Reduction and Oxidation of Annulenes

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Contents

Klaus Müllen is Professor of Chemistry at the Institute of Organic Chemistry, University of Mainz. He was born in Cologne in 1947. In 1969 he obtained a Diplomchemiker-degree at the University of Cologne after work with Prof. E. Vogel. His Ph.D. degree was granted by the University of Basel, Switzerland, in 1971 where he undertook research with Prof. F. Gerson on twisted π-systems and the ESR spectroscopic properties of their corresponding radical anions. In 1972 he joined the group of Prof. J. F. M. Oth at the Swiss Federal Institute of Technology in Zürich working in the field of dynamic NMR spectroscopy and electrochemistry. He received his Habilitation from the ETH Zürich in 1977 and was appointed Privatdozent. In 1977 he became Professor at the Institute of Organic Chemistry, University of Cologne and accepted a call to the University of Mainz in 1983. His main research interests are concerned with electron-transfer reactions as well as the structure and reactivity of carbanions.

I. Introduction

A. Definitions and Scope of the Review

This review is devoted to the study of the following sequence of electron-transfer processes within the annulene field:[1]

$$A^{2+} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{+\cdot} \underset{-e}{\overset{e}{\rightleftharpoons}} A \underset{-e}{\overset{e}{\rightleftharpoons}} A^{-\cdot} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{2-} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{3-\cdot} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{4-}$$

Chemical or electrolytic oxidation of a neutral annulene substrate A will first create a radical cation $A^{+\cdot}$ whose

$$A \xrightarrow{-e} A^{+\cdot}$$

$$A^{+\cdot} \xrightarrow{-e} A^{2+}$$

paramagnetic nature is indicated by the dot. Further oxidation leads to a diamagnetic species, the dication A^{2+}.[2]

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$$A \xrightarrow{e} A^{-\cdot}$$

$$A^{-\cdot} \xrightarrow{e} A^{2-}$$

$$A^{2-} \xrightarrow{e} A^{3-\cdot}$$

$$A^{3-\cdot} \xrightarrow{e} A^{4-}$$

Likewise a chemical, electrolytic, or photolytic reduction produces a radical anion and, subsequently, a dianion.[3-6] It is this very reaction by which Katz in his pioneering work succeeded in transforming the [8 = 4n]annulene cyclooctatetraene (**3**) into its (10 = 4n + 2)π-dianion.[7] Clearly, the ease of the above redox reactions depends on the way in which the compound accomodates the presence of extra charges,[8,9] and special emphasis will be put on electronic stabilization effects occuring in annulene ions with a particular number of electrons. The subtle competition of electronic stabilization and Coulomb effects will be influenced not only by the distribution of the π-charge within the substrate, but also by its interactions with the counterions and the solvent. The ionic products thus accessible by electron-transfer processes range from a doubly charged cation A^{2+} to a quadruply charged anion A^{4-} and constitute excellent model compounds for chemical, spectroscopic, and theoretical investigations.


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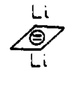
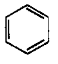


$1^{2-}/2Li^+$

$(1^{2-}/2Li^+)a$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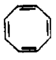
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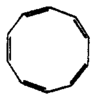
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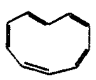
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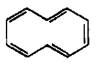
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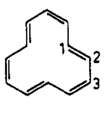
Annulenes are well known as monocyclic conjugated π-systems of the general formula $(CH)_{2i}$.[11] A neutral compound will possess (4n + 2)- or (4n)π-electrons depending on whether i is odd or even. Experience has provided convincing arguments in favor of this classification since [4n + 2]annulenes and [4n]annulenes appear to differ widely in their chemical and spectroscopic properties. It is also well known that Hückel's rule brings about a straightforward explanation for this striking difference and, indeed, one of the attractions of annulene chemistry has been found in the fruitful interplay of theoretical and experimental efforts.

If, however, the number of π-electrons involved in a conjugated monocycle plays an essential role in controlling the bonding character then *ion formation*, i.e., the removal or addition of π-electrons within one and the same molecular frame, will be regarded as *the model experiment of annulene chemistry*.

While the use of annulene ions as synthetic intermediates is touched upon briefly in section IV., emphasis is put on the spectroscopic characterization and—as a unique feature of annulene chemistry—the straightforward correlation of spectroscopic behavior and theoretical arguments.

Electrochemical, UV spectroscopic, and thermochemical evidence will be presented toward this end. However, the most significant method which has found widespread use is magnetic resonance spectroscopy: i.e., electron spin resonance (ESR) for paramagnetic[12,13] and nuclear magnetic resonance (NMR) for diamagnetic species.[14-18]

Particularly sensitive criteria for an assessment of the aromatic, antiaromatic, or olefinic character of neutral annulenes are the NMR chemical shifts of ring protons. These data reflect the influence of ring currents being induced in the monocyclic π-systems. The resulting classification of annulenes as being either diatropic or paratropic parallels the predictions of Hückel's rule concerning the aromatic character of annulenes.[19] An additional consideration when extending this reasoning to ionic annulenes, is the finding from an early application of NMR spectroscopy that the chemical shifts of protons in unsaturated molecules are also affected by the π-charge density at the carbon centers to which they are connected.[14-16,20]



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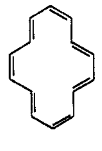
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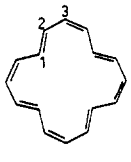

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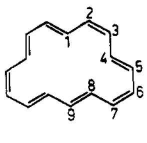

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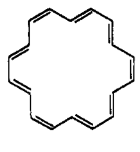
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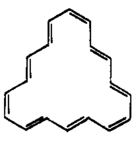
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The series of annulene compounds covered here ranges from such classical examples as [4]annulene (**1**, cyclobutadiene),[21] [6]annulene (**2**, benzene), and [8]-annulene (**3**, cyclooctatetraene),[22-24] up to the 1,3,7,9,13,15,19,21-octadehydro[24]annulene (**41**)[25] and the tetra-*tert*-butyl-1,16-bisdehydro[26]annulene (**25**).[26] In addition to the above mentioned annulene ions there is the well known series of odd-membered monocations and monoanions which comprises the cyclopropenium cation (**9**),[27] cyclopentadienyl anion (**10**),[28] tropylium cation (**11**),[29] cyclononatetraenyl anion (**12**)[30-33] and their higher homologues. Those species which do not possess a neutral diamagnetic counterpart have been extensively reviewed together with the neutral annulenes[11,34-38] and will be omitted here.


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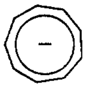
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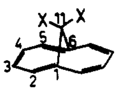
B. Significance of Ion Formation in Annulene Chemistry

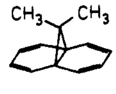
Upon oxidation of an annulene substrate an electron is removed from the highest occupied molecular orbital (HOMO) while the electron added upon reduction is accepted by the lowest unoccupied MO (LUMO). The pivotal importance of the underlying orbital scheme is obvious.

It is the consequence of the simple topology of annulenes that their orbital energies can be given in a closed form and that the resulting orbital sequence exhibits characteristic regularities.[39-42] In even-membered rings the orbitals occur in degenerate pairs except for the energetically lowest and highest which are both nondegenerate. It appears, and this has been stated by the original Hückel rule, that a closed shell ground state of a monocyclic species will only occur if it contains $(4n + 2)\pi$-electrons. Filling the orbitals with $(4n)\pi$-electrons creates a pair of degenerate nonbonding MO's containing two electrons, thus affording a biradical. By analogy with the atomic series one would expect a particular stability only for closed shell, i.e., $(4n + 2)$-π-systems. Indeed, the remarkable success of the Hückel rule has (1) readily rationalized the elusiveness of the $[4 = 4n]$annulene cyclobutadiene in contrast with the extreme persistence of the $[6 = 4n + 2]$annulene benzene; (2) encouraged the synthesis of higher membered $[4n + 2]$annulenes which turned out to exist as stable benzene like compounds.

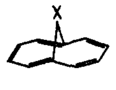


13

a X=H
b X=Cl
c X=F
d X=CH_3



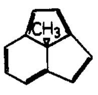
(13d)'



14

a X=>O
b X=>NH
c X=>C=O
d X=>C=C<CH_3 CH_3

Before proceeding to the corresponding ionic systems we should note that an adequate treatment of $(4n)\pi$-systems is beyond the realm of the simple Hückel model. After taking proper account of electron repulsion and correlation effects, the prediction of a degenerate ground state is not retained. However, a more sophisticated treatment arrives at systems with low lying electronically excited states which are prone to suffer a pseudo-Jahn–Teller distortion.[42-45] The latter effect includes the bond length alternation that has actually been observed for $[4n]$annulenes.[44,45] It is for the same reason that higher membered $[4n + 2]$-annulenes also show a tendency toward π-bond fixation.[45-49] Upon going to very large rings the HOMO/LUMO gap decreases and the admixture of (low-lying) electronically excited states leads again to a distorted ground-state configuration.



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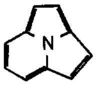

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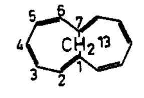

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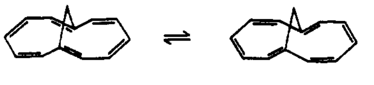


17 17'

Although the Hückel theory is on strongest grounds when applied to neutral alternant hydrocarbons the above description of the orbital scheme is valid irrespective of the charge of the π-system. The lesson to be learned from this is that *dianion or dication formation from a particular annulene is the most straightforward way of experimentally verifying Hückel's rule.* Let us, therefore, translate the underlying oxidation or reduction process, i.e., the ready interconversion of $(4n)\pi$- and $(4n + 2)\pi$-systems into the language of the simple MO model: transforming a neutral $[4n]$annulene into a dianion fills the low-lying LUMO (see Figure 1): this results in a stable ground state which is characterized by a large HOMO/LUMO gap. Conversely, the $(4n)\pi$-dianion derived from a neutral $[4n + 2]$annulene possesses a low-lying LUMO and is a potential candidate for a pseudo-Jahn–Teller distortion.

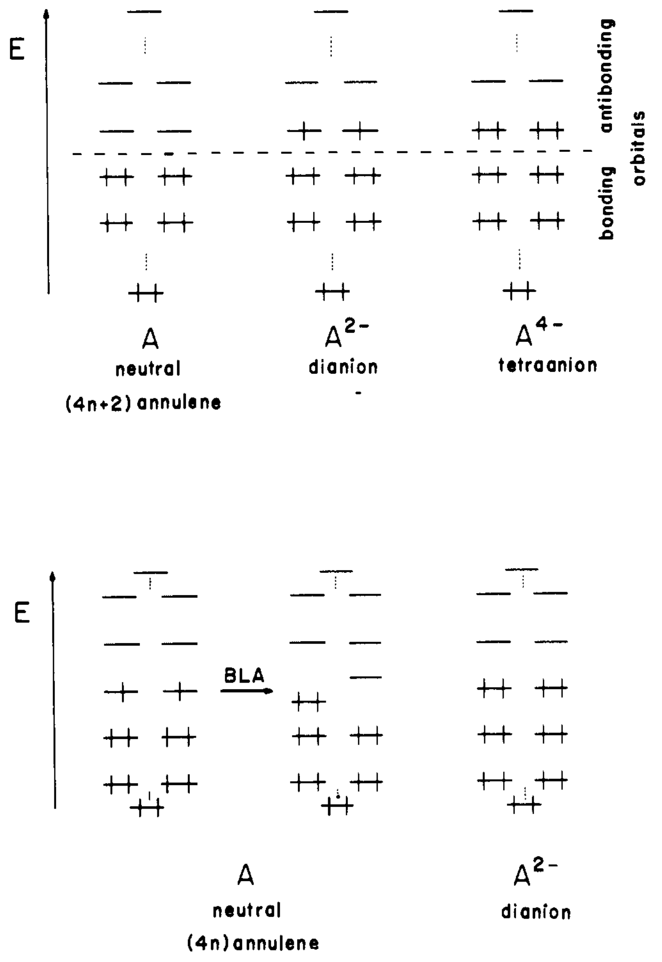
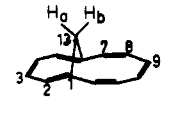
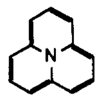
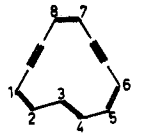
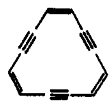


Figure 1. π-Orbital scheme of annulenes (see text).





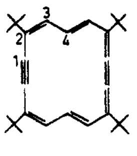




18 19 20 21

When considering Figure 1 it is important to realize that the orbital schemes are obtained irrespective of the chosen theoretical method as long as the perimeter possesses a C_n symmetry axis with $n \geqslant 3$. The degeneracy of the orbitals is maintained even when bond-length alternation (BLA) is introduced. However, this is no longer true for the nonbonding MO's in neutral $[4n]$annulenes (see Figure 1) where BLA removes the degeneracy. The degeneracy of the highest occupied orbitals of $[4n + 2]$annulene dianions is not lifted under the influence of BLA. Here further distortions of the perimeter have to be present in order to obtain closed shell structures.[396] It should be noted that the use of one-determinant approaches (Hückel or Hartree–Fock) is inadequate for π-systems with a degenerate

HOMO/LUMO pair since totally symmetric closed shells cannot be constructed.



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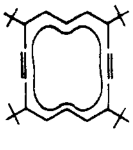

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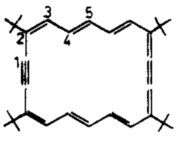
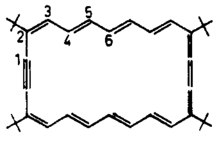


23

Starting from a neutral [4*n* + 2]annulene A the formation of a tetraanion A^{4-} is expected to be even more significant: when the intermediate dianion A^{2-} accepts two additional electrons in the next lowest unoccupied MO (NLUMO) of A the HOMO–LUMO gap of the resulting species is expected to increase, thus creating a situation similar to the one in the neutral compound A.[10]



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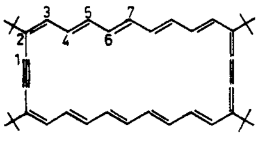

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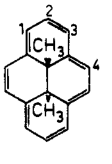
Clearly, the main emphasis in a physical description of annulenes and their corresponding ions is put on the molecular properties *structure* and *energy*. Particularly relevant to the former is the basic alternative of π-bond delocalization or π-bond localization[44,45] while a discussion of the latter brings up the concept of aromaticity. This concept, which has long been a matter of dispute,[50–53] arises from the fact that a particular cyclic π-system may possess a lower energy in its ground state than would be predicted without such a concept.[54]



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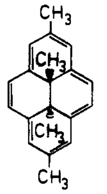

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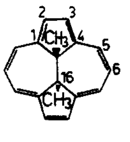

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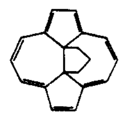

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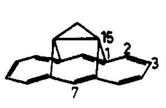
The resonance energy of a compound is thereby given by the difference between the total π-energy of the compound and that of a hypothetical nonaromatic reference structure.[48,51] The problem of choosing suitable reference structures within the theoretical treatment has been solved not only for neutral,[55–60] but also for charged π-systems.[41,61–63] It then appeared that the concept of aromaticity could be extended to ionic annulenes without violating the fascinating elegance of the simple MO model.

C. "Real" Annulenes as Perturbed Perimeters

An inherent problem of annulene chemistry is that its compounds, except for the unique case of benzene, do not conform to the full D_{nh} symmetry of the perimeter. Consequently, when describing the electronic structure of the homologous annulenes one must account for various perturbational effects.[64] The Hückel approach, while considering the π-energy alone, ignores the role of the σ-frame and can therefore only be applied to planar, strain-free π-perimeters. However, in annulenes larger than benzene the adoption of a planar conformation is unfavorable for steric reasons, because a planar ring with an all-cis configuration of the peripheral bonds suffers from increasing angle strain. On the other hand, the occurrence of trans-arranged bonds with inner hydrogens is known to cause severe nonbonding interactions.



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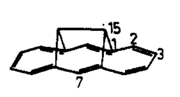

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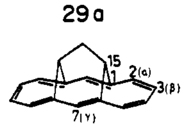

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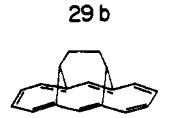

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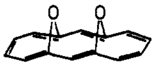

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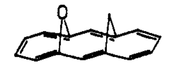

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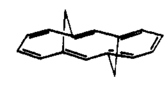

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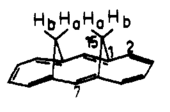

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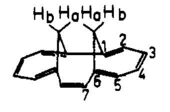

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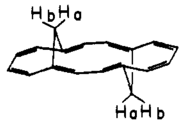

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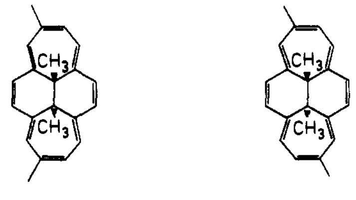

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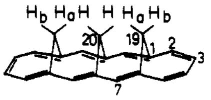
There have been different approaches toward the construction of appropriate annulene models and excellent reviews have appeared which discuss both the synthetic and structural aspects.[65–72] We will touch upon the different classes of annulenes only in so far as their particular deviations from the D_{nh} perimeters are relevant to an understanding of the corresponding ions. Depending on the sequence of cis or trans double bonds the higher homologues within the classical annulene series **1**–**8** adopt different perimeter types which, due to nonplanarity and to transannular π-interactions, may differ widely in their electronic properties. Compounds **6**,[73] **7**,[74,75] and **8**[76] are typical examples. Furthermore, the stereoisomers may interconvert at a rate corresponding to the NMR time scale and induce dynamic line-broadening effects.[77]

Within these "flexible" annulenes the profound change in the π-bonding situation that is brought about by ion formation will frequently be accompanied by a change in the ring configuration and conformation as well as in stereodynamic behavior. This will, of course, raise severe experimental problems during a structure proof (see section III). It will be shown, on the other hand, (see section XB) that these features provide sensitive criteria for monitoring the consequences of the electron-transfer processes.

As is well-known from the literature, the problem of "inner" hydrogens has been circumvented by



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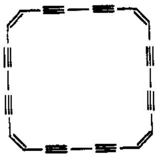


41

"bridging"[67–69,78–80,174] of the annulenes or by the transition to the dehydroannulenes.[71,73,81,82] Compound **13**[68,83] in which the inner C–H bonds of the hypothetical di-*trans*-[10]annulene **4b**[84] have been replaced by a CX_2 group constitutes a planarized [10]annulene. The same is true for the [14]annulenes **26a**,[85,86] **27a**,[79,80] and **29a**[87] with either a pyrene- or anthracene-type perimeter. Another example of an essentially planar, π-bond-delocalized 14π-perimeter is provided by the bisdehydro[14]annulene **22**[88] which incorporates an acetylene and a cumulene structure and can adequately be depicted by formula **22a**. Thus, while the perimeter character of both types of compounds can be convincingly evidenced it is clear that the presence of the bridging group or of the triple bond (i.e., an additional, although orthogonal π-system) disturbs the electronic structure. On the other hand, one can now achieve rigid annulenes with well-defined ring configuration, conformation, and, even more important, a homologous series of annulenes with identical molecular architecture. These structural features prove to be extremely useful for a study of the related ionic species which is designed *to establish the importance of particular π-electron configurations*. When changing the number of π-electrons within a *rigid* molecular frame, the spectroscopic data should reflect the pure "electronic" effects. Likewise, an investigation of the ring size within a homologous series of ions is no longer impeded by configurational and conformational interconversions.

II. Availability and Persistence of Annulene Ions

A. Experimental Techniques of Ion Formation

Radical anions and dianions are expected to undergo two general types of reactions:[5] they may transfer an electron to a suitable acceptor (e.g., oxygen!) or incorporate an electrophile. The problems concerning reactivity will be addressed in section IV. It is clear, however, that radical anions $A^{-}\cdot$ and dianions A^{2-} are powerful bases, this finding being particularly true for A^{2-}. Not surprisingly, therefore, reduction of the hydrocarbon substrates is only feasible under careful exclusion of oxygen in scrupulously dried solvents.

