

Charged paracyclophanes behave as annulenes with enhanced anisotropy

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Paracyclophanes, in which benzene units are linked at the 1,4 positions by ethylene bridges (**1–4**), show annulene characteristics upon charging. The dependence of the magnetic properties of these charged rigid systems on the number of π -electrons in the peripheries has been studied systematically. For the first time it can be shown that upon extensive reduction, **two** observable diatropic anionic stages exist (for **3**). The results of advanced DFT calculations are in line with the experimental results.

The limit on the number of π -electrons in the periphery of annulenes, which still exhibit aromatic or anti-aromatic behavior, is extended far beyond the number of 26.

Introduction

A direct consequence of the simple topology of annulenes is that, due to their orbital energies, they appear as closed shell systems and the resulting orbital sequence exhibits characteristic regularities.¹ In even-membered rings, the orbitals appear as degenerate pairs (except for the energetically lowest and highest orbitals, which are both non-degenerate), thus $[4n + 2]$ π -systems are characterized by stable closed shell ground states. Bond length alternation, according to a Jahn–Teller distortion, may also lead to closed shell ground states in the $[4n]$ annulene series.² The number of π -electrons involved in a conjugated monocycle influences the HOMO–LUMO gap; this may lead to electronic states that are close to one another. A basic property of aromatic systems is the NMR ring current which is considered as the magnetic criterion for aromaticity.^{2,3} Within the homologous series of annulenes, the measurable ring current effect usually decreases with ring size, due to the increasing tendency towards bond fixation.³ It is generally accepted that the alternating effect predicted by Hückel's rule is greatly diminished in large π -conjugated monocyclic systems (*e.g.* annulenes) when the ring size exceeds 22–26 carbon atoms.⁴ Although the Hückel theory is on its strongest ground when applied to neutral alternant hydrocarbons, the same description of the orbital scheme is valid for charged π -conjugated systems.⁵ The reduction of annulenes with alkali metals allows an alternating conversion from $[4n]$ to $[4n + 2]$ π -systems to occur with no change in the annulene backbone. Thus, this serves as a good model for studying aromaticity and anti-aromaticity, both theoretically and spectroscopically.^{6–9}

Cyclophanes, in which the aromatic units are linked at the 1,4 positions by unsaturated bridges, have been studied extensively.¹⁰ It has been previously reported that *cis*-stereoselective multiple Wittig reactions provide convenient access to $[2_4]$ cyclophanetetraene (**1**), and the application of this one-pot synthesis to macrocycles has been well demonstrated by Wennerström *et al.*¹¹ In certain types of conformation of small-sized cyclophanes, the central cavities may be of appropriate dimensions to allow host–guest inclusion complexes with small substrates.

On the other hand, the unsubstituted cyclophanes provide a playground for the study of the aromaticity of annulenes. In this paper, we report the procedure of and the effects connected with the charging of the systems **1–4**. $[2.2.2.2]$ Paracyclophane-

1,9,17,25-tetraene (**1**), $[2.2.0.2.2.0]$ paracyclophane-1,9,23,31-tetraene (**2**), $[2.2.0.0.2.2.0.0]$ paracyclophane-1,9,29,37-tetraene (**3**), and $[2.0.2.0.2.0.2.0]$ paracyclophane-1,15,29,43-tetraene (**4**) are cyclophanes that were synthesized *via* multiple Wittig reactions. Due to the benzene units, these systems behave as rigid annulenes, with well-defined ring configurations. The neutral cyclophanes, which formally have $4n$ π -electrons in the periphery (24, 32, 40, and 40, respectively), can be regarded as normal aromatic compounds, with no significant contributions from the large π -conjugated perimeter. The addition of benzene units to the annulene skeleton enables higher reduction stages relative to a typical annulene (polyene). Semi-empirical calculations assume fairly planar π -systems in the charged forms of these annulenes,¹² hence the reduced systems are expected to have a more efficiently conjugated π -system, compared with the neutral systems. It follows that the reduction is accompanied by a considerable geometrical change, as well as by an increased barrier to rotation of the benzene rings around the formal single bonds. Such stable large cyclic anions, with a fairly planar conjugated π -system, are expected to have unusual magnetic properties.¹³

Results and discussion

The preliminary quantum chemical calculations on **1**, **2**, **3**, and **4** and their anions revealed a number of interesting properties of the studied systems (for computational details see the Experimental section).

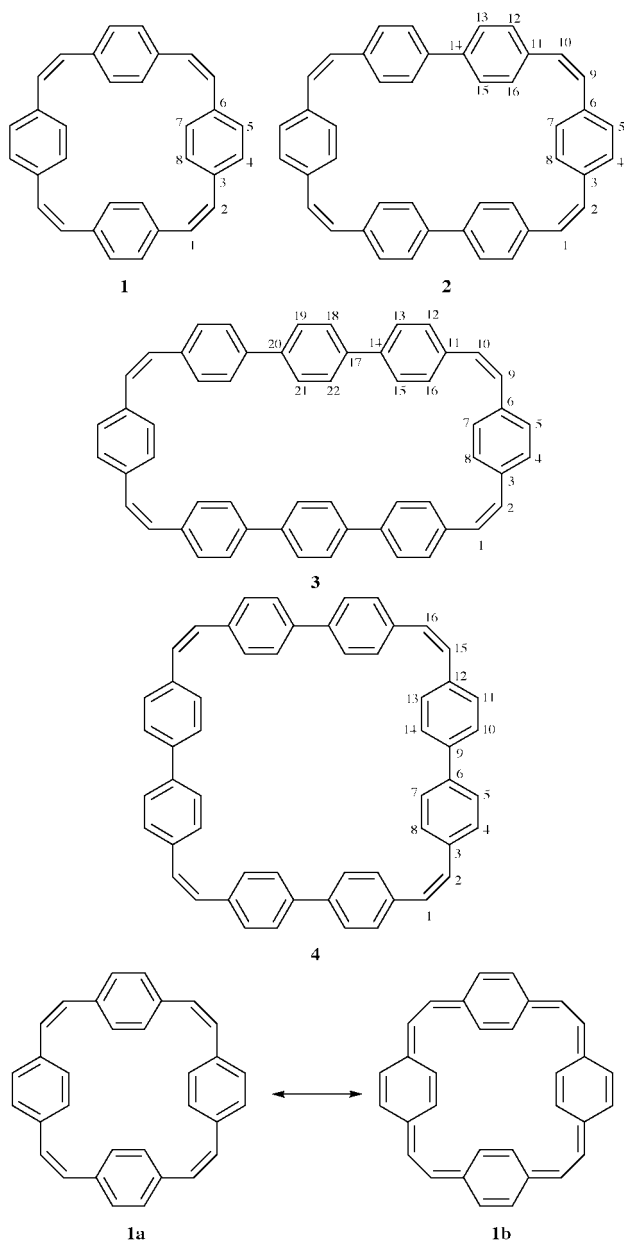
For the neutral systems, comparatively large deviations from planarity have been found (see Table 1 for geometrical data on the extent of nonplanarity), **1** and **4** refer to S_4 structures, whereas **2** is characterized by a C_2 and **3** by a C_{2h} structure (closed shell singlet states). Thus, the uncharged species can be regarded as combinations of normal aromatic six-membered rings which are linked in the 1,4-positions by olefinic double bonds.

The computed ¹H NMR chemical shifts (see Table 2) show good agreement with the values for benzene rings and olefinic fragments, respectively; no clear differentiation between inner and outer protons attached to carbon atoms of the six-membered rings could be made. Thus, a significant influence of the extended conjugated perimeter has not been found.

