radical cation $\mathbf{14}^{\bullet+}$. This holds also for a(5,6,15,16-H) = −1.61 G of $\mathbf{2b}^{\bullet+}$ [$\mathbf{14}^{\bullet+}$: a(2,3-H) = −3.25 G]. The second ring hydrogen splitting

Table 2. Isotropic hyperfine coupling constants of the radical cations **2b**$^{\bullet+}$, **3b**$^{\bullet+}$, **4d**$^{\bullet+}$, **5**$^{\bullet+}$, and **14**$^{\bullet+}$−**17**$^{\bullet+}$ in trifluoroacetic acid unless otherwise stated and *g* values

	Method	*T* [K]	*a*(H−OCH_3) [G]	*a*($H_{aromatic}$) [G]	*a*($H_{aromatic}$) [G]	*a*(H) [G]	*a*(H) [G]	*g*
2b$^{\bullet+}$	ESR	265	0.73 (12 H)	1.62 (5,6,15,16-H)	0.12 (9,10,19,20-H)	0.56 (1,2,11,12-H)	0.43 (1′,2′,11′,12′-H)	2.0029
	ENDOR	270	+0.72	−1.59	−0.13	+0.62	+0.44	
	ENDOR[a]	210	+0.76	−1.61	−0.12	+0.52	+0.36	
3b$^{\bullet+}$	ESR	270	0.79 (12 H)	1.65 (5,6,15,16-H)		3.15 (1,2,11,12-H)		2.0032
	ENDOR	270	+0.80	−1.65		+3.16		
	ESR[a]	210	0.83 (12 H)	1.70 (5,6,15,16-H)		3.33 (1,2,11,12-H)		
14$^{\bullet+}$	ESR	270	1.76 (6 H)	3.25 (2,3-H)	1.11 (6,7-H)	3.59 (H−CH_3, 6 H)		2.0033
	ENDOR	270	+1.77	−3.25	−1.11	+3.60		
4d$^{\bullet+}$	ESR[b][c]	220	1.41 (6 H)	3.01 (6,7-H)		1.80 (2-H)		2.0031
	ENDOR[b]	220	+1.43	−3.06	−0.35	+1.71		
15$^{\bullet+}$	ESR[d]	255	1.29 (6 H)	3.21 (2,3-H) [e]	0.59 (6,7-H)	0.92 (5,8-H)	3.48 (9,10-H)[e]	2.0031
	ENDOR[d]	255	+1.28	−3.21[e]	−0.59	−0.91	−3.48[e]	
16$^{\bullet+}$	ESR[d]	300	1.23 (6 H) [e]	3.30 (2,3-H) [e]	0.80 (6,7-H)	1.11 (H−CH_3, 6 H)[e]	3.45 (9,10-H)[e]	2.0031
	ENDOR[d]	255	+1.22[e]	−3.31[e]	−0.80	+1.11[e]	−3.40[e]	
17$^{\bullet+}$	ENDOR[b]	240	+1.37[e]	−3.31	−0.62	+1.12[e]	0.15[f]	2.0032
5$^{\bullet+}$	ESR	270	0.11 (12 H)	3.69 (6,13-H)	2.92 (5,7,12,14-H)	1.53 (2,3,9,10-H)		2.0028
	ENDOR	270	+0.10	−3.68	−2.92	−1.52		
	ENDOR[a]	225	+0.10	−3.57	−2.86	−1.55		

[a] In dichloromethane/trifluoroacetic acid (99:1). - [b] In toluene/trifluoroacetic acid (99:1). - [c] The hyperfine structure of 13 lines remains unchanged up to 360 K. - [d] Generated by oxidation with tris(4-bromophenyl)aminium hexachloroantimonate(V). - [e] Relative assignment tentative, see text. − [f] Apparently a splitting of 9,10-phenyl hydrogen atoms.

Figure 2. ^{1}H-ENDOR spectrum of the radical cation **2b**$^{\bullet+}$ in dichloromethane/trifluoroacetic acid (99:1) at 210 K together with a general triple-resonance spectrum, pump frequency 16.83 MHz



2b$^{\bullet+}$

a(9,10,19,20-H) = −0.12 G, however, is significantly smaller compared to *a*(6,7-H) = −1.11 G of **14**$^{\bullet+}$. The highly resolved ESR spectrum of **2b**$^{\bullet+}$ was well fitted using the values given in Table 2. Surprisingly, the ENDOR spectrum of **3b**$^{\bullet+}$ (Figure 3b) shows only three hydrogen-line pairs. A further, very small, splitting is indicated by the resonance line in the center of the ENDOR spectrum. The ESR spectrum of **3b**$^{\bullet+}$ (Figure 3a) was well simulated with *a*(H−OCH_3) = +0.79 G (12 H), *a*(5,6,15,16-H) = +1.65, and *a*(1,2,11,12-H) = +3.15 G. The assignment of the hfc constants follows that of **2b**$^{\bullet+}$. The distinct differences of the methylene hydrogen splittings of **2b**$^{\bullet+}$ and **3b**$^{\bullet+}$ may be connected with changes in the dihedral angles of the ethano bridges. Crystal structure determinations show for the *anti*-**3a**[23] a parallel arrangement of the naphthalene units, whereas in the *syn* isomers **2a**[23] and **2b**[24] the naphthalene planes are bent relative to each other by about 10°. The resulting distortions of the ethano bridges, however, cannot be directly related to the observed hfc splittings of the methylene hydrogen atoms. There is the possibility that oxidation to the radicals cations slightly changes the conformational arrangement, and furthermore, also specific through space interactions may significantly affect the methylene hydrogen splittings[25]. Unexpectedly, the second ring-hydrogen splitting *a*(9,10,19,20-H) of **2b**$^{\bullet+}$ and **3b**$^{\bullet+}$ is very small (−0.12 G) or was not observed. This splitting may also be affected by specific interactions within the [2.2](1,4)arenophane bridge. In summary, ESR and ENDOR results of **2b**$^{\bullet+}$ and **3b**$^{\bullet+}$ clearly prove the displacement of the unpaired electron over the whole molecule on the ESR time-scale in agreement with their oxidation potential difference $E_2^0 - E_1^0 \geq 0.27$ V.