Polarographic evidence (see section IXA) shows that the annulenes listed in Table I accept a first and second electron at potentials which allow their preparation via reduction with alkali metals. Indeed, all of the diamagnetic anions whose NMR spectroscopic data are given have been prepared by reduction with alkali metals in ethereal solvents. In practice, degassed solutions of the samples are kept at the bottom of a NMR tube while the alkali metals are extruded into the upper part of the suitably constricted tube.[146]

Alternatively, the metals (except lithium) can be brought in from a side arm via sublimation in vacuo and deposited as a mirror.[117,150] Cesium is thereby prepared via thermolysis of cesium azide. Lithium can be activated by sublimation with an induction furnace.[151,152] Various reductions of [4n + 2]annulenes (e.g., **8**,[146] **23**,[10] **29**,[108,109] have been reported to be successful only when the solutions are kept at −78 °C throughout the experiment.

The reaction rates are difficult to compare since the electron-transfer process depends on various experimental conditions such as concentration, temperature, and the presence of impurities or the nature of the metal surface. In describing the heterogeneous electron transfer it should be mentioned that dianion formation (lithium salt) of the [18]annulene **23** is complete within a few minutes while the same reaction in the case of the [18]annulenes **8**[146] and **39**[108,109] is reported to require several days.

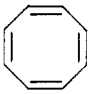
In a number of cases the progress of the reduction has been monitored by recording ^1H NMR and ESR spectra after controlled periods of time.[146] After the first contact of the solution with the alkali metal the formation of the radical anion $A^{-}\cdot$ can be detected by its ESR signals. At the same time the NMR signals of the starting compound A broaden due to an intermolecular electron-exchange process between A and $A^{-}\cdot$. The appearance of the NMR signals of A^{2-} at later stages of the reduction depends on the specific properties of the system and will be treated in the following section.

Careful kinetic control of the reduction becomes unavoidable for the case of compounds **22**–**25**.[10] While dianion formation is complete within a few minutes, the NMR signals disappear again when the solution is briefly brought into renewed metal contact. The reason is that the reduction proceeds beyond the dianion stage and produces a radical trianion and, finally, a tetraanion. These are the first examples of annulene tetraanions. It should be mentioned, however, that tetraanions have been obtained from various polycyclic alternant[154–158,401,402] and nonalternant[159] hydrocarbons. The problems of detecting radical trianions by means of ESR and ENDOR spectroscopy have been discussed elsewhere.[160]

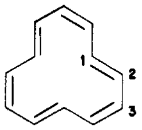
An investigation of the ion-pair structures of annulene anions[161,162] requires a systematic variation of the counterion, the solvent, and the temperature, and will be discussed in section VII. Not every ion pair can be realized experimentally due to the limited persistence; it appears that solvent-separated ion pairs are more readily protonated than contact ion pairs. Another limitation, in particular for ^{13}C NMR studies, arises from the low solubility of the dianion salts; thus, the dianion of the [12]annulene **17** can be studied by NMR only as the lithium salt.[121]

Concerning the oxidation of annulenes, radical cations of [14]annulenes (e.g., **26a**,[129] **27**,[137] **29**,[136]) have been shown to be accessible. Dications of **22**,[108] **29a**,[108] **31**,[108] **34**,[108] **37**,[144] and **39**[148] have been prepared with antimony pentafluoride as the oxidizing agent[163] using chlorosulfuryl fluoride (SO_2ClF) as the solvent. In order to minimize the amount of polymer formation it is essential that the neutral compound is slowly added to an

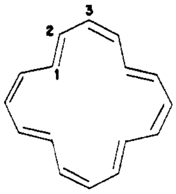
TABLE I. ${}^1H$ and ${}^{13}C$ NMR Chemical Shifts (δ_H, δ_C) of Annulenes as well as of Their Corresponding Dications, Dianions, and Tetraanions. ESR Hyperfine Coupling Constants (a_H[mT]) of Annulene Radical Anions[a]

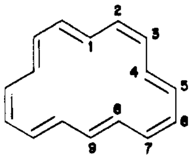


			ref
δ_H (3)	6.42		103
δ_H ($3^{2-}/2Li^+$)	5.726	THF-d_8, 29 °C	161
a_H ($3^{-\cdot}/Li^+$)	0.3209 ± 0.0005	THF	96

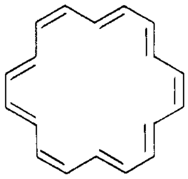


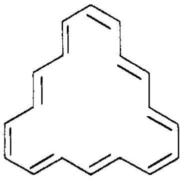
	1	2	3		
δ_H (5)	6.87	——— 5.96 ———		THF-d_8, −90 °C	112
δ_H ($5^{2-}/2Li^+$)	−4.60	6.98	6.23	THF-d_8, −90 °C	112



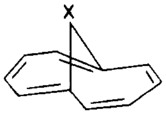


	inner				outer				
	1	4	8	10	2	3	5, 6, 7, 9		ref
δ_H (7a)	10.53				5.40	5.11		THF-d_8, −120 °C	140
δ_H ($7a^{2-}/2K^+$)	−8.17				8.83	7.45		THF-d_8, −30 °C	140
δ_H ($7b^{2+}/2FSO_3^-$)	4.48	4.10	−2.58—		———10.70———			$FSO_3H(D)/SO_2/CD_2Cl_2$, −80 °C	141
a_H ($7a^{-\cdot}/Na^+$)	0.0743				0.3958	0.0963			340

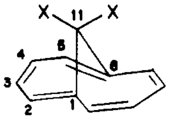




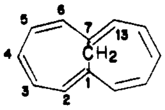
	outer	inner		ref
δ_H (8a)	9.33	−3.17	THF-d_8, −85 °C	146
δ_H ($8a^{2-}/2K^+$)	−1.13	29.5	THF-d_8, −110 °C	146
δ_H ($8b^{2-}/2K^+$)	−1.13	28.1	THF-d_8, −110 °C	146



	2	3	11 (CH_2)		ref
a_H ($13^{-\cdot}/Na^+$)	0.270	0.0099	0.115	DME, −80 °C	256

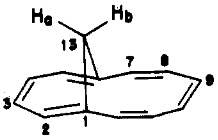


	2	3	12a (CH_3)		ref
δ_H (14d)	7.45	7.05	0.96	THF-d_8, +25 °C	108
δ_H ($14d^{2-}/2Li^+$)	4.43	4.66	1.55	THF-d_8, −30 °C	108

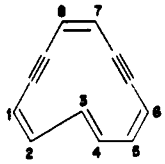


	2	3	4	5	6	13 (CH_2)		ref
δ_H (17)	5.47	5.20	5.12	5.18	5.61	5.98	THF-d_8, −135 °C	121
δ_H (17)	5.54	5.19	5.12	5.19	5.54	6.04	THF-d_8, +25 °C	121
δ_H ($17^{2-}/2Li^+$)	7.16	6.28	6.41	6.28	7.16	−6.44	THF-d_8, −80 °C	121
δ_H ($17^{-\cdot}/K^+$)	0.224	0.364	0.033			0.019	THF, −80 °C	120

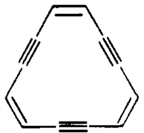
TABLE I (*Continued*)



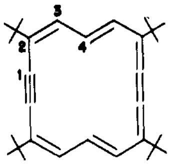
	2	3	7, 8, 9	13a (CH_2)	13b (CH_2)		ref
δ_H (18)	5.73	6.17	≈5.5	3.29	7.00	CCl_4, + 25 °C	121
δ_H ($18^{2-}/2Li^+$)	7.56	6.51	≈6.35	−5.52	−6.08	THF-d_8, − 80 °C	121



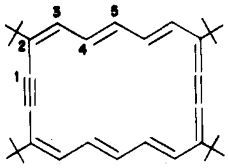
	1	2	3	4	5	6	7, 8		ref
δ_H (20)	4.18	5.03	10.90		5.03	4.18	4.53	CCl_4, − 80 °C	17, 117
δ_H ($20^{2-}/2K^+$)	6.69-5.99	7.97-7.53	(−)6.88	7.97-7.53	6.69-5.99			THF-d_8, − 35 °C	117



			ref
δ_H (21)	4.42	THF-d_8	117
δ_H ($21^{2-}/2K^+$)	6.74	THF-d_8, ca. 0 °C	117
a_H ($21^{-\cdot}/K^+$)	0.298	THF, ca. 0 °C	117

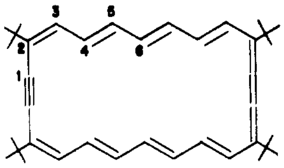


	1	2	3	4	*t*-Bu			ref
δ_C (22)	117.2	131.9	131.1	129.6	37.9	32.4	THF-d_8, − 30 °C	10
δ_C ($22^{2-}/2Li^+$)	106.0	100.0	137.4	90.7	32.3	30.2	THF-d_8, − 30 °C	10
δ_H (22)			9.32	− 4.44		1.94	THF-d_8, + 25 °C	108
δ_H ($22^{2-}/2Li^+$)			1.85	24.37		− 0.01	DME-d_{10}, − 75 °C	108
δ_H ($22^{2+}/2SbF_6^-$)			3.27	27.73		− 0.25	SO_2ClF, − 30 °C	108
a_H ($22^{-\cdot}/K^+$)			0.108	0.514			DME, − 50 °C	128

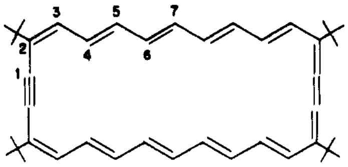


	1	2	3	4	5	*t*-Bu			ref
δ_C (23)	116.3	132.2	131.3	130.1	134.3	38.4	32.3	THF-d_8, − 30 °C	10
δ_C ($23^{2-}/2Li^+$)	107.9	109.4	136.5	107.6	137.7	31.5	28.7	THF-d_8, − 30 °C	10
δ_C ($23^{4-}/4Li^+$)	110.1	79.0	85.9	94.9	107.1	37.3	34.5	THF-d_8, − 30 °C	10
δ_H (23)			9.32	−3.64	9.82		1.92	THF-d_8, RT^b	108
δ_H ($23^{2-}/2Li^+$)			1.04	24.88	1.04		0.12	THF-d_8, − 80 °C	108
δ_H ($23^{4-}/4Li^+$)			7.95	− 8.97	9.85		2.12	THF-d_8, −40 °C	108
a_H ($23^{-\cdot}/K^+$)			0.087	0.042	0.135			DME, − 50 °C	128

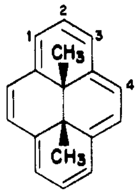
TABLE I (*Continued*)

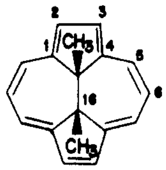


	1	2	3	4	5	6	*t*-Bu			ref
δ_C (24)	116.5	132.1	134.5 (131.1)	130.8	131.3 (134.5)	132.1	37.9	31.6	THF-d_8, −30 °C	10
δ_C ($24^{4-}/4Li^+$)	108.6	83.6	109.4 (94.3)	97.5	94.3 (109.4)	106.2	38.0	35.4	THF-d_8, −30 °C	10
δ_H (24)			8.73	−0.82	9.21	−0.82	1.82		THF-d_8, RT	108
δ_H ($24^{2-}/2Li^+$)			1.15	24.80	−0.29	23.23	−0.29		THF-d_8, −80 °C	108
δ_H ($24^{4-}/4Li^+$)			9.03	−10.67	10.61	−9.50	2.29		THF-d_8, −45 °C	108
a_H ($24^{-}\cdot/K^+$)			0.064	0.337	0.124	0.399			DME, −50 °C	128



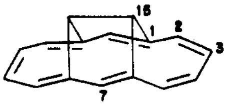
	3	4	5	6	7	*t*-Bu		ref
δ_H (25)	7.93	1.95	8.23	1.82	8.23	1.61	THF-d_8, +25 °C	108
δ_H ($25^{2-}/2Li^+$)	1.20	23.39	0.18	21.35	0.18	−0.20	THF-d_8, −80 °C	108
δ_H ($25^{4-}/4Li^+$)	9.84	−10.17	11.49	−11.27	11.49	2.44	THF-d_8, −45 °C	108
a_H ($25^{-}\cdot/K^+$)	0.061	0.285	0.114	0.310	0.122		DME, −50 °C	128





	2	3	4	15a (CH_3)		ref
δ_H (**26a**)	8.67–7.95			−4.25	THF-d_8, −65 °C	131
δ_H (**26a**$^{2-}/2K^+$)	3.19 to −3.96			21.00	THF-d_8, −65 °C	131
a_H (**26a**$^{-}\cdot/Na^+$)	0.546	0.078	0.078	0.0195	DME, −60 °C	129

	2	5	6	15a (CH_3)		ref
δ_H (**27a**)	8.74	8.77	8.04	−4.53	THF-d_8, +25 °C	108
δ_H (**27a**$^{2-}/2K^+$)	0.05	0.17	−0.85	11.96	THF-d_8, −30 °C	108
a_H (**27a**$^{-}\cdot/K^+$)	0.157	0.058	0.482	0.021	DME, −90 °C	137



	2	3	7	15 (CH)		ref
δ_H (**29a**)	8.17	7.82	8.00	−1.82	THF-d_8, −25 °C	108
δ_H (**29a**$^{2-}/2Li^+$)	2.94	1.72	2.08	13.01	THF-d_8, −30 °C	108

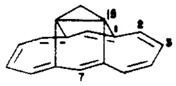
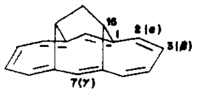
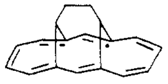
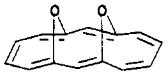
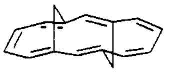
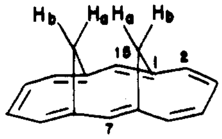
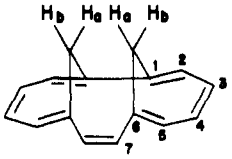
		2	3	7	15 (CH)	17 (CH_2)	ref
	a_H ($28^{-}\cdot/NR_4^+$)	0.316	0.081	0.452		0.028	135
	a_H ($30^{-}\cdot/NR_4^+$)	0.278	<0.005	0.344	0.088	0.012	135
	a_H ($31^{-}\cdot/NR_4^+$)	0.242	<0.005	0.277	0.047	0.018	135
	a_H ($32^{-}\cdot/NR_4^+$)	0.295	0.037	0.288			135
	a_H ($34^{-}\cdot/NR_4^+$)	0.164; 0.159; 0.119; 0.114; 0.020					

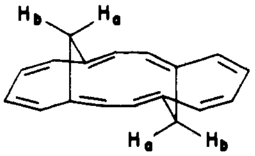
TABLE I (*Continued*)



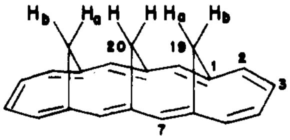
	1	2	3	7	15a (CH$_2$)	15b (CH$_2$)		ref
δ_C (35)	104.7	136.8	126.4	133.3	25.2		THF-d_8, + 25 °C	108
δ_C (35^{2-}/2Li$^+$)	136.5	97.2	118.3	81.7	49.3		THF-d_8, − 15 °C	108
δ_C (35^{2+}/2SbF$_6$)	139.9	167.9	147.3	161.2	33.0		SO$_2$ClF, − 15 °C	108
δ_H (35)		7.27	7.28	7.89	0.95	− 1.13	THF-d_8, + 25 °C	108
δ_H (35^{2-}/2Li$^+$)		2.83	3.56	2.70	11.95	8.50	THF-d_8, − 15 °C	108
δ_H (35^{2+}/2SbF$_6^-$)		7.27	7.15	6.13	9.27	6.83	SO$_2$ClF, − 10 °C	108



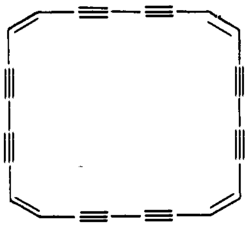
	2	3	4	5	7	15a (CH$_2$)	15b (CH$_2$)		ref
δ_H (36)^c	7.52	7.28	7.06	6.92	7.19	2.36	− 0.36	THF-d_8, + 25 °C	108
δ_H (36^2/2Li$^+$)^c	4.16	5.27	3.68	5.28	5.30	5.23	2.92	THF-d_8, − 30 °C	108



	2	3	7	17a (CH$_2$)	17b (CH$_2$)		ref
δ_H (37)	5.09	5.09	4.80	8.20	5.58	THF-d_8, + 25 °C	108
δ_H (37^{2-}/2Li$^+$)	8.24	6.93	7.92	− 8.52	−6.20	THF-d_8, +10 °C	108
δ_H (37^{2+}/2SbF$_6^-$)	11.02	10.56	11.81	− 5.71	− 2.29	SO$_2$ClF, 0 °C	108

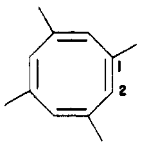


	1	2	3	7	8	19a (CH$_2$)	19b (CH$_2$)	20 (CH$_2$)		ref
δ_C (39)	107.0	138.4	126.5	137.0	96.6	26.7		14.1	CDCl$_3$, + 25 °C	148
δ_C (39^{2+}/2SbF$_6^-$)	133.9	151.6	144.6	164.8	127.4	32.8		24.7	SO$_2$ClF, − 15 °C	148
δ_C (39^{2-}/2Li$^+$)	148.4	100.9	108.8	99.9	130.0	48.4		47.2	THF-d_8, − 20 °C	108
δ_H (39)		7.55	6.95	7.62		1.32	− 0.45	0.53	THF-d_8, + 25 °C	148
δ_H (39^{2-}/2Li$^+$)		2.80	2.70	2.81		12.99	8.38	14.21	THF-d_8, − 20 °C	108
δ_H (39^{2+}/2SbF$_6^-$)		7.04	7.27	6.07		7.58	4.35	8.25	SO$_2$ClF, − 15 °C	148

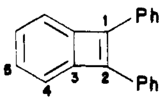


			ref
δ_H (41)	6.15	THF-d_8	149
δ_H (41^{2-}/2K$^+$)	6.12	THF-d_8	149
a_H ($41^{-\cdot}$/K$^+$)	0.166	THF-d_8	149

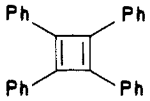
TABLE I (*Continued*)



	2	1a (CH_3)		ref
δ_H (43)	6.17	2.40	SO_2ClF	103
δ_H ($43^{2-}/2K^+$)	5.56	2.55-3.04	THF-d_8, +40 °C	104
δ_H ($43^{2+}/2SbF_6^-$)	10.80	4.27	SO_2ClF, - 70 °C	103
a_H ($43^{-\cdot}/K^+$)	0.0452	0.6414	HMPA, 0 to 65 °C	102



	1	3	4	5	q	ortho	meta	para		ref
δ_C ($45^{2-}/2Li^+$)	83.8	134.4	109.4	113.2	144.6	117.2	128.7	107.9	THF-d_8, 0 °C	91
δ_H ($45^{2-}/2Li^+$)			6.64	6.07		6.63 →	6.70	5.74	THF-d_8, 0 °C	91

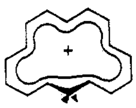


		phenyl					
	1	q	ortho	meta	para		ref
δ_C ($46^{2-}/2K^+$)	108.8	141.9	122.9	127.7	112.8	THF-d_8, 0 °C	92
δ_H ($46^{2-}/2K^+$)			6.93	6.61	5.97	THF-d_8, 0 °C	92

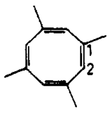
[a] δ_H and δ_C are given with respect to tetramethylsilane. The chemical shifts have frequently been measured with respect to the solvent signal and referred to the tetramethylsilane standard by using appropriate increments. [b] Room temperature. [c] The assignment is tentative.

excess of the stirred SbF_5/SO_2ClF mixture.[164]

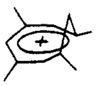
A surprising dication synthesis (7^{2+}, 39^{2+}) is observed during treatment of 7 or 39 with fluorosulfonic acid in a mixture of methylene chloride and SO_2ClF at low temperatures.[141,148] The mechanism of dication formation is not yet clear. A possible route implies primary protonation of the π-system, whereby in the case of 7 the homo[15]annulenyl cation (42) is produced.[141] Subsequent protonation of a methylene C–H bond affords 7^{2+} and H_2. Alternatively, the proton or the acid SO_2H^+ function as the oxidizing agent, a process which involves the annulene radical cation.



