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Diatropic Cyclophane Dianions

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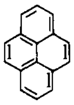
Abstract: A series of macrocyclic cyclophanes is reduced with alkali metals to yield the corresponding dianions and (in part) tetraanions. The chemical structure proof rests upon quenching and reoxidation experiments. A spectacular outcome is the pronounced ring current effect which appears from the ^{1}H NMR spectra of the ions. The diatropism of the dianions and paratropism of the tetraanions are ascribed to the formation of perimeter-type structures involving π-conjugation via aromatic moieties. The unprecedented "annulenoid" properties have been systematically affected by constructing cyclophane species with different ring size and planarity, with different aromatic subunits, and with heteroatoms. The stereodynamic behavior of the anions is rationalized in terms of simple π-bond theory. The "doping" of the cyclophanes with electrons provides adequate models for organic conductors of the polyphenylenevinylene-type.

Cyclic conjugated hydrocarbons have played a major role in the development of theoretical organic chemistry, and the monocyclic compounds, or annulenes, have been examined in detail.[2] For polycyclic compounds the question of benzenoid vs. annulenoid character arises. Typical examples of polycondensed hydrocarbons such as pyrene (**1**), coronene (**2**),[3] and Staab's well-known kekulene[4] (**3**) may either be described as a cyclic array of intact benzene units or, alternatively, as a combination of outer annulenoid rings ([14]-, [18]-, and [30]annulene in **1**, **2**, and **3**, respectively) and inner ones (a double bond in **1** and [6]- and [18]annulenes in **2** and **3**, respectively). When dealing with the significance of perimeter structures experimentally, ring current effects on the ^{1}H NMR shifts have been used as the most applicable criteria,[5] compounds such as kekulene (**3**) having, in this respect, the particular advantage of possessing "inner" protons.

Large cyclophanes in which the aromatic units are linked at the 1,4-positions by unsaturated bridges, e.g., **4–12**, constitute another series of potential annulene models with structural characteristics which lie between those of the true annulenes and those of polycondensed aromactic hydrocarbons. In the cyclophanes, and to a lesser extent in the annulenes, the structural description is further complicated by the interference of steric effects. Cyclic delocalization of the π-electrons is possible only in relatively planar conformations, the existence of which is determined by a subtle balance of resonance and strain effects.



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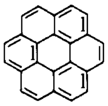

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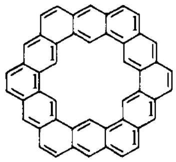

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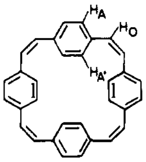

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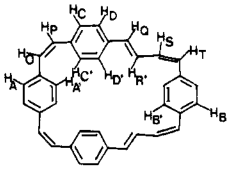

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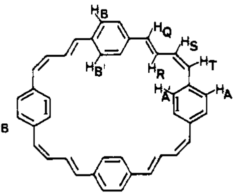

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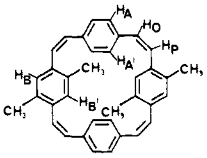
In polycyclic benzenoid hydrocarbons both experimental and theroetical evidence points toward the dominance of benzenoid character, i.e., perimeter-type structures do not contribute significantly to the electronic ground states. However, conclusions drawn from the structural description of neutral π-systems are not necessarily valid for the corresponding ions. Thus, while the properties of neutral pyrene (**1**) are dominated by the aromatic benzene units, the dianion tends to delocalize its π-charge around the periphery and exists as a true ethylene-bridged 16 π-perimeter ion.[6] The extension of this concept to the large cyclophanes **4–12** appears to be promising, since the tendency of the excess π-charge to delocalize over the whole π-system should favor perimeter structures.



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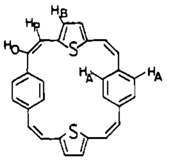

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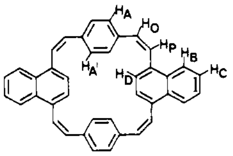

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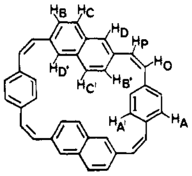

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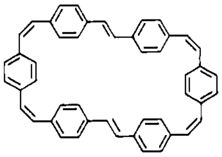

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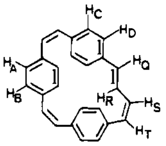

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We have indeed succeeded in generating stable dianions of cyclophanes **4–12** and even tetraanions of **4** and **9**. The most spectracular outcome of this work is that, as measured by their ^{1}H NMR spectra, the ions exhibit unusually large ring current effects. These effects have been ascribed to a perimeter-type annulenoid conjugation which, to the best of our knowledge, is unprecedented.

When describing the π-bonding of the title ions it is essential that one has available a series of closely related but structurally different model compounds. One can then investigate the effects of ring size (the dianions **4**$^{2-}$, **5**$^{2-}$, and **6**$^{2-}$ contain the same type and number of aromatic moieties), nature of the aromatic unit (the ions **5**$^{2-}$ and **10**$^{2-}$ have the same perimeter and the ions **9**$^{2-}$ and **10**$^{2-}$ are isoelectronic), planarity (**4**$^{2-}$ and **7**$^{2-}$ have identical π-systems but the former is more planar), and heteroatoms (the dianion **8**$^{2-}$ contains two thiophene units.)

It should be recalled that analogous questions have been of central interest to the structural studies of the annulenes.

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(1) (a) University of Mainz. (b) Chalmers University of Technology. (c) Present address: Department of Physical Chemistry, University of Basel, Basel, Switzerland.

(2) See, for example: Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81.

(3) Clar, E.; Zander, M. *J. Chem. Soc.* **1957**, 4616.

(4) Diederich, F.; Staab, H. A. *Angew. Chem.* **1978**, *90*, 383.

(5) For a discussion, see: Haig, C. W.; Mallion, R. E. "Progress in NMR spectroscopy"; Pergamon Press: New York 1980; Vol. 13, p 303.

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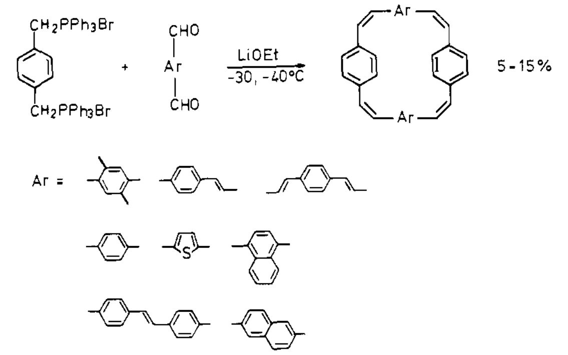
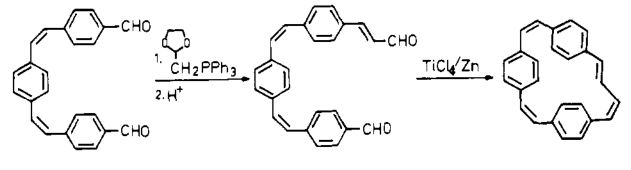
Scheme I



Scheme II



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In contrast to the annulenes the title compounds are synthetically relatively easily accessible perimeter models. The cyclophane ions also raise additional questions on the nature of charged delocalized π-systems. In such conjugated systems incorporating paraphenylene groups, different peripheral "loops" are available for perimeter conjugation, as is often the case for porphyrins.

We shall demonstrate that the presence of the "local" aromatic units in the unsaturated cyclophanes does *not* quench peripheral ring current effects in the dianions. We believe that this new discovery is of significant importance to the understanding of charge transport within polymeric conductors prepared by "doping" (oxidation or reduction) of relatively short-chain molecules containing conjugated π-systems and aromatic rings.