Table 1 Selected dihedral angles as measures for the nonplanarity of the neutral and the charged species of **1**, **2**, **3**, and **4**, stated as singlet state/triplet state. B3LYP/3-21G//B3LYP/3-21G (closed shell states), UB3LYP/3-21G//UB3LYP/3-21G (open shell states) [values in brackets: B3LYP/6-31G//B3LYP/6-31G* (closed shell states), UB3LYP/6-31G*//UB3LYP/6-31G* (open shell states)]

	1			2			3			4	
	1-2-3-8	1-2-3-8	9-10-11-16	1-2-3-8	9-10-11-16	15-14-17-22	1-2-3-8	16-15-12-13			
Neutral	31.8/—	45.0/—	−35.7/—	0.4/—	59.9/—	−41.4/—	36.6/73.2	−36.6/−33.8			
Dianion	17.6/24.4	5.6/7.4	27.4/33.2	6.7/6.0	27.9/29.8	−24.3/−33.0	20.6/19.1	−20.6/−31.7			
Tetraanion	21.3/15.2	4.6/4.1	29.5/21.5	4.2/6.3	19.8/21.1	−24.6/−16.1	19.3/17.6	−12.2/−14.0			
Pentaanion (doublet)	—	—	—	4.7 [4.7]	18.4 [18.0]	−16.5 [−15.6]	15.7 [15.3]	−11.7 [−11.7]			
Hexaanion	12.5/15.4	2.8/−3.4	17.4/12.9	5.5/3.7 [5.4]/—	15.2/12.5 [14.8]/—	10.6/17.9 [13.2]/—	12.1/10.2 [12.1]/—	−12.1/−10.3 [−12.1]/—			

“—” = structure not investigated. For numbering see formula schemes.



As expected, upon charging of the molecules the deviation of the optimized geometries from planarity decreases with increasing negative charge (see Table 1).

Comparing the total energies E_{tot} and the energy differences of the closed shell singlet states of all charging stages of **1**, **2**, **3**, and **4** (summarized in Table 3) reveals that 3^{2-} and 4^{2-} are degenerate with the reference parent neutral molecules **3** and **4**. For systems **1** and **2**, the dianions are only slightly higher in

energy than the neutral compounds;¹⁴ nonetheless, 1^{2-} and **1**, as well as 2^{2-} and **2**, can be referred to as being energetically very close if compared with the differences in energy between the relevant di- and tetraanions.

These similarities in total energy between the neutral and the twofold negatively charged **1**, **2**, **3**, and **4** clearly point to the aromatic character of the dianions. The latter can be regarded as having the Hückel numbers of 26 (1^{2-}), 34 (2^{2-}), or 42 π -electrons (3^{2-} and 4^{2-}) in their outer perimeters (where actually most of the negative charge is located). The aromatic character of the dianions also becomes evident from the calculated ^1H NMR chemical shifts (Table 2): the inner protons attached to carbon atoms within the six-membered rings are shifted upfield. In contrast, both the associated outer protons and the protons attached to carbon atoms of the olefinic double bonds are shifted downfield. Moreover, there is no substantial difference in the values of the chemical shifts for the outer protons of the last two types. This is a proof of the establishment of an outer π -conjugated ring of annulene type.

For the tetraanions, the inner protons are shifted downfield in the ^1H NMR spectra, whereas the outer protons (again, no substantial differences in the values for both types) are shifted upfield. This ‘sequential inversion’, compared with the ordering of the values for the dianions, points to the anti-aromatic character of the tetraanions which have 28 (1^{4-}), 36 (2^{4-}) or 44 (3^{4-} and 4^{4-}) π -electrons in the outer perimeter, respectively. A similar and further ‘sequential inversion’ has been found upon adding two more electrons, resulting in the hexaanion of either molecule with aromatic characteristics.

Two more properties typical of anti-aromatic systems have additionally been found for the tetraanions of each molecule:

First, very small singlet–triplet splittings have been computed. For 1^{4-} , 2^{4-} , and 3^{4-} these splittings amount to only 2.9, 2.8, and 5.8 kcal mol^{−1} in favor of the closed shell singlet states; for 4^{4-} even a triplet ground state has been found to be 1.8 kcal mol^{−1} more stable than the closed shell singlet state. In contrast, the triplet state is significantly higher in energy than the closed shell singlet state (by 36.4 kcal mol^{−1}) for uncharged **4** (being a combination of aromatic fragments bridged by formal double bonds). A similar finding applies for the hexaanions of either system (aromatic as a whole); the splittings amount to 17.7, 15.0, 12.2, and 11.3 kcal mol^{−1} for 1^{6-} , 2^{6-} , 3^{6-} , and 4^{6-} , respectively, all in favor of the closed shell singlet states.¹⁵

Second, the above described triplet states of the anti-aromatic systems 1^{4-} and 4^{4-} refer to highly symmetrical S_4 structures, the SOMOs are thus degenerate. The closed shell singlet states of the mentioned systems prevent this degeneration by undergoing Jahn–Teller distortion; their structures are characterized by only D_2 (1^{4-}) and C_2 (4^{4-}) symmetry.

The findings described above are particularly remarkable for the anions of **2**, **3** and **4**. Here, the applicability of the terms ‘aromatic’ and ‘anti-aromatic’ could clearly be extended to larger annulenes with considerably more than 26 π -electrons,

Table 2 Calculated ranges for the ^1H NMR chemical shifts (RHF/3-21G//B3LYP/3-21G) for the neutral and the charged species of **1**, **2**, **3** and **4** (closed shell singlet states) in ppm. 'Inner H' and 'outer H' refer to protons attached to carbon atoms of the six-membered rings, 'olefinic H' refers to protons attached to carbon atoms of the olefinic fragments

	1			2			3			4		
	Inner H	Outer H	Olefinic H	Inner H	Outer H	Olefinic H	Inner H	Outer H	Olefinic H	Inner H	Outer H	Olefinic H
Neutral	7.9	7.1	6.4	7.2-7.8	7.2-8.1	6.5-6.7	7.5-7.8	7.1-7.6	6.4-6.8	7.2-7.6	7.3-7.6	6.7
Dianion	-9.6	9.4	9.8	-10.4-4.4	9.3-11.0	10.4-11.1	-7.1-2.1	8.8-12.0	9.8-10.5	-8.7-5.5	10.8-12.3	11.4-11.5
Tetraanion	11.0-12.9	2.3-3.1	0.3	10.4-12.0	2.5-5.3	0.4-2.3	7.6-8.7	4.1-6.0	2.3-3.7	10.2-12.7	3.1-4.9	0.7-2.7
Hexaanion	-14.1	8.0	7.4	-18.5-12.1	9.9-11.1	10.5-10.7	-20.5-10.5	11.3-12.8	12.0-13.0	-19.4-15.7	12.9-14.4	13.1

which has previously been regarded as the upper limit for an application of the Hückel rule.

[2.2.2.2]Paracyclophane-1,9,17,25-tetraene (**1**) was first synthesized by Wennerström *et al.*¹⁶ The neutral system has 24 π -electrons in the periphery. The small contribution of the Kekulé structure **1b** to the hybrid is demonstrated by the measured proton chemical shifts of this molecule which are typical of benzene rings (7.55 ppm) and a double bond (6.38 ppm) with no significant contribution from the large conjugated perimeter. The X-ray structure of **1** shows that the olefinic fragments are arranged nearly co-planar, the individual six-membered rings are tilted towards this main molecular plane by angles in the range between 27 and 40°. The geometries of the cyclophanes are determined by the balance between the resonance energy available due to delocalization of the π -electrons, and the steric interaction which avoids planarity. Due to the tilt of the benzene rings, the UV-vis spectrum of **1** ($\lambda_{\text{max}} = 304$ nm) resembles more the stilbene unit ($\lambda_{\text{max}} = 295$ nm) than the linear analogues (triphenylenevinylene [$\lambda_{\text{max}} = 355$ nm], tetraphenylenevinylene [$\lambda_{\text{max}} = 385$ nm] and pentaphenylenevinylene [$\lambda_{\text{max}} = 386$ nm]).¹⁸ In solution the benzene rings rotate rapidly on the NMR time scale, thus exchanging inner and outer protons already at -60 °C. Accordingly, the energy needed to overcome the steric interaction and to compensate the decrease in resonance energy in the unsubstituted cyclophane is rather low (<5 kcal mol⁻¹).