42



43



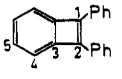
44

The oxidation of 1,3,5,7-tetramethylcyclooctatetraene (43)[103] (SbF_5, SO_2ClF) to yield the dication 43^{2+} is accompanied by the formation of the homotropylium cation 44. Ion 44 is not an intermediate in the formation of 43^{2+}, but probably results from protonation of 43 by protic impurities which are always present in the SbF_5 despite careful purification.[164]

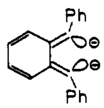
There are other techniques for the preparation of ionic annulenes which do not require reduction or oxidation of the parent compound, but start out from suitable annulene precursors. Among these are the (1) deprotonation of dihydro analogues to yield dianions, (2) solvolysis of dihalo dihydro systems to yield dications, and (3) electron-transfer-induced ring-opening reactions of polycyclic valence isomers of the annulenes.

Clearly, these routes are particularly important in those cases where the parent annulenes do not exist. These procedures are worth mentioning although this text is mainly concerned with the reduction and oxidation of annulenes.

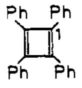
The dianions of 1,2-diphenylbenzocyclobutadiene (45) and tetraphenylcyclobutadiene (46) have been obtained from the corresponding dihydro systems 47 and 48 by deprotonation with strong bases.[91,92] Care has to be taken to exclude the existence of the corresponding monoanions 49 and 50. In fact, the dianion 45^{2-} is only produced when using activated *n*-butyllithium (*n*-butyllithium/tetramethylenediamine) as the base. In contrast, *n*-butyllithium (1.2 equiv, hexane, -30 °C) produces only 49.



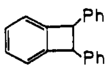
45



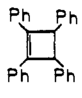
45^{2-} a



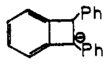
46



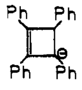
47



48

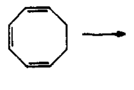


49



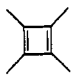
50

Potassium amide in liquid ammonia abstracts a proton from cycloocta-1,3,5-triene (**71**) to form the cyclooctatrienyl anion **51** which disproportionates into 3^{2-} and **71**.[170] The dications 46^{2+} [89] and 52^{2+} [90] can be obtained from the reaction of the dibromide **53** and the dichloride **54** with SbF_5 in SO_2. Here again the early attempts to prepare the dications led only to monocations.[171-173] The dianion 7^{2-} is achieved by the reduction of **7**, but is also accessible via alkali metal reduction of the tricyclic dimer of cyclooctatetraene **55**.[303] Obviously, electron transfer causes ring opening of both cyclooctatriene moieties. This reaction provides a convenient source of [16]annulene ions since it circumvents the laborious synthesis of the neutral annulene. According to more recent studies[175] addition of **55** to the dianion of cyclooctatetraene (3^{2-}) in HMPA (hexamethylphosphoric triamide) results in a solution which gives rise to ESR signals of both $3^{-}\cdot$ and $7^{-}\cdot$. Related valence isomerizations of anionic and cationic systems have been observed on various occasions.[176-179] This type of reaction will be referred to in section III.



71

51



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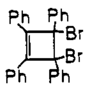
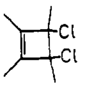
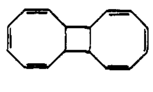


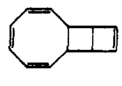
53



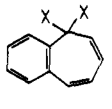
54



55



56



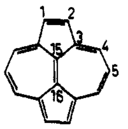
57

An astonishing thermal generation of the radical anion $7^{-}\cdot$ can be achieved by the reaction of the (electron-rich) radical anion $3^{-}\cdot$ with the (electron-deficient) neutral annulene **3**.[397]

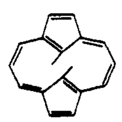
A related example is tetra-*tert*-butyltetrahedrane which upon oxidation with aluminum chloride isomerizes to tetra-*tert*-butylcyclobutadiene.[409]

Dianions of [4*n* + 2]annulenes usually decompose rapidly when warmed to temperatures above 0 °C in ethereal solvents. It is significant in this context that dianions of [4*n*]annulenes are more persistent: the NMR spectra of 7^{2-} [140] and 17^{2-} [121] have been recorded at temperatures up to +90 °C. The ^1H NMR spectrum of 5^{2-} was found to be unaffected when the sealed sample tube warmed to +30 °C. It should be noted that 5^{2-} is much more stable than the corresponding neutral compound which at −50 °C rearranges into *cis*-tricyclo[6.4.0.0^{9,19}]dodeca-2,4,6,10-tetraene (**56**).[111]

Problems with the occurrence of side and intermediate products during dianion formation (see, e.g., the preparation of 45^{2-} and 46^{2-} via deprotonation) are also encountered during the reduction of the neutral annulenes. The reduction of the bridged [10]annulenes **13** and **14** is particularly critical. Reductive formation of the radical anions may lead to the rupture of a C–X bond in **13**,[181] to extrusion of the bridging group X in **14c**,[107,181] or even to some valence isomerization.[182] Thus, species **13d** which exists preferentially as the tricyclic isomer **13d′**, affords a stable radical anion only at −110 °C. Even at −90 °C, $\mathbf{13d}^{-}\cdot$ undergoes a Berson–Willcott rearrangement to yield $\mathbf{57}^{-}\cdot$.[187] The analogous rearrangement, i.e., a sigmatropic 1,5-migration of the bridging group, occurs upon thermolysis of the neutral compound. The latter, however, reacts by a factor of 10^{15} slower than the radical anion. Consequently, compound **13d** is not a favorable candidate for dianion formation. The only example of a [10]-annulene dianion is achieved upon reduction of **14d**.[108,109]



58



58a

58b

A related outcome results from the redox behavior of **27a** and **27b**.[137] While the corresponding radical anions possess an intact molecular frame, this is no longer true for the radical cations. In the latter case oxidations of the neutral compounds causes immediate cleavage of the central C-15–C-16 single bond. ESR spectroscopic evidence indicates that the radical cations formed possess a cyclophane-type structure, i.e., $\mathbf{58a}^{+}\cdot$ and $\mathbf{58b}^{+}\cdot$. It should be noted that a similar ring opening can be induced photochemically for the neutral [14]annulene **26a**.[183-185] In contrast, the isomer **27a** is recovered unchanged after photolysis.

B. Kinetics of Electron Transfer and Disproportionation Effects

Monitoring the reduction of annulenes has been shown in the previous section to be essential for obtaining pure solutions of the ionic products. In addition, recording the intermediate NMR and ESR spectra can tell a lot about the rates of electron transfer as well as about the relative energies of the species involved.[156]

When treating cyclooctatetraene (**3**) in tetrahydrofuran (THF) with potassium, one observes the following ^1H NMR spectroscopic behavior of the system:[7] (1) the sharp resonance of **3** decreases in intensity without significant line broadening; (2) after the signal has decreased to less than about 10% of its original intensity a very broad absorption is superimposed on the initial peak; (3) the latter disappears while the broad absorption, which is assigned to the dianion 3^{2-}, narrows; (4) the resulting sharp singlet has the same intensity as that of the starting material.

The appearance of the broad signal of 3^{2-} just before 2 equiv of the metal has been consumed can be rationalized by a rapid electron transfer between 3^{2-} and the intermediate radical anion $3^{-}\cdot$. The observed line width of the broad signal, the concentration ratio of 3^{2-} to $3^{-}\cdot$ at this stage (100:3), and the known equilibrium constant for the disproportionation of $3^{-}\cdot$ (see below) allow a determination of the rate constant of the bimolecular electron transfer between $3^{-}\cdot$ and 3^{2-}. The value obtained is ca. 10^9 L mol^{-1} s^{-1}.[7] On the other hand, it is obvious from the NMR spectroscopic findings that the electron exchange both between **3** and $3^{-}\cdot$ as well as **3** and 3^{2-} is much slower than the exchange between $3^{-}\cdot$ and 3^{2-}. This result has been explained by the fact that the tub-shaped ring of the neutral compound is flattened upon reduction, with the radical anion and dianion adopting essentially planar perimeters.[7,101]

Independent evidence for this interpretation is obtained from ESR measurements for $3^{-\cdot}$: the bimolecular electron-exchange process limits the lifetime of the radical anion and determines the line width of the ESR signals. A complicating factor in this interpretation lies in the fact that a regular octagonal structure of $3^{-\cdot}$ should suffer a Jahn–Teller distortion.[96] This would again lead to large line widths. It has been argued, however, that planar distortions within the cyclooctatetraene radical anion exert only a small influence on its ESR spectrum,[96] and the experimental results have been interpreted as indicating the absence of any large effects attributable to the Jahn–Teller theorem.

Another characteristic feature of the cyclooctatetraene reduction is that the disproportionation equilibrium

$$2\,3^{-\cdot} \rightleftharpoons 3^{2-} + 3$$

lies largely to the right. The equilibrium constant K has been estimated from intensity measurements and from polarographic data as 2.5×10^8 and 1.1×10^8 for the systems K–THF and Li–THF, respectively.[96]

The rates of the bimolecular electron-transfer process and the disproportionation constant appear to depend sensitively upon the nature of the counterion and the solvent. These phenomena will be revisited in the discussion of ion-pairing effects (see section VII).

According to the following evidence the reduction of cyclooctatetraene appears to be in striking contrast to the reduction of benzenoid hydrocarbons and other [4*n* + 2]-[146] and [4*n*]annulenes.[117]

Electron exchange between aromatic radical anions and their parent hydrocarbons is extremely fast.[186–190] The rates have been determined from line-broadening effects in the ESR spectra to be of the order of 10^8 L mol^{-1} s^{-1}.

For many benzenoid aromatic hydrocarbons which have been reduced in ethereal solvents the disproportionation equilibrium is strongly in favor of the radical anion.[191,192] This is in line with the argument that the dianions are destabilized by Coulomb repulsion between the two excess electrons.

Brief contact of an ethereal solution of **17** with lithium wire produces a small concentration of the radical anion $\mathbf{17}^{-\cdot}$ which is detected by its ESR signal. The ^{1}H NMR spectrum taken at the same stage shows no absorptions from either **17** or $\mathbf{17}^{2-}$. The observation of a rapid equilibrium between $\mathbf{17}^{-\cdot}$ and **17** has been ascribed to the fact that the [12]annulene, unlike cyclooctatetraene, does not have to overcome a barrier to ring flattening upon the electron transfer.[121]

Similarly, a very short contact time between a potassium mirror and a solution of the [16]annulene **7** induces a significant broadening of its proton resonance which is due to the fast exchange between **7** and $\mathbf{7}^{-\cdot}$. The stability of the radical anion with respect to disproportionation can be inferred from the following experiment.[140] First, **7** is electrochemically reduced in a flow cell with the potential of the mercury cathode at a value sufficiently negative to produce $\mathbf{7}^{2-}$. Then, the flow rate is adjusted so that 1 F per mole is transferred. Under these conditions UV and ESR spectroscopic measurements indicate $\mathbf{7}^{-\cdot}$ to be the dominant product. Apparently, the initially formed dianion reacts with the neutral compound as soon as it diffuses away from the cathode. This outcome clearly reveals that the disproportionation equilibrium lies on the side of the radical anion.

The thermodynamic stabilities as well as the stabilization energies of charged annulenes will be discussed in section X.

III. Structure Proof of Ionic Species

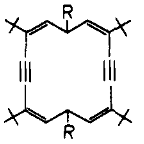
A. Constitution and Charge

The low persistence of the ionic annulenes, on the one hand, and their importance as model compounds, on the other hand, call for a reliable structure proof. It generally rests upon the following pieces of evidence:

(1) The kinetics of the reduction, i.e., the appearance and disappearance of the respective NMR and ESR spectra which characterize the sequence of successive electron transfers (see section IIA).[10,140,146]

(2) Voltammetric experiments provide the number of separate one-electron redox steps as well as the relevant redox potentials (see section IX).[10,140,146]

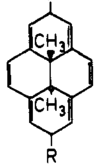
(3) Quenching experiments (via the number of added electrophiles) indicate the number of charges in the dianions and tetraanions; moreover, together with reoxidation experiments, they reveal the intact molecular frameworks. Thus, the tetraanions $\mathbf{23}^{4-}$–$\mathbf{25}^{4-}$ provide mixtures of tetramethyl adducts when reacted with dimethyl sulfate. Protonation of the dianions $\mathbf{22}^{2-}$, $\mathbf{26a}^{2-}$,[142] $\mathbf{27a}^{2-}$,[108] and $\mathbf{30}^{2-}$ [108] gives rise to the dihydro derivatives **59a**, **60a**, **61a**, and **62a**. The regioselective attack of the protons will be touched upon in the following section.[5,193,194] It should be pointed out, however, that the identification of the quenching products chemically proves the structure of the intermediate dianions. Care should be exercised when interpreting such experiments for highly reduced π-systems since it has been observed that intermolecular electron-transfer processes may compete with the quenching reaction.[195] As a consequence, the protonation of a tetraanion A^{4-} may produce a mixture of di-, tetra-, hexa-, and even octahydro derivatives. Thereby, an intermediate protonation product $(\mathrm{A{-}H}_n)^{(4-n)-}$ may accept additional electrons, e.g., from the remaining tetraanion A^{4-}. These complications can be largely avoided by an "inverse" quench whereby the anion is slowly added to



59

a R=H

b R=CH$_3$

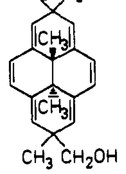


60

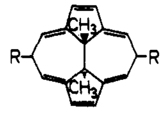
a R=H

b R=CH$_2$OH

c R=CH$_3$



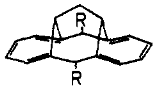
60d



61

a R=H

b R=CH$_3$

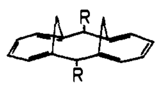


62

a R=H

b R=CH$_3$

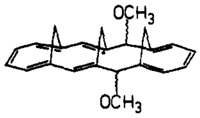
c R=COOCH$_3$



63

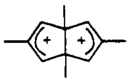
a R=OCH$_3$

b R=CN



64

an excess of the electrophile. Related quenching experiments can be performed when annulene dications are brought in contact with nucleophilic agents. This is documented by the formation of **63a** and **63b** from $\mathbf{35}^{2+}$ as well as **64** from $\mathbf{39}^{2+}$.[109,146] A structure proof by chemical means is also possible if the annulene ion undergoes a well defined valence isomerization. When the SbF_5/SO_2ClF solution of $\mathbf{43}^{2+}$ is warmed to −20 °C an irreversible isomerization to the *cis*-2,3a,5,6a-tetramethyldihydropentalene dication (**65**) is observed.[103] The analogous reaction occurs upon oxidation of octamethylcyclooctatetraene (**66**).[196] The rearrangement of $\mathbf{43}^{2+}$ to **65** via a concerted mechanism is in disagreement with orbital-symmetry considerations;[197,198] it can be rationalized by the thermodynamic stability of the cis—relative to the trans (3a,6a)—product and by the importance of maintaining the p_π-overlap in the allylic moiety. Moreover, one cannot exclude that the rearrangement occurs at the radical-cation stage. A related experiment is the reductive cyclopropane ring opening of semibullvalene (**67**) which affords the bisallylic dianion **68** (lithium salt).[199] Warming to temperatures above 0 °C causes a rearrangement to the cyclooctatetraene dianion. In contrast, the analogous dianion **70** does not isomerize.[200]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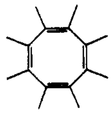
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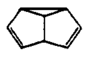
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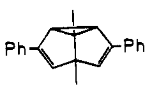
68



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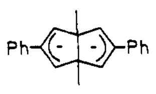


70

(4) The ^1H and ^{13}C NMR spectra of annulene ions, besides being significant for the π-bonding, indicate the intact monocyclic π-systems and show the number of charges having been transferred (see section VB). The case of the rigid annulenes, e.g., $\mathbf{26a}^{2-}$[131] and $\mathbf{29}^{2-}$,[108,109] is relatively simple. The extreme ring current induced ^1H chemical shifts are only compatible with an intact π-perimeter which is further evidenced by the splitting patterns of the proton absorptions and by the number of ^{13}C signals. The latter criteria take on particular significance for those cases in which the electron transfer might be expected to induce side reactions. Two types of examples should be mentioned. In dehydroannulenes such as **22–25** or **20**, **21**, and **41** one might have expected the in-plane π-systems to function as separate electrophores or anionic polymerization to occur. Both possibilities can be rejected from the NMR spectra.[117,201] It has been postulated[202] that the dianion of cyclobutadiene (lithium salt) ($1^{2-}/2Li^+$) prefers an open structure [e.g., $(1^{2-}/2Li^+)$**a**] instead of a monocyclic one. The dianion 1 has been claimed to exist as a labile intermediate in solutions of THF which suffers from ready protonation by the solvent.[167] The related species $\mathbf{45}^{2-}$ and $\mathbf{46}^{2-}$ are stable in solution and can be studied via NMR.[91,92] Quenching experiments (i.e., incorporation of two electrophiles) together with the symmetry inherent in the ^{13}C NMR spectrum of $\mathbf{45}^{2-}$ exclude the possible existence of monoanions (**49**, **50**). Moreover, the resonance of C_1 (C_2) of $\mathbf{45}^{2-}$ at δ 84 is not compatible with a ring-opened valence isomer such as $\mathbf{45}^{2-}\mathbf{a}$. Related arguments can be applied when assessing the structures of $\mathbf{46}^{2+}$ and $\mathbf{52}^{2+}$.[89,90]

B. Configuration and Conformation

The problem of structural assignment is particularly severe for flexible annulenes where ion formation may change the configuration and conformation of the ring. Let us—as a representative example—consider the [16]annulene **7** as well as its dianion and dication.

The neutral compound appears from extended ^1H NMR spectroscopic studies to exist as an equilibrium mixture of the two configurations **7a** and **7b**.[74,75,77] Both isomers exhibit π-bond fixation in their ground state, but differ in the number and sequence of cis and trans double bonds. Moreover, each **7a** and **7b** undergo rapid conformational interconversions and π-bond shifts.

When one looks at the ^1H NMR spectrum of the dianion[140] it can be anticipated from section V that $\mathbf{7}^{2-}$ is a diatropic species with a large deshielding of outer and shielding of inner protons. Three separate resonances of relative intensities 8:4:4 and chemical shifts δ 8.77, 7.40, and −8.07 are observed. The simple triplet structure of the high-field signal indicates immediately that there are four isochronous inner protons each of them being equally coupled with the outer protons at δ 8.77. These findings point toward a π-bond-delocalized perimeter $\mathbf{7a}^{2-}$ which possesses D_{4h} (D_4 or D_{2d} are also possible) symmetry.

In the dication $\mathbf{7}^{2+}$ the situation is totally different since the relative intensities of signals due to inner and outer protons as well as the number of ^{13}C signals are only compatible with a C_{2v} symmetry.[141] Accordingly, the dication has to adopt structure $\mathbf{7b}^{2+}$.

Electron-transfer-induced changes of the conformational behavior in annulenes will be important for an understanding of the π-bonding situation (see section XB). In view of the discussion on structure elucidation two features deserve special comment: dianion formation from [4*n*]annulenes frequently causes some flattening of the perimeter; in these instances the dianion turns out to be less flexible than the neutral compound. (As becomes obvious from the properties of compound **8** (see below), this finding must not be true for dianions derived from [4*n* + 2]annulenes.)

