1,2,3,4,5-[1′,8′]Anthra-8,9;10,11-dibenzo[13]annulene and 1,8-Distyrylanthracene as Models for Phenylenevinylene Species. Syntheses, Structures, and Redox Properties

Kay-Uwe Klabunde[a], Walter Huber[b], Johann Lex[c], and Klaus Müllen*[a]

Institut für Organische Chemie der Universität Mainz[a],
J. J. Becher-Weg 18–20, D-6500 Mainz 1

Institut für Physikalische Chemie der Universität Basel[b],
Klingelbergstr. 80, CH-4056 Basel

Institut für Organische Chemie der Universität Köln[c],
Greinstraße 4, D-5000 Köln 41

Received March 6, 1987

The synthesis of the title compound **4**, formally a [13]perimeter, and of its acyclic model system, 1,8-distyrylanthracene (**6**) is described. The crystal structure of **4** reveals the configuration of the double bonds and the conformation of the macrocycle. Related findings come from the ^{1}H-NMR spectroscopic characterization of **4** and **6** in solution. The spin density distribution of the radical anions $\mathbf{4}^{-\cdot}$ and $\mathbf{6}^{-\cdot}$ is interpretet in terms of the singly occupied molecular orbital and of the prevailing geometry. In contrast to **4**, compound **6** proves to be an efficient electron acceptor since it can even be reduced to a tetraanion salt. The complete redox sequence is characterized by NMR and ESR spectroscopy.

1,2,3,4,5-[1′,8′]Anthra-8,9;10,11-dibenzo[13]annulen und 1,8-Distyrylanthracen als Modelle für Phenylenvinylen-Systeme. Synthesen, Strukturen und Redoxeigenschaften

Die Synthesen der formal als [13]Perimeter aufzufassenden Titelverbindungen **4** und ihres acyclischen Modellsystems 1,8-Distyrylanthracen (**6**) werden beschrieben. Die Kristallstruktur von **4** zeigt die Konfiguration der Doppelbindungen und die Konformation des Makrocyclus auf. Entsprechende Befunde ergeben sich aus den ^{1}H-NMR-Spektren von **4** und **6** in Lösung. Die Spindichteverteilung in den Radikalanionen $\mathbf{4}^{-\cdot}$ und $\mathbf{6}^{-\cdot}$ wird im Hinblick auf die Art des einfach besetzten Molekülorbitals und auf die Molekülgeometrie diskutiert. Verbindung **6** erweist sich als effizienter Elektronenakzeptor, denn es kann zu einem Tetraanionsalz reduziert werden. Die komplette Redoxsequenz wird mit Hilfe der NMR- und ESR-Spektroskopie charakterisiert.

The hydrocarbons **1**–**4** can be regarded as polycycles incorporating a central [11]-, [12]- or [13]perimeter. While **3** and **4** are still elusive, compounds **1**$^{1,2)}$ and **2**$^{3,4)}$ have been prepared. How these macrocycles accommodate the appreciable ring strain, and to what extent there is transannular interaction between their C=C double bonds are basic questions concerning the structure of these hydrocarbons. The most important chemical property of **1** and **2** is the thermal or photochemical [2+2] cycloaddition of their olefinic bonds to yield cyclobutane species.

Transformation of **1** or **2** into radical anions via electron-transfer reactions should be promising since the prevailing spin density distribution could be used to probe the bonding situation. Upon attempted radical anion formation through chemical or electrochemical reduction of **1** and **2** we found that even at −80°C the electron transfer induced a rapid [2+2] cycloaddition$^{5)}$. Under the reaction conditions the cyclobutane products could not be isolated, but underwent a subsequent [2+2] cycloreversion to yield phenanthrene and acenaphthylene, respectively. Thus the reduction of **1** and **2** provides another example of rapid electron-transfer induced valence isomerization$^{6,7)}$. We also found that incorporation of the ethylene moieties into a rigid macrocycle is not a prerequisite for ring formation. While the structurally related 2,2′-distyrylbiphenyl (**5**)$^{8,9)}$ gives rise to a stable radical anion at −90°C reduction of **5** at slightly higher temperatures stereospecifically produces a cyclobutane species by an intramolecular [2+2] cycloaddition$^{5)}$.

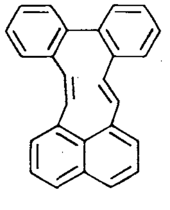
In the light of these results compounds **4** and **6** appeared to be suitable model systems; **4** possesses a central [13]perimeter and is closely related to the [11]perimeter system **1**. The acyclic analogue **6** can formally be derived from **4** by hydrogenolysis of the biphenyl single bond. The larger distance between the ethylene π systems in **4** and **6** compared to that in **1** is expected to prevent cyclobutane formation by intramolecular [2+2] cycloaddition. As an important consequence the corresponding ionic species, with intact molecular framework, should be susceptile to spectroscopic studies. We describe the synthesis of the yet unknown title systems **4** and **6** and their structural elucidation by X-ray analysis and NMR spectroscopy. Furthermore, the mono- and polycharged ions resulting from alkali metal reduction of **4** and **6** are studied by NMR and ESR spectroscopy. This work is part of a project concerning the redox behavior of linear and cyclic polyphenylenevinylenes$^{10,11)}$.