The ENDOR spectra of the reference radical cations **15**$^{\bullet+}$−**17**$^{\bullet+}$ show five hydrogen line pairs in agreement with the molecular C_{2v} symmmetry, and general triple resonance provided the relative signs of these splittings. Accordingly, the highly resolved ESR spectra of **15**$^{\bullet+}$ and **16**$^{\bullet+}$ were well simulated with the data given in Table 2. In the case of **17**$^{\bullet+}$, however, the ESR spectrum was not sufficiently resolved to allow a detailed analysis. The assignments of the splittings were made by means of their relative signs, the different substitution pattern, and in relation to reported ESR results of the anthracene radical cation[26][27] and its 2,3-[28] and 9,10-dimethyl derivatives[27][29]. Even with all this infor-

Figure 3. a) ESR spectrum of the radical cation $\mathbf{3b}^{\bullet+}$ in dichloromethane/trifluoroacetic acid (99:1) at 210 K; b) ^{1}H-ENDOR spectrum of $\mathbf{3b}^{\bullet+}$ in trifluoroacetic acid at 270 K; c) general triple-resonance spectrum of $\mathbf{3b}^{\bullet+}$ in trifluoroacetic acid at 270 K, pump frequency 18.77 MHz

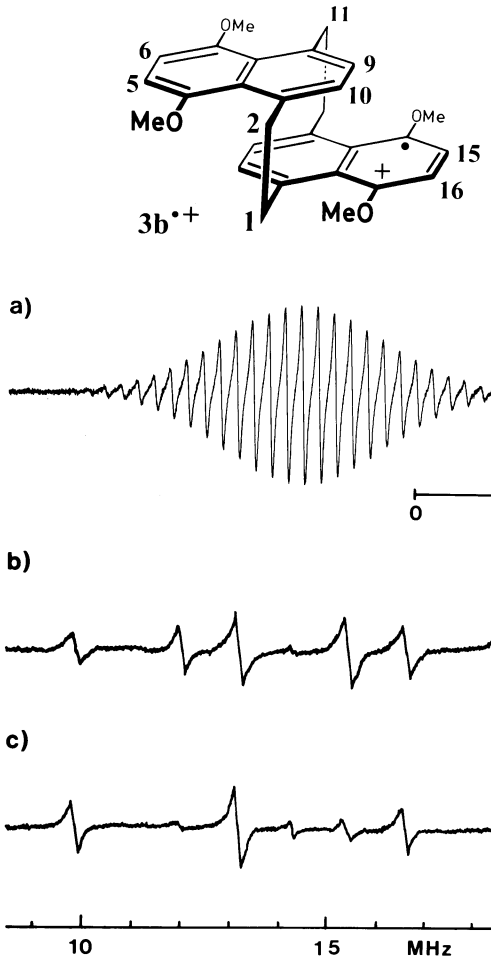
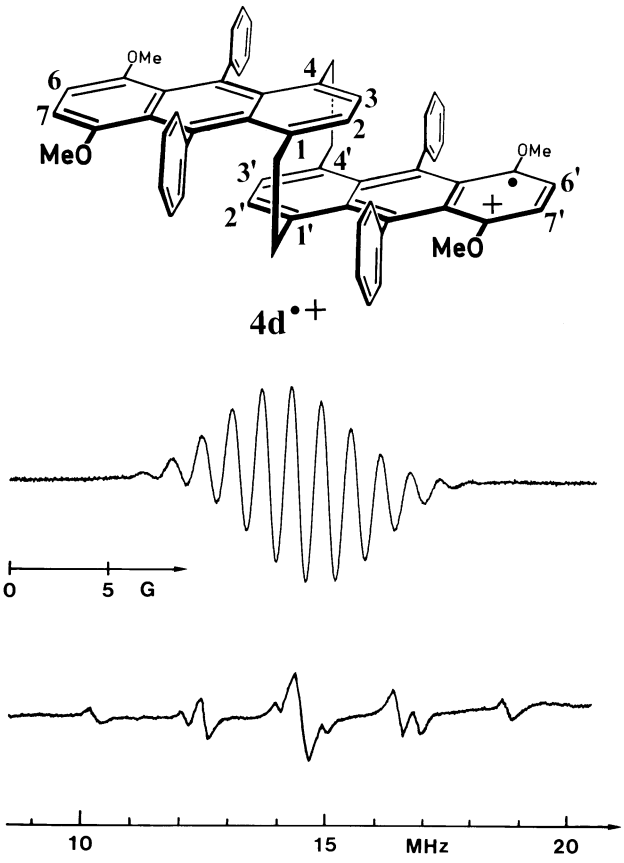


Figure 4. ESR spectrum (top) and ^{1}H-ENDOR spectrum (bottom) of the radical cation $\mathbf{4d}^{\bullet+}$ in toluene/trifluoroacetic acid (99:1) at 220 K