The best documented example of a charge-induced conformational change in [4*n*]annulenes is the transition from the tub-shaped, conformationally mobile cyclooctatetraene to its planar dianion.[87] The same holds for the alkyl-substituted derivatives, e.g., 1,2-dimethyl- and 1,3,5,7-tetramethylcyclooctatetraene (where a flattening of the ring is opposed by the steric interference of the substituents[101,103,105]). Moreover, it was concluded from the rates of bimolecular electron transfer (see section IIB) and from the ^{13}C hyperfine spectrum of $\mathbf{43}^{-\cdot}$ that the intermediate radical anions are also planar.[102]

Even in more rigid [4*n*]annulenes dianion formation goes along with a flattening of the perimeter. This has been convincingly demonstrated for the example of the [12]annulene **18**.[121]

The situation for [4*n* + 2]annulenes and their dianions is somewhat different. While the bridged [4]-

annulenes **26**–**31**[108,109] and the bisdehydro[4*n* + 2]annulenes **22**–**25**[10] have an extremely rigid σ-frame and are not expected to suffer from charge-induced conformational changes, the case of the flexible [18]annulene **8** appears to be more complicated.[146] The neutral compound is described as conforming approximately to D_{6h} symmetry which is compatible with structure **8a**.[76,145] Moreover, the molecule exhibits a conformational mobility[77] by which three isodynamic structures of type **8a** are interconverted. Thereby, conformers of the type **8b** are probable intermediates.

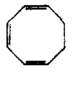
The dianion $\mathbf{8}^{2-}$ exists in solution as an equilibrium of the conformers $\mathbf{8a}^{2-}$ and $\mathbf{8b}^{2-}$.[146] (Note that the two conformers have the same number and sequence of cis and trans double bonds.) A detection of both conformers by means of their individual NMR signals is only possible at −110 °C. At higher temperatures a rapid interconversion of both conformers, as well as a π-bond shift in each one, occur. As a consequence of the exchange behavior, all protons become equivalent in the NMR time scale above −70 °C.

IV. Reactions of Annulene Dianions

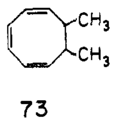
Annulene dianions can function as storage devices for electrons and therefore as potential reducing agents, and as dicarbanions which are prone to accepting two electrophiles.

From the foregoing section it was shown that such reactions (protonation, alkylation, acylation) can be applied to chemically prove the structure of the intermediate ions. The present discussion is mainly concerned with dianion reactions having obtained some preparative use. The favorite subject, clearly, is the dianion of cyclooctatetraene[203,204] since it constitutes the only example of an annulene dianion which is available within large-scale processes. The present discussion will be restricted to a few characteristic features since full accounts of the related dianion chemistry have been given elsewhere.

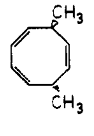
The dianion of cyclooctatetraene $\mathbf{3}^{2-}$ has been applied as reducing agent in the reactions with various classes of compounds. Among these are π-systems such as nitro derivatives of benzene and of related benzenoid hydrocarbons,[205,206] fulvenes,[207] stilbenes,[207] quinones,[205] but also cations like the tropylium ion[208] or the 2,4,6-trimethylpyrylium ion.[209] In the latter instances the reduction is followed by the dimerization of the originally formed neutral radicals.


71

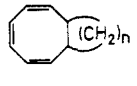

72



73
a: cis
b: trans



74



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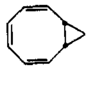
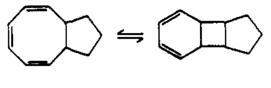
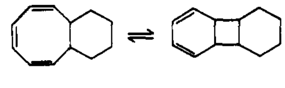

76

The protonation of $\mathbf{3}^{2-}$ which has been prepared under different conditions yields a mixture of the cyclooctatrienes **71** and **72**.[203,204] In a similar fashion alkylation produces dialkylcyclooctatrienes. Thus, the products formed from the reaction of $\mathbf{3}^{2-}$ with methyl iodide are *cis*- (**73a**) and *trans*-1,2-dimethylcyclooctatriene (**73b**) (4:1) and *trans*-dimethylcycloocta-1,3,6-triene (**74**) (total yield 84%).[210,211] In the silylation of $\mathbf{3}^{2-}$ the relative amounts of the 1,2- and 1,4-bisadduct can be controlled by the choice of the chloroalkylsilane.[212]

An interesting variation of the alkylation process is realized when introducing bifunctional alkylating agents such as 1,*n*-dihaloalkanes. The reaction affords bicyclo[6.*n*.0]alkatrienes of the general type **75**.

Among these processes the application of *gem*-dihalides which produces bicyclo[6.1.0]nonatrienes (**76**) has attracted the greatest attention.[213,215] Although various counterion/solvent systems have been applied for the preceding reduction of **3**, the use of $\mathbf{3}^{2-}/2\mathrm{Li}^+$ in liquid ammonia appears to be favorable.[216] Under these reaction conditions one may also employ 1,2-dibromoethane,[217,218] 1,3-dibromopropane,[218,219] and 1,4-dibromobutane as annelating agents. It is remarkable that the introduction of the C_3 and the C_4 units affords mixtures of the bicyclic and tricyclic valence isomers (**77a** and **77b** as well as **78a** and **78b**).

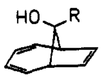

77a 77b


78a 78b

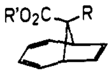
The acylation of $\mathbf{3}^{2-}$ may provide a manifold of products. A typical example is the reaction with acyl chlorides,[220,221] which gives rise to the bicyclo[4.2.1]nonatrienes **79** and **80**, the bicyclo[6.1.0]nonatrienes **81** as well as the acyclic tetraenes **82**. Aldehydes and ketones initially lead to mixtures of cyclooctatrienes related to the alkylation products. Here again, however, the diadducts may isomerize to the bicyclo[4.2.0] systems or to acyclic tetraenes.[220,222] Similar reactions have recently been studied by using alkyldichloro or chlorodiphenylphosphanes.[398]

Finally, it must be mentioned that the dianion $\mathbf{3}^{2-}$ is frequently used as a precursor for the synthesis of various metal derivatives.[223,224] The most famous example comprises the reaction of $\mathbf{3}^{2-}$ with actinide(IV) metal complexes which affords complexes of the type **83**.[225–227] These complexes which are termed "uranocene", etc., and which possess sandwich structures have been the subject of numerous preparative, spectroscopic and theoretical studies.[22]

In the case of $\mathbf{3}^{2-}$, which for reasons of symmetry adopts a uniform π-charge distribution, each ring carbon possesses the same probability to be attacked by the first electrophile. Dianions of higher annulenes which do not conform to the ideal D_{nh} symmetry are characterized by a nonuniform π-charge distribution. We will touch upon the NMR spectroscopic determination of the local π-charge densities in a subsequent section. It is known from broad experience, however, that the kinetically controlled addition of an electro-



79



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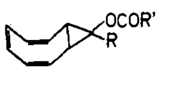

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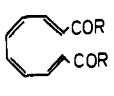

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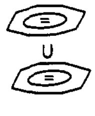

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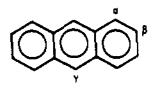


84

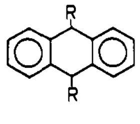
phile to an anionic π-system preferentially attacks the position of the highest π-charge.[79,229]

Not surprisingly, from both the protonation experiment (see section III) and from spectroscopic evidence (see section VIB) the reaction of the [14]annulene dianion $\mathbf{26a}^{2-}$ with formaldehyde yields the bis(hydroxymethyl) species **60b**.[142]

The solvolysis of the corresponding ditosylate did not afford the ring-opened product, the latter constituting another bridged [16]annulene, but only gave rise to elimination products. The problem was circumvented by transforming $\mathbf{26a}^{2-}$ into the dimethyldihydroannulene **60c**. Dehydrogenation to the annulene **26b**, reduction to the corresponding dianion, and subsequent hydroxymethylation yielded the derivative **60d** which, according to the above procedure, could be transformed into a mixture of the *syn*- and *anti*-dimethyl[16]annulenes **38**.[131]

The structural elucidation of bridged annulenes with acene perimeter may depend on the question whether these species constitute homoacenes or true peripheral π-systems. It is, therefore, straightforward to refer the chemical and physical properties of, e.g., the [14]annulene **30** to those of the isoelectronic anthracene (**84**). Such a comparison is particularly meaningful in view of the very similar LUMO's. Concerning the reactivity of the corresponding dianions, it has been well established that anthracene can be reductively alkylated in liquid ammonia to yield the dialkyl dihydro derivatives **85**.[228] Recent NMR measurements point out that $\mathbf{84}^{2-}$ does not resist protonation in liquid ammonia and transforms into a monohydro monoanion.[410] The alkylation of the latter provides a monoalkyl dihydro product, which, after deprotonation by the amide ion, can undergo a second alkylation process. The best yields of dialkyldihydroanthracenes are obtained when the reaction is performed in boiling ammonia in the presence of additional sodium amide.

Reductive alkylation of **30**[108] (NH_3, Li, CH_3Br) provides a nearly quantitative yield of a 3:1 mixture of the dimethyl adducts **62b** and **86b**. The higher regioselectivity in $\mathbf{84}^{2-}$ can be explained by the fact that the difference of the π-charge densities at C_γ (with the highest local π-charge) and at C_α is more pronounced in $\mathbf{84}^{2-}$ than in $\mathbf{30}^{2-}$. One also concludes that under the prevailing conditions $\mathbf{30}^{2-}$ does not suffer from protonation.



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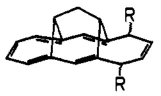
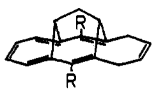


86

a R=H
b R=CH_3
c R=$COOCH_3$



87

a R=H
b R=CH_3
c R=$COOCH_3$

If a solution of $\mathbf{30}^{2-}$ in THF is quenched with chloroformic ester one isolates the bisacylation products **62c** and **87c**. It is reasonable to consider **87c** as a secondary product which is formed from **62c** by a base-induced hydrogen shift. This process is favorable due to the formation of an extended π-system. It should be noted that the above dihydro derivatives can easily be dehydrogenated to the corresponding annulenes and that the direct alkylation or acylation of the annulene has not been possible.

V. Qualitative Assessment of Ring-Current Effects

It has been concluded from convincing evidence that protons outside a [4*n* + 2]annulene experience an additional deshielding while those inside the rings are shielded.[14-18,65-72] These features are ascribed to a diamagnetic ring current induced in the monocyclic loop. The converse is true for [4*n*]annulenes (shielding of outer and deshielding of inner nuclei) an effect which is interpreted as being due to a paramagnetic ring current. Moreover, the ring-current-induced shielding effects of protons in the interior are generally more pronounced. While the differentiation of inner and outer protons is straightforward for the "true" annulenes we note that in bridged annulenes the aliphatic "bridge" protons play the role of inner nuclei.

When these principles are extended to ionic annulenes an interpretation of the ^1H shift data in Table I is compelling: upon reduction (oxidation) of [4*n* + 2]annulenes one obtains strongly paratropic dianions (dications) with $(4n)\pi$-electrons. When going from the neutral [18]annulene **8** to its 20π-dianion the resonances of inner protons are shifted downfield by $\Delta\delta = 32$ while those of outer protons move upfield by $\Delta\delta = 12$.[146]

It was shown in section IIIB that ionic annulenes, depending on the number of π-electrons, may differ in their conformational behavior. This feature poses experimental problems for the evaluation of ring-current effects. Thus, the paratropism of $\mathbf{8}^{2-}$ can only be detected at temperatures below −110 °C. This temperature domain constitutes the slow exchange limit of the conformational process which interconverts the magnetic sites of inner and outer protons.

While in the [14]annulene **22** the inner protons absorb at δ −4.4 (thus, indicating the expected shielding) they appear at δ 27.7 in the 12π-dication[108] and at δ 20 in the 16π-dianion.[10] Similar effects are observed for bridged [14]annulenes: thus, while the (inner) methyl protons of **26a** resonate at δ −4.3, dianion formation induces a downfield shift of their signal by about 25 ppm.[131] Since these data are from a few representative cases, the reader is recommended to consult the other entries of Table I to fully realize the astonishing magnitude of the shift effects.

An additional aspect is revealed during the reduction of the [22]annulene **24** (see Figure 2). Not surprisingly now, the inner protons of the corresponding dianions resonate at about δ 24 (which means a downfield shift of 25 ppm upon dianion formation).[10] Further reduction of $\mathbf{24}^{2-}$ affords the tetraanion $\mathbf{24}^{4-}$. The latter possesses $(22 = 4n + 2)\pi$-electrons and should, therefore, exist as a diatropic species. Indeed, the absorp-

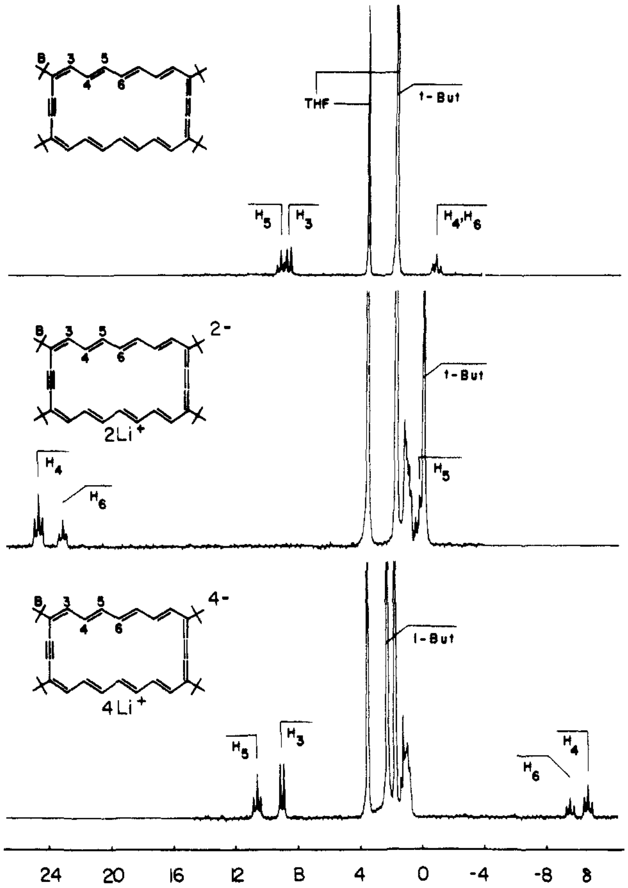


Figure 2. ^{1}H NMR spectra of the [22]annulene 24 and its corresponding dianion and tetraanion.

tions of the inner protons are again at δ −10. Moreover, from the shift difference of inner and outer protons in $\mathbf{24}^{4-}$ one would characterize the tetraanion as being even more diatropic than its neutral annulene.

It is for the same reason that dianions and dications of [4*n*]annulenes can be characterized as strongly diatropic. Selecting from Table I a few examples of [16]- and [12]annulenes we arrive at the following conclusions: The paratropic *anti*-bismethano[16]annulene **37** yields a 14π-dication and a 18π-dianion whose diatropism is evident by the high-field resonances of the bridge protons ($\mathbf{37}^{2+}$: δ −5.7, δ −2.3; $\mathbf{37}^{2-}$: δ −8.5, δ −6.2). Similarly, reductive formation of the dianion $\mathbf{17}^{2-}$ moves the signals of inner protons upfield by $\Delta\delta$ = 12.4. The inner bridge protons of the [12]annulene dianions $\mathbf{17}^{2-}$ and $\mathbf{18}^{2-}$ as well as the inner (olefinic) protons of the isoelectronic dianion $\mathbf{20}^{2-}$ resonate at about δ −6. In accordance with findings both from neutral annulenes and [4*n* + 2]annulene dianions the ring-current-induced shielding effects of outer protons are smaller. As a consequence, the interpretation of the relevant shift data is less straightforward, especially so, since the ring protons are under the additional influence of the π-charge within the anions. It is expected that ring protons of dianions experience a shielding due to the higher π-charge while those of dications are deshielded due to the lower π-charge. Thus, the "olefinic" resonances observed for the outer protons of the dianions of cyclooctatetraene ($\mathbf{3}^{2-}$), 1,7-methano[12]annulene ($\mathbf{17}^{2-}$), 1,5-bisdehydro[12]annulene ($\mathbf{20}^{2-}$), 1,6:9,14-bismethano[16]annulene ($\mathbf{37}^{2-}$), and 1,3,7,9,13,15,19,21-octadehydro[24]annulene ($\mathbf{41}^{2-}$) result from the competition of a ring-current-induced deshielding and a charge-induced shielding. In a related fashion, the charge-induced deshielding within the dication of 1,3,5,7-tetramethylcyclooctatetraene [δ(H-2) +10.1] adds up to the diamagnetic ring-current effect.

Ring-current-induced shielding effects should be detectable from the chemical shifts of nuclei other than hydrogen. This is true for carbon— as long as the carbon center is not situated in the annulene periphery and, thus, in the node of the π-system.[230-233] Studies of ring-current effects upon ^{13}C chemical shifts have been reported for bridged annulenes where the bridge carbons are positioned above the unsaturated ring.[230] Different from ^{1}H NMR the ring-current effects upon ^{13}C resonances are expected to be small with respect to the total shift scale. An interpretation of the data is further impeded by the occurrence of additional shielding terms such as strain-induced rehybridization effects of the carbon or, in the case of ionic annulenes, electric-field effects of the excess π-charge.[121,230]

The ^{7}Li chemical shifts of the lithium counterions of various aromatic ions have been shown to sensitively depend on the mode of ion pairing.[161] Nevertheless, it was possible to detect a shielding of the Li nucleus in ion pairs from diatropic dianions such as $\mathbf{3}^{2-}$ and a deshielding in ion pairs from paratropic dianions such as the [14]annulene dianion $\mathbf{26a}^{2-}$.[234-237] These results were rationalized by assuming that the cation was located directly above the plane of the carbanion, e.g., in the shielding region of a diatropic system such as the dianion of cyclooctatetraene.

Already in this qualitative overview it is worth mentioning that any perturbations of the cyclic π-conjugation are predicted to partly quench the observed ring-current effects.[17,42,238] Among these perturbations which have been sketched in section IC, are nonplanarity, transannular (homoconjugative) π-conjugation as well as the electronic effects of bridges, triple bonds, or substituents. A detailed discussion of ring-current effects in annulene ions and, in particular, an interpretation in terms of bond theory will require a careful consideration of those shift effects (charge, geometry, ion pairing) which are superimposed on the influence of ring currents. This will be done in the following sections.

VI. Spin-Density Distribution and Charge Distribution

A. ESR Hyperfine Coupling Constants and Spin Density

Knowledge of the spin-density distribution in radical ions and of the charge distribution in the corresponding diamagnetic ions is significant for both structural and synthetic considerations.

As is well documented, ESR spectroscopy of paramagnetic π-systems provides proton hyperfine coupling constants a_H which can be used for estimating local spin densities ρ[13]. The McConnell expression[239,240]

$$a_H = Q \cdot \rho$$

which relates both parameters, bears some uncertainty due to the choice of the proportionality constant Q. A value of 2.25 mT is adequate for the benzene radical anion.[94] For larger π-systems, in order to obtain agreement with the total unpaired spin density, one occasionally has to adopt greater values.[5,12]

In a crude approach, ρ at a particular π-center is calculated from the square of the AO coefficient of the singly occupied molecular orbital. In a refined treatment the McLachlan procedure[241] can be used to account for the effects of π,π-polarization.

From the correlation of ESR spectroscopic and MO theoretical parameters one can, therefore, predict the symmetry of the singly occupied molecular orbital of the paramagnetic annulene species.[13] The importance of such information for an understanding of the bonding situation in annulenes will become obvious from the following.

It has been pointed out above that in neutral [4n + 2]annulenes with ideal D_{nh} symmetry the lowest antibonding (Ψ_{a+},Ψ_{a-}) and the highest bonding (Ψ_{b+},Ψ_{b-}) molecular orbitals are degenerate. The probability for the unpaired electron of the corresponding radical anion to be distributed in Ψ_{a+} is the same as in Ψ_{a-}. The ground state of such an ion (analogous arguments hold for the radical cation) is thus doubly degenerate, and it should be subject to Jahn–Teller distortions.[242] It was suggested[93] that such a situation is detectable by three experimental observations: an increase of the g value with respect to the one of the free electron; a large line width,[243,244] and a decrease in the spin-lattice relaxation time since the existence of a degenerate or nearly degenerate[245] electronic ground state creates additional relaxation mechanisms.[243,244,246]

When identical contributions from Ψ_{a+} and Ψ_{a-} to the ground state of an annulene radical anion $A^{-}\cdot$ are assumed, the spin density should be the same at any carbon center of the ring. This prediction is supported by the ESR spectrum of the benzene radical anion[94] (see Table I).