Experimental Section

The cyclophanes **4**–**11** were prepared by multiple Wittig reactions between the appropriate aromatic dialdehydes and bisphosphonium salts from bis(bromomethyl)arenes, as described elsewhere[7,11,16] (Scheme I).

Cyclophane **12** ([2.2.4]paracyclophanetetraene) was prepared from the dialdehyde **13** (Scheme II) which on treatment with 1 equiv of (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide and base, followed by hydrolysis, gave the cis,cis,trans dialdehyde **14**. This was then treated with a low-valent titanium species ($TiCl_4/Zn$)[8] in refluxing THF to give the cyclophane **12**. The configuration at the double bonds was deduced from the method of syntheses (the trans,trans configuration at the butadiene moiety is ruled out for steric reasons), and the ^{1}H NMR spectrum, which shows three AA'BB' multiplets for the aromatic protons, was consistent only with the expected trans,cis butadiene configuration. The extreme complexity of the olefinic proton resonances made a complete assignment of these difficult.

Table I. Potentials (V vs. SCE) for the Reversible Two-Electron Reduction of Cyclophanes **4**–**12**

compd	reduction potential[a]	ref
4	−1.70	11
5	−1.60	7b
6	−1.53	11
7	−1.91	11
8	−1.56	11
9	*b*	16
10	−1.71	16
11	−1.70	7c
12	−1.85	this work

[a] Cyclic voltammograms obtained at a hanging mercury drop electrode in dry *N*,*N*-dimethylformamide containing tetraethylammonium perchlorate (0.1 M). All data were obtained at room temperature. [b] No reversible reduction observed under these conditions.

***cis*,*cis*,*cis*,*trans*-[2.2.4]Paracyclophanetetraene (12).** 1,4-Bis(4-formylstyryl)benzene[9] (**13**) (3.0 g) and (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide[10] (3.98 g) were dissolved in warm (90 °C) dimethylformamide (100 mL, dried over calcium hydride) under nitrogen. A solution of lithium ethoxide in ethanol (0.2 M) was slowly added with stirring. The solution was stirred overnight at room temperature, water (200 mL) was added, and the mixture was carefully extracted with ether several times. The solvent was removed, and the residue was dissolved in tetrahydrofuran (75 mL) and treated with hydrochloric acid (10%, 50 mL) with stirring overnight. The mixture was extracted with ether and, finally, dichloromethane. The combined organic solvents were removed and the residue chromatographed on silica gel with dichloromethane to give unreacted aldehyde **13** (0.55 g) and the vinylogous dialdehyde **14** (0.82 g, 25%, mp 34–38 °C). MS: 364 (M^+, 100%); absolute mass 3624.146; calcd for $C_{26}H_{20}O_2$ 364.146. ^{1}H NMR (270 MHz, $CDCl_3$): δ 9.92 (s, 1 H, aldehyde), 9.65 (d, 1 H, aldehyde, J = 7.5 Hz), 7.69 (m, 2 H, aromatic), 7.37 (d, 1 H, olefinic, J_{trans} = 16 Hz), 7.35 (m, 4 H, aromatic), 7.26 (m, 2 H, aromatic), 7.08 (m, 4 H, aromatic), 6.63 (dd, 1 H, J = 16, 7.5 Hz), 6.61 (AB m, 2 H, J_{cis} = 12 Hz), 6.56 (AB m, 2 H, J = 12 Hz).

Titanium tetrachloride (2.2 mL, 20 mmol) was added with stirring under argon to dry THF (100 ml) at 0 °C to give a clear yellow mixture. Zinc powder (2.62 g, 40 mg-atom) was then added carefully in small portions, followed by dry pyridine (0.5 mL). The resultant black mixture was refluxed for 1 h before slow dropwise addition of a solution of the dialdehyde **14** (0.73 g, 2 mmol) in dry THF (100 mL). The reaction mixture was held at reflux until TLC showed complete disappearance of the dialdehyde and then cooled to 0 °C and quenched by careful addition of 10% aqueous potassium carbonate. The grey precipitate was filtered off and both filter cake and filtrate extracted thoroughly with dichloromethane. The combined organics were washed with brine and dried over magnesium sulfate, and the solvent was evaporated. The yellow residue was chromatographed on a short column of silica gel (dichloromethane eluent) to yield the title compound as a pale yellow solid (0.32 g, 48%). MS: 332 (M^+, 100%); absolute mass 332.157; calcd for $C_{26}H_{20}$ 332.157. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.22 (AA'BB' m, 4 H, aromatic), 7.04 (AA'BB' m, 4 H, aromatic), 6.76 and 6.50 (AA'BB' m, 4 H, aromatic), 6.78–6.61 (complex m, 5 H, olefinic), 6.51–6.33 (complex m, 3 H, olefinic).

Results

When the cyclophanes **4**–**12** are reduced at a mercury drop electrode in dimethylformamide they undergo a reversible *two-electron* transfer[11] (Table I). One can conclude from the data that the dianions should also be accessible via alkali metal reduction, and successful preparation of the alkali metal salts of the dianionic species **4**$^{2-}$–**12**$^{2-}$ has indeed allowed the detection of their unusual ^{1}H NMR spectroscopic properties.

The alkali metal reduction of cyclophanes **4**–**10** under proper experimental conditions generally produces solutions of pure dianions. The reductive formation of **11**$^{2-}$ and **12**$^{2-}$ is, however, accompanied by side reactions giving rise to broad NMR signals. Moreover, despite spectroscopic monitoring of the reduction process, the ^{1}H NMR signals of **11**$^{2-}$, appearing at both very high and very low field, exhibit line broadening which we believe is due to electron-transfer processes involving paramagnetic species. For example, bringing the solution of the dianion of **11** into further contact with the alkali metal for only a few seconds causes the NMR signals to disappear into the noise.

What is not anticipated from the electrochemical data is that alkali metal reduction proceeds beyond the dianion stage to yield

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(7) (a) Thulin, B.; Wennerström, O.; Högberg, H.-E. *Acta Chem. Scand., Ser. B* **1975**, *B29*, 138. (b) Thulin, B. *J. Chem. Soc., Perkin Trans. 1* **1981**, 664. (c) Raston, I.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 655.