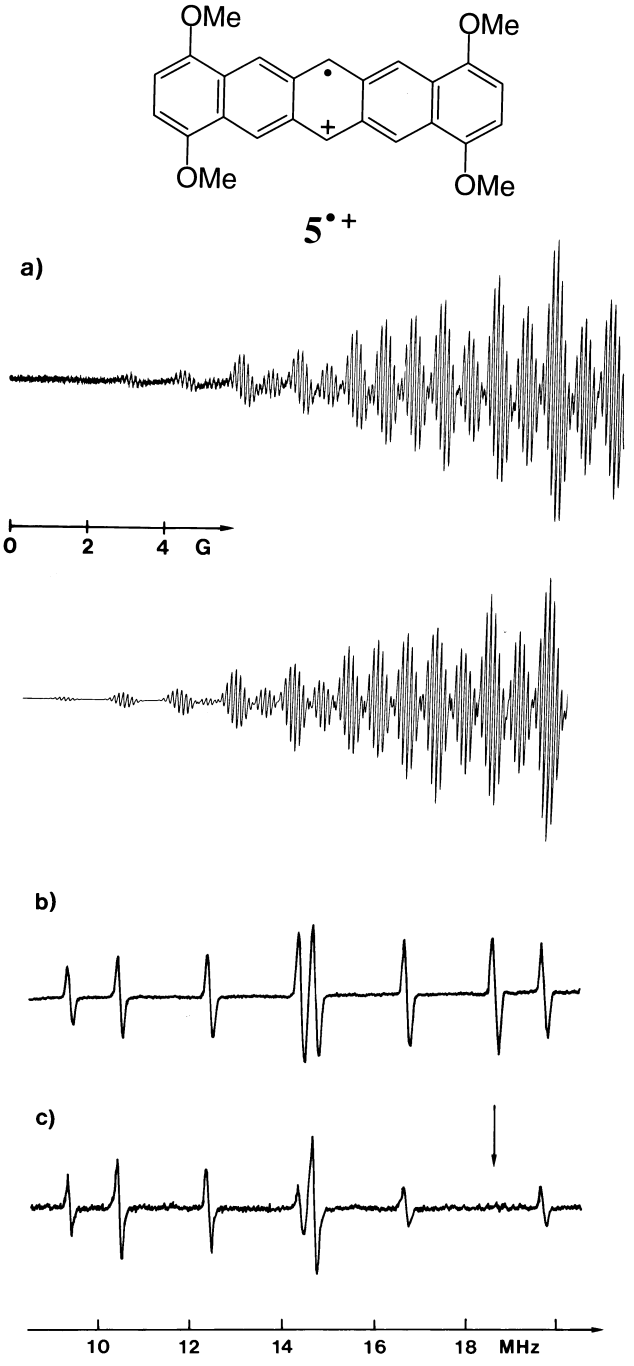


mation the specific assignment of the nearly equal a(2,3-H) and a(9,10-H) in $\mathbf{15}^{\bullet+}$–$\mathbf{17}^{\bullet+}$ and a(H-OCH_3) and a(H-CH_3) in $\mathbf{16}^{\bullet+}$ still remains tentative.

The ENDOR spectrum of $\mathbf{4d}^{\bullet+}$ (Figure 4) shows four line pairs and an additional intense center line, which probably originates from very small hfc splittings of the 9,10-phenyl hydrogen atoms. Relative signs of the hfc constants were obtained by general triple resonance. In the ESR spectrum (Figure 4), which was well fitted with a(H) = −3.01 (2 H), a(H) = +1.80 (2 H), and a(H−OCH_3) = +1.41 G (6 H), the small a(H) = −0.35 G is not resolved. This splitting is tentatively assigned to the 2,3-hydrogen atoms. However, we cannot exclude yet the possibility that this splitting might stem from a phenyl hydrogen set. The large a(6,7-H) = −3.01 G splitting corresponds to a(2,3-H) of the reference radical cations $\mathbf{15}^{\bullet+}$–$\mathbf{17}^{\bullet+}$. Based on the positive sign, a(H) = +1.80 G (2 H) can be unambiguously assigned to two methylene bridge hydrogen atoms. The obtained results give clear evidence that the electron transfer between the two electrophores in $\mathbf{4d}^{\bullet+}$ is slow on the ESR time-scale up to 360 K, in accordance with the very small oxidation potential difference $E_2^0 - E_1^0$ = 0.10 V. The radical cations $\mathbf{3b}^{\bullet+}$ and $\mathbf{4d}^{\bullet+}$ illustrate clearly, how the extension of the relative spatial arrangement of the electrophores by benzoanellation affects decisively the intramolecular electron transfer, although there are still substantial spin populations within the [2.2]paracyclophane bridge of $\mathbf{4d}^{\bullet+}$.

In agreement with the molecular D_{2h} symmetry, the ENDOR spectrum of $\mathbf{5}^{\bullet+}$ (Figure 5b) consists of four line pairs. Based on these splittings and their relative signs, the highly resolved ESR spectrum (Figure 5a) was well simulated with the data given in Table 2. The assignments of a(2,3,9,10-H) = −1.53 and a(5,7,12,14-H) = −2.92 G are based on a McLachlan[31] calculation of the spin-population distribution (Table 3). Radical cation $\mathbf{5}^{\bullet+}$ is related to the pentacene radical cation, which displays a comparable electron delocalization: a(1,4,8,11-H) = 0.975, a(2,3,9,10-H) = 0.757, a(5,7,12,14-H) = 3.554, a(6,13-H) = 5.083 G[32]. Despite the extensive 1,4,8,11-OCH_3 substitution in $\mathbf{5}^{\bullet+}$ the spin-population distribution is only partly changed, and the major part of the spin population still resides in the central anthracene segment of the molecule. In contrast to the 1,4,8,11-pentacenetetrone radical anion[9][10] with conjugated but weakly coupled quinone electrophores, the terminal 1,4-dimethoxybenzene units in $\mathbf{5}^{\bullet+}$ are integral parts of a strongly delocalized system. This is substantiated by

Figure 5. a) Low-field half of the ESR spectrum of the radical cation $\mathbf{5}^{\bullet+}$ in trifluoroacetic acid at 270 K together with a simulation using the data in Table 2; b) ^{1}H-ENDOR spectrum of $\mathbf{5}^{\bullet+}$ in trifluoroacetic acid at 270 K; c) general triple-resonance spectrum of $\mathbf{5}^{\bullet+}$ in trifluoroacetic acid at 270 K, pump frequency 18.60 MHz



the distinct oxidation potential difference $E_2^0 - E_1^0 = 0.41$ V.

Experimental Section

General: Melting points were recorded with 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 and G Princeton Applied Research 263 A potentiostat attached to an EG and 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 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}. Oxidation potentials are referred to ferrocene, $FeCp_2^{+/0}$ was 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 cations $\mathbf{2b}^{\bullet+}$, $\mathbf{3b}^{\bullet+}$, $\mathbf{4d}^{\bullet+}$, $\mathbf{5}^{\bullet+}$, and $\mathbf{14}^{\bullet+}$−$\mathbf{17}^{\bullet+}$ were generated in trifluoroacetic acid (99.7% for protein sequencing, Merck), in dichloromethane (99.9%, HPLC grade, Aldrich)/trifluoroacetic acid (99:1) or in toluene/trifluoroacetic acid (99:1) by adding a few drops of a diluted solution (ca. 1 mg in 2 ml) of lead tetracetate or tris(4-bromophenyl)aminium hexachloroantimonate(V) in dichloromethane to dilute solutions (ca. 1 mg in 2 ml) of the parent compounds in the given solvents, followed by careful deoxygenation under high-vacuum conditions.