1. Results and Discussion

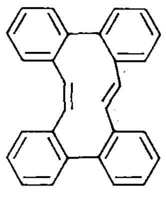
1.1. Synthesis

Our synthesis of **4** implies a twofold Wittig reaction between 2,2′-biphenyldicarbaldehyde (**7**)$^{12)}$ and the bisylide ob-

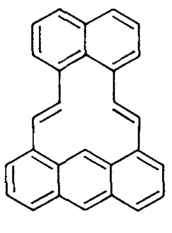
0009–2940/87/0909–1491 $ 02.50/0



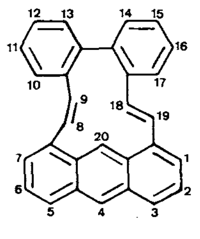
1



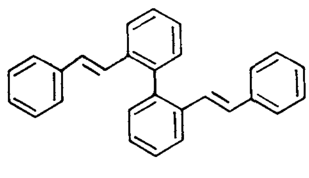
2



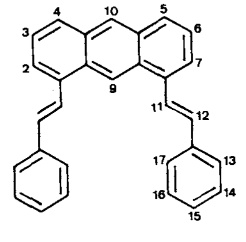
3



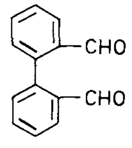
4



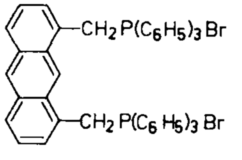
5



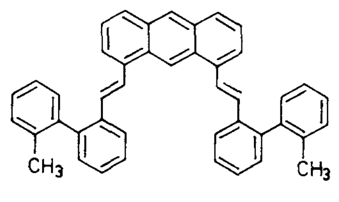
6



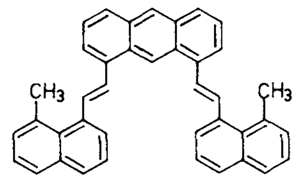
7



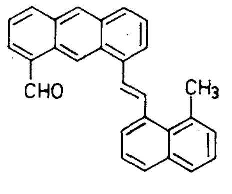
8



9



10



11

tained from [1,8-anthracenediylbis(methylene)]bis(triphenylphosphonium bromide) (**8**)[13]. Although the experimental conditions have been systematically varied the yield of the cyclization reaction does not exceed 10% which is similar to that obtained for the synthesis of **1**[1]. The choice of **7** and **8** as reaction partners is essential since the corresponding Wittig process involving 1,8-anthracenedicarbaldehyde provides compound **9**, while **4** is obtained in less than 1% yield. The model system **6** is prepared by a Wittig reaction from **8** and benzaldehyde in ethanol (lithium ethoxide, yield 79%). The photochemical behavior of **6** will be described elsewhere[14]. All attempts to synthesize the [12]perimeter system **3** from 1,8-anthracenedicarbaldehyde and [1,8-naphthalenediylbis(methylene)]bis(triphenylphosphonium bromide) failed. The only products identified are **10** and **11**. The failure to observe ring formation to **3** must be ascribed to the steric hindrance between the three internal hydrogen atoms of the macrocycle.

1.2. Crystal Structure of 4

In a formel sense **4** establishes a [13]perimeter fused with an anthracene unit and two benzene rings. Model considerations indicate that the perimeter should be far from planarity; crucial questions are how the central ring accommodates the high degree of strain and where the largest torsional angles are. It appears from our analysis of the crystal structure of **4** that there is both a *cis*-(C-8 – C-9) and a *trans*-(C-18 – C-19) configurated double bond, so that the molecule possesses only C_1 symmetry[15]. Moreover, the two phenyl rings of the biphenyl moiety are more or less orthogonal with respect to each other (angle C-13, C-13A, C-13B, C-14 106°) and the corresponding formal single bond (C-13A – C-13B: 1.50 Å) is rather long. The bond lengths of the other single bonds are about 1.47 Å, and the corresponding angles of torsion are smaller than 30° except angle C-19B, C-19A, C-19, C-18 which is 43°. It follows from the structural data that **4** can be described as a bent 1,8-distyrylanthracene with both a *cis*- and *trans*-double bond.

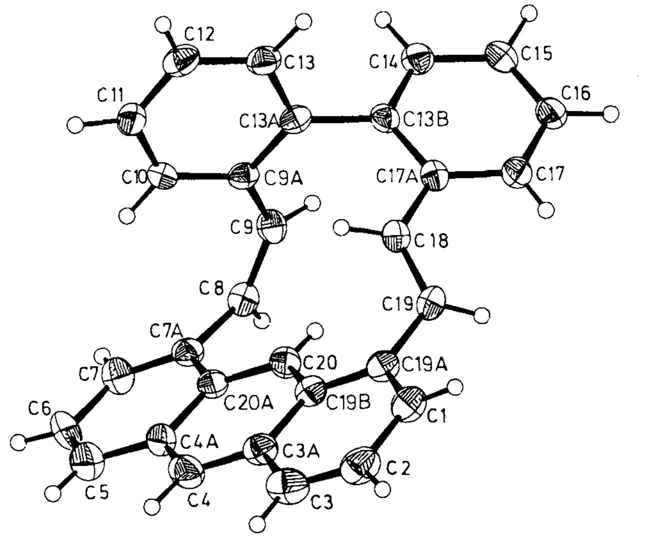


Figure 1. Molecular structure of **4**

Table. ^{1}H-NMR chemical shifts δ_H and vicinal coupling constants ^3J (Hz, in parentheses) of **4**, **6**, and **6**$^{4-}$/4Li$^+$ (see Experimental)

	2-H 7-H	3-H 6-H	4-H 5-H	9-H	10-H	11-H	12-H	13-H 17-H	14-H 16-H	15-H
δ_H (6)$^{b)}$	7.72 (7.5)	7.48 (7.5,8.5)	7.97 (8.5)	9.11	8.55	8.01 (16.0)	7.23 (16.0)	7.63 (7.5)	7.39 (7.5)	7.30 (7.5)
δ_H (6^{4-}/4Li$^+$)$^{c)}$	4.33 (7.3)	4.15 (7.9)	5.6-5.8	-5.39(s) and 5.6-5.8(m)		4.61 (11.0)	3.35 (11.0)	5.92 6.22	5.52 5.6-5.8	4.82
	1-H to 3-H, 5-H to 7-H 14-H to 17-H$^{a)}$			20-H	4-H	19-H	18-H	14'-H to 17'-H$^{a)}$		
δ_H (4)$^{d)}$	8.03 (7.3) (1H,d); 7.95 (1H,m); 7.85 (8.1) (1H,d); 7.5-7.6 (3H,m); 7.3-7.5 (4H,m);			9.32	8.30	7.38 (16.9)	6.60 (16.9)	7.13 (1H,d); 6.98 (1H, d); 6.77 (2H,m)		
						8-H and	9-H			
						6.87 (12.2)	6.81 (12.2)			

a) Assignments uncertain; b) $CDCl_3$, 400 MHz; c) [D_8]-THF, 200 MHz; d) CD_2Cl_2, 300 MHz.