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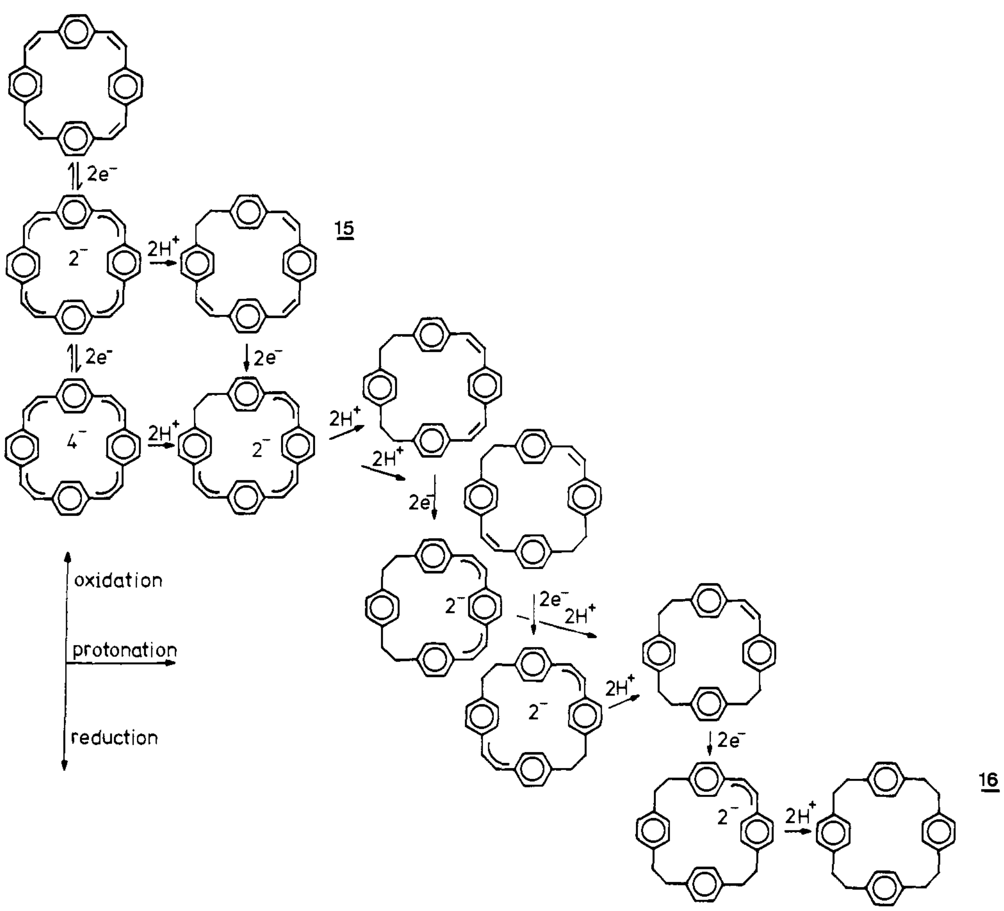
(13) Olsson, T.; Tanner, D.; Thulin, B.; Wennerström, O. *Tetrahedron* **1981**, *37*, 3491.

(14) Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *Tetrahedron* **1983**, *39*, 1575.

(15) Liljefors, T.; Wennerström, O. *Tetrahedron* **1977**, *33*, 2999.

(16) See also: Tanner, D.; Thulin, B.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1979**, *B33*, 443.

Scheme III



more highly charged species. Thus, we are able to obtain and to characterize the tetraanions $\mathbf{4}^{4-}$ and $\mathbf{9}^{4-}$.

The above dianions give rise to well-resolved ^{1}H NMR spectra only if present as sole products. Careful spectroscopic monitoring of the reduction process toward the dianions is essential to avoid line broadening due to rapid electron transfer between doubly and singly (or triply) charged species.

All dianions $\mathbf{4}^{2-}$–$\mathbf{12}^{2-}$ can readily be re-oxidized with air to give the neutral cyclophanes. Quenching of the dianions with electrophiles yields the corresponding diadducts, e.g., dimethyl derivatives, which are identified by mass spectrometry. On protonation with methanol, the dianion $\mathbf{4}^{2-}$, generated electrochemically or by metal reduction, provides the dihydro derivative **15**. Protonation of the tetraanion $\mathbf{4}^{4-}$ (as its lithium salt) gives a complex mixture of reduction products of which the dihydro derivative **15** and the octahydro derivative **16** are major components. This can be rationalized by assuming that electron-transfer processes compete with the protonation steps, as indicated in Scheme III. The tetraanion serves as the reducing agent for the protonated species, whereas the dianion is only slowly protonated. Inverse quenching gives a similar complex mixture with, however, a greater abundance of the tetrahydro derivatives. We conclude that the electrochemical behavior of the cyclophanes, the re-oxidation and quenching experiments, the kinetics of the reductions as followed by ESR and NMR spectroscopy, and the ^{1}H NMR spectra of the reduced species provide convincing proof of the structural identity of the dianions.

The neutral cyclophanes **4**–**12** are characterized by their normal values for the chemical shifts of their aromatic and olefinic protons, and there is little indication for additional anisotropic shielding effects other than those due to the local aromatic and olefinic subunits. In sharp contrast, the corresponding dianions exhibit ^{1}H NMR resonances at very low fields (δ 9–10) and at very high fields (δ -6 to -10, see Table II). For an interpretation of these surprising chemical shifts one is urged to invoke ring current effects. Toward this end, however, reliable signal assignments have to be made, and it is necessary to be able to differentiate aromatic and olefinic protons as well as protons inside and outside the macrocyclic ring.

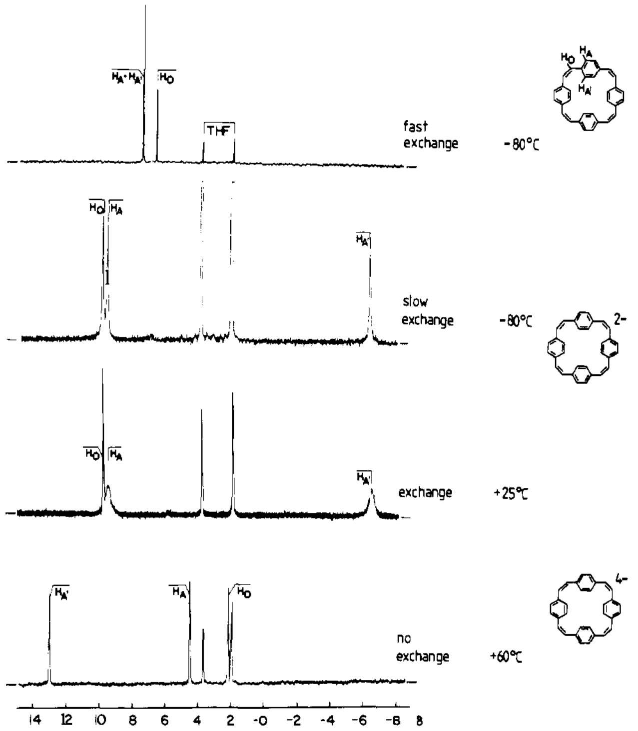


Figure 1. ^{1}H NMR spectra (300 MHz, THF-d_8) of **4**, $\mathbf{4}^{2-}$, and $\mathbf{4}^{4-}$.

From an inspection of structural formulae **4** or $\mathbf{4}^{2-}$ one readily identifies three different types of hydrogen, namely, the inner and outer aromatic hydrogens and the olefinic ones. This is done under

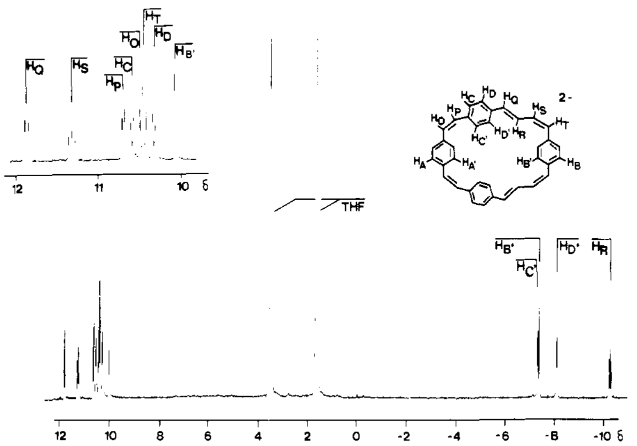


Figure 2. ^{1}H NMR spectrum (300 MHz, THF-d_8, −40 °C) of $\mathbf{5}^{2-}$.

the assumption that the benzene rings are tilted significantly less than 90° from the average plane of the double bonds and that no exchange of inner and outer aromatic hydrogens occurs. Due to the symmetry of the neutral molecule (D_{2d})[12] and its dianion, the olefinic protons of $\mathbf{4}^{2-}$ are expected to resonate as one sharp signal and the aromatic ones as two "singlets" only slightly broadened by meta couplings. Thus the two low-field signals have to be identified as being due to the outer protons and the high-field signal as due to the inner aromatic protons. One of the low-field signals is slightly broadened, as is the high-field signal, and these are assigned to the aromatic protons. By careful analysis of all of the spectra from the cyclophane dianions one obtains a consistent scheme of assignments (Figure 1 and Table II) with inner protons at high fields and outer protons at low fields. This assignment is clearly supported by inspection of the spectra from dianions $\mathbf{8}^{2-}$ to $\mathbf{10}^{2-}$ (in these cases, the olefinic protons are readily identified as giving rise to an AB pattern at low field), the number of protons in $\mathbf{9}^{2-}$ which resonate at high or at low field (it is assumed that for steric reasons the naphthalene units point away from the macrocyclic center), and the high-field resonance of four inner olefinic protons in $\mathbf{6}^{2-}$ (a triplet at δ −12).