Table 3. Experimental [$a(H_i) = -27\rho(C_i)$[30]] and calculated (McLachlan[31]) spin populations of $\mathbf{5}^{\bullet+}$

Position	$a(H_i)_{exp}$ [G]	$\rho(C_i)_{exp}$	$\rho(C_i)$[a]	$\rho(C_i)$[b]
1,4,8,11	−	−	+0.061	+0.058
2,3,9,10	−1.52	+0.056	+0.049	+0.044
4a,7a,11a,14a	−	−	−0.019	−0.018
5,7,12,14	−2.92	+0.108	+0.103	+0.110
5a,6a,12a,13a	−	−	−0.023	−0.024
6,13	−3.68	+0.136	+0.117	+0.129

[a] In analogy to ref.[22]: $a_O = a_C + 1.57\,\beta_{CC}$; $\beta_{C(1)O(1)} = \beta_{C(4)O(4)} = \beta_{C(8)O(8)} = \beta_{C(11)O(11)} = 1.03\,\beta_{CC}$; $\lambda = 1.2$. − [b] $a_O = a_C + 1.7\,\beta_{CC}$; $\lambda = 1.2$.

The compounds *syn*- (**2b**)[20] and *anti*-4,7,14,17-tetramethoxy[2.2](1,4)naphthalenophane (**3b**)[20], and 1,4-dimethoxy-5,8-dimethylnaphthalene (**14**)[10] were available in our laboratory or were prepared as described in the literature.

syn,syn-9,10:9′,10′-Diepoxy-9,9′,10,10′-tetrahydro-5,5′,8,8′-tetramethoxy-9,9′,10,10′-tetraphenyl-anti-[2.2](1,4)anthracenophane (**8a**), *anti,syn-9,10:9′,10′-Diepoxy-9,9′,10,10′-tetrahydro-5,5′,8,8′-tetramethoxy-9,9′,10,10′-tetraphenyl-anti-[2.2](1,4)anthracenophane* (**8b**), *and anti,anti-9,10:9′,10′-Diepoxy-9,9′,10,10′-tetrahydro-5,5′,8,8′-tetramethoxy-9,9′,10,10′-tetraphenyl-anti-[2.2](1,4)anthracenophane* (**8c**): To a stirred mixture of 4,5,12,13-tetrabromo[2.2]paracyclophane[12] (457 mg, 0.87 mmol) and 4,7-dimethoxy-1,3-diphenylisobenzofuran[13] (573 mg, 1.74 mol) in anhydrous THF (50 ml) was added dropwise at −40°C a 0.32 M butyllithium hexane solution (10 ml, 3.3 mmol) over a period of 30 min. After warming up to room temperature and addition of methanol (10 ml) and water (100 ml), the mixture was extracted with dichloromethane (2 × 100 ml). The combined extracts were washed with water, dried (Na_2SO_4) and concentrated under reduced pressure.

The residue obtained was treated with acetone (100 ml), and the precipitated colourless solid was filtered and dried to afford the isomer mixture **8a−c** (555 mg, 74%). − LSIMS (3-nitrobenzyl alcohol); *m/z* (%): 866 (4) [$M^{\bullet+}$ + 2 H], 865 (7) [MH^+], 864 (2) [$M^{\bullet+}$]. − HR MS: calcd. 865.3529; found 865.3564 [MH^+]. The isomer mixture was separated by flash chromatography on silica gel (Amicon, 35−70 mm, 60 Å; *h* = 40 cm, *d* = 5 cm) with toluene/dichloromethane (2:1) as eluent to give **8a**, **8b**, and **8c**.

syn,syn Isomer **8a**: Minor isomer, R_f = 0.67, dichloromethane, mp. > 340°C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.05−3.20 (m, 4 H, CH_2), 3.45 (s, 12 H, OCH_3), 3.50−3.60 (m, 4 H, CH_2), 5.98 (s, 4 H, 2,2′,3,3′-H), 6.42 (s, 4 H, 6,6′,7,7′-H), 7.35−7.50 (m, 12 H, H_{phenyl}), 8.35−8.45 (m, 8 H, H_{phenyl}); irradiation of the OCH_3 signal at δ = 3.45 yielded a positive NOE response for the 6,6′,7,7′-H at δ = 6.42.

anti,syn Isomer **8b**: Minor isomer, R_f = 0.54, dichloromethane, mp. > 340°C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.95−2.05 (m, 2 H, CH_2), 2.20−2.30 (m, 2 H, CH_2), 2.40−2.50 (m, 2 H, CH_2), 3.15−3.25 (m, 2 H, CH_2), 3.50 (s, 6 H, *syn*-OCH_3), 3.76 (s, 6 H, *anti*-OCH_3), 4.63 (s, 2 H, *syn*-2,3-H), 5.98 (s, 2 H, *anti*-2′,3′-H), 6.47 (s, 2 H, *syn*-6,7-H), 6.77 (s, 2 H, *anti*-6′,7′-H), 7.20-7.30 (m, 6 H, H_{phenyl}), 7.40−7.50 (m, 2 H, H_{phenyl}), 7.50−7.58 (m, 4 H, H_{phenyl}), 7.60−7.70 (m, 4 H, H_{phenyl}), 8.45−8.55 (m, 4 H, H_{phenyl}); irradiation of the *syn*-OCH_3 signal at δ = 3.50 yielded a positive NOE response for the *syn*-6,7-H at δ = 6.47 and irradiation of the *anti*-OCH_3 signal at δ = 3.76 yielded a positive NOE response for the 2,3-H at δ = 4.63 and for the *anti*-6′,7′-H at δ = 6.77.

anti,anti Isomer **8c**: Major isomer, R_f = 0.54, dichloromethane, mp. > 340°C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.60−2.75 (m, 4 H, CH_2), 2.75−2.85 (m, 4 H, CH_2), 3.86 (s, 12 H, OCH_3), 4.80 (s, 4 H, 2,2′,3,3′-H), 6.88 (s, 4 H, 6,6′,7,7′-H), 7.28−7.38 (m, 12 H, H_{phenyl}), 7.70−7.78 (m, 8 H, H_{phenyl}); irradiation of the OCH_3 signal at δ = 3.85 yielded a positive NOE response for the 2,2′,3,3′-H at δ = 4.80 and for the 6,6′,7,7′-H at δ = 6.88.