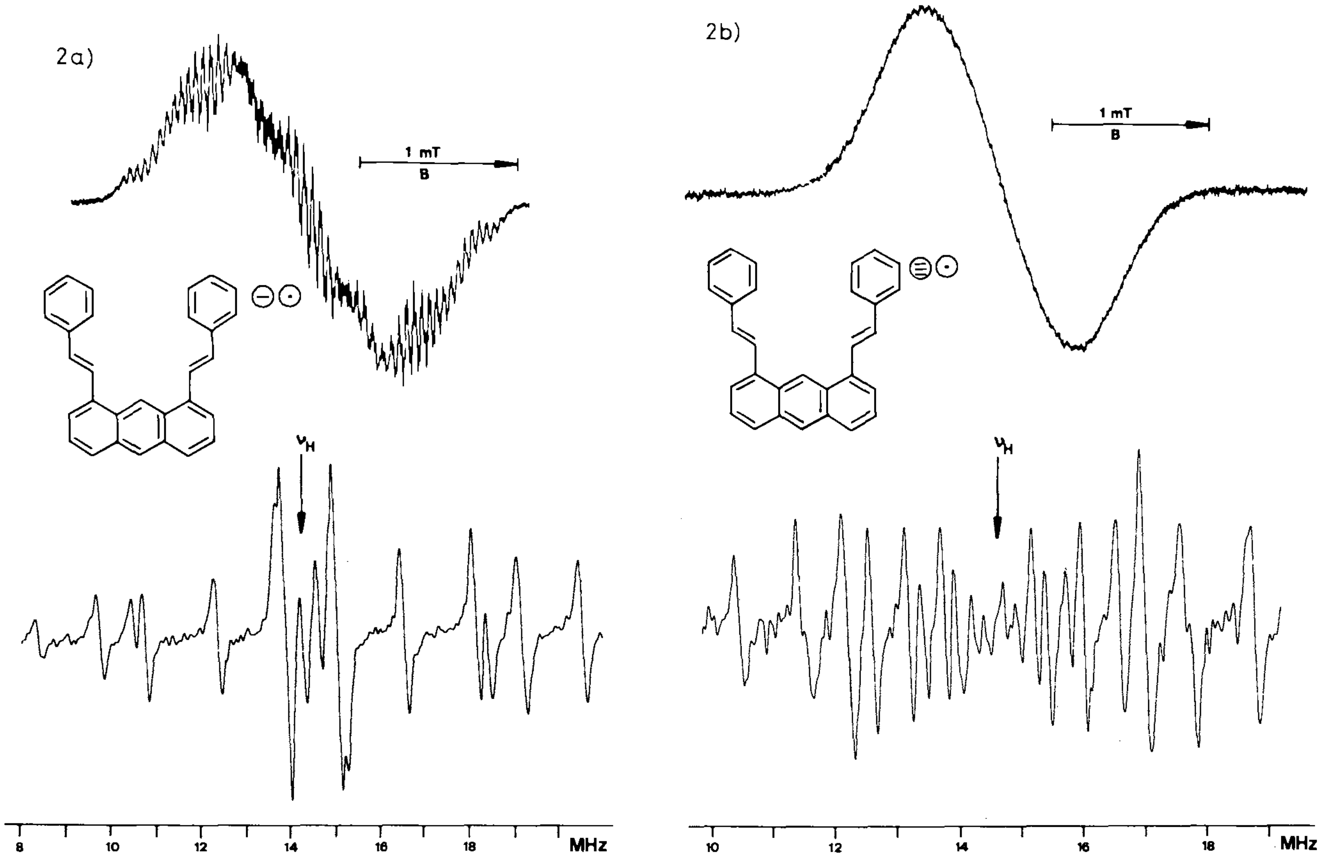


Figure 2. ESR and ENDOR spectra of a) the radical anion $6^{-\bullet}$/ K$^+$ and b) the radical trianion $6^{-\bullet}$/3K$^+$

1.3. Structures of 4 and 6 in Solution

The number of ^{13}C-NMR signals of **4** supports its C_1 symmetry. The assignments of the ^{1}H-NMR signals (see Table) follow from both H,H decoupling experiments and difference-NOE measurements. The vicinal coupling constants of the olefinic protons, $^3J_{8,9}$ = 12.2 and $^3J_{18,19}$ = 16.9 Hz, indicate a *cis*- and *trans*-double bond and are in accord with conclusions drawn from the crystal structure.

NOE experiments reveal that the anthracene proton resonating at δ 9.32 (singlet) must be close to 18-H and can therefore be identified as 20-H. The highfield absorption of 18-H, in spite of a potential van der Waals deshielding due to the interaction with 20-H, can be rationalized by the fact that it is located in the shielding region of the benzene unit at C-9A, C-13A. Conversely, 19-H (δ 7.38) is deshielded due to the influence of both the benzene moiety at C-13B, C-17A, and the anthracene ring. Finally, the highfield resonance lines of the protons of one benzene unit (10-H to 13-H) with respect to those of the neighboring one come from their position above the anthracene ring.