The orbital degeneracy may be removed under the influence of the counterion or upon transition to deuterated or alkylated benzene species.[247] A different situation is encountered in the higher [4n + 2]-annulenes. Considering the particular example of a [14]annulene it should be mentioned that within the Hückel model a deformation of the D_{14h} perimeter to D_{2h} symmetry (with either anthracene—Figure 3a or pyrene—Figure 3b configurations) will not affect the orbital energies. The degeneracy is removed, however, when accounting for the perturbation brought about by the bridging.

Related ESR studies of the radical anions **12a**$^{-}\cdot$,[106] **12c**$^{-}\cdot$,[248] **13a**$^{-}\cdot$,[248] **13c**$^{-}\cdot$[249] have revealed that the dominant substituent effect of the bridging group on the π-orbitals of the perimeter is inductive and electron repelling.[250] A similar effect of the bridging groups in, e.g., the [14]annulene radical anion **30**$^{-}\cdot$ will destabilize Ψ_{a-} with respect to Ψ_{a+}. Accordingly, the latter should accept the unpaired electron upon formation of the radical anion. Consider the ESR hyperfine coupling constants of the radical anions **29**$^{-}\cdot$–**35**$^{-}\cdot$ which are given in Table I and note that the sequence of their absolute values is a_{H} (H-7) > a_{H} (H-2) > a_{H} (H-3). From a comparison of the hyperfine constants with the diagram of Ψ_{a+} and Ψ_{a-} it is evident that the singly occupied orbital in the radical anions strongly resembles Ψ_{a+}. This is in full accord with the above prediction.

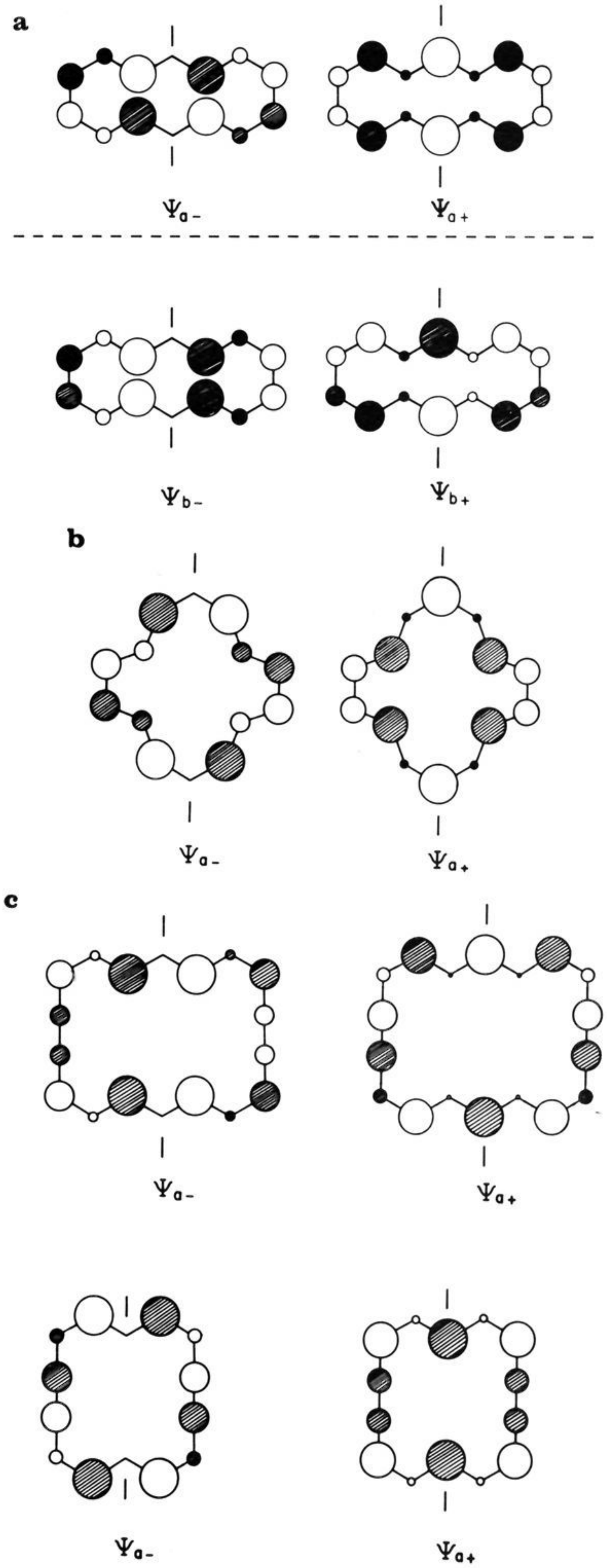


Figure 3. Schematic representation of the frontier orbitals of annulenes. (The areas of the circles are proportional to the squares of the LCAO coefficients, dotted and blank circles symbolize different signs.) (a) [14]Annulene with anthracene perimeter. (b) [14]Annulene with pyrene perimeter (LUMO's only). (c) Bisdehydro[18]annulene and bisdehydro[14]annulene (LUMO's only).

Knowledge of the relative energies of the two lowest antibinding MO's and of the two highest bonding MO's is essential for a description of the electronic structure of annulenes. In addition to the above ESR work, extended PE[251] and UV[252–255] spectroscopic studies have been devoted to this feature.

In the case of the above radical anions the homoconjugative effects act in the same direction as the inductive one, i.e., both perturbations tend to destabilize Ψ_{a-}. The effects are counterproductive for the corresponding HOMO pair, and this situation has been dealt with through the ESR investigation of the corresponding radical cations.[136]

The ESR spectroscopic properties of **26a**$^{-}\cdot$[129] and **27a**$^{-}\cdot$[137] are extraordinary in that both radical anions and cations exhibit the unpaired electron in an orbital symmetric with respect to the mirror plane indicated in Figure 3b. This outcome has been rationalized by a strong hyperconjugative interaction between the bridge and the perimeter orbitals.

These models have been further tested[130] by including compound **26b** with additional substituent effects. It appears that the final spin-density distribution results from a delicate balance of the various perturbational effects.

Proceeding along the series **29**$^{-}\cdot$–**34**$^{-}\cdot$ one realizes that the absolute values of related coupling constants decrease. Also characteristic is the decrease of the sum of the ring coupling constants $\sum a_{\mathrm{H}}$. In restricting the comparison to the latter term one can ignore slight redistributions of the π-charge densities and also include compound **34**$^{-}\cdot$ where reliable assignments have not been achieved. In the above series of compounds—with **34**$^{-}\cdot$ representing the borderline case—one knows from model considerations and also from X-ray studies that the perimeter successively deviates from coplanarity. The decrease of $\sum a_{\mathrm{H}}$ in the series, thus, reflects the increasing degree of twisting among the peripheral π-orbitals. In view of the rigidity of the molecules, which excludes charge-induced conformational changes, the ESR data are expected to also reflect the planarity of the neutral perimeter.[135]

The above finding can be rationalized by the fact that the spin density within the 1s orbital of the ring hydrogen is created via two mechanisms:

(1) The "through-bond" mechanism implies a σ,π-polarization within the C–H bond. The spin density is, thus, produced "indirectly" and has a sign opposite to that of the π-spin density at the carbon center.

(2) A "through-space" mechanism implies a direct transfer of spin density from neighboring π-orbitals into the 1s orbital. The resulting spin density has the same sign as the π-spin density and will partially cancel the 1s density which is due to the indirect effect. The bending of the perimeter thus produces an increasing positive contribution to the negative 1s spin population at the ring hydrogens. The characterization of annulene radical anions which is based on the above arguments has led to the proposal of a modified McConnell equation for radical ions derived from nonplanar π-systems.[256]

A decision as to the type of the singly occupied frontier MO is also possible for the radical anions **22**$^{-}\cdot$–**25**$^{-}\cdot$. Figure 3c depicts the two low-lying LUMO's for **22** and **23** whereby the perimeter has been distorted to the appropriate configuration. Among the perturbations that have to be considered the existence of two short "acetylenic" bonds within the periphery is the most important one. Simulating the shortening of the relevant C–C bonds by increasing the corresponding β-values, again, lifts the degeneracy of the LUMO pair. Interestingly, however, while in **22** the orbital Ψ_{a+} becomes more stable than Ψ_{a-}, the sequence in **23** is reversed (note the relative signs of the AO coefficients at the formal triple bonds). This feature can be found to be generally valid, since the energetic sequence of the MO's Ψ_{a+} and Ψ_{a-} alternates along the homologous series **22**–**25**. As a result the LUMO in **23** and **25**, i.e., the orbital accepting the unpaired electron, possesses a nodal plane through the central ring carbons [C-5, C-14 in **23**, C-7, C-20 in **25**]. Not, surprisingly, therefore, the a_{H} values of H-4 (H-11) in **22**$^{-}\cdot$ and of H-6 (H-17) in **24**$^{-}\cdot$ are large while those of H-5 (H-14) in **23**$^{-}\cdot$ and H-7 (H-20) in **25**$^{-}\cdot$ are small.

The [4*n*]annulenes differ from their [4*n* + 2] counterparts in that they possess a pair of degenerate nonbonding molecular orbitals Ψ_{n+} and Ψ_{n-}. In the corresponding radical anions these orbitals are filled by three electrons, two of which are spin paired. This contrasts the situation in [4*n* + 2]annulene radical anions, where a single unpaired electron has the choice between two degenerate MO's.

The possibility of a Jahn–Teller distortion of the radical anion of cyclooctatetraene (**3**$^{-}\cdot$) has been carefully studied.[257,258] It was concluded that **3**$^{-}\cdot$ should differ from radical anions such as the one derived from benzene (the latter possessing a threefold axis of symmetry) in that planar distortions should exert only a small influence on the ESR spectrum. The nine-line spectrum of **3**$^{-}\cdot$ (indicating the interaction of the unpaired electron with eight equivalent hydrogens) and the UV spectrum of **3**$^{-}\cdot$[259] were interpreted as indicating the absence of any large effects resulting from the Jahn–Teller deformation.

As has been mentioned in section IC the situation is different in radical anions derived from higher [4*n*]-annulenes: even assuming all bonds to be equal in length, the bond-angle strain will prevent a regular D_{nh} structure and the degeneracy of the nonbonding MO's may no longer exist.[140]

The case of the [12]annulene radical anion **17**$^{-}\cdot$ is relatively simple since the inductive effect of the bridge removes the degeneracy of the nonbonding MO's, and the excess electron is accepted by the MO that is higher in energy.[120] A more interesting question concerns the behavior of the nonbonding MO's in the presence or absence of π-bond alternation. When simulating the electronic structure, e.g., of the [16]annulene radical anion **7**$^{-}\cdot$ within a simple Hückel model,[140] the introduction of bond alternation will remove the degeneracy of the nonbonding MO's. Applying such arguments during an ESR spectroscopic description of [4*n*]-annulene radical anions, a decision can be made whether or not the ions exist as π-bond-delocalized systems. This will be discussed in section X which is devoted to the fundamental alternative of π-bond delocalization and π-bond localization.

B. NMR Chemical Shifts and π-Charge Densities

As is well-known the local spin densities of a radical ion can be estimated from the π-charge densities within the molecular orbital occupied by the unpaired electron. Under the reasonable assumption that the doubly occupied HOMO of the dianion A^{2-} is the same as the singly occupied MO in the intermediate radical anion $A^{-}\cdot$ one would conclude that the spin-density distribution in $A^{-}\cdot$ provides a suitable basis for predicting the π-charge distribution in A^{2-}. (A similar relation is expected to hold for the pairs $A^{3-}\cdot/A^{4-}$ and $A^{+}\cdot/A^{2+}$ where in the latter case one must encounter the half or fully empty frontier MO of the neutral compound.)

Therefore, a critical aspect in a study of ionic annulenes is the correlation of the spin-density distribution in annulene radicals and of the π-charge distribution in the related diamagnetic ions whereby both properties should be determined experimentally.

NMR chemical shifts have frequently been invoked to describe the π-charge distribution within unsaturated compounds.[7,14,15,20] Monocyclic ions such as the cyclopropylium cation (**9**), cyclopentadienyl anion (**10**), tropylium cation (**11**), cyclononatetraenyl anion (**12**), as well as the dianion of cyclooctatetraene ($\mathbf{3}^{2-}$) have appeared as most suitable model compounds since due to their D_{nh} symmetry they establish a uniform charge distribution. Several workers have noted a linear relationship between the proton chemical shift δ_H and the excess π-charge according to[260-265]

$$\delta_H = 7.27 + K_H \cdot \Delta q_\pi$$

The definition of the excess π-charge adopts benzene ($\Delta q = 0$) as a reference case so that the related monocyclic ions obtain the values $+^1/_3$ (**9**), $-^1/_5$ (**10**), $+^1/_7$ (**11**), $-^1/_4$ ($\mathbf{3}^{2-}$), and $-^1/_9$ (**12**). The gradient K_H amounts to about 10 ppm per unit charge. A similar correlation was later found for ^{13}C chemical shifts with $K_C \approx 160$ ppm/e.[260,263,266,267]

The linear shift/π-charge density relationship proved to be still valid when extended to various cyclic and acyclic ions.[268] It was concluded from the satisfying correlation obtained from average ^{13}C chemical shifts within species of nonuniform charge distribution that the local π-charge density is, indeed, the main factor influencing the individual ^{13}C chemical shifts.[268] One should be aware that the empirical charge dependence of δ_H and δ_C values has no firm theoretical foundation.[269-272] Nevertheless, it could be demonstrated that such relations are applicable to series of closely related compounds[268] provided that one accounts for ion pairing and ring-current effects.[159,400]

Considering the case of annulene dianions and dications it is clear that ^{1}H chemical shifts cannot be taken as a reliable probe for π-charge densities since they are heavily influenced by anisotropic ring-current effects. (Note that the early ^{1}H shift/π-charge density plot has only included diatropic ions.)

An interesting extension of this work comes from the progress of solid-state NMR which draws attention to the tensorial features of the chemical shielding. The principle values of the ^{13}C chemical shift tensor have been measured for the cyclopentadienyl anion (**10**), for benzene (**2**) and for the tropylium cation (**11**).[273,274] Based on single crystal studies the σ_{11} value is assigned along the C–H axis, while σ_{22} lies in the molecular plane perpendicular to the C–H bond and σ_{33} perpendicular to the molecular plane. The isotropic shift dependence upon the π-electron density q_π which has been reported above results primarily from variations in σ_{22} and σ_{11} while the dependence of σ_{33} upon q_π is negligible. When the average of σ_{11} and σ_{22} is plotted against q_π one obtains a linear relationship with a slope of −218 ppm/e.

On the other hand, when systematically studying ^{1}H chemical shifts in terms of ring-current effects one needs δ_H values which have been corrected for the influence of charge. From the change of the local π-charge densities Δq_π one might obtain the charge-induced signal shift by

$$\Delta\delta_H = K_H \cdot \Delta q_\pi$$

The Δq_π can, thereby, be calculated from MO methods or determined experimentally according to the following procedure. As previously mentioned ^{13}C chemical shifts are insensitive to ring-current effects as long as the carbons are within the π-periphery. Given reliable signal assignments one might then determine Δq_π from the shift of an individual resonance which is observed upon ion formation. The problem, however, is the choice of the proportionality constant $K_C = \Delta\delta_C/\Delta q_\pi$.[268] "Compound-specific" proportionality constants of annulenes have been determined[10] by dividing the charge-induced upfield shift of the center of gravity of the ^{13}C signals by the average change of the π-charge densities. The K_C values of the tetraanions $\mathbf{23}^{4-}$ and $\mathbf{24}^{4-}$ are 154.1 and 164.5 ppm/e, respectively. These values are close to the ones that have been given in the literature for various monoanions. The K_C values of the related dianions which are calculated via the same procedure, are 112.0 and 93.6 ppm/e. Similarly low proportionality constants K_C are observed for the dianions of the bridged[14]annulenes

$$\mathbf{29c}^{2-}\text{: } K_C = 23.1 \text{ ppm/e}$$

and

$$\mathbf{35}^{2-}\text{: } K_C = 84.0 \text{ ppm/e}$$

Facing the strange behavior of the paratropic dianions one notes that they constitute $(4n)\pi$-systems while the diatropic tetraanions possess $(4n + 2)\pi$-electrons. Not unexpectedly, therefore, the dianions of [12]annulenes, (e.g., $\mathbf{17}^{2-}$ and $\mathbf{18}^{2-}$, the latter species again representing $(4n + 2)\pi$-systems) show K_C values of about 169 ppm/e. It is noteworthy in this context, that polycyclic π-systems behave in a similar fashion, i.e., normal K_C values are only observed for diatropic ions. A few examples may be cited: the diatropic tetraanion $\mathbf{111}^{4-}$, but not the paratropic dianion $\mathbf{111}^{2-}$ possesses a K_C value close to 160 ppm/e. Likewise, the K_C value of the diatropic dianion $\mathbf{114}^{2-}$ is 194, while compound $\mathbf{58}^{2-}$, whose ^{1}H chemical shifts fail to indicate significant ring-current effects, has a K_C value of 156.5.

We conclude this section by pointing out that Δq_π values obtained from either MO calculations or ^{13}C chemical shifts are in reasonable agreement although the former have been shown to indicate a more uniform charge distribution.[10] Care should be exercised, however, when attempting to use these data in a quantitative fashion.[159]

An interesting case could be made for methano-bridged annulenes and their ionic derivatives where the ^{13}C shift average of the ring carbons and the shift of the bridge carbons were shown to correlate well with the average π-electron density.[399]

When one interprets the ^{13}C chemical shifts as well as the resulting $\Delta\delta_C$ values of the dianions $\mathbf{29a}^{2-}$, $\mathbf{29c}^{2-}$, and $\mathbf{35}^{2-}$, one readily concludes on the basis of the above discussion that the π-charge distribution is grossly nonuniform. The central carbons C-7 (C-14) adopt the greatest portion of the excess π-charge. In contrast, the signals of the quaternary centers C-1 (C-6, C-8, C-13) suffer from a downfield shift in the dianions. This outcome can tentatively be ascribed to some partial positive charge on these centers as a consequence of π,π-charge polarization. A related mechanism is responsible for the occurrence of negative spin densities in radical anions.

The π-charge distribution in these annulene dianions appears very similar to the one in the closely related, isoelectronic anthracene dianion[403] (see section IX).

An important realization from the above is that the type of π-charge distribution within the dianions could have been properly predicted from the spin-density distribution within the intermediate radical anions. A similar finding is derived for the dianions $\mathbf{22}^{2-}$ and $\mathbf{23}^{2-}$. While in $\mathbf{22}^{2-}$ the signal of the central carbon C-4 is strongly shifted upfield (with a downfield shift of the C-3 resonance), the most pronounced upfield shift in the higher homologue $\mathbf{23}^{2-}$ is now observed for C-4. This behavior is in complete accord with the ESR data derived for $\mathbf{22}^{-}\cdot$ and $\mathbf{23}^{-}\cdot$ and can be rationalized by the nodal properties of the relevant frontier orbitals.

VII. Ion Pairing in Annulenes

A. Additional Aspects in the Structural Description

Research in the field of ionic annulenes has mainly been focused on the behavior of the "pure" π-systems (see section X). While the success of this approach is beyond any doubt, its limitations are particularly striking when invoking aspects such as "stability", resonance energy, or intermolecular electron transfer. Clearly, one now must consider the interaction of the organic anion with the counterion and the solvent. Starting from the calculated pyramidal C_{5v} structure of the lithium salt of the cyclopentadienyl anion (**10**)[275,276] one observes the interaction of ionic annulene systems with their counterions as the combination of a ring and a capping group—a concept which is already well established within the chemistry of boranes and carboranes as well as of various transition-metal systems.[277,278] The π-electrons of the ring and the electrons contributed to the ring/cap binding by the cap are termed interstitial electrons. In general, pyramidal systems with $(4n + 2)$ interstitial electrons are expected to be stable, a prediction which is nothing else than an extension of Hückel's aromaticity rule to three-dimensional systems.[278] It is important in that respect that X-ray studies of lithium complexes of polycyclic benzenoid compounds (e.g. naphthalene, anthracene)[279,280] indicate a symmetric bridging with the lithium atom lying on the local C_6 axis of the benzene moiety.