The quantum-chemical calculation of **1** points to a low-lying LUMO (-0.0712 a.u.) and two degenerate NLUMOs (= LUMO + 1) (-0.0381 a.u.). The reduction of **1** with lithium yielded stable di- and tetraanions¹⁹ that showed a pronounced anisotropic effect. The reduction with lithium was repeated and compared with the behavior upon reduction with potassium. The dianion of **1**, with the more reductive metal *i.e.* potassium, appears immediately after a short contact with the metal. Further reduction of **1**²⁻ with potassium led to the formation of the tetraanion only after a long period of time (four weeks). This tetraanion shows a very weak, broad, and temperature dependent ^1H NMR spectrum whereas no ^{13}C NMR spectrum could be recorded. The ^1H and ^{13}C NMR spectra of the anions of **1**, both with lithium and potassium as counter ions (**1**⁴⁻/4Li⁺, **1**⁴⁻/4K⁺), are similar with only minor differences in chemical shifts and temperature dependence (Table 4).

[2.2.0.2.2.0]Paracyclophane-1,9,23,31-tetraene (**2**) was first synthesized and characterized by Wennerström *et al.*^{11a} The ^1H and ^{13}C NMR spectra of the neutral cyclophane, which formally has 32 π -electrons ($4n$) in the perimeter, again point to insignificant contributions of the large conjugated perimeter to the chemical shifts.²⁰ As the result of a lower symmetry relative to **1**, the quantum-chemical calculations predicted a set of non-degenerate LUMO and NLUMO (-0.0655 and -0.0487 a.u., respectively), thus annulene **2** is expected to yield stable di- and tetraanions upon reduction.

Annulene **2** was reduced with both lithium and potassium. Careful contact with lithium metal at low temperature (195 K) led to a color change of the solution to violet at which point a new temperature dependent ^1H NMR spectrum could be recorded (Fig. 1). The dianion, **2**²⁻/2Li⁺, possesses $4n + 2$ π -electrons (34) and should therefore exist as a diatropic species. Due to a strong diatropic ring current the inner protons are shifted to a higher field (up to -3.4 ppm), whereas the opposite effect appears to control the peripheral protons (up to 8.0 ppm). Further contact of **2**²⁻ with lithium metal did not yield the expected tetraanion. Even after a prolonged period of time the stable dianion was the only species in solution. Quenching the dianion with oxygen yielded the starting material as the only product thus indicating that no other chemical reaction (like rearrangements or decompositions) had taken place during the reduction.

The reduction of **2** with potassium, however, progressed differently. In the first stage, the solution changed color to violet

Table 3 Total energies E_{tot} for the singlet states and selected doublet and triplet states of the neutral and the charged species of **1**, **2**, **3**, and **4**; singlet–triplet splittings $\Delta E_{\text{S-T}} = E_{\text{tot}}(\text{S}) - E_{\text{tot}}(\text{T})$ where applicable, B3LYP/3-21G//B3LYP/3-21G (closed shell states), UB3LYP/3-21G//UB3LYP/3-21G (open shell states) [values in brackets: B3LYP/6-31G*/B3LYP/6-31G* (closed shell states), UB3LYP/6-31G*/UB3LYP/6-31G* (open shell states)]. Symmetry point groups as stated after the state term

	E_{tot} (a.u.)			$\Delta E_{\text{S-T}}/\text{kcal mol}^{-1}$
	Singlet state	Doublet state	Triplet state	
1				
Neutral	${}^1\text{E}(\text{S}_4) - 1,227.03104$		—	—
Dianion	${}^1\text{E}(\text{S}_4) - 1,226.99835$		${}^3\text{B}_3(\text{D}_2) - 1,226.96998$	-17.8
Tetraanion	${}^1\text{A}(\text{D}_2) - 1,226.47286$		${}^3\text{E}(\text{S}_4) - 1,226.46827$	-2.9
Hexaanion	${}^1\text{E}(\text{S}_4) - 1,225.50187$		${}^3\text{B}_2(\text{D}_2) - 1,225.47366$	-17.7
2				
Neutral	${}^1\text{A}(\text{C}_2) - 1,686.60260$		—	—
Dianion	${}^1\text{A}_g(\text{S}_2) - 1,686.58125$		${}^3\text{A}_u(\text{C}_{2h}) - 1,686.57046$	-6.8
Tetraanion	${}^1\text{A}_g(\text{S}_2) - 1,686.18227$		${}^3\text{B}_g(\text{C}_{2h}) - 1,686.17742$	-3.0
Hexaanion	${}^1\text{A}_g(\text{C}_{2h}) - 1,685.40307$		${}^3\text{A}_u(\text{S}_2) - 1,685.37920$	-15.0
3				
Neutral	${}^1\text{A}_g(\text{C}_{2h}) - 2,146.16891$		—	—
Dianion	${}^1\text{A}_g(\text{C}_{2h}) - 2,146.17038$		${}^3\text{A}_u(\text{C}_{2h}) - 2,146.17127$	+0.6
Tetraanion	${}^1\text{A}_g(\text{C}_{2h}) - 2,145.85580$		${}^3\text{B}_g(\text{C}_{2h}) - 2,145.84649$	-5.8
Pentaanion		${}^2\text{A}_g(\text{C}_{2h}) - 2,145.56916$ [-2,157.44993]		
Hexaanion	${}^1\text{A}_g(\text{C}_{2h}) - 2,145.20233$ [-2,157.08736]		${}^3\text{A}_u(\text{C}_{2h}) - 2,145.18285$	-12.2
4				
Neutral	${}^1\text{E}(\text{S}_4) - 2,146.17598$		${}^3\text{A}(\text{C}_1) - 2,146.10995$	-36.4
Dianion	${}^1\text{E}(\text{S}_4) - 2,146.17685$		${}^3\text{B}(\text{C}_2) - 2,146.17273$	-2.6
Tetraanion	${}^1\text{A}(\text{C}_2) - 2,145.85737$		${}^3\text{E}(\text{S}_4) - 2,145.86018$	+1.8
Pentaanion		${}^2\text{B}_3(\text{D}_2) - 2,145.58135$ [-2,157.45974]		
Hexaanion	${}^1\text{E}(\text{S}_4) - 2,145.22195$ [-2,157.10296]		${}^3\text{B}_2(\text{C}_{2v}) - 2,145.20397$	-11.3

Table 4 ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR values of **1** and its anions

	$\delta({}^1\text{H})$			
	H-4/C-4	H-8/C-8	C-3	H-1/C-1
Neutral	7.55	7.55	—	6.38
$\text{1}^{2-}/2\text{Li}^+$	9.33	-7.19	—	9.62
$\text{1}^{2-}/2\text{K}^+$	9.35	-7.02	—	9.64
$\text{1}^{4-}/4\text{Li}^+$	3.77	15.05	—	1.31
$\text{1}^{4-}/4\text{K}^+$	3.26	16.44	—	0.92
	$\delta({}^{13}\text{C})$			
	H-4/C-4	H-8/C-8	C-3	H-1/C-1
Neutral	129.6	129.6	136.6	129.9
$\text{1}^{2-}/2\text{Li}^+$	123.9	116.5	123.9	108.8
$\text{1}^{2-}/2\text{K}^+$	123.7	116.4	119.7	108.6
$\text{1}^{4-}/4\text{Li}^+$	122.4	121.6	133.3	95.9

and a broad, temperature-dependent ${}^1\text{H}$ NMR spectrum of the dianion was recorded. Unlike the dianion of **2** with lithium, which was best resolved at 230 K, a highly resolved ${}^1\text{H}$ NMR spectrum of the dianion with potassium could be detected only at a very low temperature (175 K). Increasing the temperature to 230 K led first to a fast broadening of the signals and finally to the disappearance of the spectrum. The peripheral ring current effect of the dianion, $\text{2}^{2-}/2\text{K}^+$, as reflected by the proton chemical shifts, was dramatically amplified, relative to the dianion of **2** with lithium (Fig. 1). It is to be expected from the polarizing power of the counterions that they will influence the mode of the π -charge distribution within the anion.⁷ Any perturbations in the cyclic π -conjugation are predicted to partly quench the observed ring current effects. The small lithium cation is more effective in attracting the π -charge and thus decreasing the ring current effect, hence the extreme shift

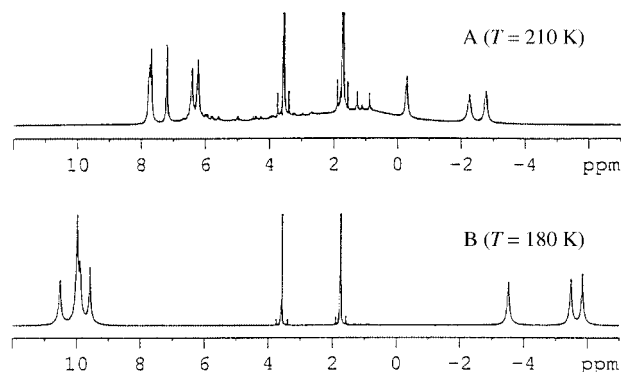


Fig. 1 Dianions of **2** with lithium (A) and potassium (B) in THF-*d*₈.

differences of inner and outer protons are usually achieved by potassium reduction.