Two conclusions may be drawn from the ^{13}C-NMR spectrum of **6**: (i) unlike **4**, the molecule adopts a structure with an effective C_{2v} symmetry, and (ii) the rotation of the phenyl rings about the neighboring single bonds is rapid on the NMR time scale. The H,H coupling constant of the olefinic protons ${}^{3}J_{11,12} = 16.0$ Hz points toward a *trans* configuration of the double bonds. A difference-NOE measurement provides evidence that the anthracene proton resonating at δ 9.11 (singlet) is located close to the olefinic proton resonating at δ 8.01. While this finding allows an identification of the anthracene protons 9-H and 10-H, a differentiation of the olefinic protons 11-H and 12-H is less straightforward. In principle, **6** could exist in two conformations which interconvert by a rotation about the C-1 – C-11 (C-8 – C-11′) single bond. According to model considerations, however, the conformer, in which 11-H and 11′-H point toward each other (see formula), is much more favorable. Consequently, the signal at δ 8.01 can be assigned to 11-H (11′-H) and that at δ 7.23 to 12-H (12′-H). That 11-H (11′-H) absorb at rather low field may be caused by a nonbonded interaction between these hydrogen atoms and/or by the anisotropy of the anthracene π system.

1.4. The Chemical and Electrochemical Reduction of 4 and 6

The cyclic voltammograms of compounds **4** and **6** show a well defined wave at $E_{1/2} = -1.90$ and -1.75 V (vs SCE), respectively. Their shape is indicative of reversible one-electron transfers producing radical anion species which are stable for the duration of the experiment. The difference of the $E_{1/2}$ values observed for the isoelectronic compounds **4** and **6** may be ascribed to geometric factors, i.e. the strong deviation from planarity in compound **4** raises the LUMO energy[16].

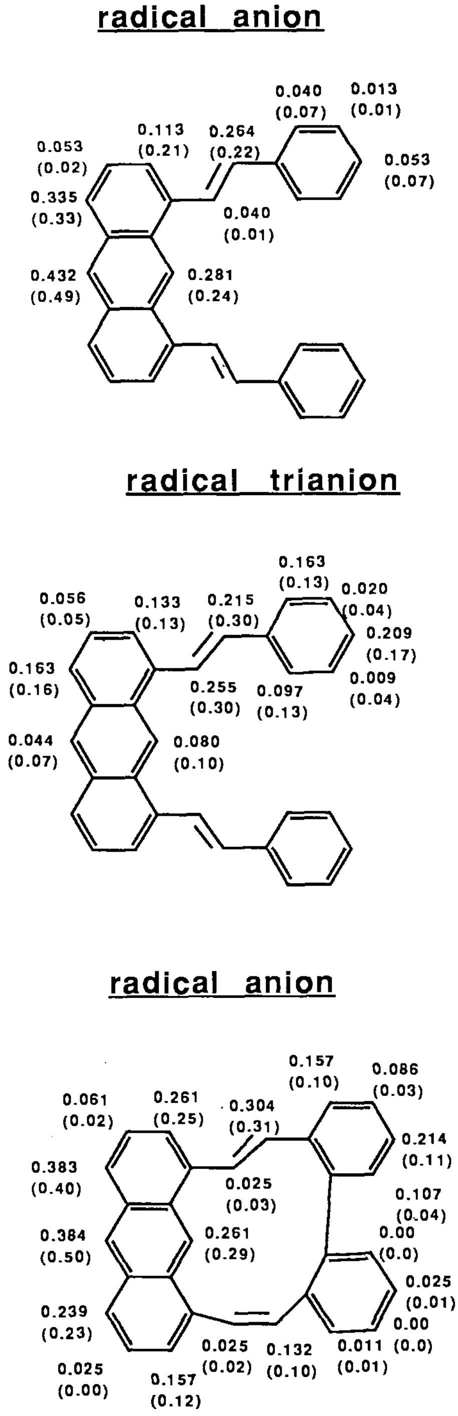
Within the potential range ($0\ \mathrm{V} \geq E \geq -2.4\ \mathrm{V}$) available the cyclic voltammograms of both compounds show a second cathodic wave placed at a potential 0.45 V (for **4**) and 0.35 V (for **6**) more negative from the first wave. The second waves could not be investigated properly because they fall into a potential range where the *i-E* characteristic is influenced by reactions of the medium. The slope and the intensity of the cathodic part of these waves seem to indicate the transfer of two electrons, a process which is irreversible under the given experimental conditions.

As expected from the cyclovoltammetric experiments brief contact of ethereal solutions of the neutral compounds **4** and **6** with a potassium mirror produces the radical anions $4^{-\bullet}$ and $6^{-\bullet}$, respectively. Both radical anions are persistent even at high temperatures ($T \geq 298$ K).

The relatively simple ESR and ENDOR spectra of the radical anion $6^{-\bullet}$ (potassium salt) are depicted in Figure 2a.

A simulation of the ESR spectrum with coupling constants taken from the ENDOR experiment yields the following hyperfine data (in mT): 0.432 (1 H), 0.335 (2 H), 0.281 (1 H), 0.264 (2 H), 0.113 (2 H), 0.053 (4 H), 0.040 (6 H), 0.013

Scheme 1. Experimental hyperfine coupling constants [mT] of the radical anions $4^{-\bullet}/\mathrm{K}^+$ and $6^{-\bullet}/\mathrm{K}^+$ as well as of the radical trianion $6^{-\bullet}/3\mathrm{K}^+$; calculated values are given in parenthesis



(4H) (see Scheme 1). The assignment of the two large one-proton coupling constants to the protons in the central positions (9-H, 10-H) of the anthracene moiety is straightforward. The distinction between these two positions and the assignment of the remaining coupling constants given in Figure 2a follow from a comparison of experimental and theoretical values which have been calculated by the HMO-McLachlan procedure[17] ($\beta = 1$) and the McConnell relationship[18]. Support for such an approach comes from the agreement between experimental and theoretical data for positions with large coupling constants. Although the small hyperfine couplings cannot be assigned reliably, the singly occupied MO can easily be identified as a divinylanthracene orbital with high spin density at C-9, C-10, and C-12.