5,5′,8,8′-Tetramethoxy-9,9′,10,10′-tetraphenyl-anti-[2.2](1,4)anthracenophane (**4d**): To a stirred suspension of **8c** (100 mg, 0.116 mmol) in anhydrous acetonitrile, tetramethylsilyl iodide (0.1 ml, 0.7 mmol) was added at −20°C, and the mixture was stirred at room temperature for 12 h. Then again trimethylsilyl iodide (0.05 ml, 0.35 mmol) was added and stirring was continued for further 6 h. The reaction was quenched by the addition of water (40 ml) and dichloromethane (40 ml). The organic layer was separated, and the aqueous phase was extracted with dichloromethane (2 × 40 ml). The combined organic extracts were washed with a saturated aqueous sodium thiosulfate solution (50 ml) followed by water, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Amicon, 35−70 mm, 60 Å; *h* = 40 cm, *d* = 2.5 cm) with hexane/dichloromethane (3:1) as eluent to give compound **4d** (19 mg, 20%; R_f = 0.71, dichloromethane) as yellow crystals, m.p. > 310°C (dec.). − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.10−1.30 (m, 4 H, CH_2), 2.10−2.30 (m, 4 H, CH_2), 3.21 (s, 12 H, OCH_3), 5.78 (s, 4 H, 2,2′,3,3′-H), 6.56 (s, 4 H, 6,6′,7,7′-H), 7.20−7.34 (m, 20 H, H_{phenyl}); irradiation of the OCH_3 signal at δ = 3.21 yielded a positive NOE response for the 6,6′,7,7′-H at δ = 6.56. − LSIMS (3-nitrobenzyl alcohol); *m/z* (%): 836 (8) [$M^{\bullet+}$ + 4 H], 835 (18) [M^+ + 3 H], 834 (30) [$M^{\bullet+}$ + 2 H], 833 (18) [MH^+], 832 (6) [$M^{\bullet+}$]. − HR MS: calcd. 833.3631; found 833.3607 [MH^+].

1,4,8,11-Tetramethoxypentacene-6,13-dione (**11**): A stirred mixture of 3,6-dimethoxybenzocyclobuten-1-ol[15][33] (180 mg, 1 mmol), 5,8-dimethoxy-1,4-anthraquinone[15] (268 mg, 1 mmol), and benzyl alcohol (10 ml) in an autoclave was heated to 200°C for 24 h. On cooling the precipitated product was filtered and washed with dichloromethane to yield compound **11** as sparingly soluble red crystals (374 mg, 87%), m.p. > 340°C. On a small scale the product can be further purified by sublimation at 340°C/2·10^{-4} bar. − ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 4.07 (s, 12 H, OCH_3), 7.20 (s, 4 H, 2,3,9,10-H), 9.13 (s, 4 H, 5,7,12,14-H). − EI MS; *m/z* (%): 430 (23), 429 (30), 428 (100) [$M^{\bullet+}$], 414 (16), 413 (31) [M^+ - CH_3], 399 (16), 398 (36) [$M^{\bullet+}$ - 2 CH_3], 384 (14), 383 (43) [M^+ - 3 CH_3], 223 (11), 199 (14), 44 (34), 18 (16). − HR MS: calcd. 428.1259; found 428.1268 [$M^{\bullet+}$].

6,13-Dihydro-1,4,8,11-tetramethoxypentacene (**12**): To a stirred suspension of **11** (175 mg, 0.41 mmol) in anhydrous THF (70 ml) under argon, lithium aluminium hydride (120 mg, 3.2 mmol) was added. Stirring under argon at ambient temperature was continued for further 2 h. Then the mixture was hydrolysed by addition of water (150 ml) and 2 N hydrochloric acid (30 ml) and extracted with dichloromethane (3 × 150 ml). The combined extracts were washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to yield an orange residue (102 mg). To this product, dichloromethane (20 ml), trifluoroacetic acid (99%, 40 ml) and triethylsilane (30 ml) were added, and the suspension was stirred for 24 h at ambient temperature. To the clear solution water (100 ml) was added, and the mixture was extracted with dichloromethane (3 × 100 ml). The combined extracts were washed twice with a saturated aqueous hydrogen carbonate solution (100 ml) followed by water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Amicon, 35−70 mm, 60 Å; *h* = 25 cm, *d* = 2.5 cm) with dichloromethane as eluent to give compound **12** (28 mg, 17%; R_f = 0.67, dichloromethane) as colourless needles from acetone, m.p. 238−239°C. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.94 (s, 12 H, OCH_3), 4.25 (s, 4 H, 6,6,13,13-H), 6.66 (s, 4 H, 2,3,9,10-H), 8.12 (s, 4 H, 5,7,12,14-H). − EI MS; *m/z* (%): 401 (28), 400 (100) [$M^{\bullet+}$], 385 (20) [M^+ - CH_3], 370 (30) [$M^{\bullet+}$ - 2 CH_3], 356 (11), 355 (39) [M^+ - 3 CH_3]. − HR MS: calcd. 400.1675; found 400.1673 [$M^{\bullet+}$]. − $C_{26}H_{24}O_4$: calcd. C 77.98, H 6.04; found C 77.76, H 6.11.