Further reduction of 2^{2-} with potassium revealed a change in the color of the solution to purple and a new ${}^1\text{H}$ NMR spectrum attributed to the tetraanion could be detected (Fig. 2). Addition of four electrons to the perimeter of the neutral molecule rendered the system anti-aromatic (36 π -electrons). As is known for π -conjugated systems in general, due to a more effective conjugation in the tetraanion 2^{4-} a strong paramagnetic behavior could be expected. As a result of the two additional electrons the inner protons are shifted from a very high field in the dianion $\text{2}^{2-}/2\text{K}^+$ to a very low field in the tetraanion $\text{2}^{4-}/4\text{K}^+$ and *vice versa* for the outer protons. As expected for such systems, due to the higher intensity of the magnetic flux, the greater change in chemical shifts was observed for the inner protons.^{6,7,9} The observed chemical shifts of **2** and its anions are summarized in Table 5. Further reduction of 2^{4-} with potassium led to the disappearance of the

Table 5 ^1H and ^{13}C NMR values of **2** and its anions

	$\delta(^1\text{H})$										
	H-4/C-4	H-8/C-8	C-3	H-2/C-2	H-1/C-1	C-11	H-12/C-12	H-16/C-16	H-13/C-13	H-15/C-15	C-14
Neutral	7.35	7.35	—	6.57	6.62	—	7.53	7.53	7.79	7.79	—
$2^{2-}/2\text{Li}^+$	7.35	-2.89	—	6.45	6.64	—	7.87	-3.40	7.95	-0.89	—
$2^{2-}/2\text{K}^+$	9.60	-5.89	—	9.99	9.90	—	9.99	-5.50	10.53	-3.52	—
$2^{4-}/4\text{K}^+$	2.48	17.86	—	0.60	0.02	—	2.75	18.71	3.00	18.04	—
	$\delta(^{13}\text{C})$										
	H-4/C-4	H-8/C-8	C-3	H-2/C-2	H-1/C-1	C-11	H-12/C-12	H-16/C-16	H-13/C-13	H-15/C-15	C-14
Neutral	129.4	129.4	136.9	130.2	130.2	136.8	129.9	129.9	126.8	126.8	139.4
$2^{2-}/2\text{K}^+$	125.2	117.4	122.9	113.9	111.1	125.7	129.7	117.9	117.4	112.8	125.2
$2^{4-}/4\text{K}^+$	120.7	125.8	^a	115.1	100.4	^a	^a	^a	^a	^a	^a

^a Broad ^1H and ^{13}C NMR signals did not allow correlation and full assignment.

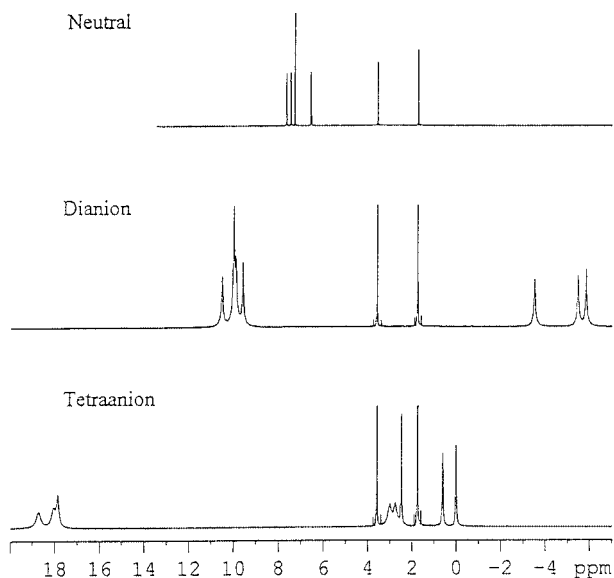


Fig. 2 ^1H NMR spectra of **2**, its dianion and tetraanion with potassium in THF- d_8 at 180 K.

spectrum as a result of the formation of a new paramagnetic species, probably 2^{5-} . Quenching all anions 2^{2-} , 2^{4-} , and 2^{5-} with oxygen yielded quantitative amounts of the starting material **2**, which supports the assumption that the last stage of charging was indeed a pentaanion.

The subtle competition of electronic stabilization and coulomb effects is influenced not only by the distribution of the π -charge within the substrate, but also by its interaction with the counter ions and the solvent. Whereas the reduction of **1** with lithium led to stable di- and tetraanions, the reduction with potassium yielded a stable dianion, which only after a long period of contact time with the metal could be further reduced to the temperature-sensitive tetraanion. The opposite behavior was found in compound **2**. While the reduction with lithium terminates at the dianionic stage, upon using potassium, compound **2** could be reduced to its tetraanion and even further. It has been observed previously²¹ that small π -conjugated compounds yield stable anions with lithium while larger systems prefer a larger alkali metal like potassium. The explanation for this is based mainly on the differences in ion pairing equilibria and the tendency of the lithium cations to aggregate and thus to stabilize the smaller anions.

Generally, anions in solution exist as rapidly equilibrating mixtures of solvent-separated and contact ion pairs whose ratio sensitively depends on the experimental conditions. Particularly in anions with efficient π -charge delocalization like annulenes it is expected that solvent separated ion pairs are favored. The efficiency of reduction of small systems with lithium results from the relatively high charge density and hence the tendency

of lithium cations to support the formation of stable anions. As we switch to extended π -conjugated systems, it is not the reduction potential of lithium but the stable lithium salt which is formed in the early reduction state that impedes the progress of the reduction. However, with the potassium metal where a stable structure cannot be formed in the preliminary stages of the reduction, the reducing ability depends on whether the system is large enough to accommodate the extra charge and can be accompanied by the larger potassium cations. This ability usually leads to stable highly reduced hydrocarbons.

The ^7Li chemical shifts of the lithium counterions have been shown to be sensitive to the mode of ion pairing. The ^7Li NMR measurements can point towards different types of contact ion pairs that differ by the distance between the ring and the coordinated metal above and below the π -cloud.²² In dianions $2^{2-}/2\text{Li}^+$ and $1^{2-}/2\text{Li}^+$, ^7Li chemical shifts of -4.7 and -2.0 ppm, respectively, have been found. It seems that in the larger cyclophane (**2**), as the internal cavity becomes more spacious, the preferred position of lithium cations is still above the cavity but closer to the molecular framework (*i.e.* higher tendency to form contact ion pairs).

[2.2.0.0.2.2.0.0]Paracyclophane-1,9,29,37-tetraene (**3**) was synthesized by Wittig reaction of equivalent amounts of terphenyl-4,4'-dicarbaldehyde and the bistrisphenylphosphonium salt prepared from α,α -dibromoparaxylene. The addition of two benzene rings to the skeleton of **2** results in 40 π -electrons in the perimeter. Due to the low symmetry (C_{2h}), both the LUMO (-0.0601 a.u.) and the NLUMO (-0.0543 a.u.) are non-degenerate, thus the formation and the detection by NMR techniques of both diamagnetic dianion and tetraanion could be expected. The reduction of **3** with potassium led to three species that allowed the detection of the ^1H NMR spectra, but only near the freezing point of the solvent (THF). As found for the smaller annulenes, the first diamagnetic species, the dianion, showed a diamagnetic ring current effect. Further contact with the potassium metal led to the tetraanion 3^{4-} (Fig. 3). The inner protons of 3^{2-} and 3^{4-} resonated at about -2 and 15 ppm, respectively, reflecting a decrease in ring current effects relative to the anions 1^{2-} and 1^{4-} (-7 and 16 ppm) as well as to the anions 2^{2-} and 2^{4-} (-5 and 18 ppm). Further contact with the potassium metal led to the disappearance of the spectra but, eventually, a new diamagnetic species could be detected: a hexaanion (Fig. 3).