Moreover, recent calculations[202] point out that the dilithio salt of the dianion of cyclobutadiene could exist in an open "Hückel–Moebius-stabilized" configuration ($\mathbf{1}^{2-}/2\mathrm{Li}^+$)**a** which is bridged by the lithium atoms above and below the plane of the carbon centers. It should be mentioned, however, that the dianions obtained from cyclobutadiene derivatives **45** and **46** possess an intact σ-frame.[91,92]

Experimental studies of the annulene anion/counterion interaction in solution have been performed by invoking the concept of ion pairing.[191] It is known from ample experience that solutions of anionic π-systems contain more than one kind of thermodynamically distinct ion pair.[191,281–285] This is due to the fact that the polarizing counterions may disturb the extended π-system in different fashions. For the corresponding carbocations which possess weakly polarizing polyatomic counterions such as $\mathrm{SbF_6}^-$ the formation of specific solvate structures is probably less significant.[20]

The organic anion/cation interaction, on the other hand, may produce solvent-separated (free) ions, solvent-separated (loose) ion pairs, contact (tight) ion pairs, or larger aggregates. For the highly conjugated title anions existing in ethereal solvents, loose solvent-separated and contact ion pairs are dominant. Concerning the latter species, it has been shown that there are at least two different types of contact ion pairs which are thought to exist in different solvation states.[161] Even in a nonethereal solvent as polar as dimethyl sulfoxide, ion pairing of benzenoid radical anions and dianions with tetraalkylammonium ions is significant.[285,286]

The properties of annulene ion pairs are of both practical and fundamental importance. This shall be outlined by only a few aspects: (1) the persistence of dianions and tetraanions derived from **22**–**25** appears to sensitively depend on the counterion and the solvent;[10] the dianion of cyclooctatetraene is an outstanding example in that it can be prepared by using ethereal solvents as well as ammonia and the strongly cation-solvating hexamethylphosphoric triamide (HMPA); (2) the interaction of the annulene radical anion with the counterion is important in the examples of orbital degeneracy ($\mathbf{2}^{-}\cdot$, $\mathbf{3}^{-}\cdot$) since it can affect MO's in a different fashion (see below); it is to be expected from the polarizing power of the counterions that they influence the mode of the π-charge distribution within the anion. As indicated by the ^{13}C chemical shifts of the ion pairs of $\mathbf{22}^{2-}$ and $\mathbf{23}^{2-}$, the small lithium cation is most effective in attracting the π-charge to those positions which a priori have a high q_π value; (3) ion pairing is an important, although sometimes ill-defined, factor in the reactions of paramagnetic and diamagnetic anions;[5] (4) electrolyte effects severely influence the electrochemical reduction of annulenes; a typical example is provided by the electrochemical formation of an annulene dianion: ion pairing and solvation act to decrease the energy necessary to transfer a second electron to the intermediate radical anion (see section IX). It follows that MO calculations restricted to the "pure" ionic π-system (e.g., $\mathbf{3}^{2-}$ [287]) may not be applied to electrochemical measurements in solution.

An important structural detail of the description of ion pairs concerns the location of the cations with respect to the organic substrate. X-ray data of annulene ions have been described for the dianions of cyclooctatetraene[288] and of its 1,3,5,7-tetramethyl derivative,[289] where the crystalline ion pairs exist in a solvated state, that is the cations are further coordinated with chelating agents such as diglyme. The carbocyclic ring, e.g., of the potassium diglyme 1,3,5,7-cyclooctatetraene dianion is not significantly puckered and exhibits an eightfold symmetry with equilibrated bond lengths. The two counterions are related by inversion and lie on either side of the ring such that all the K–C bond lengths are equal.

With respect to solutions of $\mathbf{3}^{2-}$, the large upfield shift measured for the Li signal of the salt $\mathbf{3}^{2-}/2\mathrm{Li}^+$ indicates that counterions are again positioned above and below the π-system in a sandwich arrangement.[161] As can easily be anticipated, a description of less symmetric ion pairs is more complicated. The example of polycyclic dianions reveals that the results of an X-ray analysis and of a NMR measurement in solution are not necessarily compatible.[404]

Various spectroscopic techniques have been applied to study ion-pairing phenomena for ions derived from mono- and polycyclic benzenoid hydrocarbons.[191] The latter are generally more stable and more easily accessible than annulene ions. It is not surprising, therefore, that—except for $\mathbf{3}^{2-}$—related studies within the annulene field have been rare.

The importance of ion pairing for ESR spectral parameters of organic radical anions has been convincingly documented.[5] It became obvious from these studies that the metal may retain some of the unpaired spin density. This behavior, which can be proven by an ESR hyperfine coupling of the metal, has been reported for the unstable benzene radical anion[93,94] and for other annulene ions.[290] The physical origin of the alkali metal coupling is still a matter of debate; we only mention here that the detection of some splitting points toward the occurrence of ion pairing while the converse conclusion is not necessarily valid.[5,291,292] Even in the absence of a metal hyperfine coupling constant one can detect the interaction between the organic substrate and the counterion by systematically studying the dependence of the spin-density distribution upon solvent, cation, and temperature. Radical anions derived from cyclophanes constitute particularly promising subjects for these investigations.[293]

Naturally, the benzene radical anion $\mathbf{2}^{-\cdot}$ has attracted special interest. One main question, thereby, has concerned the vibronic interaction of the nearly degenerate electronic states[93,94,242-246] in deuterium[247] or alkyl[12] substituted benzene radical anions. Another deals with the structure of the ion pair.[294-298] Toward an understanding of the latter problem, the g values, the metal hyperfine splitting, and the ESR line widths of $\mathbf{2}^{-\cdot}$ were carefully measured as a function of the alkali metal, the temperature, and the solvent.[298] A model for the ion pair was suggested in which the counterion lies on the sixfold axis of the organic anion.[299] However, in order to rationalize the temperature dependence of the g values and the metal coupling constants it was necessary to assume an oscillation of the cation parallel to the ring plane and with an average position on the C_6 axis.

In the case of highly reduced derivatives (radical trianions[300]) of polycyclic hydrocarbons one has observed symmetry deformations of the organic π-system due to a strong interaction with the counterions. There is no report on similar effects within the annulene field.

The following discussion will summarize a few significant ion-pairing effects for both (paramagnetic) monoanions and (diamagnetic) dianions.

B. Ion-Pairing Effects on Disproportionation Processes

Knowledge of the thermodynamic and kinetic parameters of ion-pair formation has sometimes proven more significant than conductivities or ESR/NMR data. The example of cyclooctatetraene, with the disproportionation equilibrium very much in favor of the dianion, is revealing.

The equilibrium constant K has been determined in THF (see section IIB)[96] and in ammonia[98] where in the latter solvent K varies by a factor of 10^6 with the counterion. It has been shown[97] that stronger ion pairing shifts the equilibrium toward the dianion. A useful extension of the above studies, therefore, was the measurement of K in HMPA solution, since hydrocarbon radical anions had been considered to be fully dissociated in this powerful solvating agent. Even in the latter case, however, K varies with the counterion with the lowest value for the sodium reduction. One concluded that the sodium ion must be better solvated in HMPA than potassium or lithium.

The apparent equilibrium constant of the disproportionation of $\mathbf{3}^{-\cdot}$ in HMPA has been related to the dissociation constant of the ion pair $\mathbf{3}^{2-}/2\mathrm{M}^+$.[302] As expected the entropies turn out to be negative. Quite surprisingly, however, the ion pairs $\mathbf{3}^{2-}/2\mathrm{Cs}^+$ and $\mathbf{3}^{2-}/2\mathrm{Li}^+$ dissociate endothermically into the solvent-separated ion pairs.[303] Upon going to the larger [16]-annulene system no ion association could be detected. This finding can be explained in terms of the lower charge densities at the carbons due to the larger ring. In a related attempt, ESR spectroscopy has been applied to determine the enthalpy for the electron-transfer reaction from $\mathbf{3}^{-\cdot}$ to substituted cyclooctatetraenes or to **7**.[304] There is a correlation between the experimental $\Delta H°$ value and the splitting $\Delta\epsilon$ of the nonbonding cyclooctatetraene orbitals that is induced by the substituent. It appears, however, that $\Delta H°$ for the electron transfer is much more sensitive to the existence of the substituent than is $\Delta\epsilon$ itself. One concludes, in agreement with what has been said in section VIA, that $\Delta\epsilon$ is largely influenced by solvation effects.[304]

The rate constant of disproportionation of $\mathbf{3}^{-\cdot}$ is also indicative of ion pairing. One technique of estimating this value considers line-broadening effects in the ESR (see section IIB). Alternatively, one may subject the system of neutral compound, radical anion, and dianion to near UV irradiation.[305] The resulting photooxidation of $\mathbf{3}^{2-}$ creates an increased (nonequilibrium) concentration of $\mathbf{3}^{-\cdot}$ whose decay can be followed.[306]

In a discussion of the ion-pairing effects upon the rate constant of disproportionation one will have to consider not only the reaction of the free ions

$$2\,\mathbf{3}^{-\cdot} \xrightarrow{k_0} \mathbf{3}^{2-} + \mathbf{3}$$

but also the following processes:

$$2\,\mathbf{3}^{-\cdot}\mathrm{M}^+ \xrightarrow{k_1} \mathbf{3}^{2-}\cdot 2\mathrm{M}^+ + \mathbf{3}$$

$$\mathrm{M}^+\cdot\mathbf{3}^{-\cdot} + \mathbf{3}^{-\cdot} \xrightarrow{k_2} \mathbf{3}^{2-}\cdot\mathrm{M}^+ + \mathbf{3}$$

It appears from the kinetic data of the systems **3**/Na(K)/(methyltetrahydrofuran) that $k_1 > k_2 > k_0$, i.e., disproportionation takes place primarily via the rate process k_1 (disproportionation rates measured in HMPA are much smaller than in ethereal solvents). One can also conclude that the electron-transfer rate k_1 increases drastically with increasing size of the counterions. This finding parallels the dependence of the electron-transfer rate between $\mathbf{3}^{-\cdot}$ and $\mathbf{3}^{2-}$ upon the

TABLE II. ^{1}H NMR Chemical Shifts (δ_H) of the Cyclooctatetraene Dianion (3^{2-}) for Different Counterions and Solvents[161]

	DEE	THF	DME
$3^{2-}/2Li^+$	5.914	5.726	5.773
$3^{2-}/2Na^+$	5.885	5.797	5.844
$3^{2-}/2K^+$	5.841	5.754	5.773
$3^{2-}/2Rb^+$	5.694	5.700	5.747

counterion. It has been suggested that the cations function as bridges during the electron transfer, thereby playing an important role in minimizing the electrostatic repulsion of the approaching organic anions.[306]

C. Ion-Pairing Effects on NMR Chemical Shifts

NMR spectroscopic studies have confirmed the results of other methods[191,281-284] that diamagnetic anions exist in solution as rapidly equilibrating mixtures of solvent-separated and contact ion pairs whose ratio sensitively depends on the experimental conditions.

It appears that solvent-separated ion pairs are favored by smaller cations, lower temperatures, more polar solvents, and larger anions (with π-charge delocalization). The latter finding is supported within the annulene field by the fact that the cyclopentadienyl anion[278] forms only contact ion pairs while the lithium and sodium salts of the cyclononatetraenyl anion[161] (THF, DME) exist as equilibrium mixtures of both ion-pair structures.

The ^{1}H chemical shift data of 3^{2-} for various counterions and solvents[161] are found in Table II. In diethyl ether (DEE) the hydrocarbons are shielded depending on the metal in the order Rb > K > Na > Li which, in accordance with related results, indicates the predominance of contact ion pairs. In THF and dimethoxyethane (DME) the analogous sequence is Rb > Li > K > Na. The immediate conclusion that a small fraction of solvent-separated ion pairs is formed for the lithium salt is not in full accord with the effects of solvent variation. Thus, the resonance of $3^{2-}/2Li^+$ is further downfield in DME than in THF. The bidentate coordination of DME is generally predicted to favor solvent-separated ion pairs. Consequently, if $3^{2-}/2Li^+$ forms solvent-separated ion pairs, the protons of 3^{2-} should be more shielded in DME than in THF. The resulting inconsistency could be solved by the inclusion of ^{7}Li NMR measurements.[161] The latter point toward different types of contact ion pairs which differ by the distance between the ring and the coordinated metal above and below the π-cloud.[161]

In a different approach the interaction of the dianions 3^{2-} and 7^{2-} with their counterions in HMPA was described by monitoring the ^{1}H chemical shifts as alkali metal cations were added to the solutions.[302] The ^{1}H resonance of $3^{2-}/2K^+$ appears to shift downfield as the concentration of added potassium perchlorate increases. This outcome indicates the formation of a tight ion pair. Under similar conditions the dianion of [16]annulene (7^{2-}) fails to exhibit any chemical shift changes. It is straightforward to assume that due to the smaller π-charge densities in 7^{2-} the Coulomb attraction between the dianion and the cation is not sufficient to result in the formation of contact ion pairs.

A NMR spectroscopic study of ion pairing-effects has also been performed for the series of paratropic dianions 22^{2-}–25^{2-}.[162] Particularly advantageous is the accessibility of the homologous series so that one can investigate the effect of ring size in addition to the effects of counterion, temperature, and solvent (see Table III).

The sodium, potassium, and cesium salts of 22^{2-} in THF (temperature-independent chemical shifts) predominantly exist as contact ion pairs while for $22^{2-}/2Li^+$ one detects a temperature-dependent equilibrium of both contact and solvent-separated ion pairs. The latter finding is also true for the Li and K salts of the higher membered homologous dianions. Not unexpectedly, the relative fraction of solvent-separated ion pairs increases with increasing ring size. The borderline case is 25^{2-} which as its Li salt (THF) seems to exclusively exist as a solvent-separated ion pair.

Substituting THF by either dimethoxyethane or diethyl ether favors solvent-separated or contact ion pairs, respectively. By a proper choice of the counterion/solvent system one succeeds for the case of 3^{2-} in obtaining NMR chemical shifts of the pure contact (δ_C) and solvent-separated (δ_S) ion pair. From the measured chemical shift (δ) under equilibrium conditions one obtains the equilibrium constant K via the equation

$$K = \frac{\delta_C - \delta}{\delta - \delta_S}$$

The temperature dependence of K (via a plot of ln K vs. reciprocal temperature) allows a determination of the relevant thermodynamic parameters ($\Delta H° = -14.5$ kJ mol^{-1}, $\Delta S° = 74.8$ J mol^{-1} K^{-1}).

It is clear from an inspection of the data in Table III that the ion-pairing-induced changes of ^{1}H chemical shifts are much larger for the paratropic dianions 22^{2-}–25^{2-} than for the diatropic dianion 3^{2-}, the diatropic monoanion cyclononatetraenyl[161] or the aromatic monoanions of the indenyl and fluorenyl type.[276,307-309]

Protons attached to annulene ions should experience the influence of a counterion in three ways: (a) via the (direct) electric field effect along the C–H axis, (b) via the induced modification of the local π-charge densities, and (c) by the perturbed electronic structure and magnetic anisotropy of the entire π-system.[162]

It would seem from the large shift effects in Table III that a change of the mode of ion pairing severely affects the observable paratropic ring-current phenomena. This conclusion is supported by the fact that the chemical shifts of inner protons show much larger ion pairing effects than those of outer protons. On the other hand, it is well-known from a consideration of the isoshielding lines of diatropic or paratropic annulenes that the resonances of inner protons reflect ring-current effects in a more sensitive way than those of outer protons. Moreover, it appears from the above investigation that an increased tendency toward solvent-separated ion pairs also increases the degree of paratropism of the dianions.

The observation of much more pronounced ion-pairing effects in paratropic than in diatropic systems implies (1) that paratropic species, if they are stable enough, are extremely well suited for a study of ion-pairing effects and (2) that a systematic analysis of ring-current effects must account for the variable counterion effects. Clearly, in order to come as close as possible to the situation of an "unperturbed" π-system one should refer to the properties of the solvent-separated ion pairs.

TABLE III. ^{1}H NMR Chemical Shifts (δ_H) of Dianions Derived from the Bisdehydro[4*n* + 2]annulenes 22–25 for Different Counterions, Solvents, and Temperatures[162]

		temp, °C	3	4	5	6	7	*t*-Bu
δ_H (**22**$^{2-}$/2Li$^+$)	THF	+6	3.22	18.88				0.37
		−42	3.10	19.90				0.35
		−75	2.95	19.66				0.30
		−82	2.89	19.84				0.29
δ_H (**22**$^{2-}$/2Li$^+$)	DME	−10	2.52	21.24				0.18
		−45	2.18	22.60				0.11
		−75	1.85	24.37				−0.01
δ_H (**22**$^{2-}$/2K$^+$)	THF	+11	2.74	20.96				0.22
		−42	2.68	20.98				0.21
		−75	2.66	20.94				0.21
		−82	2.65	20.89				0.20
δ_H (**22**$^{2-}$/2K$^+$)	DME	−5	2.63	21.37				0.19
		−45	2.61	21.41				0.19
		−18	2.50	21.76				0.17
δ_H (**22**$^{2-}$/2Cs$^+$)	THF	−35	2.77	23.27				0.20
	THF/HMPA 10:1	−40	*a*	23.11				0.16
δ_H (**23**$^{2-}$/2Li$^+$)	THF	−15	*a*	22.47	*a*			−0.12
		−42	1.50	23.33	1.04			−0.12
		−75	*a*	24.56	*a*			−0.11
		−82	1.04	24.88	1.04			−0.11
δ_H (**23**$^{2-}$/2K$^+$)	THF	−15	*a*	21.10	*a*			0.06
		−45	*a*	21.22	*a*			0.06
		−60	2.07	21.50	1.57			0.07
		−80	2.02	21.65	*a*			0.07
δ_H (**23**$^{2-}$/2K$^+$)	DME	−25	*a*	22.41	*a*			−0.04
		−75	2.05	24.51	*a*			−0.19
		−80	*a*	24.68	*a*			−0.19
δ_H (**24**$^{2-}$/2Li$^+$)	THF	−15	*a*	24.20	*a*	22.70		−0.25
		−45	*a*	24.80	*a*	23.20		−0.29
		−80	1.15	24.80	−0.29	23.23		−0.29
δ_H (**24**$^{2-}$/2K$^+$)	THF	−45	1.95	21.29	1.22	19.84		−0.06
δ_H (**24**$^{2-}$/2K$^+$)	THF/DEE 1:1	+4	2.16	20.24	*a*	18.90		0.01
		−15	2.07	20.45	1.45	19.06		0.01
		−45	1.93	20.84	1.26	19.47		−0.02
		−80	1.78	21.90	*a*	20.40		−0.17
δ_H (**24**$^{2-}$/2K$^+$)	THF/DEE 1:2	−4	2.21	20.05	1.70	18.74		0.03
		−19	2.19	20.13	*a*	18.71		0.03
		−40	2.08	20.41	*a*	18.97		0.00
		−70	1.92	20.89	*a*	19.46		−0.09
δ_H (**25**$^{2-}$/2Li$^+$)^b	THF	−15	*a*	23.28 (21.35)	0.18	21.35 (23.28)	0.18	−0.20
		−45	*a*	23.32 (21.37)	*a*	21.37 (23.32)	*a*	−0.20
		−80	1.20	23.39 (21.35)	0.18	21.35 (23.39)	0.18	−0.20
δ_H (**25**$^{2-}$/2K$^+$)^b	THF	−15	2.08	20.41 (18.71)	*a*	18.71 (20.41)	*a*	−0.18
		−45	*a*	20.91 (19.14)	*a*	19.14 (20.91)	*a*	−0.09
	THF	−80	1.70	21.58 (19.72)	1.50	19.72 (21.58)	1.50	−0.09

[a] Covered by the signal of an impurity or of the solvent. [b] It is not possible from experimental evidence to discriminate between the signals of H-4 and H-6.