The spectra of $\mathbf{5}^{2-}$ and $\mathbf{6}^{2-}$ deserve special comment (Table II). It follows from decoupling experiments that the triplet from $\mathbf{5}^{2-}$ at high field (δ −10.4) is due to H_R (Figure 2). The high-field signals which give an AB pattern are thus ascribed to the inner protons of the unsymmetrically substituted benzene units ($H_{C'}$ and $H_{D'}$). The remaining singlet must then be assigned to the inner protons ($H_{A'}$ or $H_{B'}$). Irradiation at the resonance frequency of H_R causes the two signals at lowest field to collapse to a singlet and a doublet, respectively, and these signals can thus be assigned to H_Q and H_S. The aromatic protons H_C and H_D and the olefinic protons H_O and H_P give rise to the two AB systems which can be differentiated by the magnitude of the vicinal coupling constants. The remaining singlet is assigned to H_A or H_B.

Apparently, the signals from one of the benzene rings of $\mathbf{5}^{2-}$ are not observed which must be due to site exchange via ring rotation/flipping. At the same temperature, such processes in $\mathbf{4}^{2-}$ and $\mathbf{6}^{2-}$ are completely frozen out, and from comparison of the spectra we deduce that for $\mathbf{5}^{2-}$ the missing signals are those of H_A and $H_{A'}$. In $\mathbf{5}^{2-}$ the benzene ring bearing H_A and $H_{A'}$ is, for steric reasons, more twisted out of the macrocyclic ring plane than the other three, and this results in a lower barrier to the ring flip or rotation.

The higher symmetry of **6** as compared to **5** simplifies the ^{1}H NMR spectra of both the neutral cyclophane and its dianion. Signal assignments of the protons in the butadiene bridges in $\mathbf{6}^{2-}$ are achieved as for $\mathbf{5}^{2-}$. Due to the higher symmetry, the aromatic protons H_A, $H_{A'}$, H_B, and $H_{B'}$, in $\mathbf{6}^{2-}$ appear as singlets. The vicinal coupling constants in $\mathbf{5}^{2-}$ and $\mathbf{6}^{2-}$ are given in Table II.

Discussion

(1) Unprecedented Ring Current Effects. Two major conclusions emerge from these NMR spectroscopic findings: (a) All the dianions from the cyclophanes **4**–**12** have in common that inner (outer) protons are strongly shielded (deshielded). Such large chemical shifts are normally considered as typical for [4n + 2]annulenes and are caused by large diatropic ring currents. (b) The rotation of the paraphenylene moieties about the adjacent single bonds is slow in most of the dianions, in contrast to the neutral compounds in which such rotation is fast[13] on the NMR time scale at the temperatures at which the dianions are generated.

The most important structural prerequisite for such behavior is the existence of conjugated [4n] π-perimeters in the neutral cyclophanes. Formally, the paraphenylene unit can be regarded as consisting of a butadiene moiety, incorporated into the conjugated perimeter, and an isolated ethylene unit. Thus the resulting perimeters contain 24 π-electrons in cyclophanes **4**, **7**, **8**, and **9**; 28 π-electrons in **5** and **10**; 32 π-electrons in **6**; 36 π-electrons in **11**; and 20 π-electrons in **12**. On reduction, the two extra electrons enter a delocalized molecular orbital thus creating the new [4n + 2] perimeter. Although the perimeter model is irrelevant to a description of the neutral cyclophanes, it is highly relevant to the description of the dianions, as demonstrated by the large ring current effects on the ^{1}H NMR shifts. The dianions $\mathbf{4}^{2-}$–$\mathbf{12}^{2-}$ thus appear as true diatropic [4n + 2] π-perimeter systems!

Convincing evidence in favor of this interpretation is also obtained from an inspection of the spectroscopic data of the tetraanions $\mathbf{4}^{4-}$ and $\mathbf{9}^{4-}$ (Table II and Figure 1). If the dianions contain [4n + 2] π-perimeters, then the corresponding tetraanions should have [4n] π-perimeters and therefore show *paratropic* properties. On reduction of the dianions to the tetraanions, the ^{1}H NMR signals for inner and outer protons are, indeed, reversed in order, i.e., inner protons are strongly deshielded.

Recalling from the introduction the structural varieties within the series **4**–**12** and $\mathbf{4}^{2-}$–$\mathbf{12}^{2-}$, we point out some obvious trends in the NMR spectroscopic behavior of the dianions. The shift difference between inner and outer aromatic protons increases upon going from $\mathbf{4}^{2-}$ (16.3 ppm), to $\mathbf{5}^{2-}$ (average 17.8 ppm) to $\mathbf{6}^{2-}$ (average 20.8 ppm). The trend is even more pronounced when comparing the shift difference of inner and outer olefinic protons in $\mathbf{5}^{2-}$ (21 ppm) and $\mathbf{6}^{2-}$ (24–25 ppm). Returning to the shift difference between inner and outer benzene protons (paraphenylene rings), one notes that the value is only slightly smaller for the less planar $\mathbf{7}^{2-}$ (16 ppm) and for the benzocondensed derivative $\mathbf{9}^{2-}$ (15.3 ppm) and essentially unchanged for the thiophene derivative $\mathbf{8}^{2-}$ (17.3 ppm) as compared with $\mathbf{4}^{2-}$ (Table II). Even in $\mathbf{11}^{2-}$, the periphery of which incorporates six benzene rings and six double bonds, the diatropic ring current is not quenched ($\Delta\delta$ = ca. 14 ppm).

The small amounts of material available and, more critically, the low solubility of the dianion salts have prevented a thorough study of the relevant ion-pair structures. We have recently studied the dependence of ring current effects upon ion pairing in charged annulenes[14] and concluded that solvent-separated ion pairs are favored over contact ion pairs by lower temperatures, larger organic anions, and smaller alkali metal counterions. While in the large title dianions one would generally expect solvent-separated ion pairs to predominate, a comparison of the lithium and potassium salts of $\mathbf{4}^{2-}$ does reveal significant chemical shift differences. The measurable ring current effects are larger for the lithium salt than for the potassium salt and, in accordance with previous findings, the difference is most pronounced for the inner protons (Table II). A slight temperature dependence of the proton chemical shifts in the potassium salt of $\mathbf{4}^{2-}$ (which also is largest for the inner protons) might indicate a contribution of contact ion pairs which decrease the observed ring current effects. However, within the qualitative discussion of ring current effects in the present cases neither serious ion-pairing effects nor symmetry deformations due to tight bonding of cations need to be taken into account.