Taking into consideration that **1** could be reduced to its tetraanion and **2** to a pentaanion, the ability of **3** to accommodate six electrons is not unexpected. The hexaanion, which includes $4n + 2$ π -electrons (46), is qualitatively expected to behave like the dianion. However, to our knowledge, this is the first observation of a second negatively charged (aromatic) species of the same π -perimeter of an annulene. The outer proton chemical shifts of 3^{6-} are similar to those in 3^{2-} (*ca.* 9 ppm). However, there is a difference between the chemical shifts of the inner proton of 3^{2-} (*ca.* -2 ppm) and 3^{6-} (*ca.* -6 ppm).

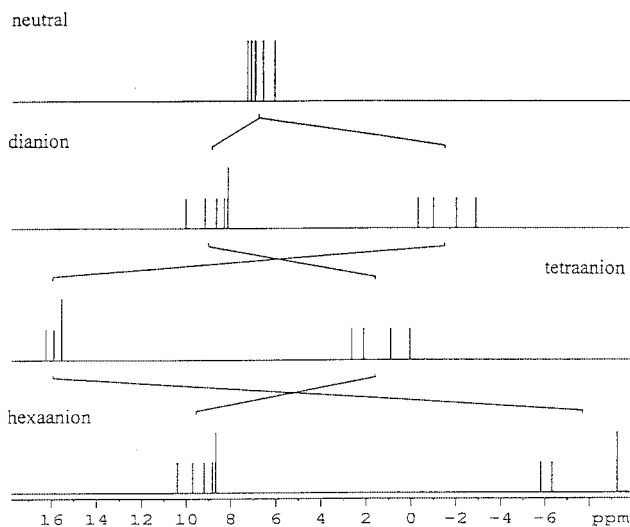


Fig. 3 ^1H NMR spectra of **3**, its dianion, tetraanion and hexaanion with potassium in THF-*d*₈ at 167 K (scheme).

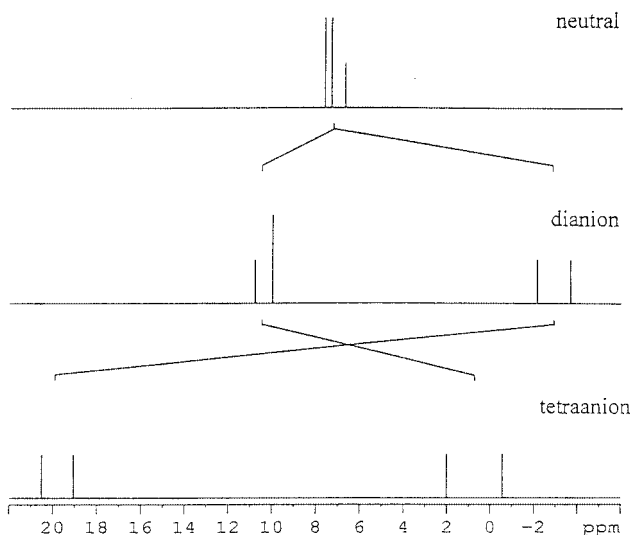


Fig. 4 ^1H NMR spectra of **4**, its dianion and tetraanion with potassium in THF-*d*₈ at 167 K (scheme).

The two additional benzene rings of **3** compared to **2** extended the perimeter by the elongation of the annulene in one dimension. It seems that this change in geometry is responsible for the ability of the annulene to accept up to six electrons. Investigations on an isoelectronic annulene with higher symmetry may indicate whether the geometry or the total number of electrons is responsible for the decrease in ring current.

[2.0.2.0.2.0.2.0]Paracyclophane-1,15,29,43-tetraene (**4**) was synthesized by reaction of equivalent amounts of biphenyl-4,4'-dicarbaldehyde and the bistrisphenylphosphonium salt prepared from 4,4'-bis(bromomethyl)biphenyl. This cyclophane, which has the same number of π -electrons (40) in the perimeter as **3**, is characterized by a higher potential symmetry. For **4**, which has the same geometry (S_4) as **1**, a low-lying LUMO (-0.0621 a.u.) and two degenerate NLUMOs (-0.0496 a.u.) have been found. The extenuation of the π -system should make the reduction of annulene **4** easier than that of **1**, therefore, the formation of both 4^{2-} and 4^{4-} is expected. The reduction of **4** with potassium led first to the diamagnetic dianion that could be further reduced to the tetraanion. The ring current effect, as reflected by the chemical shifts of the internal protons, was less pronounced for 4^{2-} compared to 1^{2-} (-3 vs. -7 ppm) but more pronounced when considering the reference tetraanions (16 ppm for 1^{4-} vs. 20 ppm for 4^{4-} , Fig. 4). Differing from **3**, the reduction does not proceed beyond the eventually detected pentaanion 4^{5-} .

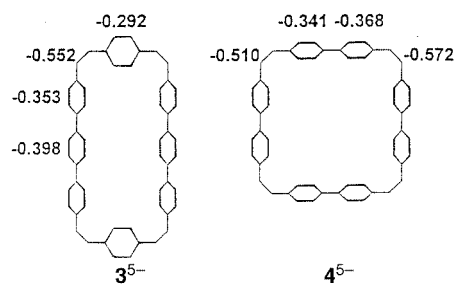


Fig. 5 Charge distribution for the doublet states of 3^{5-} and 4^{5-} . UB3LYP/6-31G*//UB3LYP/6-31G*, Mulliken analysis.

The reasons that annulene **3** could be further reduced to the hexaanion and **4** could not, although both systems have the same number of peripheral π -electrons, could be related to the geometry of the annulene or the effect of the counter cations and the solvent on the charge distribution. Experimentally, charge distribution is deduced from the change in carbon chemical shifts upon the reduction. Since these large annulenes are temperature-sensitive and their carbon spectra could not be detected, we approached the question of the different behavior of the two annulenes 3^{4-} and 4^{4-} upon reduction by looking at theoretical calculations.

Given the importance of these computations, the basis set 6-31G* has been employed. According to our optimizations, the SOMOs and LUMOs of the doublet states of both 3^{5-} and 4^{5-} show no evident differences in shape and in the coefficients of the contributing atomic orbitals. Moreover, there is minimal support for the assumption that the different topologies of both systems lead to a concentration of charges in specific structural fragments which are unique for either **3** or **4**. Principally, the negative charges are quite evenly distributed all over the rings and the olefinic fragments of either molecule (see Fig. 5).

To find the preferred site for an approaching reducing agent to attack 3^{5-} and 4^{5-} and to deliver the extra electron to, SCF single point calculations of the closed shell singlet states of 3^{6-} and 4^{6-} have been performed by using the optimized geometries of the doublet states of 3^{5-} and 4^{5-} , respectively. However, no structural elements for any of the molecules have been located where the 'additional' negative charges are primarily located after reduction. The electron affinities estimated from the computed energetic differences between the pentaanions (optimized doublet state structures) and the hexaanions (SCF single point calculation as described above) are comparable (230.9 kcal mol $^{-1}$ for 3^{5-} vs. 226.1 kcal mol $^{-1}$ for 4^{5-}).

Interestingly, the overall energetic differences between the pentaanion and the hexaanion are very similar for **3** (227.5 kcal mol $^{-1}$) and for **4** (223.9 kcal mol $^{-1}$). Obviously, the differences in the chargeability of 3^{5-} and 4^{5-} , which both formally contain 45 π -electrons in their outer perimeters, are not (at least not primarily) caused by the topological differences.

Nonetheless, there are many other circumstances which might influence chargeability, that could not be modeled computationally, such as the influences of the solvent, the counter-cations or the solvation of the latter. Most probably, the last two factors play an essential role.

Conclusion

The size and the geometry of the annulenes influence the degree of reduction. In correlation with the increased size of the annulenes, the highest reduction stages with potassium were 1^{4-} , 2^{5-} , 3^{6-} and 4^{5-} , respectively.