1,4,8,11-Tetramethoxypentacene (**5**): Compound **12** (17.4 mg, 0.044 mmol) was finely powdered in a mortar and intensively mixed with copper powder (1.2 g, 19 mmol). This mixture was transferred to a sublimation apparatus, flushed with argon and heated at 260°C for 15 min. Then the apparatus was evacuated to ca. 10^{-7} bar, and the formed pentacene **5** (9.8 mg, 57%; R_f = 0.47, toluene) was condensed at the cold finger trap as dark violet lustrous crystals, m.p. > 320°C. The pentacene is very sensitive in solution and could not be further purified. On air the violet solutions bleach within 1 h. − UV/Vis (DMF): λ_{max} (lg ε) = 595 nm (3.58), 550 (3.58), 510 (3.36), 475 (3.21), 4.17 (3.52), 307 (5.21). − ^{1}H NMR (500 MHz, CD_2Cl_2, flushed with argon, 1 min after dissolution): δ = 4.04 (s, 12 H, OCH_3), 6.50 (br. s, 4 H, 2,3,9,10-H), 9.00 (br. s, 6 H, 5,6,7,12,13,14-H); (15 min after dissolution): δ = 4.04 (s, 12 H, OCH_3), 6.50 (s, 4 H, 2,3,9,10-H), 9.00 (s, 6 H, 5,6,7,12,13,14-H) and δ = 3.94 (s, 12 H, OCH_3), 6.26 (s, 2 H, 6,13-H), 6.77 (s, 4 H, 2,3,9,10-H), 8.23 (s, 4 H, 5,7,12,14-H) representing the formed compound **13**. − EI MS; *m/z* (%): 408 (11), 404 (12), 400 (20), 399 (42), 398 (100) [$M^{\bullet+}$], 383 (14) [M^+ - CH_3], 376 (19), 375 (73), 369 (14), 368 (47) [$M^{\bullet+}$ − 2 CH_3], 353 (29) [M^+ − 3 CH_3], 338 (19) [$M^{\bullet+}$ − 4 CH_3], 329 (18), 199 (14) [M^{2+}], 191.5 (6) [M^+ - CH_3]$^{\bullet+}$, 184 (12) [$M^{\bullet+}$ − 2 CH_3]$^{\bullet+}$. − HR MS: calcd. 398.1518; found 398.1523 [$M^{\bullet+}$].

6,13-Dihydro-6,13-epidioxy-1,4,8,11-tetramethoxypentacene (**13**): A solution of **5** (3 mg) in dichloromethane (5 ml) was stirred for 45 min at ambient temperature. The violet colour of the solution

changed to yellow. Concentration of the solution under reduced pressure afforded a yellow solid. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.94 (s, 12 H, OCH_3), 6.26 (s, 2 H, 6,13-H), 6.77 (s, 4 H, 2,3,9,10-H), 8.23 (s, 4 H, 5,7,12,14-H). – EI MS; *m/z* (%): 431 (31), 430 (100) [$M^{\bullet+}$], 401 (23), 400 (38), 97 (40), 95 (28), 85 (29), 83 (46), 81 (30), 71 (43), 69 (55), 57 (73), 44 (30), 43 (56), 41 (33). – HR MS: calcd. 430.1416; found 430.1424 [$M^{\bullet+}$].

1,4-Dimethoxyanthracene (**15**): To 1,4-anthraquinone (1.00 g, 4.8 mmol) in diethyl ether (30 ml) a solution of sodium dithionite (3.00 g, 17.2 mmol) in water (40 ml) was added, and the mixture was stirred at ambient temperature for 3 h. On addition of diethyl ether (100 ml) and water (100 ml) the organic phase was separated, and the aqueous phase was extracted with diethyl ether (2 × 50 ml). The combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. To the residue dissolved in a solution of potassium hydroxide (7.00 g, 125 mmol) in water (50 ml) was added dropwise at 0°C dimethyl sulphate (4.7 ml, 50 mmol). After stirring the mixture at 0°C for 1 h, it was heated to 80°C. Then again dimethyl sulphate (4.7 ml, 50 mmol) was added, and stirring at 80°C was continued for 3 h. On cooling water (200 ml) was added, and the mixture was extracted with dichloromethane (3 × 80 ml). The combined extracts were washed with water (3 × 50 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Amicon, 35–70 mm, 60 Å; *h* = 25 cm, *d* = 4 cm) with cyclohexane/dichloromethane (1:1) as eluent to give compound **15** (661 mg, 58%; R_f = 0.61, toluene) as yellow needles from cyclohexane, m.p. 132–133°C (ref.[18]: m.p. 136–137°C). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.04 (s, 6 H, OCH_3), 6.62 (s, 2 H, 2,3-H), 7.47 (dd, ^3J = 6.4, ^4J = 3.2 Hz, 2 H, 6,7-H), 8.04 (dd, 2 H, 5,8-H), 8.78 (s, 2 H, 9,10-H); irradiation of the 9,10-H signal at δ = 8.78 yielded a positive NOE response for the 5,8-H at δ = 8.04.

1,4-Dimethoxy-5,8-dimethyl-9,10-anthraquinone (**20**): A mixture of 5,8-dimethoxy-1,4-naphthoquinone (**18**,[34] 436 mg, 2.0 mmol) and 2,4-hexadiene (**19**, Tokyo Kasei Chemicals, mixture of isomers, 0.5 ml, 4.4 mmol) in toluene (30 ml) was heated in an autoclave at 150°C for 3 h. The mixture was transferred into a round-bottom flask and, after addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.0 g, 4.4 mmol), heated at reflux for 1 h. Then again 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.0 g, 4.4 mmol) was added and heating at reflux was continued for 2 h. The hot mixture was filtered and the filtrate was concentrated under reduced pressure. The red residue was purified by flash chromatography on silica gel (Amicon, 35–70 mm, 60 Å; *h* = 30 cm, *d* = 3.5 cm) with dichloromethane followed by ethyl acetate as eluent to give compound **20** (264 mg, 45%; R_f = 0.52, ethyl acetate) as yellow crystals from acetone, m.p. 262–263°C. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.67 (s, 6 H, CH_3), 3.94 (s, 6 H, OCH_3), 7.19 (s, 2 H, 2,3-H), 7.29 (s, 2 H, 6,7-H); irradiation of the OCH_3 signal at δ = 3.94 yielded a positive NOE response for the 2,3-H at δ = 7.19. – EI MS; *m/z* (%): 297 (20), 296 (100) [$M^{\bullet+}$], 281 (33) [$M^+ - CH_3$], 279 (22), 278 (17), 266 (32) [$M^{\bullet+} - 2\ CH_3$], 264 (29), 263 (64), 251 (40), 249 (30), 238 (17), 236 (43), 235 (29), 221 (16), 181 (19), 179 (16), 178 (25), 165 (36), 154 (23), 153 (30), 152 (28). – $C_{18}H_{16}O_4$: calcd. C 72.96, H 5.44; found C 73.05, H 5.65.