(2) Conformations and Configurations of the Dianions. The neutral cyclophanes, as well as their dianions, may adopt structures differing widely in their conformations and configurations. The following discussion will pay special attention to the charge-induced conformational changes as well as to the interdependence of

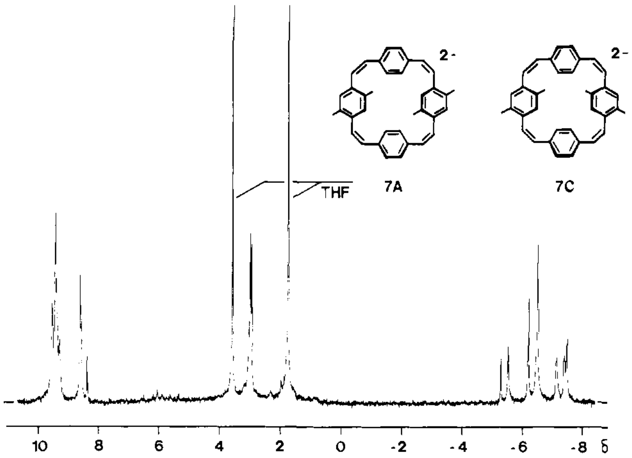


Figure 3. ^{1}H NMR spectrum (300 MHz, THF-5_8, −40 °C) of 7^{2-} (mixture of isomers). See text for discussion and Table 11 for a more complete assignment.

geometric and electronic factors.

The crystal structure[12] of **4** reveals that the benzene units are, on average, twisted from the mean molecular plane by about 35°, a value reproduced by molecular mechanics calculations.[15] In solution, the paraphenylene rings rotate rapidly on the NMR time scale,[13] thus exchanging inner and outer protons. As already mentioned, this process is slow in the dianion of **4**, allowing easy differentiation of inner and outer protons.

For cyclophane **5**, the configuration at the "butadiene" bridges follows from the method of synthesis and the ^{1}H NMR spectrum (Table II). Four of the six double bonds have the cis configuration and two have the trans. Although the compound cannot be planar, the preferred conformation has s-trans orientation at the "butadiene" bridges, as deduced from the vicinal $J_{\mathrm{H,H}}$ coupling constants. A molecular mechanics calculation (Allinger's MMP2 program) confirms this structure. The ^{1}H NMR data reveal that in $\mathbf{5}^{2-}$ both configuration and conformation are fixed and essentially the same as those in the neutral cyclophane (Table II).

The cis, trans, trans, cis, cis, trans, trans, cis configuration of **6** can be deduced from the method of synthesis and from the simple ^{1}H NMR spectrum. Again, the preference for the s-trans conformation at the bridges is apparent from the chemical shifts and coupling constants of the olefinic protons (Table II). The ^{1}H NMR data of $\mathbf{6}^{2-}$ reveal that configuration and conformation are fixed in the dianion and essentially the same as in the neutral compound. However, when $\mathbf{6}^{2-}$ is allowed to stand at −20 °C for several hours a second product, presumably a configurational isomer of $\mathbf{6}^{2-}$, is formed which shows high-field NMR signals with shifts similar to those of the major product.

Although cyclophanes **4**, **5**, and **6** are not planar molecules, charge delocalization over the entire macrocyclic loop is not seriously inhibited in their dianions, and the results imply that transformation of the flexible and conformationally mobile neutral [4*n*]cyclophanes into their dianions is accompanied by flattening of the π-system to less flexible, and more planar, structures. For the more planar conformations within the series **4**–**6** it is clear that the interaction between inner hydrogens and carbons decreases with increasing ring size. In contrast, the introduction of four methyl substituents into **4** to give **7** increases the steric interaction in the planar conformations. Due to hindered rotation of the benzene rings bearing two methyl substituents through the central cavity in **7**, two slowly interconverting isomers become observable by ^{1}H NMR spectroscopy.[13] In the neutral cyclophane these two conformers are present in roughly a 2:1 ratio and interconvert very slowly at the temperature at which the dianion is formed. In the dianion, the rotation or flipping of both types of benzene rings is hindered, and this leads to a total of four possible low-temperature conformations of $\mathbf{7}^{2-}$ (**7A**–**D** in Scheme IV). The two pairs **7A**/**7B** and **7C**/**7D** should be present in a 2:1 ratio, but the ^{1}H NMR spectrum of $\mathbf{7}^{2-}$ (Figure 3, Table II) is consistent with the exclusive presence of only two isomers, $\mathbf{7A}^{2-}$ and $\mathbf{7C}^{2-}$ (ratio 2:1). This can be rationalized by inspection of CPK molecular models. In the "missing" conformers, a sandwiched arrangement of pairs of benzene rings results in increased steric crowding in the central cavity (see also Scheme IV). The two conformers which are actually present exhibit similar ^{1}H NMR resonances (Table II) and an unambigous assignment cannot be made. A reasonable guess is that the more abundant isomer has a twofold axis of symmetry, $\mathbf{7A}^{2-}$, and that the less abundant isomer has a plane of symmetry, $\mathbf{7C}^{2-}$, and thus the nonbonding interactions between the inner methyl groups determine the conformational population.

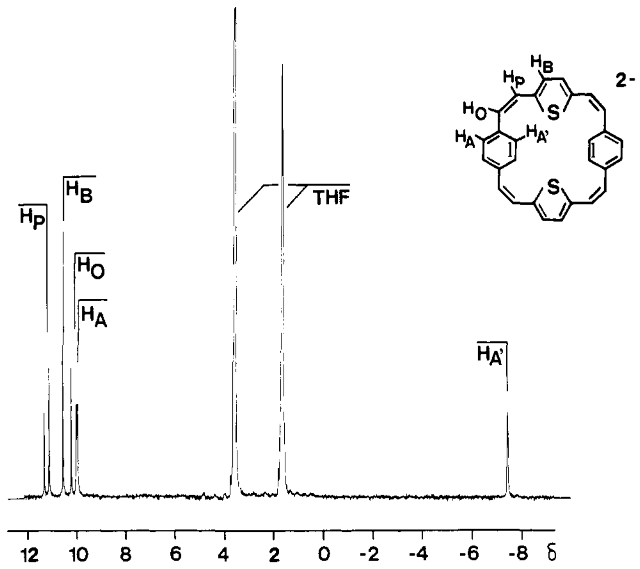
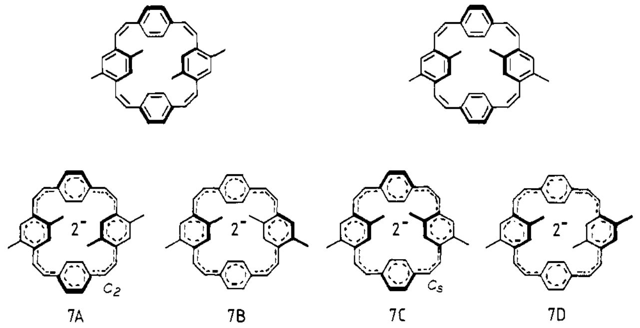
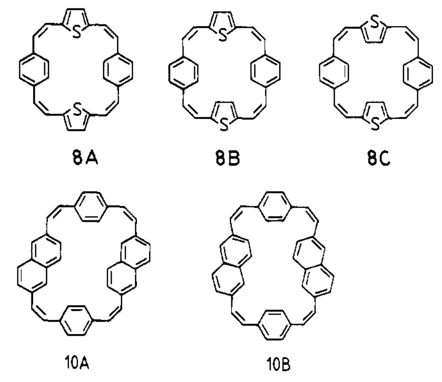


Figure 4. ^{1}H NMR spectrum (90 MHz, THF-d_8, +38 °C) of $\mathbf{8}^{2-}$.