VIII. Structural Dependence of Ring-Current Effects. Annulene Ions as Ideal Models

The most spectacular outcome of the ^{1}H NMR spectroscopic description of ionic annulenes in section V is the pronounced ring-induced shielding effects which allow the straightforward identification of either diatropic or paratropic species. Recalling the introductory remarks, such a classification within neutral [4*n* + 2]annulenes has found extended use as an experimental, yet somewhat undefined, criterion of aromaticity. The present section will systematically evaluate the structural dependence of ring-current effects by using charged annulenes as model compounds. Experience from the study of the neutral compounds would strongly suggest focusing on the influence of ring size, planarity, the number of electrons (in one and the same substrate), and the HOMO/LUMO gap. The discussion will first compile empirical results; their interpretation in terms of bond theory[310] will be given in section X.

A. Influence of Ring Size

An intriguing problem in the concept of aromaticity is the influence of the perimeter size. Theoretical predictions claim that toward the upper range of ring sizes the aromatic character will disappear, with the molecules simply behaving as olefins.[46-49] While the importance of the ring current criterion is evident, there have been disagreements about which class of annulenes is best suited for actually assessing the "borderline of aromaticity".[64]

Compounds **22**–**25** constitute a homologous series of planar [4*n* + 2]annulenes with the same type of perimeter.[71] The successful preparation of the corresponding

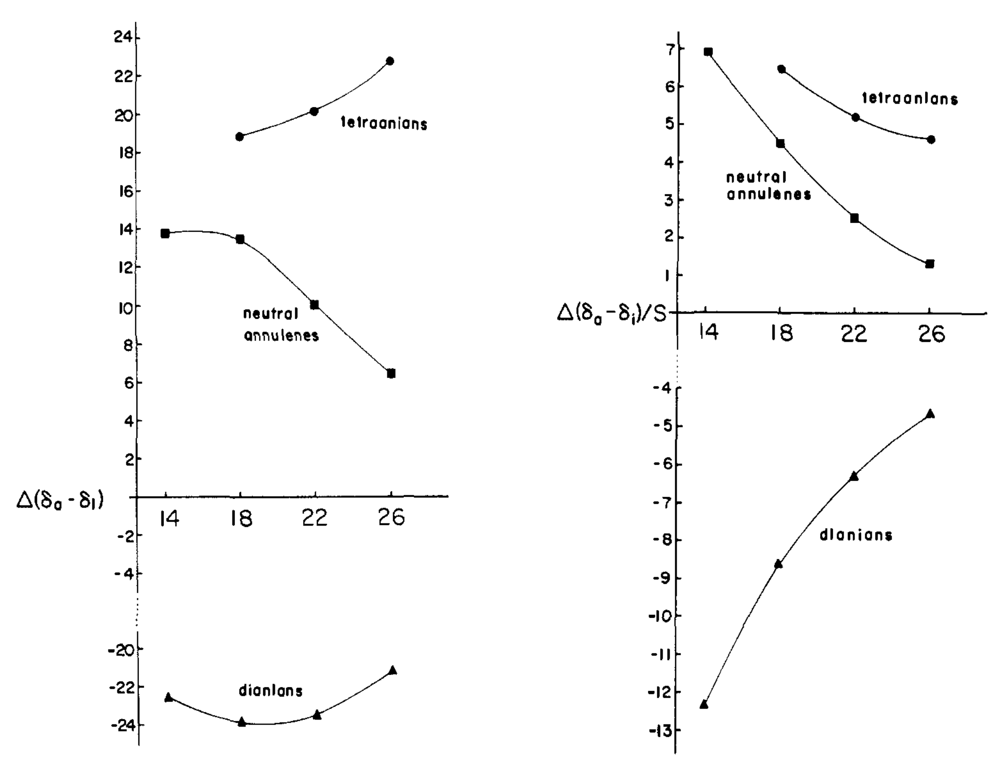


Figure 4. Ring-current effects in neutral, dianionic, and tetraanionic annulenes as a function of ring size (see text).[10]

dianions and tetraanions[10] offers the unique opportunity of probing the influence of ring size for both paratropic and diatropic π-systems. Thereby, the ^1H chemical shifts which have been corrected for the charge and ion-pairing effects provide reliable criteria.

Two complicating factors have to be considered, however, when comparing ring-current effects within annulenes of different ring size: the role of geometry and of the local anisotropic shielding phenomena. A classical treatment of the deshielding of hydrogens in polycyclic benzenoid hydrocarbons[311] reveals that the nonspherical electronic environment of carbon causes a local magnetic anisotropy which, within the chemical shift scale, can dominate the "nonlocal" ring-current effects. The unique structural properties of [4n + 2]-annulenes create a somewhat different situation, since the contribution of delocalized shielding terms is much more significant.

The ^1H chemical shifts of the annulenes **22**–**25** have been calculated in a quantum mechanical approach[312] whereby both ring current ($\Delta\delta^{RC}$) and local contributions ($\Delta\delta^{LC}$) have been taken into account. The latter comprise the influence of the π-bond-delocalized ring, the orthogonal (acetylene-type) π-moiety and the σ-frame. For protons outside the ring the term $\Delta\delta^{LC}$ is about 1 ppm and, thus, definitely smaller than $\Delta\delta^{RC}$, both contributions inducing some deshielding. For protons inside the ring the dominant role of $\Delta\delta^{RC}$ is even more distinct since the shielding effect of $\Delta\delta^{RC}$ is only slightly decreased due to the influence of $\Delta\delta^{LC}$.

An analogous treatment of the corresponding dianions and tetraanions,[313] again, points toward the dominant role of nonlocal effects. Moreover, when considering the ^1H chemical shifts of $\mathbf{22}^{2-}$–$\mathbf{25}^{2-}$ as a function of perimeter size, the local anisotropic shielding effects can be assumed to be constant. The main consequence of the ring-current effects in the neutral and anionic annulenes can be seen in the large chemical-shift difference of inner and outer protons. A suitable ring-current criterion, therefore, is the (charge-corrected) difference of the related resonances, which in Figure 4 is plotted as a function of ring size.

A second problem during a semiquantitative analysis of experimentally detected ring-current effects is the role of the molecular geometry. The secondary magnetic field at an individual proton depends not only on the ring current intensity per unit applied field but also on the location of the proton and the shape of the perimeter.[314] These spatial effects have been dealt with in both classical[315–318] and quantum-mechanical[319–321] treatments. While these arguments have been reviewed in great detail,[314] it is worth mentioning an approximate equation[42] in which the ring-current-induced proton shift is proportional to the product of ring-current intensity, the area of the ring S and the inverse-cube distance of the individual proton from the center of the perimeter. In the homologous series of the bisdehydroannulenes[10] the distance dependence is negligible and the term $(\delta_o - \delta_i)/S$ can safely be regarded as an empirical measure of ring-current effects (see Figure 4b).

Figure 4 provides a systematic description of the change of ring-current effects in differently charged annulenes. The following features are obvious: (1) diamagnetic ring-current effects in the annulene tetraanions are always larger than in the corresponding neutral annulenes; (2) in the neutral species the diamagnetic ring-current effect decreases with increasing ring size. The decay in the corresponding tetraanions is much smoother; (3) a similar trend is observed for the paratropic dianions, the decay is much more rapid than for the diatropic tetraanions.

Within the present discussion of ring size, it seems tempting to include other classes of annulenes such as **1**–**8** or **28**–**34** and **39**. The possibility of different ring configurations in **7** and **8** as well as their ions makes it difficult, however, to evaluate the ring-current effects within the series **1**–**8**. On the other hand, when considering dianions and dications of bridged annulenes with identical perimeter type (configuration), one realizes the major importance of the ring conformation, i.e., of the planarity of the π-systems.

B. Influence of Planarity

A significant flattening of the annulene perimeter is known to be a prerequisite for the formation of π-bond-delocalized structures. Thereby, it is an open question as to what degree of bending a monocyclic $(4n + 2)\pi$-system can tolerate without undergoing a total quench of its diatropism.

Compounds **29**, **30**, and **31** constitute a series of bridged [14]annulenes whose perimeters increasingly deviate from a coplanar arrangement. This structural feature follows from the size of the bridging group and, thus, the distance of the bridge centers C-15 and C-16.[69] Various spectroscopic properties (e.g., the ESR hyperfine coupling constants of the corresponding radical anions) have been shown to sensitively reflect the above conformational effect and to reveal the subtle interdependence of steric and conjugational phenomena.

^{1}H NMR spectroscopy proves to be of special value since the chemical shifts of both ring and bridge protons depict the decreasing diatropism within the less planar analogues [δ_H (H-15): −1.8 (**29a**), −1.16 (**30**), −0.96 (**31**)]. In a related fashion the higher degree of bending within the dianions causes a decrease of the paratropism[108,109] [δ_H (H-15): 13.0 (**29a**$^{2-}$), 10.4 (**30**$^{2-}$), and 9.9 (**31**$^{2-}$)]. However, the paratropic effects of the $(4n)\pi$-dianions reflect the conformational changes in a much more sensitive way than the diatropic ones in the neutral compounds.

Further support in favor of this finding is obtained from the couple **36**/**36**$^{2-}$ which appears to represent the borderline case within the present evaluation of ring-current effects.[238] It follows from an X-ray analysis that the π-system of **36** within the present series has the highest degree of bending; nonetheless, the ^{1}H NMR chemical shifts of **36** leave no doubt that the annulene exhibits a small, but significant diatropism. An outstanding feature of the ^{1}H NMR spectrum of **36**$^{2-}$ is that the resonances of both ring and bridge protons appear in the same shift range (two signals of perimeter protons, 2 H each, appear at δ 3.7 and δ 4.2, while the bridge protons give rise to the signals of an AB system at δ 2.9 and δ 5.2).[108,109] Obviously, the indications pointing toward a paratropic character of the π-system are much less pronounced than in the dianions with an anthracene-type perimeter. A comparison with the isoelectronic dianions of anthracene and phenanthrene reveals that the ring protons of the benzenoid species suffer from a much stronger shielding than those of **36**$^{2-}$.[403]

It is due to the insufficient flattening of the perimeter that an analysis of the homologous series **14d**$^{2-}$, **35**$^{2-}$, and **39**$^{2-}$ does not provide results which are comparable to those obtained from **22**$^{2-}$–**25**$^{2-}$. Compound **14d** is outstanding in that its ^{1}H chemical shifts indicate a distinct diatropic behavior while the paratropic character of its corresponding dianion is weak.[108,109]

TABLE IV. ^{1}H NMR Chemical Shifts (Center of Gravity of Signals Obtained for Inner and Outer Protons) of Isoelectronic Neutral Annulenes, Dianions, and Dications

	$\delta_{H,outer}$	$\delta_{H,inner}$
($5^{2-}/2Li^+$)	6.73	−4.60
6	7.6	0.0
($7^{2-}/2K^+$)	8.34	−8.17
8	9.33	−3.17
$18^{2-}/2Li^+$	6.62	−5.80
35	7.39	−0.09
($37^{2-}/2Li^+$)	7.69	−7.36
39	7.37	0.47
($37^{2+}/2SbF_6^-$)	11.13	−4.00
35	7.39	−0.09
($7^{2+}/2FSO_3^-$)	10.70	3.52
6	0.60	0.0

So far we have compared the diatropism of bridged $[4n + 2]$annulenes and the paratropism of their dianions as a function of planarity. We have, thereby, made the reasonable assumption that the electron-transfer processes do not significantly change the geometry of the rigid framework. As a consequence, the assessment of the ring conformation in the neutral compounds will also hold for the radical anions and dianions.

Dianion formation upon reduction of $[4n]$annulenes has been shown above to be accompanied by a flattening of the perimeter, and a decrease in the conformational mobility. An important observation in the present context is that the diatropic $(4n + 2)\pi$-dianions sustain a pronounced diamagnetic ring-current effect even in those cases where the perimeter cannot adopt a strictly planar conformation. This conclusion holds for the bridged [12]annulene dianions **17**$^{2-}$ and **18**$^{2-}$ as well as for the isoelectronic system **5**$^{2-}$ where the nonbonded interaction of the inner hydrogens opposes a further flattening of the ring. Note that structurally different [12]annulene dianions such as **17**$^{2-}$, **18**$^{2-}$, and **20**$^{2-}$ exhibit resonances of the inner protons at about δ 6. (Similar shifts are observed for the bridge protons of the [16]annulene dianions **37**$^{2-}$ [144] and **38**$^{2-}$.[142]) Obviously, the diatropic species reflect a bending of the π-perimeter in a less sensitive way than the paratropic ones.

C. Influence of the Number of π-Electrons

An attractive feature in the study of neutral and charged annulenes is the inspection of one and the same electronic configuration in different rings, and of different electronic configurations in one and the same ring. The former approach will contrast an annulene dianion (dication) with the isoelectronic next higher (next lower) neutral annulene. The latter will compare $[4n + 2]$annulenes with their corresponding tetraanions or compare dianions and dications derived from the same annulene.

From the data presented in Table I, one may conclude as a general rule that the diatropism of $[4n]$annulene dianions is significantly more pronounced than the one of the next higher (neutral) $[4n + 2]$annulene with the same number of π-electrons. Table IV provides the pairs of compounds **5**$^{2-}$/**6**, **7**$^{2-}$/**8**, **18**$^{2-}$/**35**, **37**$^{2-}$/**39**, **7**$^{2+}$/**6**, and **37**$^{2+}$/**35** as representative examples.

A similar relation (i.e., greater diatropism within an ionic annulene than within an isoelectronic neutral compound) holds for dications. This conclusion is drawn from a comparison of the pairs of 14π-systems **37**$^{2+}$/**35** or **7**$^{2+}$/**6** (see Table IV).

TABLE V. ^{1}H NMR Chemical Shifts (Center of Gravity of Signals Obtained for Ring and Bridge Protons) of the Bridged [14]annulenes 26a, 27a, and 29c as well as of Their Corresponding Dianions

	δ_{ring}	δ_{bridge}	ref
26a	8.54	−4.25	131
$\mathbf{26a}^{2-\,a}$	−3.60	21.00	
Δ ($\mathbf{26a}^{2-}$ − **26a**)	−12.14	25.25	
27a	8.61	−4.53	108
$\mathbf{27a}^{2-\,a}$	−0.14	11.96	
Δ ($\mathbf{27a}^{2-}$ − **27a**)	−8.75	16.49	
$\mathbf{29c}^{b}$	7.99	−1.85	108, 109
$\mathbf{29c}^{2-}$	1.48	7.70	
Δ ($\mathbf{29c}^{2-}$ − **29c**)	−6.51	9.55	

[a] THF-d_8, potassium salt. [b] THF-d_8, lithium salt.

Considering the existence of different electronic configurations within one and the same ring it is obvious from section VIIIA that [4*n* + 2]annulenes A exhibit a weaker diatropism than their corresponding tetraanions A^{4-}. The pairs of diatropic ions $\mathbf{37}^{2+}/\mathbf{37}^{2-}$ and $\mathbf{7}^{2+}/\mathbf{7}^{2-}$ may be regarded as a related case since the number of π-electrons again differs by 4. The dianions appear to be slightly more diatropic than the dications.

An extension of these arguments to pairs of paratropic dianions and dications, e.g., $\mathbf{22}^{2+}/\mathbf{22}^{2-}$, $\mathbf{35}^{2+}/\mathbf{35}^{2-}$ or $\mathbf{39}^{2+}/\mathbf{39}^{2-}$ using charge-corrected ^{1}H chemical shifts, does not lead to straightforward conclusions. Even more so, since the ^{1}H resonances of paratropic systems have been shown to depend sensitively upon the mode of ion pairing.

D. HOMO/LUMO Gap

In section VIIIB we have discussed the dia- and paratropism within perimeters of varying conformation but well-defined configuration. A complementary approach is possible for those annulenes which are more or less *planar*, but possess different sequences of double-bond configurations. Compounds **26a**, **27a**, and **29c** as well as their dianions $\mathbf{26a}^{2-}$, $\mathbf{27a}^{2-}$, and $\mathbf{29c}^{2-}$ seem to fit these criteria. These [14]annulenes have in common a dimethylethanediylidene group as a bridge, where **26a** and **27a** adopt a pyrene-type, and **29c** an anthracene-type perimeter. While the ring of the latter deviates only slightly from coplanarity, those of the former are known from X-ray evidence to be essentially planar.

Let us consider the average signal of the perimeter protons (δ_{ring}) and the resonance of the (bridge) methyl protons (δ_{bridge}) for the neutral and dianionic species (see Table V). Not unexpectedly from what has been said above, **26a** and **27a** appear to be very similar while the diatropism of **29c** is less pronounced. The spectacular low-field absorption of the methyl protons in $\mathbf{26a}^{2-}$, $\mathbf{27a}^{2-}$, and $\mathbf{29c}^{2-}$ supports the paratropic character of the dianions. Remarkably enough, the corresponding signal shifts are $\Delta\delta = +25.25$, +16.49, and +9.55. These data point toward considerable differences between the dianions; differences which cannot be explained by simple geometric effects and the concomitant tendency toward π-bond fixation.

It should be recalled from the orbital scheme in section IC (see Figure 1) that formation of (4*n*)π-dianions from [4*n* + 2]annulenes creates species with low-lying electronically excited states. Their interaction with the ground state gives rise to paramagnetic ring-current effects superimposed on the diamagnetic ones. Thus, within the limits of a simple MO model a decreasing HOMO/LUMO gap of the dianions is expected to increase the paratropic effects. The ESR study of the corresponding radical anions (see section VIA) has made quite clear that the relative energies of the low-lying annulene LUMO's result from a delicate balance of inductive, homoconjugative, and hyperconjugative perturbations. Without going into further details, it should be noted that due to the actual HOMO/LUMO gap the magnitude of paratropic effects may differ widely, even for structurally similar species.

Supporting evidence comes from an inspection of the [18]annulene dianions $\mathbf{8}^{2-}$ and $\mathbf{23}^{2-}$. In $\mathbf{8}^{2-}$ the shift difference of inner and outer protons is much greater than in $\mathbf{23}^{2-}$, i.e., the former exhibits a stronger paratropism. As has been mentioned previously, the degeneracy of the two LUMO's in **23** is destroyed because of the inherent perturbation. These two annulene MO's are degenerate as long as a C_3 axis is preserved in the perimeter, a situation which is expected to prevail in **8**. Even if the degeneracy is removed in $\mathbf{8}^{2-}$ due to some distortion of the perimeter (bond lengths alternation is not sufficient) one will expect a relatively small HOMO/LUMO gap and, thus, a strong paratropic effect. (It is recalled from section IB that the case of HOMO/LUMO degeneracy cannot be described adequately within the one-electron or Hartree–Fock model.)

IX. Ground-State and Excited-State Energies

An important property of any radical anion is the ease with which it is formed via reduction of the neutral π-system, or, to be more specific, the free energy of the corresponding electron-transfer reaction. The demand for energetic considerations is particularly severe for the chemistry of neutral and charged annulenes since (1) the inherent concept of aromaticity implies the occurrence of electronic stabilization effects, and (2) the experimental experience accumulated above leaves no doubt that it is easier to add extra electrons to a [4*n*]- than to a [4*n* + 2]annulene.

Sections IXA and IXB include electrochemical and calorimetric criteria for the energetic description of ionic annulenes, the subsequent interpretation of the data in terms of bond theory will be presented in section X.

A simple NMR spectroscopic result might serve as an introductory example.[322] The dianion of **3** was produced by reduction with sodium in HMPA and detected by its ^{1}H resonance. Addition of an equal molar amount of the [16]annulene **7** led to the appearance of an intense signal of neutral **3**. Consequently, the dianion $\mathbf{3}^{2-}$ has been oxidized by **7** to yield neutral cyclooctatetraene and the [16]annulene dianion $\mathbf{7}^{2-}$. (The latter does not give rise to a NMR signal because of its rapid electron transfer with small amounts of the corresponding radical anion.) Formation of the dianion $\mathbf{7}^{2-}$ is energetically more favorable than that of $\mathbf{3}^{2-}$ (see section X), and the above equilibrium is shifted far to the right.

$$\mathbf{3}^{2-} + \mathbf{7} \rightleftharpoons \mathbf{7}^{2-} + \mathbf{3}$$

A. Electrochemistry

A more systematic description of annulenes follows from electrochemical measurements which will be re-

TABLE VI. Polarographic Half-Wave Potentials (E_1, E_2) of Annulenes

	E_1, V	E_2, V	ref
3	−1.98	-2.80^a	101, 329
5	−1.35	-2.00^b	112
7	−1.23	-1.52^c	140
8	−1.56	-1.90^c	146
17	−1.47	-1.79^d	121
18	−1.51	-1.72^d	121
26a	−2.22	-3.01^e	324
91	−2.33	-3.0^a	101
92a	-3.6^f		105
92b	-3.7^f		105

[a] THF, Bu_4NClO_4 (0.1 M); SCE. [b] THF-d_8, Bu_4NClO_4; relative to Hg pool; −80 °C. [c] Dimethylformamide (DMF), Bu_4NClO_4; relative to Hg/Hg_2Cl_2 (0.1 M KCl), 0 °C. [d] DMF; Bu_4NClO_4; SCE. [e] DMF; Bu_4NClO_4 (0.1 M); relative to $Ag/AgNO_3$. [f] SCE.

ported for **3** (and alkyl substituted derivatives), **5**, **7**, **8**, **17**, **18**, and **26a**.