Even above the assumed 'magic' limit of 26 π -electrons, a ring current effect has been observed. For the diatropic $4n + 2$ π -electron systems 1^{2-} , 2^{2-} , 3^{2-} , and 4^{2-} , this could be demonstrated by the chemical shifts of the outer protons which amount to 9.64, 10.53, 10.69, and 10.65 ppm, respectively (maxi-

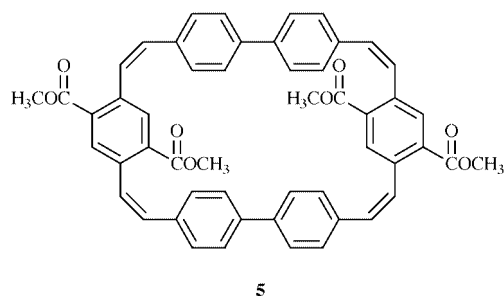
mum values, reduction with potassium). A similar behavior has been seen in the paratropic tetraanions. The chemical shifts of the outer protons are 0.92, 0.02, 0.55 and -0.54 ppm for 1^{4-} , 2^{4-} , 3^{4-} , and 4^{4-} respectively (minimum values, reduction with potassium). The dependency of the proton chemical shifts on the size of the annulene rings, in both dia- and paratropic annulenes, is mainly demonstrated by the chemical shifts of the inner protons.

Reduction of **3** with potassium led to a dianion, a tetraanion and eventually a hexaanion. For the first time, we could observe two different diamagnetic anions derived from the same carbon framework. The proton chemical shifts point to a similar anisotropy while the main difference of the magnetic properties is seen in the induced magnetic field inside the cavity of the annulenes. This result is in line with the general behavior of the series.

Outlook

Small-sized cyclophanes, like **1** and **2**, with an average molecular plane being formed by the (nearly) co-planar olefinic fragments, have the aromatic rings rotated out of this plane to a large extent. In certain types of conformation, the central cavities may be large enough to allow host-guest inclusion complexes with small substrates. Due to the rigidity of the framework, such a cavity is stable and would not collapse in the absence of a guest molecule. Therefore, substituted cyclophanes may function as multidentate ligands or as organic matrices for an inclusion of the desired guest. The influence of the unique magnetic behavior of these charged annulenes on a guest molecule can lead to interesting characteristics.

In an earlier work we reported the synthesis and characterization of two substituted [2.2.2.2]paracyclophanes which are derivatives of **1**, containing carboxylic acid ester groups.²³ Cyclophane **5** was also synthesized recently, and its X-ray struc-



ture (Fig. 6) showed a large deviation of the two substituted benzene rings relative to the average molecular plane (*ca.* 82°), and a twisting conformation of the biphenyl unit above and below the molecular plane (*ca.* 7°).²⁴ The formed internal cavity seems to be large enough to host small guest molecules.

Experimental

Computational details

All computations described herein were carried out using the program package GAUSSIAN '98.²⁵

The structures of the lowest lying closed shell singlet states and selected lowest lying triplet states of **1**, **2**, **3**, and **4** and of the reference di-, tetra- and hexaanions, and the structures of the lowest lying doublet states of 3^{5-} and 4^{5-} have been optimized without any restrictions. For each system under investigation, frequency analyses were carried out; all described optimized structures refer to minima on the corresponding potential energy hypersurfaces. All total energies, orbital energies and charge distribution data given in the 'Results and discussion' section are as derived from the optimizations on the B3LYP/3-21G//B3LYP/3-21G (closed shell states) or UB3LYP/

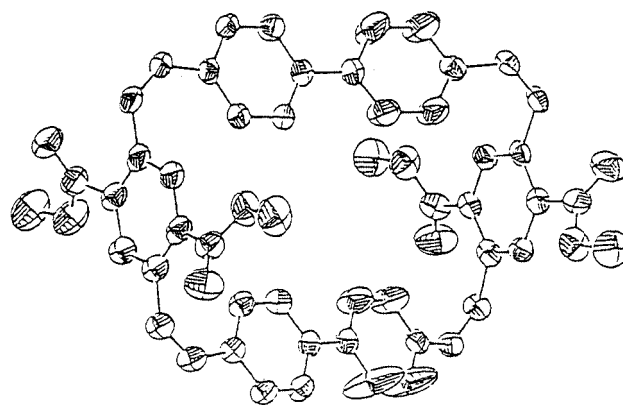


Fig. 6 Molecular structure of **5**.

3-21G//UB3LYP/3-21G (open shell states) level unless explicitly referred to as being derived from optimizations on the B3LYP/6-31G**/B3LYP/6-31G* or UB3LYP/6-31G**/UB3LYP/6-31G* level.²⁶ NMR chemical shifts (for the closed shell singlet states only) are as derived from additional RHF/3-21G//B3LYP/3-21G single point calculations employing the GIAO method as implemented in GAUSSIAN '98.

To find an estimate for the electron affinities of 3^{5-} and 4^{5-} , SCF single point calculations for the singlet states of 3^{6-} and 4^{6-} were performed using the optimized geometries of the doublet states of 3^{5-} and 4^{5-} , respectively.

NMR spectroscopy

All NMR analyses were performed on Bruker AMX-400 and DRX-400 pulsed FT-spectrometers in $CDCl_3$ ($\delta_H = 7.275$ ppm, $\delta_C = 77.00$ ppm) and THF-*d*8 ($\delta_H = 3.579$ ppm and $\delta_C = 67.16$ ppm), operating at 400.13, 100.62 and 155.51 MHz for 1H , ^{13}C and 7Li NMR, respectively. Coupling constants (*J*) are given in Hz. Full structure assignment was obtained by applying 2D-NMR spectroscopy techniques such as COSY, NOESY, CH-Correlation and LRCH-Correlation.

X-Ray crystal structure analyses

Intensity data were measured with a RRAF-NONIVS CAD-4 computer controlled diffractometer, using graphite crystal-monochromated Cu-K α radiation ($\lambda = 1.54178$ Å).

Materials

Potassium and lithium (Aldrich) were kept in paraffin oil and were rinsed shortly before use with petroleum ether (bp 40–60 °C). THF-*d*8 (Deutero GmbH) was dried over sodium-potassium alloy under vacuum.

General procedure for the reduction process

Lithium wire or potassium mirror was introduced to the upper part of an extended NMR tube containing the compounds dissolved in THF-*d*8. The sample was degassed and sealed under vacuum. The solution was brought into contact with the metal solution by turning the tube upside down.

Quenching of the anions

All anions were quenched with oxygen. The quenching experiments were carried out by bubbling the gas into the NMR tube *via* a syringe under anhydrous conditions. The deep colors disappeared, and the 1H NMR spectra were recorded.

[2.2.2.2]Paracyclophane-1,9,17,25-tetraene (**1**)

1 was prepared according to the literature.¹⁶ 1H NMR ($CDCl_3$, 298 K) δ 7.33 [s, 16 H, 4(8)-H], 6.44 [s, 8 H, 1-H] ppm, ^{13}C NMR ($CDCl_3$, 298 K) δ 128.9 [C-4(8)], 136.2 [C-3], 129.8 [C-1] ppm.

^1H NMR (THF-*d*₈, 180 K) δ 7.55 [s, 16 H, 4(8)-H], 6.38 [s, 8 H, 1-H] ppm, ^{13}C NMR (THF-*d*₈, 298 K) δ 129.6 [C-4(8)], 136.6 [C-3], 129.9 [C-1] ppm.

Lithium salt ($1^2\text{-}^2\text{Li}^+$). ^1H NMR (THF-*d*₈, 200 K) δ 9.33 [s, 8 H, 4-H], -7.19 [s, 8 H, 8-H], 9.62 [s, 8 H, 1-H] ppm. ^{13}C NMR (THF-*d*₈, 298 K) δ 123.9 [C-4], 116.5 [C-8], 123.9 [C-3], 108.8 [C-1] ppm. ^7Li NMR (standard LiCl/D₂O 298 K) δ -2.7 ppm (298 K), δ -2.8 ppm (200 K), ^7Li NMR (external standard LiBr/THF) δ -1.7 ppm (298 K), -1.8 ppm (200 K).