Scheme IV



Scheme V



The thiophene derivative **8** can adopt three conformations (Scheme V) of which **8A** is the least crowded and most planar. All the ^{1}H NMR data (Figure 4) are indeed consistent with this being the preferred structure. While no absolute proof can be given for this conclusion, the structural assignment is compelling in the case of the dianion. The lone signal for the thiophene protons appears at very low field, strongly supporting the idea that

Table II. ^{1}H NMR Data (300, 270, 90, or 60 MHz) of the Cyclophanes **4–12** and Their Dianions (and Tetraanions of **4** and **9**) in THF-d_8 at −40 °C (Chemical Shifts in δ, Coupling Constants in Hz)

	aromatic protons				olefinic protons						inner aromatic protons[a]				
compd	A	B	C	D	O	P	Q	R	S	T	A'	B'	C'	D'	methyl protons
4	7.32				6.45						7.32				
4^{2-}/2Li$^+$	9.26				9.56						−7.07				
4^{2-}/2K$^+$	9.33				9.58						−6.73				
4^{4-}/4Li$^+$	4.48				2.09						12.76				
5	7.45/7.47		7.38/7.53		6.44/6.39		6.65	7.57	6.38	6.48	7.45/7.47		7.38/7.53		
			(J_{CD} = 8.5)		(J_{OP} = 12)		(J_{QR} = 16)	(J_{RS} = 11)	(J_{ST} = 11.5)				($J_{C'D'}$ = 8.5)		
5^{2-}/2Li$^+$	*b*	10.04	10.57/10.31		10.47/10.67		11.84	−10.21	11.29	10.42	*b*	−7.32	−7.24/−8.05		
			(J_{CD} = 8.4)		(J_{OP} = 11.2)		(J_{QR} = 13.3 = J_{RS})		(J_{ST} = 9.6)				($J_{C'D'}$ = 8.4)		
6	7.54/7.58						6.60	7.89	6.35	6.35	7.54/7.58				
							(J_{QR} = 16)	(J_{RS} = 12)	(J_{ST} = 11)						
6^{2-}/2Li$^+$	11.4/12.1						13.6	−12.0	12.8	11.8	−8.9/−9.1				
							(J_{QR} = 13.3 = J_{RS})		(J_{ST} = 11)						
7	6.96	6.97			6.47/6.57						6.96	6.97			2.05,^{c} 2.10^d
7^{2-}/2Li$^+$	8.58 to 8.36				9.29 to 9.52						−7.11 to −7.46/−5.25^c to −5.51^d				2.93,^{c} 2.99,^{d} −6.15,^{c} −6.45^d
8	7.24	6.80			6.45/6.38						7.24				
8^{2-}/2Li$^{+\,e}$	9.92	10.54			10.1/11.2						−7.34				
9	6.90	8.05	7.40		6.80/6.92						6.90			7.33	
9^{2-}/2Li$^+$	9.00	8.71	7.40		9.74/9.18						−5.29			−5.75	
9^{4-}/4Li$^+$	*f*	5.6	6.1		2.2/2.8						13.84			13.84	
10	7.39	7.63	7.45	7.94	6.57/6.60						7.39	7.63	7.45	7.94	
10^{2-}/2Li$^+$	9.45 to 9.30	9.44/8.74		10.48	9.35 to 9.74	9.90 to 10.18					−6.20 to −6.41	−5.79/−4.35		−7.23	
12	7.22/7.04/6.76/6.50				6.78 to 6.61/6.51 to 6.33						7.22/7.04/6.76/6.50				
12^{2-}/2Li$^+$								−8.46			−6.25/−4.41/−3.78/−3.57/−3.00				

[a] Inner and outer aromatic protons exchange rapidly in the neutral cyclophane. [b] Signals missing probably due to slow exchange processes. [c] Minor isomer ca. $^1/_3$. [d] Major isomer ca. $^2/_3$. [e] Temperature +38 °C. [f] Signal covered by solvent and/or impurity.

$\mathbf{8A}^{2-}$ is the sole conformer present (Figure 4, Table II).

The same type of argument is also valid for the structure of $\mathbf{9}^{2-}$. The unsubstituted rings of the naphthalene units must be outside the center of the macrocycle for steric reasons, and this structure alone is consistent with the relative numbers of shielded and deshielded protons.

In cyclophane **10**, with the two olefinic bridges attached to the 2- and 6-positions of the naphthalene units, two conformations differing in the orientation of the naphthalenes are possible, **10A** and **10B**. Due to the large cavity, these interconvert rapidly on the NMR time scale, as is evident from the simple spectrum[16] of **10** (Table II). The restricted rotation or flipping of the aromatic units in the dianion should in principle provide an opportunity to observe both $\mathbf{10A}^{2-}$ and $\mathbf{10B}^{2-}$, but the experimental NMR data are consistent with the presence of one major isomer, $\mathbf{10A}^{2-}$, in which the inner benzene protons are part of an ABCD-spin system with large ortho couplings resulting in broad signals. In contrast, the inner benzene protons of $\mathbf{10B}^{2-}$ should give rise to two fairly sharp sets of signals (AA′XX′ patterns, meta couplings). It should be noted that the naphthalene units in $\mathbf{10}^{2-}$ function as 2 six-electron bridges within the macrocyclic loop of 30 π-electrons.

(3) Effects of Ring Size. The three cyclophanes **4**, **5**, and **6** form a series of macrocycles containing the same number of benzene rings but with an increasing number of "butadiene" bridges. It is well-known that a consistent evaluation of ring current effects within such a series requires a consideration of the molecular geometries. Within Waugh's approach, the ring current induced shift of a proton resonance signal is proportional to the product of ring current intensity, the area of the ring, and the inverse cube distance of the nucleus from the ring center.[5]

As a first crude approximation of the ring current effect within the series above, we have considered the chemical shift difference of outer and inner paraphenylene protons divided by the ring area, S. While the $\Delta\delta$ values of $\mathbf{4}^{2-}$, $\mathbf{5}^{2-}$, and $\mathbf{6}^{2-}$ can be obtained directly from the spectra and found to be 16.33, 17.84 (average value), and 20.75 ppm (average value), respectively, complications arise when estimating the ring sizes. It is not clear, for example, whether it is correct to choose the outer or inner loop through the benzene rings as the preferred path of the ring current. Choosing the outer loop, we determined the relative ring areas of $\mathbf{4}^{2-}$, $\mathbf{5}^{2-}$, and $\mathbf{6}^{2-}$ from molecular models to 1.00, 1.35, and 1.74, respectively. The relative ring current effects, measured as $\Delta\delta/S$, are then 1.00, 0.81, and 0.73, rerespectively. A steady decrease of $\Delta\delta/S$ with increasing ring size has also been observed for various neutral and charged annulenes.[17] For a more accurate approach we must first take into account two characteristic properties of the present series of cyclophane dianions: the effects of the aromatic subunits which are expected to represent varying "resistances" to the induced ring currents and the steric transannular interactions which cause deviations from coplanar arrangements of the aromatic units and the unsaturated bridges. It is then necessary to find a simple but improved model for the ring current effect and to consider the relevance of the question of the inner vs. the outer loop in estimating the effective ring area, S.

(4) Effects of the Different Aromatic Units and of Variations in Planarity. The most striking result of this investigation is that the title dianions are formed from a variety of precursors of different macrocyclic ring sizes containing different numbers and types of aromatic subunits, the ring current effects being similar in all cases. The small variations which actually are observed are discussed below.

The ring current effects cannot be discussed adequately without consideration of the degree of planarity of the π-systems in the dianions. There are many examples of ring current effects being sensitive to deviations of the π-system from planarity as has been particularly well documented for bridged [14]annulenes.[18,19]

In order to minimize the influence of electronic factors and restrict the discussion to geometrical ones, the species **4**, $\mathbf{4}^{2-}$ and **7**, $\mathbf{7}^{2-}$ should be compared. As already stated, nonbonded interactions in **7** are much more serious than those in **4**. Electrochemically, however, these cyclophanes behave similarly and both give stable dianions on reduction. The tetramethyl derivative does require a more negative potential than expected from considerations of inductive effects only, and this can be rationalized as being due to increased steric strain in $\mathbf{7}^{2-}$ as compared to $\mathbf{4}^{2-}$. Interestingly enough, the $\Delta\delta$ value for the paraphenylene protons in $\mathbf{7}^{2-}$ (ca. 15.9 ppm) is only slightly smaller than that of $\mathbf{4}^{2-}$ (16.3 ppm) which indicates that the effects of nonbonded interactions are much less pronounced in the dianions. For the entire series of dianions discussed here ring current effects are not very sensitive to small variations in planarity.