The ESR and ENDOR spectrum of the radical anion $4^{-\bullet}(K^+)$ are given in Figure 3. Due to the C_1 symmetry of the molecular framework 20 different coupling constants a_H are expected. The ENDOR spectrum shows 14 pairs of lines indicating that some of the a_H values are degenerate. This expectation is fully borne out by the simulation of the ESR spectrum which yields the following hyperfine data (in mT): 0.383 (1H), 0.381 (1H), 0.304 (1H), 0.261 (2H), 0.239 (1H), 0.214 (1H), 0.157 (2H), 0.132 (1H), 0.107 (1H), 0.086 (1H), 0.061 (1H), 0.025 (4H), 0.011 (the number of protons possessing a coupling of 0.011 mT is not clear since this coupling constant is not resolved in the ESR spectrum) (see Scheme 1). In calculating the hyperfine coupling constants (see above), twisting of the π system is accounted for by estimating the resonance integral β from the cosine of the torsional angle[19] as determined from the crystal structure of **4**. There is not doubt that the singly occupied MO of $4^{-\bullet}$ must be similar to that of $6^{-\bullet}$. Nevertheless, the agreement between experimental and calculated hyperfine coupling constants is rather poor. This may be due to the fact that the variation of the individual resonance integrals in the bent macrocycle is not treated adequately in our simple approach. Additionally, because of the nonplanarity of the molecule, the σ/π separation breaks down. This allows for a direct spin transfer from the surrounding p_z orbitals into the 1s hydrogen orbital[20–22]. Since our MO treatment does not account for such a transfer mechanism, a quantitative agreement of experimental and calculated data cannot be expected. It is a characteristic finding, incidentally, that among the large experimental coupling constants one parameter cannot be reproduced by the calculation (see Figure 3). Deviations between experimental and calculated ESR hyperfine coupling constants have been reported for a large number of twisted π systems and are ascribed to the occurrence of a direct spin transfer.

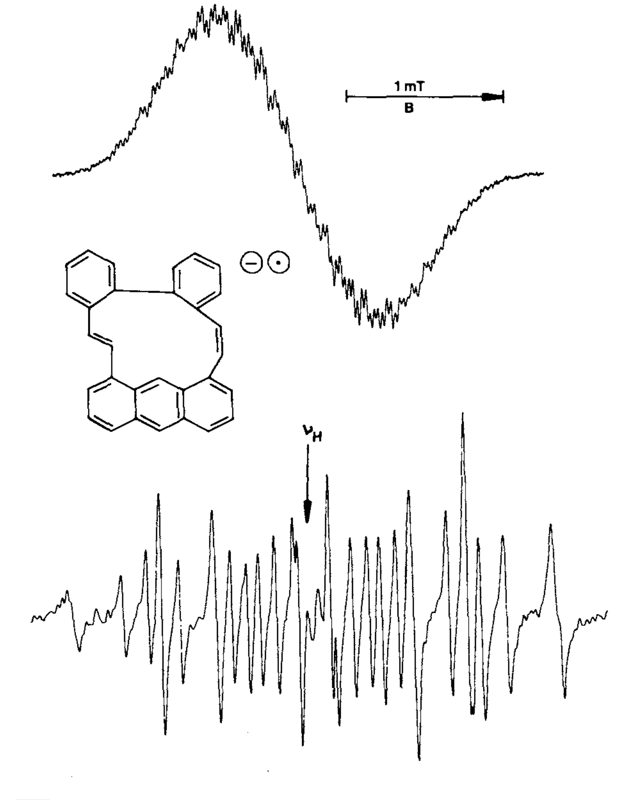


Figure 3. ESR and ENDOR spectra of the radical anion $4^{-\bullet}/K^+$

If a solution of $4^{-\bullet}$ is brought into further contact with potassium, the ESR signals of the radical anion merge into the base line. There is no indication from ESR spectroscopy for the formation of a secondary paramagnetic species. In the NMR spectroscopic control of the lithium reduction no signals are detected of a diamagnetic reduction product. Reoxidation with oxygen recovers only small amounts of the starting material. Obviously reduction of **4** beyond the radical anion stage causes decomposition.

Prolonged metal contact of a solution of $6^{-\bullet}$ gives rise to a broad ^{1}H-NMR absorption between $\delta = 6.2$ and 7.7 in addition to less intense signals at $\delta = 5.35$ and 5.85 which are tentatively assigned to the dianion salt $6^{2-}/2\,Li^+$. The ESR spectra taken at the same stage of reduction reveal that the signals of $6^{-\bullet}/K^+$ are slowly replaced by those of a second paramagnetic species. The presence of radical species throughout the reduction process explains why a highly resolved NMR spectrum of the dianion cannot be obtained. Thus the reduction of **6** differs from that of structurally related oligophenylenevinylenes[10,11,23]. In the latter case reduction of the radical anions to dianions produces highly resolved ^{1}H-NMR spectra. At the same reduction stage no ESR signal can be detected, and only further metal contact produces the ESR signals of a trianion radical[23]. The ENDOR spectrum of the secondary radical obtained upon reduction of **6** exhibits 11 pairs of lines. They are due to coupling constants of 0.255, 0.215, 0.209, 0.163, 0.133, 0.097, 0.056, 0.044, 0.02, and 0.009 mT (see Scheme 1 and Figure 2b). Due to the low resolution of the corresponding ESR spectrum the multiplicities of these coupling constants cannot be determined by a simulation of the ESR spectrum. From the width of the ESR signal, however, the multiplicities of coupling constants larger than 0.1 mT can be estimated. This estimation clearly indicates that the coupling constants of 0.255, 0.215, 0.209, and 0.133 mT must be assigned to two equivalent protons and the coupling constant of 0.163 mT to four equivalent protons. The higher multiplicity of the latter is also obvious from the ENDOR spectrum, in which the corresponding line is significantly more intense then the others. The agreement with values calculated for the radical trianion of **6** suggests that the secondary paramagnetic species detected is, indeed, $\mathbf{6}^{3-\bullet}$. This assignment is further supported by the existence of a stable tetraanion (see below). The experimental and theoretical hyperfine coupling constants of $\mathbf{6}^{3-\bullet}$ reveal an important difference between the mono- and trianion. In the latter case the singly occupied MO (with a nodal plane through C-9 and C-10) has small AO coefficients on the anthracene moiety, i.e. the spin density is essentially localized within the styryl units.