Potassium salt ($1^2\text{-}^2\text{K}^+$). ^1H NMR (THF-*d*₈, 180 K) δ 9.35 [s, 8 H, 4-H], -7.02 [s, 8 H, 8-H], 9.64 [s, 8 H, 1-H] ppm. ^{13}C NMR (THF-*d*₈, 180 K) δ 123.7 [C-4], 116.4 [C-8], 119.7 [C-3], 108.6 [C-1] ppm.

Lithium salt ($1^4\text{-}^4\text{Li}^+$). ^1H NMR (THF-*d*₈, 200 K) δ 3.77 [s, 8 H, 4-H], 15.05 [s, 8 H, 8-H], 1.31 [s, 8 H, 1-H] ppm. ^{13}C NMR (THF-*d*₈, 180 K) δ 122.4 [C-4], 121.6 [C-8], 133.3 [C-3], 95.9 [C-1] ppm. ^7Li NMR (standard LiCl/D₂O 298 K) δ 0.3 ppm (298 K), 0.8 ppm (200 K). ^7Li NMR (external standard LiBr/THF) δ 0.8 ppm (298 K), 1.3 ppm (200 K).

Potassium salt ($1^4\text{-}^4\text{K}^+$). ^1H NMR (THF-*d*₈, 180 K) δ 3.26 [s, 8 H, 4-H], 16.44 [s, 8 H, 8-H], 0.92 [s, 8 H, 1-H] ppm.

[2.2.0.2.2.0]Paracyclophane-1,9,23,31-tetraene (2)

Biphenyl-4,4'-dicarbaldehyde was prepared according to a modified procedure.^{11a,27} A solution of butyllithium (45 ml, 1.6 M in hexane) was added to 4,4'-dibromobiphenyl (7.5 g) dissolved in dry cooled (0 °C) diethyl ether (165 ml), and the mixture was allowed to stand for four hours. Following the addition of dry DMF (9 ml), the mixture was refluxed for three more hours and then quenched with HCl (3 M). Extraction with methylene chloride led to the dialdehyde [62%, mp 165–168 °C].²⁸ ^1H NMR (CDCl₃, 298 K) δ 10.10, 8.01, 7.80 ppm]. Cyclophane **2** was prepared by the Wittig reaction between the above mentioned dialdehyde and the phosphonium salt derived from α,α -dibromoparaxylene, according to the literature^{11a} (yellow crystals, 10%, mp 246–248 °C, λ_{max} = 312 nm, ^1H NMR (CDCl₃, 295 K) δ 7.25 [s, 8 H, 4(8)-H], 6.57 [d, 4 H, J_{HH} = 12.3 Hz, 2-H], 6.62 [d, 4 H, J_{HH} = 12.3 Hz, 1-H], 7.39 [d, 8 H, J_{HH} = 8.3 Hz, 12(16)-H], 7.49 [d, 8 H, J_{HH} = 8.3 Hz, 13(15)-H] ppm, ^{13}C NMR (CDCl₃, 295 K) δ 128.8 [C-4(8)], 136.3 [C-3], 130.0 [C-2], 129.8 [C-1], 136.2 [C-11], 129.4 [C-12(16)], 126.4 [C-13(15)], 139.2 [C-14] ppm. ^1H NMR (THF-*d*₈, 180 K) δ 7.35 [s, 8 H, 4(8)-H], 6.57 [d, 4 H, J_{HH} = 12.4 Hz, 2-H], 6.62 [d, 4 H, J_{HH} = 12.4 Hz, 1-H], 7.53 [d, 8 H, J_{HH} = 8.0 Hz, 12(16)-H], 7.79 [d, 8 H, J_{HH} = 8.0 Hz, 13(15)-H] ppm, ^{13}C NMR (THF-*d*₈, 180 K) δ 129.4 [C-4(8)], 136.9 [C-3], 130.2 [C-2], 130.2 [C-1], 136.8 [C-11], 129.9 [C-12(16)], 126.8 [C-13(15)], 139.4 [C-14] ppm.

Lithium salt ($2^2\text{-}^2\text{Li}^+$). ^1H NMR (THF-*d*₈, 190 K) δ 7.35 [4 H, 4-H], -2.89 [4 H, 8-H], 6.45 [4 H, 2-H], 6.64 [4 H, 1-H], 7.87 [4 H, 12-H], -3.40 [4 H, 16-H], 7.95 [4 H, 13-H], -0.89 [4 H, 15-H] ppm. ^7Li NMR (external standard LiCl/H₂O, 298 K) δ -3.7 ppm (298 K), -4.7 ppm (200 K).

Potassium salt ($2^2\text{-}^2\text{K}^+$). ^1H NMR (THF-*d*₈, 180 K) δ 9.60 [4 H, 4-H], -5.89 [4 H, 8-H], 9.99 [4 H, 2-H], 9.90 [4 H, 1-H], 9.99 [4 H, 12-H], -5.50 [d, 4 H, 16-H], 10.53 [4 H, 13-H], -3.52 [4 H, 15-H] ppm. ^{13}C NMR (THF-*d*₈, 180 K) δ 125.2 [C-4], 117.4 [C-8], 122.9 [C-3], 113.9 [C-2], 111.1 [C-1], 125.7 [C-11], 129.9 [C-12], 117.9 [C-16], 117.4 [C-13], 112.8 [C-15], 125.2 [C-14] ppm.

Potassium salt ($2^4\text{-}^4\text{K}^+$). ^1H NMR (THF-*d*₈, 180 K) δ 2.48 [4 H, 4-H], 17.86 [4 H, 8-H], 0.60 [4 H, 2-H], 0.02 [4 H, 1-H], 2.75 [4 H, 12-H], 18.71 [4 H, 16-H], 3.00 [4 H, 13-H], 18.04 [4 H,

15-H] ppm. ^{13}C NMR (THF-*d*₈, 180 K) δ 120.7 [C-4], 125.8 [C-8], 115.1 [C-2], 100.4 [C-1] ppm.

[2.2.0.0.2.2.0]Paracyclophane-1,9,29,37-tetraene (3)

4,4''-Dibromoterphenyl was prepared according to a modified reaction.²⁹ A solution of terphenyl (3 g) dissolved in acetic acid (300 ml) with a catalytic amount of iodine (I₂) was heated to 100 °C for an hour. After the addition of bromine (2.2 ml), the mixture was refluxed for eight hours. The precipitate was filtered and washed with hot ethanol to give a mixture of bromo- and dibromoterphenyl. Recrystallization from bromobenzene enhanced the concentration of dibromoterphenyl.

Terphenyl-4,4''-dicarbaldehyde was prepared from the dibromopropene according to a known procedure.^{27a,28} ^1H NMR (CDCl₃, 298 K) δ 10.16, 8.00, 7.82, 7.79 ppm. Cyclophane **3** was prepared by the Wittig reaction between the above mentioned dialdehyde (2.3 g) and the phosphonium salt from α,α -dibromo-*p*-xylene (5.9 g) in dry DMF (280 ml). Lithium ethoxide (0.1 g lithium in 30 ml ethanol) was added dropwise (25 h) to the cold solution (-40 °C), followed by the addition of water (250 ml). Extraction with ether and purification by column chromatography (silica gel, 6:4 petroleum ether 40–60 °C and chloroform) led to a mixture that was further chromatographed (silica gel, 8:2 petroleum ether 40–60 °C and ethyl acetate). Elution with ethyl acetate led to a yellow oil (λ_{max} = 318 nm). ^1H NMR (CDCl₃, 298 K) δ 7.24 [s, 8 H, 4(8)-H], 6.68 [d, 4 H, J_{HH} = 12.1 Hz, 2-H], 6.66 [d, 4 H, J_{HH} = 12.1 Hz, 1-H], 7.35 [d, 8 H, J_{HH} = 8.2 Hz, 12(16)-H], 7.51 [d, 8 H, J_{HH} = 8.2 Hz, 13(15)-H], 7.64 [s, 8 H, 18(22)-H] ppm. ^{13}C NMR (CDCl₃, 298 K) δ 128.8 [C-4(8)], 136.4 [C-3], 130.3 [C-2], 130.0 [C-1], 136.2 [C-11], 129.6 [C-12(16)], 126.3 [C-13(15)], 139.0 [C-14], 139.4 [C-17], 127.1 [C-18(22)] ppm. ^1H NMR (THF-*d*₈, 180 K) δ 7.33 [s, 8 H, 4(8)-H], 6.64 [AB-System, 8 H, 1(2)-H], 7.50 [d, 8 H, J_{HH} = 8.2 Hz, 12(16)-H], 7.79 [d, 8 H, J_{HH} = 8.2 Hz, 13(15)-H], 7.90 [s, 8 H, 18(22)-H] ppm. ^{13}C NMR (THF-*d*₈, 180 K) δ 128.9 [C-4(8)], 136.8 [C-3], 130.2 [C-2], 130.1 [C-1], 136.8 [C-11], 129.5 [C-12(16)], 127.0 [C-13(15)], 139.4 [C-14], 139.6 [C-17], 127.6 [C-18(22)] ppm.