It is more difficult to elucidate the extent to which variation of the aromatic units affects the magnitude of the induced ring currents. The dianions of the three cyclophanes **4**, **8**, and **9** have the same size of the perimeter (26 π-electrons) but contain different aromatic units, the same being true for the pair of dianions $\mathbf{5}^{2-}$ and $\mathbf{10}^{2-}$ (30 π-electron perimeters). By again using the chemical shift difference ($\Delta\delta$) of inner and outer paraphenylene proton signals as a probe of the induced ring current, the following conclusions can be made. (a) The exchange of two benzene rings in $\mathbf{4}^{2-}$ for thiophene rings, as in $\mathbf{8}^{2-}$, has no effect on the total ring current ($\Delta\delta = 16.3$ ppm for both $\mathbf{8}^{2-}$ and $\mathbf{4}^{2-}$). (b) Twofold benzocondensation of the parent dianion as in $\mathbf{9}^{2-}$ decreases the ring current effect ($\Delta\delta = 14.3$ ppm in $\mathbf{9}^{2-}$). One obvious explanation is that the naphthalene unit linked in the 1- and 4-positions constitutes a higher resistance to the induced shift than does the paraphenylene moiety, and it is known that benzoannelation of $[4n + 2]$annulenes decreases diatropic ring current effects.[20] The role of the effective ring size will be considered later. (c) The incorporation of a 2,6-naphthalene unit as in $\mathbf{10}^{2-}$ instead of a vinylbenzene unit as in $\mathbf{5}^{2-}$ (both dianions having 30 π-electron perimeters) decreases the ring current effect ($\Delta\delta = 15.7$ ppm in $\mathbf{10}^{2-}$ and 17.4 ppm in $\mathbf{5}^{2-}$). Geometrical factors can be important here as the two dianions have different conformations, resulting in a slightly larger area for $\mathbf{5}^{2-}$. Further, for $\mathbf{10}^{2-}$ there are several possible peripheral loops which the ring current can follow (see below).

(5) Semiquantitative Evaluation of Ring Current Effects. In order to arrive at a better understanding of ring current phenomena in the dianions $\mathbf{4}^{2-}$–$\mathbf{12}^{2-}$ one has to consider the influence of two local effects on the total ring current. The aromatic units may sustain a local diatropism, the effect of which is superimposed on the peripheral diatropism, resulting in a larger overall deshielding of the outer protons and a slightly smaller total shielding of the inner protons. For the total ring current this would mean an apparent preference for the outer peripheral loop. However, there are various alternative pathways available for perimeter conjugation in the dianions. In $\mathbf{4}^{2-}$, the ring current may follow the inner and/or outer loop through the benzene rings, and in $\mathbf{10}^{2-}$, as in $\mathbf{9}^{2-}$, one has to consider three different routes through the naphthalene rings (Scheme VI and VII). It is obvious that the various loops define rings of differing areas and peripheral geometries—two features which are of prime importance for any interpretation of ring current phenomena.

The question of inner/outer loop is intimately bound to the question of charge distribution in the dianions. For purely electrostatic reasons one would predict the extra charge to be delocalized mainly over the outer loop. However, if the counterions were located in the central cavity of the macrocycle, their polarization effect might enhance the density of the extra charge on the inner loop. So far, we have not observed any experimental evidence for the latter effect. It is well documented that relative local π-electron densities can be deduced from ^{1}H and ^{13}C chemical shifts,[21] provided that one can properly account for additional

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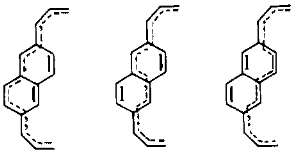
Scheme VI



shielding effects.[22] In the case of the title dianions the ring current effects exerted upon the proton resonances are much more pronounced than any charge effects. The same argument applies to the "aromatic" carbons of the dianions. If these are not located on the perimeter route their chemical shifts will still be affected by the anisotropic ring current phenomena, and our attention is therefore drawn from the ^{13}C chemical shifts to the one-bond $J_{\mathrm{C,H}}$ coupling constants. The latter are known from related π-systems to decrease with increasing π-charge on the carbon atom.[23,24] From inspection of the experimental data on **4**$^{2-}$ one sees that upon formation of the dianion, the outer aromatic and olefinic $^{1}J_{\mathrm{C,H}}$ values decrease more than do the corresponding values for the inner ones.[31] However, one should remember that the dianion is more planar than the neutral cyclophane and that the inner protons might be subject to steric distortions. ESR data[25] on the anion radicals **4**$^{-}\cdot$ and **8**$^{-}\cdot$ show that the hyperfine coupling constants are different at the outer and inner paraphenylene positions. Although an unambigous assignment cannot be made, one might assume that the outer carbons bear the highest spin density. If so, the ratio of inner and outer spin densities is 0.6 and 0.89 in **4**$^{-}\cdot$ and **8**$^{-}\cdot$, respectively. Again, the data must be used with caution because of the nonplanar structure of the anion radicals, and the fact that the spin densities need not be proportional to the charge. Although definite proof is lacking, all the data are consistent with a preference of the extra charge in **4**$^{2-}$ to be delocalized on the outer loop.

An evaluation of the ring current induced shielding phenomena within the entire series **4**$^{2-}$–**12**$^{2-}$ can be made, by calculating the secondary magnetic field at the position of any particular proton, through application of the Biot–Savart law.[26] Accordingly, one assigns a total ring current intensity which can be distributed over the various loops in several ways. The contribution from each peripheral bond to the secondary field is then summed. Our calculations were performed assuming planar structures and standard bond lengths. Surprisingly enough, this simple model allows us to rationalize most of the experimental results and gives insight on the problem of inner and/or outer loop alternatives. A few selected examples will now be discussed. Hückel bond orders in the cyclophanes and their dianions have also proven to be of considerable value for the evaluation of alternative pathways for the ring current in less symmetrical cases.

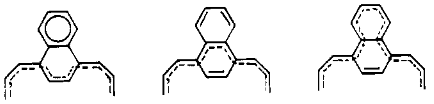
The chemical shifts for the naphthalene protons in **10**$^{2-}$ are easily deduced from the ^{1}H NMR spectrum (Table II). Somewhat surprisingly, the signal for the inner isolated protons ($\mathrm{H_{D'}}$) is observed at very high field (−7.23 ppm). This is not consistent with the simple idea that the ring current effect is most pronounced at the center of the macrocycle, but the observed relative shifts can be reproduced by Biot-Savart-type calculations. Three different routes for the ring current through the naphthalene units are possible (Scheme VI). The large internal shift difference for the outer (as well as the inner) naphthalene protons is best explained by assuming that the central route in Scheme VI is of importance. Electron densities and bond orders in **10**$^{2-}$ from Hückel calculations confirm that the central route through **10**$^{2-}$ must be considered when discussing the global ring current (Table III).