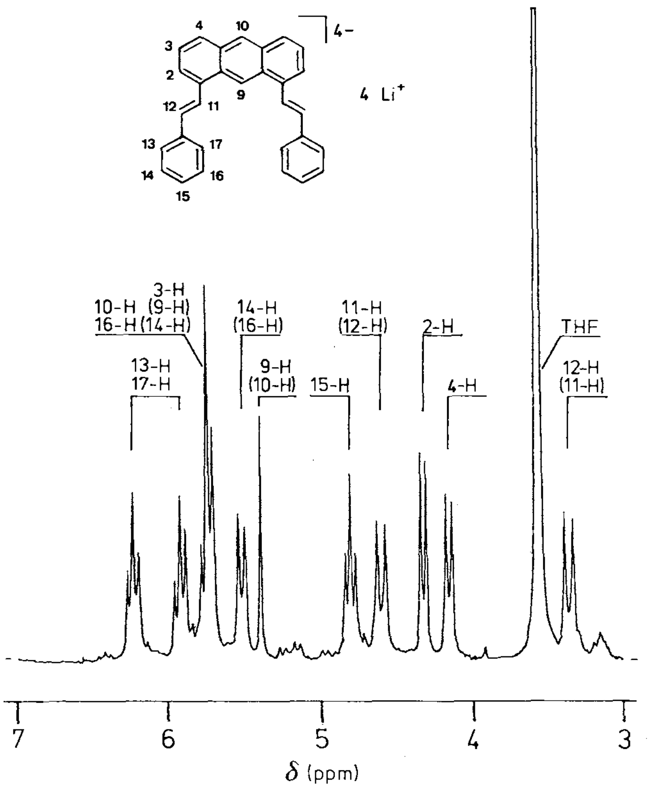


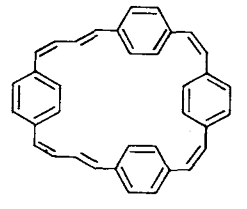
Figure 4. ^{1}H-NMR spectrum of the tetraanion $6^{-\bullet}/4Li^+$ ([D$_8$]THF, −40°C, 200 MHz)

Upon further reduction of the trianion solution the ^{1}H-NMR signals of a diamagnetic product grow out of the noise. The spectrum finally obtained (see Figure 4) leaves no doubt as to the intact framework of the ion. Quenching of the solution whith dimethyl sulfate gives a tetramethyl adduct as determined by MS analysis. This finding as well as the NMR and ESR spectroscopic monitoring of the successive electron transfers point toward the formation of tetraanion salts of $\mathbf{6}^{4-}$. Its spectroscopic characterization is given in the Table. Toward that end the Li salt has been studied instead of the K salt since the spectral resolution is better in the former case (see Figure 4). The signal assignments rest upon the splitting patterns and upon extensive H,H decoupling experiments.

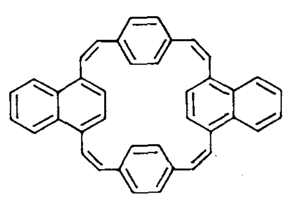
From the LUMO and NLUMO of **6** it is expected that the highest local π charge is located at C-12 of the olefinic unit. Not surprisingly, therefore, an olefinic proton suffers the strongest shielding and appears at highest field (δ 3.35, d). The vicinal H,H coupling constant ($^3J_{H,H}$ = 11.0 Hz) is much smaller than for the corresponding neutral compound ($^3J_{H,H}$ = 16.0 Hz). Reduction of related phenylenevinylene systems reveals the same trend[24,25]. This is not due to a configurational change but to a stronger π bond delocalization which decreases (increases) the π bond order of formal double (single) bonds. This conclusion is supported by the fact that the rotation of the phenyl groups of $\mathbf{6}^{4-}/4Li^+$ is slow on the NMR time scale.

2. Conclusion

We have shown recently that the reduction of phane-type oligoarylenevinylene macrocycles such as **12** or **13** produces stable dianions whose (4n + 2) π perimeter character can be detected by a strong diatropism[24,25]. Further reduction of such species even proceeds beyond the dianion stage. A potential cyclic conjugation in ions derived from **4** is inhibited by the appreciable strain which forces the phenyl rings of the biphenyl unit into a nearly orthogonal arrangement. Only the radical monoanion persists. On the other hand, "cleavage" of the biphenyl single bond upon going to the isoelectronic distyrylanthracene model compound **6** produces an efficient electron acceptor. The distance of the olefinic units is large enough to avoid both electron-transfer induced valence isomerizations and unfavorable electrostatic interactions in the resulting ions.



12



13

Experimental

^{1}H- and ^{13}C-NMR spectra: AC 200 ($\mathbf{6}^{4-}/4Li^+$), WM 300 (**4**), AM 400 (**6**). – ESR and ENDOR spectra: Bruker ESP 300 spectrometer system. – Cyclovoltammetry: Metrohm VA-scanner E612, Polarocord E 506. – MS: Varian MAT CH 7A with data system AMD Intectra DP 10. – Melting points are not corrected.

Crystal Structure Analysis of **4**[15,26]: The data were collected on an automatic diffractometer (Enraf-Nonius CAD4, Mo-K_α radiation, graphite monochromator, ω-2θ scanning). The solution of the structure with direct methods and refinement in full matrix technique were carried out with the Enraf-Nonius SDP program system.