1,4-Dimethoxy-5,8-dimethylanthracene (**16**): To a solution of **20** (148 mg, 0.5 mmol) in anhydrous THF (40 ml) under argon, lithium aluminium hydride (50 mg, 1.35 mmol) was added, and the mixture was stirred at ambient temperature for 30 min. Then the mixture was hydrolysed by addition of water (10 ml) and extracted with dichloromethane (3 × 50 ml). The combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. To a solution of the residue in acetic acid (5 ml), phenylhydrazine (1 ml) was added, and the mixture was heated at reflux for 2 h. On cooling the solution was diluted with water (50 ml) and extracted with dichloromethane (3 × 50 ml). The combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Amicon, 35–70 mm, 60 Å; *h* = 20 cm, *d* = 2.5 cm) with dichloromethane as eluent to give compound **16** (88 mg, 66%; R_f = 0.79, dichloromethane) as yellow needles from cyclohexane, m.p. 191–192°C. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.81 (s, 6 H, CH_3), 4.05 (s, 6 H, OCH_3), 6.64 (s, 2 H, 2,3-H), 7.21 (s, 2 H, 6,7-H), 8.89 (s, 2 H, 9,10-H). – EI MS; *m/z* (%): 267 (20), 266 (99) [$M^{\bullet+}$], 252 (18), 251 (100) [$M^+ - CH_3$], 236 (43) [$M^{\bullet+} - 2\ CH_3$], 235 (12), 221 (13), 208 (12), 165 (11), 154 (13), 118 (76). – $C_{18}H_{18}O_2$: calcd. C 81.17, H 6.81; found C 80.96, H 7.01.

9,10-Dihydro-cis-9,10-dihydroxy-1,4-dimethoxy-5,8-dimethyl-9,10-diphenylanthracene (**21a**) *and 9,10-Dihydro-trans-9,10-dihydroxy-1,4-dimethoxy-5,8-dimethyl-9,10-diphenylanthracene* (**21b**): To a stirred solution of **20** (200 mg, 0.675 mmol) in anhydrous THF (30 ml) under argon was added dropwise at 0°C a 1.6 M phenyllithium hexane/diethyl ether (7:3) solution (1.5 ml, 2.4 mmol) over a period of 5 min. After the addition the mixture was stirred at ambient temperature for further 2 h. Then the mixture was hydrolysed by addition of water (30 ml) and 2 N hydrochloric acid (30 ml) and extracted with dichloromethane (3 × 40 ml), and the combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Flash chromatography of the residue on silica gel (Amicon, 35–70 mm, 60 Å; *h* = 25 cm, *d* = 2.5 cm) with cyclohexane/ethyl acetate (3:1) as eluent separated the products being biphenyl, the *trans* isomer **21b** , and the *cis* isomer **21a**.

21a: From acetone colourless needles [191 mg, 63%, R_f = 0.29, cyclohexane/ethyl acetate (2:1)], m.p. 292–295°C. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.20 (s, 6 H, CH_3), 3.52 (s, 6 H, OCH_3), 5.23 (s, 2 H, OH), 6.75 (s, 2 H, 2,3-H), 6.90 (s, 2 H, 6,7-H), 7.10–7.18 (m, 2 H, 4-H_{phenyl}), 7.19–7.25 (m, 4 H, 3,5-H_{phenyl}), 7.56–7.62 (m, 4 H, 2,6-H_{phenyl}); irradiation of the CH_3 signal at δ = 2.20 yielded a positive NOE response for the OH–H at δ = 5.23, for the 6,7-H at δ = 6.90, and for the 2,6-H_{phenyl} at δ = 7.56–7.62. – EI MS; *m/z* (%): 452 (16) [$M^{\bullet+}$], 376 (26), 375 (100) [$M^+ - C_6H_5$], 357 (11), 329 (12), 298 (12), 283 (18).

21b: From acetone colourless needles [87 mg, 29%, R_f = 0.79, cyclohexane/ethyl acetate (2:1)], m.p. 314–316°C. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.23 (s, 6 H, CH_3), 3.58 (s, 6 H, OCH_3), 5.71 (s, 2 H, OH), 6.63 (s, 2 H, 2,3-H), 6.84 (s, 2 H, 6,7-H), 6.98–7.05 (m, 2 H, 4-H_{phenyl}), 7.11–7.18 (m, 4 H, 3,5-H_{phenyl}), 7.31–7.39 (m, 4 H, 2,6-H_{phenyl}). – EI MS; *m/z* (%): 453 (26), 452 (79) [$M^{\bullet+}$], 451 (18), 434 (11), 377 (22), 376 (100), 375 (100) [$M^+ - C_6H_5$], 357 (13), 345 (15), 343 (17), 329 (20), 299 (13), 298 (50), 284 (12), 283 (58), 269 (12), 268 (17), 105 (11).