Table III. Calculated Bond Orders and Excess Electron Densities from Hückel Calculations in the Naphthalene Units in **9**$^{2-}$ and **10**$^{2-}$

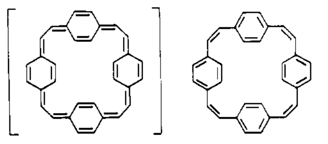
compd	bond	bond orders[a]	carbon	excess electron density
9^{2-}	1–2	0.59 (0.65)	1	0.08
	2–3	0.52 (0.54)	2	0.05
	3–4	0.76 (0.74)	3	0.01
	1–9	0.62 (0.58)	4	0.04
	4–10	0.51 (0.54)	9	0.02
	9–10	0.49 (0.51)		
10^{2-}	1–2	0.63 (0.56)	1	0.08
	2–3	0.71 (0.65)	2	0.06
	5–6	0.69 (0.71)	5	0.02
	6–7	0.63 (0.61)	6	0.02
	1–9	0.46 (0.49)	9	0.01
	5–10	0.59 (0.58)		

[a] Bond orders in parentheses refer to the neutral compounds.

Scheme VII



Scheme VIII



A different situation prevails in the dianion **9**$^{2-}$. Again, three routes for the ring current are possible (Scheme VII). From the chemical shifts of **9**$^{2-}$ (Table II) it is clear that the outer naphthalene rings are not much affected by the macrocyclic ring current whereas the singlet due to the inner naphthalene protons is shifted to higher field than the inner paraphenylene proton signal. This is a strong indication that the ring current follows the inner route (Scheme VII). Inspection of bond orders and electron densities in **9**$^{2-}$ (Table III) leads to the same conclusion, the LUMO orbital of **9** having only small coefficients at the outer naphthalene rings.

In contrast, the macrocyclic ring current in **8**$^{2-}$ apparently shows a preference for the outer loop, as the thiophene protons are more deshielded than the paraphenylene protons. The shift difference of 1.07 ppm, observed for the olefinic protons, can also be explained on this basis, as the Biot–Savart calculations predict a larger induced shift for the olefinic protons adjacent to the thiophene rings.

As demonstrated above, the global ring current may follow an outer, an inner, or, where possible, a middle route through a local aromatic unit. For the series of dianions **4**$^{2-}$–**12**$^{2-}$ it is observed that the olefinic proton shifts are generally more affected by the ring current than the paraphenylene proton shifts, indicating that both inner and outer loops through the paraphenylene rings are of importance. We conclude from the experimetal data and our rather crude models that the observed ring current effects can be understood in terms of a macrocyclic diamagnetic ring current modified by the local diamagnetic ring currents. The latter have the effect of decreasing the contribution from inner loops and increasing those from outer loops. Another result from the Biot–Savart-type calculations is that we calculate relatively larger ring current effects in the smaller rings, e.g., the inner paraphenylene protons in **4**$^{2-}$ and **6**$^{2-}$ show the relative shifts of δ 1.00 (**4**$^{2-}$) and δ 0.93 ($\mathrm{H_A}$, in **6**$^{2-}$) and δ 0.84 ($\mathrm{H_B}$, in **6**$^{2-}$) for the same absolute ring current through an outer loop. If this effect is real, it means that the extent to which the ring current is quenched with increasing ring size has been overestimated.[17]

(6) π-Bond Delocalization. There is convincing experimental evidence that various $[4n + 2]$annulenes exist as π-bond delocalized species.[2] However, as n increases there exists a marked tendency toward π-bond fixation[17,27–29] which decreases the dia-

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tropism of the π-system. Although $[4n + 2]$annulenes with nonequivalent Kekule structures have been described,[30] the delocalization energy is generally highest for those with equivalent Kekulé structures.

The neutral cyclophanes **4–12** have been shown by X-ray crystallographic[12] and NMR methods to contain π-bond localized unsaturated bridges. The two Kekulé structures of the neutral cyclophane **4** shown in Scheme VIII differ widely in energy and only the one with intact benzene rings is relevant.

The tendency of the excess charge in the ionic species to be uniformly distributed is expected to enhance π-bond delocalization. Partial equilibration of π-bond orders within the $[4n + 2]\pi$ perimeter is expected to occur, particularly at the bridges. What is the experimental evidence which supports this assumption?

The most obvious symptom of π-bond delocalization is the pronounced diatropism of the dianions. The magnitude of the relevant π-bond orders is reflected in the activation energy of the barriers to rotation or flipping of the aromatic units. As noted previously, this process is usually a facile one for the neutral cyclophanes on the NMR time scale. However, in the anion radical $\mathbf{4}^{-\cdot}$ the barrier to flipping is observable by ESR techniques[25] and was calculated to 9 kcal mol^{-1}, while for the dianion the nonequivalence of inner and outer protons in the ^{1}H NMR spectra shows the rotation or flipping of the aromatic units to be frozen out, and the spectrum of $\mathbf{4}^{2-}$ below −20 °C consists of three sharp signals (Table II). At temperatures above −20 °C the signals from H_A and $H_{A'}$ undergo line broadening while the signal from H_O remains sharp. Although the fast-exchange domain cannot be reached for reasons of thermal instability of the dianion, it is clear that the broadening is due to the flipping of the paraphenylene rings whereby the magnetic sites of H_A and $H_{A'}$ are interconverted, while that of H_O is unaffected. From a line-shape analysis, the enthalpy of activation was determined to ca. 15 kcal mol^{-1}. The same type of barrier is significant in all of the dianions and is probably lowest in the strained tetramethyl derivative $\mathbf{7}^{2-}$ and the large paracyclophanehexaene ($\mathbf{11}^{2-}$).

Vicinal coupling constants ($^3J_{H,H}$) in cyclic π-systems have been shown to be proportional to the corresponding π-bond orders and thus to reflect the π-bond situation.[32] It is clear from the ^{1}H NMR spectra of $\mathbf{5}^{2-}$ and $\mathbf{6}^{2-}$ that the two trans coupling constants $^3J_{H_O,H_R}$ and $^3J_{H_R,H_T}$ are the same so that the signal due to H_R appears as a triplet. This seems to indicate an equilibration of the π-bond order in the dianions as compared to the neutral cyclophanes. A closer inspection of Table II reveals other examples of this phenomenon. The unusual properties of the dianions $\mathbf{4}^{2-}$–$\mathbf{12}^{2-}$ classify them as $[4n + 2]$annulene derivatives. $[4n + 2]$Annulenes have been regarded as resonance stabilized species and much effort has been devoted toward a quantification of their resonance energy.[33] For the $[4n + 2]$annulene-type dianions discussed here such efforts seem almost to be useless. The major contribution to the total resonance stabilization must come from the local aromatic units and any extra stabilization from the macrocycle will be small in comparison and difficult to quantify.

(7) Outlook. The fundamental phenomenon of π-electron delocalization in neutral hydrocarbon molecules and their ions is far from understood in spite of numerous investigations of annulenes and polycondensed aromatics and their charged derivatives. The unsaturated cyclophanes discussed here constitute another interesting group of compounds with great potential as model compounds for the study of conjugation and delocalization, their diatropic dianions revealing the fundamental difference between the charged and the neutral π-systems. It is important to note the close resemblance between the behavior of these cyclophanes and polymeric species which consist of chains of para-phenylene rings linked by vinylene or other unsaturated bridges.[34] The neutral polymers of this type display only low conductivity whereas the "doped" species are highly conductive, a phenomenon which is parallelled by the behavior of the neutral and "doped" (i.e., reduced) $[4n]$cyclophanes **4–12**. More recently, we have shown that within the Hückel approximation, small ring compounds with conjugated π-systems and macrocycles and polymers built from the same repetitive units, e.g., a *p*-vinylphenylene unit, all have the same frontier orbitals under certain conditions.[35] This further demonstrates the utility of unsaturated cyclophanes as model compounds for the evaluation of the fundamental electronic properties of organic molecules with delocalized π-systems.

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