The *Wittig reactions* were performed under argon in a three-necked round-bottomed flask equipped with magnetic stirring, gas-inlet tube, and dropping-funnel. The solvents were dried according to standard procedures. The bases were freshly prepared from alcohol and alkali metal.

1,2,3,4,5-[1′,8′]Anthra-8,9;10,11-dibenzo[13]annulene (**4**): Lithium (20 mg, 2.9 mmol) was dissolved in 5 ml of dry methanol and the solvent removed under reduced pressure. The base was dissolved in 50 ml of dry dimethylformamide (DMF) and the solution was added dropwise to a solution of 2,2′-biphenyldicarbaldehyde

(**7**) (210 mg, 1.0 mmol)[12] and [1,8-anthracenediylbis(methylene)]-bis(triphenylphosphonium bromide) (**8**)[13] (890 mg, 1.0 mmol) in 100 ml of dry DMF under argon over a period of 24 h. The reaction mixture was stirred at room temp. for 4 d and poured into 600 ml of ice/water containing 20 ml of conc. hydrochloric acid. The mixture was extracted with ether, and the organic layer dried with magnesium sulfate. The residue obtained after evaporation of the solvent was chromatographed on silica gel (10 cm × 2 cm; hexane/chloroform, 20 : 1). After recrystallization from hexane 38 mg of pure **4** (10%) was obtained, mp. 171 – 172°C (yellow needles). – ^{1}H NMR (300 MHz, CD_2Cl_2): Table. – ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 141.6 (q); 140.9 (q); 138.6 (t); 138.5 (q); 137.6 (q); 136.3 (q); 133.7 (t); 132.9 (q); 132.1 (q); 131.1 (q); 130.6 (q); 129.5 (t); 129.4 (t); 128.5 (t); 128.4 (q); 128.3 (t); 128.0 (t); 127.4 (t); 127.1 (t); 127.0 (t); 126.8 (t); 125.9 (t); 125.5 (t); 125.3 (t); 124.8 (t); 123.7 (t); 123.3 (t). – MS (70 eV): *m/z* (%) = 380 (100, $M^{+\bullet}$), 215 (95, $M^{+\bullet} - C_{12}H_8$). – UV (cyclohexane): λ = 254 nm (ε = 75280), 388 (8330). – Exact mass calcd. for $C_{30}H_{20}$ 380.1565, found 380.1561.

Attempted Synthesis of **4**: 1,8-Anthracenedicarbaldehyde (300 mg, 1.29 mmol)[27] and [2,2′-biphenyldiylbis(methylene)]bis(triphenylphosphonium bromide)[28] (1110 mg, 1.29 mmol) were treated as described above. Chromatography over silica gel (10 cm × 2 cm, hexane/tetrachloromethane, 6 : 1) gave a mixture of **4** and **9** which was separated by preparative TLC (silica gel, hexane/tetrachloromethane, 6 : 1). The first fraction gave 2 mg of **4** (0.4%), the second fraction gave 60 mg of **9** (8%) which was recrystallized from hexane.

9: M.p. 161 – 162°C (yellow needles). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 6H, CH_3), 8.30 and 8.87 (s, 1H each, 9- and 10-H anthracene), 6.85 (d, 2H, *J* = 15.0 Hz, A-part of the AB spin system of the olefine double bonds), 7.10 – 8.0 (m, 24H). – UV (cyclohexane): λ = 262 nm (ε = 99100), 325 (12200), 396 (14600). – MS (70 eV): *m/z* (%) = 562 (100, $M^{+\bullet}$), 205 (23), 191 (25), 179 (72), 165 (25), 152 (5); exact mass calcd. for $C_{44}H_{34}$ 562.2621, found 562.2668.

1,8-Distyrylanthracene (**6**): A solution of **8** (450 mg, 0.50 mmol) and benzaldehyde (200 mg, 1.89 mmol) in 80 ml of dry ethanol was added dropwise to 20 ml of an ethanolic solution of lithium ethoxide [prepared from 50 mg (7.1 mmol) of lithium] over a period of 2 h and the stirring was continued for 1 h. The solvent was removed under reduced pressure and the remaining residue filtered over silica gel (10 cm × 4 cm, petroleum ether/dichloromethane, 10 : 1). Evaporation of the solvent and recrystallization from tetrachloromethane gave 152 mg (79.5%) of **6**, m.p. 195°C (yellow needles). – ^{1}H-NMR (400 MHz, $CDCl_3$): Table. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7; 135.6; 132.2; 131.9; 130.0; 128.8; 128.1; 127.9; 127.5; 126.7; 126.1; 125.4; 123.5; 119.1. – UV (CH_2Cl_2): λ = 259 nm (ε = 144300), 325 (11700), 399 (15200). – MS (70 eV): *m/z* (%) = 382 (100, $M^{+\bullet}$), 291 (17, $M^{+\bullet} - C_7H_7$).

$C_{30}H_{22}$ (382.0) Calcd. C 94.24 H 5.76 Found C 94.08 H 5.79

The reduction of **4** and **6** with lithium and potassium as well as the NMR spectroscopic characterization of the diamagnetic products were performed as described elsewhere[24].

Compound **4** (4 mg) in 0.5 ml of [D$_8$]THF was allowed to get into contact with active lithium within a sealed NMR tube at −78°C. Upon metal contact the color of the solution turned to grey-green and, after 1 d, to brown. The ^{1}H-NMR signals of the starting compound disappeared rapidly; however, even after prolonged metal contact the brown solution did not give rise to signals of a diamagnetic product. Reoxidation with oxygen gave small amounts of the starting compound and decomposition products.