1,4-Dimethoxy-5,8-dimethyl-9,10-diphenylanthracene (**17**): A stirred solution of **21a** (300 mg, 0.66 mmol) and phenylhydrazine (1 ml) in acetic acid (5 ml) was heated at reflux for 1 h. After addition of water (40 ml) the mixture was extracted with dichloromethane (3 × 80 ml), and the combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Amicon, 35–70 mm, 60 Å; *h* = 30 cm, *d* = 4 cm) with cyclohexane/diethyl ether (10:1) as eluent to give compound **17** (127 mg, 46%; R_f = 0.73, toluene) as dark yellow lustrous crystals from hexane, m.p. 191–192°C. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.68 (s, 6 H, CH_3), 3.24 (s, 6 H, OCH_3), 6.51 (s, 2 H, 2,3-H), 6.90 (s, 2 H, 6,7-H), 7.25–7.45 (m, 10 H, H_{phenyl}); irradiation of the CH_3 signal at

δ = 1.68 yielded a positive NOE response for the 6,7-H at δ = 6.90. − EI MS; *m/z* (%): 420 (14), 419 (83), 418 (100) [$M^{\bullet+}$], 403 (23) [$M^+ - CH_3$], 388 (31) [$M^{\bullet+} - 2\ CH_3$], 375 (21), 373 (31) [$M^+ - 3\ CH_3$], 372 (33), 359 (13), 358 (14) [$M^{\bullet+} - 4\ CH_3$], 357 (13), 356 (28), 345 (15), 327 (15), 311 (14), 303 (11). − $C_{30}H_{26}O_2$: calcd. C 86.09, H 6.26; found C 86.06, H 6.40.

[1] B. Becker, A. Bohnen, M. Ehrenfreund, W. Wohlfahrt, Y. Sakata, W. Huber, K. Müllen, *J. Am. Chem. Soc.* **1991**, *113*, 1121−1127, and references therein.
[2] H. Hope, J. Bernstein, K. N. Trueblood, *Acta Crystallogr., Sect. B* **1972**, *28*, 1733−1743.
[3] F. Gerson, W. B. Martin, Jr., *J. Am. Chem. Soc.* **1969**, *91*, 1883−1891.
[4] F. Gerson, W. B. Martin, Jr., C. Wydler, *J. Am. Chem. Soc.* **1976**, *98*, 1318−1320.
[5] J. Bruhin, F. Gerson, W. B. Martin, Jr., C. Wydler, *Helv. Chim. Acta* **1977**, *60*, 1915−1923.
[6] V. Hamacher, M. Plato, K. Möbius, *Chem. Phys. Lett.* **1986**, *125*, 69−73.
[7] F. Nemeto, K. Ishizu, T. Toyoda, Y. Sakata, S. Misumi, *J. Am. Chem. Soc.* **1980**, *102*, 654−656.
[8] A. R. Wartini, J. Valenzuela, H. A. Staab, F. A. Neugebauer, *Eur. J. Org. Chem.* **1998**, 139−148.
[9] S. F. Rak, L. L. Miller, *J. Am. Chem. Soc.* **1992**, *114*, 1388−1394.
[10] A. R. Wartini, J. Valenzuela, H. A. Staab, F. A. Neugebauer, *Eur. J. Org. Chem.* **1998**, 211−227.
[11] B. König, B. Knieriem, K. Rauch, A. de Meijere, *Chem. Ber.* **1993**, *126*, 2531−2534.
[12] B. König, B. Knieriem, A. de Meijere, *Chem. Ber.* **1993**, *126*, 1643−1650.
[13] L. Lepage, Y. Lepage, *Synthesis* **1983**, 1018−1019.
[14] K. Jung, J. Koreeda, *J. Org. Chem.* **1989**, *54*, 5667−5675.
[15] J. E. Almlöf, M. W. Feyereisen, T. H. Jozefiak, L. L. Miller, *J. Am. Chem. Soc.* **1990**, *112*, 1206−1214.
[16] E. Clar, F. John, *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 3021−3029.
[17] D. B. Bruce, R. H. Thomson, *J. Chem. Soc.* **1952**, 2759−2766.
[18] Cf.: Y. Lepage, *Ann. Chim. (Paris)* **1959**, *13*, 1137−1181.
[19] C. Krieger, A. R. Wartini, F. A. Neugebauer, *Acta Crystallogr., Sect. C*, in press.
[20] H. A. Staab, C. P. Herz, *Angew. Chem.* **1977**, *89*, 406−407; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 392−393.
[21] H. Kurreck, B. Kirste, W. Lubitz, *Angew. Chem.* **1984**, *96*, 171-193; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 173-195, and references given therein.
[22] P. D. Sullivan, *J. Phys. Chem.* **1970**, *74*, 2563−2569.
[23] A. V. Fratini, M. L. Chabinyc, T. J. Perko, W. W. Adams, *Acta Crystallogr.* **1995**, *C51*, 904−908.
[24] R. Gleiter, K. Staub, H. Irngartinger, T. Oeser, *J. Org. Chem.* **1997**, *62*, 7644−7649.
[25] Compare, for example, the ESR/ENDOR results of the *pseudogeminal* (**1b**$^{\bullet+}$) and *pseudoortho* 4,7,12,15-tetramethoxy[2.2]paracyclophane radical cations[8].
[26] A. Carrington, F. Dravnieks, M. C. R. Symons, *J. Chem. Soc.* **1959**, 947−952.
[27] A. C. Buchanan, R. Livingston, A. S. Dworkin, C. P. Smith, *J. Phys. Chem.* **1980**, *84*, 423−427.
[28] J. A. Valenzuela, A. J. Bard, *J. Phys. Chem.* **1969**, *73*, 779−788.
[29] J. R. Bolton, A. Carrington, A. D. McLachlan, *Mol. Phys.* **1965**, *5*, 31−41.
[30] H. M. McConnell, *J. Chem. Phys.* **1956**, *24*, 632, 764−766; E. T. Strom, G. R. Underwood, D. Jurkowitz, *Mol. Phys.* **1972**, *24*, 901−904.
[31] A. D. McLachlan, *Mol. Phys.* **1960**, *3*, 233−252.
[32] J. R. Bolton, *J. Chem. Phys.* **1967**, *46*, 408−409.
[33] M. Azadi-Ardakani, T. W. Wallace, *Tetrahedron* **1988**, *44*, 5939−5952.
[34] Y. Tanoue, K. Sakata, M. Hashimoto, S. Morishita, M. Hamada, N. Kai, T. Nagai, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2593−2595.

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