Potassium salt ($3^2\text{-}^2\text{K}^+$). ^1H NMR (THF-*d*₈, 167 K) δ -2.31 [4 H], -1.53 [4 H], -0.38 [4 H], 0.08 [4 H], 8.83 [8 H], 8.97 [4 H], 9.18 [4 H], 9.84 [4 H], 10.69 [4 H] ppm.

Potassium salt ($3^4\text{-}^4\text{K}^+$). ^1H NMR (THF-*d*₈, 167 K) δ 0.55 [4 H], 1.28 [4 H], 2.74 [4 H], 3.22 [4 H], 16.03 [8 H], 16.40 [4 H], 16.56 [4 H] ppm.

Potassium salt ($3^6\text{-}^6\text{K}^+$). ^1H NMR (THF-*d*₈, 167 K) δ -9.2 [4 H], -8.5 [4 H], -5.68 [4 H], -5.37 [4 H], 9.17 [12 H], 9.70 [4 H], 10.12 [4 H], 10.87 [4 H] ppm.

[2.0.2.0.2.0.0]Paracyclophane-1,15,29,43-tetraene (4)

4,4'-Bis(bromomethyl)biphenyl was prepared according to a modified procedure.³⁰ A mixture of 4,4'-dimethylbiphenyl (5 g), *N*-bromosuccinimide (9.7 g) and carbon tetrachloride (75 ml) was refluxed by using two tungsten lamps (150 W) for eight hours. The precipitate was filtered (hot funnel) and recrystallized from carbon tetrachloride [82%, mp 171 °C, ^1H NMR (CDCl₃, 298 K) δ 7.57, 7.46, 4.75 ppm].³¹ 4,4'-Bis(bromomethyl)biphenyl (4.3 g) and triphenylphosphine (7.2 g) were dissolved in dry DMF (30 ml) and the mixture was refluxed for five hours. The precipitate was collected and washed first with DMF and then with a small amount of ether [52%, burned >350 °C, ^1H NMR (CDCl₃, 298 K) δ 7.85, 7.73, 7.57, 7.05, 6.82, 5.79 ppm]. Cyclophane **4** was prepared by the multiple Wittig reaction between the phosphonium salt (2.5 g) and dialdehyde (0.61 g) in dry DMF (100 ml). To the cold solution (-40 °C) lithium ethoxide (13 ml) was added dropwise during 30 h. After quenching with water (250 ml) the mixture was extracted with

ether and washed; and the ether was evaporated. The yellow oil was further purified first by column chromatography (silica gel, 1:1 petroleum ether 40–60 °C and chloroform) and then on silica (PTLC silica, 6:4 petroleum ether 40–60 °C and chloroform) to give the final product as the last fraction (yellow oil, $\lambda_{\text{max}} = 322 \text{ nm}$, 1–2%), $^1\text{H NMR}$ (CDCl_3 , 298 K) δ 7.47 [d, 16 H, $J_{\text{HH}} = 8.23 \text{ Hz}$, 5(7)-H], 7.36 [d, 16 H, $J_{\text{HH}} = 8.23 \text{ Hz}$, 4(8)-H], 6.65 [s, 8 H, 1-H] ppm. $^{13}\text{C NMR}$ (CDCl_3 , 298 K) δ 126.7 [C-5(7)], 129.4 [C-4(8)], 129.9 [C-1], 136.3 [C-3], 139.4 [C-6] ppm. $^1\text{H NMR}$ (THF-*d*8, 180 K) δ 7.61 [d, 16 H, $J_{\text{HH}} = 8.07 \text{ Hz}$, 5(7)-H], 7.39 [d, 16 H, $J_{\text{HH}} = 8.07 \text{ Hz}$, 4(8)-H], 6.70 [s, 8 H, 1-H] ppm. $^{13}\text{C NMR}$ (THF-*d*8, 180 K) δ 127.2 [C-5(7)], 130.1 [C-4(8)], 130.3 [C-1], 136.8 [C-3], 139.7 [C-6] ppm.

Potassium salt ($4^{2-}/2\text{K}^+$). $^1\text{H NMR}$ (CDCl_3 , 298 K) δ –3.82 [8 H], –2.11 [8 H], 10.05 [16 H], 10.65 [8 H] ppm.

Potassium salt ($4^{4-}/4\text{K}^+$). $^1\text{H NMR}$ (CDCl_3 , 298 K) δ –0.54 [8 H], 1.06 [8 H], 2.05 [8 H], 18.86 [8 H], 20.21 [8 H] ppm.

Tetramethyl [2.2.0.2.2.0]paracyclophane-1,9,23,31-tetraene-4,7,26,29-tetracarboxylate (5)

Cyclophane **5** was prepared by the Wittig reaction between the phosphonium salt derived from dimethyl 2,5-bis(bromomethyl)terephthalate²³ (8.85 g), biphenyl-4,4'-dicarbaldehyde (3.8 g) (see **2**) and dry DMF (18 ml). A solution of lithium ethoxide (see **3**) (18.5 ml) was added dropwise during 30 h. After quenching with water (180 ml) the mixture was extracted with ether and washed. The ether was evaporated to give a yellow oil. The product was purified by column chromatography (silica gel, methylene chloride) followed by recrystallization from methylene chloride (2–3%, mp 320 °C, $^1\text{H NMR}$ (CDCl_3 , 295 K) δ 7.89 [s, 4H, 5(8)-H], 7.50 [d, 8H, $J_{\text{HH}} = 8.1 \text{ Hz}$, 13(15)-H], 7.09 [d, 8H, $J_{\text{HH}} = 8.1 \text{ Hz}$, 12(16)-H], 7.02 [d, 4H, $J_{\text{HH}} = 12.0 \text{ Hz}$, 2-H], 6.68 [d, 4H, $J_{\text{HH}} = 12.0 \text{ Hz}$, 1-H], 3.77 [s, 12H, CH_3] ppm. $^{13}\text{C NMR}$ (CDCl_3 , 295 K) δ 139.1 [C-3(6)], 138.2 [C-14(17)], 135.6 [C-11(20)], 133.0 [C-5(8)], 132.8 [C-4(7)], 129.8 [C-12(16)], 129.8 [C-2(9)], 129.6 [C-1(10)], 125.9 [C-13(15)], 166.3 [CO], 52.3 [CH_3] ppm.

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- The 'outer' perimeter has been deduced from $J_{\text{C-H}}$ coupling constants.⁸
- This is obviously due to the fact that the structures of 1^{2-} and 2^{2-} cannot compensate intramolecular repulsive forces well especially between the internal hydrogen atoms. They cannot do so either by large deviation from planarity (as the uncharged **1** and **2** can do) or by taking advantage of a higher 'structural flexibility' (as 3^{2-} and 4^{2-} can do by having a larger sized internal cavity).
- A very interesting and rather surprising behavior has been found for the formally aromatic dianions. For 1^{2-} the singlet–triplet splitting as expected is rather large (17.8 kcal mol⁻¹) in favor of the closed shell singlet state. This splitting is dramatically smaller for 2^{2-} and 4^{2-} (6.8 and 2.6 kcal mol⁻¹, both in favor of the singlet states, respectively). For 3^{2-} (with a structure of C_{2h} symmetry!), even a triplet ground state has been found, which is by 0.6 kcal mol⁻¹ more stable than the closed shell singlet state. This trend is obviously due to the increased size of the molecules, but the actual reason for this unexpected finding is still subject to speculation.
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