Compound **6** (5 mg) in 0.5 ml [D$_8$]THF was reduced with lithium as described above. Upon metal contact the color of the solution turned to blue, green and then brown, The ^{1}H-NMR signals of **6** disappeared. However, after 10 min of metal contact a broad, poorly resolved signal between δ = 6.2 and 7.7 (maxima at δ = 6.3, 6.45, 6.55, 6.80, and 6.95) was recorded (200 MHz, −50°C) in addition to less intense signals at δ = 5.35 and 5.85. Further reduction (2 min) broadened these signals into the noise. After two weeks of metal contact the brown solution gave rise to the well resolved ^{1}H-NMR signals of $\mathbf{6}^{4-}/4\,Li^+$ discussed above. Breaking off the tube under argon and addition of an excess of freshly distilled dimethyl sulfate caused an immediate change of the color from brown to yellow. Evaporation of the solvent under reduced pressure and filtration of the residue over aluminium oxide afforded a mixture of methyl adducts. The mass spectrum [*m/z* (%) = 442 (16, starting compound + $4\,CH_3$), 412 (8%), 397 (10%)] indicated the formation of a tetramethyl derivative.

CAS Registry Numbers

4: 108816-42-8 / $\mathbf{4}^{-\bullet}/K^+$: 108867-38-5 / **6**: 108816-44-0 / $\mathbf{6}^{-\bullet}/K^+$: 108867-39-6 / $\mathbf{6}^{3-\bullet}/3\,K^+$: 108816-46-2 / $\mathbf{6}^{4-}/4\,Li^+$: 108816-45-1 / **7**: 1210-05-5 / **8**: 34824-23-2 / **9**: 108816-43-9 / benzaldehyde: 100-52-7 / 1,8-anthracenedicarbaldehyde: 34824-75-4 / [2,2′-biphenyldiyl-bis(methylene)]bis(triphenylphosphonium bromide): 4283-98-1

---

[1] R. H. Mitchell, F. Sondheimer, *Tetrahedron Lett.* **1968**, 2873.

[2] P. R. Houlton, W. Kemp, *Tetrahedron Lett.* **1968**, 1045.

[3] K. Grohmann, P. D. Howes, A. Monahan, R. H. Mitchell, F. Sondheimer, *J. Org. Chem.* **38** (1973) 808.

[4] G. Wittig, G. Skipka, *Liebigs Ann. Chem.* **1975**, 1157.

[5] K. Müllen, W. Huber, *Helv. Chim. Acta* **61** (1978) 1310.

[6] F. Gerson, W. Huber, K. Müllen, *Angew. Chem.* **90** (1978) 216; *Angew. Chem. Int. Ed. Engl.* **17** (1978) 208.

[7] K. Müllen, *Pure Appl. Chem.* **58** (1986) 177.

[8] W. H. Laarhoven, Th. J. H. M. Cuppen, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2074.

[9] C. D. Tulloch, W. Kemp, *J. Chem. Soc. C*, **1971**, 2824.

[10] W. Huber, K. Müllen, *Acc. Chem. Res.* **19** (1986) 300.

[11] J. Heinze, J. Mortensen, K. Müllen, R. Schenk, *J. Chem. Soc., Chem. Commun.* **1987**, 701.

[12] P. S. Bailey, R. E. Erickson, *Org. Synth.* **41** (1961) 41.

[13] S. Akiyama, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **44** (1971) 3158.

[14] E. Prass, K.-U. Klabunde, H. Meier, K. Müllen, to be published.

[15] Crystal data for **4**: $C_{30}H_{20}$, M = 380.49, orthorhombic, *Pbca* (No. 61), a = 7.592(2), b = 21.485(4), c = 24.071(4) Å, V = 3926.3 Å^3, Z = 8, D(calcd.) = 1.287 g cm^{-3}, μ(Mo-K_α) = 0.678 cm^{-1}. After data reduction of 4272 unique reflections 1520 reflections with $I > 2\,\sigma(I)$ were taken as observed. Final residuals R = 0.055, R_w = 0.059. The highest peak in the final difference Fournier map was 0.21 $e \cdot$ Å^{-3}.

[16] G. Cauquis in: M. M. Baizer, H. Lund (Eds.), *Organic Electrochemistry*, p. 65, Marcel Dekker, New York 1983.

[17] A. D. McLachlan, *Mol. Phys.* **3** (1966) 233.

[18] H. M. McConnell, *J. Chem. Phys.* **24** (1956) 632.

[19] E. Heilbronner, H. Bock, *Das HMO-Modell und seine Anwendung, Grundlagen und Handhabung*, 2nd edition, p. 135, Verlag Chemie, Weinheim, New York 1987.

[20] F. Gerson, K. Müllen, E. Vogel, *J. Am. Chem. Soc.* **94** (1972) 2924; F. Gerson, K. Müllen, C. Wydler, *Helv. Chim. Acta* **59** (1976) 1357.

[21] K. Müllen, *Helv. Chim. Acta* **57** (1974) 2399.

[22] W. Huber, *Helv. Chim. Acta* **67** (1984) 625.

[23] W. Huber, R. Schenk, K. Müllen, to be published.

[24] D. Tanner, O. Wennerström, U. Norinder, K. Müllen, R. Trinks, *Tetrahedron* **42** (1986) 4499.

[25] W. Huber, K. Müllen, O. Wennerström, *Angew. Chem.* **92** (1980) 636; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 624.

[26] Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (W. Germany), by specifying registry number CSD 52357, author, and the reference to this publication.

[27] S. Akiyama, S. Misumi, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **35** (1962) 1829.

[28] D. M. Hall, B. Prakobsantisuk, *J. Chem. Soc.* **1965**, 6311; H. J. Bestmann, W. Häberlein, H. Wagener, O. Kratzer, *Chem. Ber.* **99** (1966) 2848; E. D. Bergmann, P. Bracha, I. Agranat, M. A. Kraus, *J. Chem. Soc. C*, **1967**, 328.

[81/87]