As is well-known, standard redox potentials can be obtained from polarographic or voltammetric measurements as long as subsequent chemical transformations (e.g., protonation) are much slower than the electron transfer and the electrochemical redox process can be regarded as reversible.[5]

The latter requirement is fulfilled for **7** and **8** while the situation in cyclooctatetraene and its derivatives is more complicated (see below).

The essential factors which determine the potential at which an electron is transfered to the annulene species are the electron affinity of the neutral compound—this is generally correlated with the energy of the LUMO, the energies of interaction with the solvent and the counterions (including outer-sphere solvent reorganization energies), the compressional energy of geometric changes of the substrate, as well as the electron–electron repulsion energies.

Before commenting on the first factor, it should be mentioned that the correlation of half-wave potentials with the energies of Hückel LUMO's has been one of the early successes of the Hückel model.[39,323] The transfer of an electron to a [4*n*]annulene should be favorable because the electron is injected into a nonbonding MO with extremely low energy. Inspection of Table VI reveals that the half-wave potentials of [4*n*]annulenes are, indeed, relatively low. The comparison of **7** ($E_1 = -1.23$ V)[140] and **8** ($E_1 = -1.56$ V)[146] (under the same experimental conditions) is indicative: the [16]annulene is more easily reduced although the reduction of the larger π-system (**8**) should be more favorable from electrostatic arguments.

Another interesting feature of ionic annulenes can be derived by considering the formation of the radical anion (at potential E_1) together with the successive formation of the dianion (at potential E_2):[324,325]

$$A + e \rightleftharpoons A^{-\cdot} \quad E_1$$

$$A^{-\cdot} + e \rightleftharpoons A^{2-} \quad E_2$$

By subtracting the first from the second equilibrium one arrives at the expression

$$2A^{-\cdot} \rightleftharpoons A^{2-} + A$$

which is nothing other than the well-known disproportionation equilibrium. Thereby, one relates the free energy of the disproportionation reaction with the spacing between E_1 and E_2.

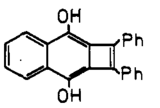
$$\Delta G = -F(E_2 - E_1) = -F\Delta E$$

ΔE values have been determined for a wide variety of benzenoid hydrocarbons and found to lie in the narrow range of 0.5–0.6 V (absolute values). Recalling from section VII that ion pairing and solvation are more important for the dianion than for the radical anion, thus driving the disproportionation equilibrium to the right, one concludes from the small range of ΔE values that solvation effects upon the disproportionation are quite similar for the different benzenoid species. It has been noted, on the other hand, that ΔE is larger for the [14]annulene **26a** ($\Delta E = 0.68$ V, Me_2SO) than for benzenoid hydrocarbons, e.g., for the structurally related pyrene ($\Delta E = 0.55$ V).[285,324] It has been claimed that this is due to a steric inhibition of the cation–anion association within the reduction product. This conclusion is confirmed by the fact that increasingly bulky bridging groups of the annulene increase ΔE.

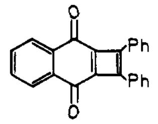
Subsequent experiments revealed, however, that additional *electronic* effects must be operative. Thus, the ΔE value for **3** is extremely small ($\Delta E < 0.2$ V) although the ion-pairing situation in the planar species $\mathbf{3}^{2-}$ should be sterically similar to the one in the pyrene dianion $\mathbf{110}^{2-}$. The explanation given for the contrasting behavior of the [14]- and [8]annulenes is essential for an understanding of annulene ions in general:[285,324] [4*n* + 2]annulenes give rise to (4*n*)π-dianions, the relative instability of which should shift the above disproportionation equilibrium to the left, while the converse is true for the reduction of [4*n*]annulenes. ΔE should, therefore, be small for [4*n*]- and large for [4*n* + 2]-annulenes, and this is, indeed, supported by the data given in Table VI.

Similar arguments hold for the formation of the (4*n* + 2)π-tetraanions $\mathbf{23}^{4-}$ and $\mathbf{25}^{4-}$. Cyclic voltammetry[10] shows a small difference in the potentials (<80 mV) of the tetraanion formation (redox step $\mathbf{24}^{3-\cdot}/\mathbf{24}^{4-}$), on the one hand, and of the mono-, di-, and trianion formation, on the other hand. Under the assumption that the entropy changes of the single redox reactions are of similar magnitude and that there is no dramatic change in the solvation effects, this finding might, indeed, indicate some electronic stabilization in the tetraanion.

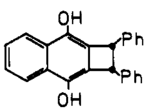
The electronic destabilization induced by a cyclobutadiene moiety has also been determined electrochemically.[326] The polycyclic hydroquinone **88** can be oxidized electrochemically to the quinone **89** the latter being much more labile than the starting compound. It was shown that this oxidation is less easy than the one of naphthohydroquinone while the greatest tendency toward oxidation is exhibited by the dihydro derivative **90**. The destabilizing effect of the cyclobutadiene unit which is produced upon oxidative formation of **89** was estimated as ca. 50 kJ/mol.



88

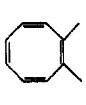


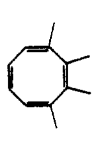
89

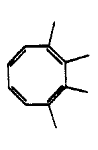


90

Related information is obtained from the electrochemical reduction of a series of 1,*n*-dimethylcyclooctatetraenes.[101] The fact that E_1 of 1,2-dimethyl-cyclooctatetraene (**91**) is significantly cathodic with respect to E_1 of the parent compound is believed to reflect the strong interaction of the substituents upon ring flattening. Even more convincing are the extremely negative E_1 values determined from the polarographic reduction of 1,2,3,4-tetramethylcyclooctatetraene (**92**) which, due to the severe van der Waals interaction of the substituents upon flattening of the molecule, forms two stable bond-shift isomers **92a** and **92b**[105] (see Table VI).


91


92a


92b

In conducting the "electrochemical" determination of the relative stabilities of annulene redox products the significance of ion pairing must, again, be emphasized (see also section VII). More recent measurements[405] indicate that the $\Delta E = E_2 - E_1$ values of benzenoid hydrocarbons, indeed, depend on the mode of ion pairing (e.g., $\Delta E = 0.66$ V for the reduction of pyrene in THF using sodium tetraphenylborate as supporting salt). Moreover, there is electrochemical evidence that the stabilization of the cyclooctatetraene dianion is largely due to ion-pairing effects.[406]

Having estimated the free enthalpy of the disproportionation reaction from the polarographic ΔE value one can consider electrolyte effects upon the disproportionation of the cyclooctatetraene radical anion. The conclusions obtained are in full accord with the results from section VII: ion pairing will be less important as the size of the counterion increases; and ion pairing is more important for the dianions than for the radical anions. Not surprisingly, therefore, ΔE decreases—with more effective ion pairing—in the following order: (i) tetrabutylammonium ion, polar solvent, (ii) tetramethylammonium ion, polar solvent, (iii) alkali metal ion, nonpolar solvent, so that in the latter case one observes a single two-electron polarographic wave.[330,331] This finding is in agreement with the early NMR results, namely that the disproportionation of the cyclooctatetraene radical ion is actually exothermic in the presence of alkali metal counterions.

The electrochemical reversibility of the first reduction step of benzenoid hydrocarbons is generally explained by the assumption that the electron transfer simply implies the injection of an electron into the LUMO. This process has a low activation energy since it involves no bond breaking and little changes in geometry. Upon the electrochemical reduction of **3** in aprotic solvents[97,327–329] two waves have been detected with the shape of the first wave somewhat drawn out, i.e., log plot slope > 59 mV.

Related findings appear from the polarographic reduction of various cyclooctatetraene derivatives.[101] One concluded that, in contrast to, e.g., **7** and **8**, the electron-transfer processes are irreversible. (It should be noted in this respect that the slopes of the polarographic curves have only limited significance as criteria of electrochemical reversibility. Slopes deviating from 59 mV may indicate a hindered heterogeneous charge transfer or a subsequent chemical process.) The irreversibility in the case of **3** has been explained by the assumption that the electron transfer induces a change of the geometry (see above) as a result of which the activation barrier of the first electron transfer is significantly increased. These arguments have been a matter of dispute,[329,330] it would seem, however, that double-layer effects play an important role in the electrochemical reduction of **3**.[330]

B. Thermochemistry

According to the electrochemical results the great ease with which a [4*n*]annulene accepts additional electrons is due to the formation of an electronically stabilized product. This is not expected to hold for [4*n* + 2]annulenes. In dealing with the thermodynamic significance of such a classification, knowledge of the heats of formation of the dianion salts would be highly desirable. Measurement of the heats of combustion, generally applied toward that goal, are not practical for organometallic compounds,[332] mainly due to their air sensitivity. In order to circumvent that problem, one can calorimetrically measure the heats of reaction of the alkali metal salts of $\mathbf{3}^{2-}$[54,333] and $\mathbf{7}^{2-}$[322] with water. For the sake of comparison acene dianions (e.g., anthracene) have also been included.[334]

Interestingly, the acene dianions react with water much more exothermically than does sodium metal itself. On the other hand, the $(4n + 2)\pi$-dianions $\mathbf{3}^{2-}$ and $\mathbf{7}^{2-}$ react less exothermically with water than the acene dianions possessing $(4n)\pi$-electrons. It is also found that the [16]annulene dianion reacts less than one-third as exothermically with water than does the cyclooctatetraene dianion. One is led to the conclusion that $\mathbf{3}^{2-}$ is less thermodynamically stable than $\mathbf{7}^{2-}$, a finding which is in full accord with the outcome of the NMR experiment described above.

More significant for a thermodynamic description of the dianions is the enthalpy of the reaction between the alkali metal and the hydrocarbon to yield the dianion. This value can be obtained from the thermodynamic cycle to be discussed in section XB. One may anticipate, however, that the heats of formation of the dianion salts are negative, those of the $(4n + 2)\pi$-dianions being about 200 kJ/mol more exothermic than those of the $(4n)\pi$-acene dianions.

Having learned about the basically different stabilities of [4*n* + 2]- and [4*n*]annulene dianions, a challenging question concerns the thermodynamic stabilities of the radical anions formed in the course of the reduction. It has been described that the radical anions of [8]- and [16]annulenes ($\mathbf{3}^{-}\cdot$ and $\mathbf{7}^{-}\cdot$, ions representing $(4n + 1)\pi$-systems) possess a special stability. Interestingly, the transfer of an extra electron to benzene, thus producing a $(4n + 3)\pi$-system, appears to be much more difficult. The question arises whether the low thermodynamic stability of $(4n + 3)\pi$- with respect to $(4n + 1)\pi$-radical anions may be indicative of a general principle similar to the one governing the behavior of $(4n + 2)\pi$- and $(4n)\pi$-dianions.

In order to gain insight into the stability of radical anions formed by the reduction of [4*n* + 2]annulenes, the properties of the potassium salt of the 1.6 methano[10]annulene radical anion ($\mathbf{13a}^{-}\cdot$,K^+)[335] were investigated. The latter species can be kept in ethereal solutions at room temperature, while the benzene radical anion is only stable at low temperatures.[335]

The enthalpies of the reaction ΔH° of both solvated and solid $\mathbf{13a}^{-}\cdot/K^+$ with water were measured by calorimetric techniques similar to those applied in the case of the dianion salts. The ΔH° value of the reaction

$$\mathbf{13a}^{-}\cdot/K^+ \text{ (s)} + H_2O(l) \rightleftharpoons {}^1/_2\mathbf{13a} - H_2 + KOH(aq) + {}^1/_2\mathbf{13a} \text{ (l)}$$

is −121 kJ/mol, while for the isoelectronic naphthalene radical anion (K^+ salt), ΔH° amounts to −163 kJ/mol. One might argue whether the remarkable relative stability of $\mathbf{13a}^{-}\cdot$—much larger than that of the naphthalene radical anion and nearly as large as that for the anthracene radical anion—is not simply a consequence of the prevailing crystal lattice energies. However, related measurements for the solvated π-systems reveal the same sequence of stabilities.

As has been mentioned on several occasions the conclusions regarding the relative stabilities of the ionic π-systems can be supported by investigating their relative reducing power. When anthracene (**84**) was added to a THF solution of $\mathbf{13a}^{-}\cdot$ the ESR signal of the latter was replaced by that of $\mathbf{84}^{-}\cdot$. In contrast, addition of naphthalene to the $\mathbf{13a}^{-}\cdot/K^+$/THF system does not cause any change in the ESR spectrum. A strict comparison of the thermodynamic stabilities of $\mathbf{13a}^{-}\cdot$ and of the naphthalene radical anion must refer to the heat of formation of the anion radical salts from the relevant hydrocarbon and the alkali metal (see section XB).

C. Electron Absorption Spectroscopy

Electron absorption spectra have been taken for radical and dianions derived from [4*n*]annulenes. The main goal is to confirm structural conclusions drawn from other spectroscopic measurements, whereby one is mainly concerned with the symmetry and conformation of the perimeter. Such a procedure will compare experimentally observed transitions with those calculated via MO models on the basis of the different possible geometries (e.g., with/without π-bond alternation, planar/nonplanar) and scrutinize which assumption fits the experimental data best. According to this approach the cyclooctatetraene radical anion $\mathbf{3}^{-}\cdot$[336] [produced by electrolysis in liquid ammonia; $\lambda_{max} = 300$; $\lambda = 324$; $\lambda = 395$] differs little, if at all, from D_{8h} symmetry.[337]

The radical anion $\mathbf{7}^{-}\cdot$ has been generated electrolytically (in dimethylformamide/Hg pool, tetra-*n*-butylammonium perchlorate as supporting salt) and characterized through its UV and visible spectra [$\lambda = 664$ ($\epsilon = 10600$); 690 (10000); 380 (190000); 330 (51500)].[140] A satisfactory agreement is obtained between experimental results and theoretical predictions based on the simple Hückel model (D_{16h}) or the variable β-approximation (D_{4h}).

The ground state and the excited states of the [16]-annulene radical anion ($\mathbf{7}^{-}\cdot$) have subsequently been investigated by different groups.[338–340] It was concluded from the temperature-dependent ESR hyperfine coupling constants of $\mathbf{7}^{-}\cdot$ that there is a low-lying, thermally accessible electronically excited state of A_{2u} symmetry, 1140 cm^{-1} (8772 nm) above the A_{1u} ground state.[338] Due to the possibility of degenerate states and, therefore, of angular momenta, $\mathbf{7}^{-}\cdot$ appeared as suitable subject for the study of magnetic circular dichroism (mcd). It was, indeed, observed that large angular momenta give large molar mcd values. The question of which is the ground state of $\mathbf{7}^{-}\cdot$ seems to be settled since recent calculations[340] provide strong evidence in favor of the ${}^2A_{1u}$ state. Another important result of the study of $\mathbf{7}^{-}\cdot$ is the detection of the theoretically predicted band at very long wavelength (1473 nm).[340]

It is interesting to note from the case of the [16]-annulene **7** that the splitting between the highest bonding and lowest antibonding orbitals decreases along the series **7**, $\mathbf{7}^{-}\cdot$, and $\mathbf{7}^{2-}$. As has been mentioned on several occasions the magnitude of this splitting depends on the variation of the peripheral resonance integrals. It follows that the distribution of the β-values is increasingly homogeneous in the series **7**, $\mathbf{7}^{-}\cdot$, $\mathbf{7}^{2-}$.

As anticipated from a simple MO model the dianion $\mathbf{7}^{2-}$ exhibits only two absorption bands [$\lambda = 560$ (13750)/600 (15800); $\lambda = 412$ (175000)].[140,340] These two bands as well as the two broad absorptions of the cyclooctatetraene dianion $\mathbf{3}^{2-}$, correlate well with the three transitions observed for the aromatic [4*n* + 2]-annulenes, thus providing additional support for the close relationship between [4*n*]annulene dianions and their neutral [4*n* + 2]counterparts.[407]

X. *π*-Bonding Situation in Ionic Annulenes

A. Structure and Energy of Annulenes

Regarding the *structure* and *energy* of an organic compound as its most important ground-state properties, the special significance of these features in the annulene field should be clarified.

It has been recognized that for a series of [4*n* + 2]-annulenes, the molecular symmetry of the ground state is that suggested by the resonance, i.e., superposition with equal weight of the two Kekulé structures (with alternating bond lengths). The actual structure possesses equal bond lengths. On the other hand it was pointed out in the introductory section that [4*n*]-annulenes in their ground state should not adopt the fully symmetric framework predicted on the basis of resonance theory. The distorted structure is characterized by alternating bond lengths.

Therefore, when assessing the structure of annulenes, in particular when contrasting neutral annulenes and their ionic derivatives, one is mainly concerned with the fundamental alternative of π-bond delocalization vs. π-bond localization.[44,45]

If one considers the ground state of an annulene as the resonance of two Kekulé structures, one will necessarily raise the question of the resonance energy. According to the Hückel approach a planar 2*i*-membered annulene should possess a total π-energy which is lower than that of a hypothetical nonconjugated reference structure. The most simple model, thereby, predicts both [4*n* + 2]- and [4*n*]annulenes as being stabilized by cyclic π-conjugation. More sophisticated calculations (on the basis of SCF-MO procedures, but also within the realm of the Hückel theory)[48,57–62] ascribe a positive resonance energy to [4*n* + 2]annulenes and a negative resonance energy to [4*n*]annulenes. It is not within the scope of this review to touch upon the great number of investigations devoted to resonance energies or delocalization[341,342] energies in annulenes. It is clear, however, from the preceding section IX that stabilization effects resulting from cyclic π-conjugation have to be invoked in order to properly account for the dramatic differences in the redox behavior of [4*n*]- and [4*n* + 2]annulenes.

The problem with the use of resonance energies as criteria of aromaticity is the choice of suitable reference structures,[342] a point which is further aggravated in the treatment of ionic annulenes. One approach originates from the finding that the π-energy of neutral linear polyenes can be written as a sum of bond-energy terms. The bond-energy terms of acyclic radicals and ions are then taken to define reference structures for cyclic radicals and ions. Difficulties in using open-chain references have led to an alternative procedure in which the energies of annulene ions are compared to infinitely large annulenes with additional formal charges.

Having accepted the aromaticity criteria which are based on the HMO resonance energies of neutral annulenes one can then show that HMO theory may also be used to analyze the aromaticity of annulene ions. Indeed, $(4n + 2)\pi$-ions have been characterized as aromatic and $(4n)\pi$-ions as antiaromatic, however, there are some striking disagreements among the published predictions.[60–63,343]

Within the realm of a perturbational treatment the distortion of a fully symmetric structure, i.e., the process of π-bond fixation, can be described by the first and higher derivatives of the π- and σ-energy with respect to the bond lengths.[44,45] One arrives at first-order bond fixation terms which lead to the linear relationship of bond length and bond order, and second-order bond fixation terms. Only the latter induce a distortion of the original symmetry. Thereby, the σ-compression energy must be overcompensated by the gain in the π-energy. The structural features, therefore, are a direct consequence of the inherent energetics so that the above-mentioned energetic and structural descriptions of annulene species are complementary.

It should be realized that a bond alternation corresponding to one of the two equivalent Kekulé structures is often, but not always the most favorable bond distortion. However, the above theories are capable of examining all types of bond distortion. They can, therefore, be extended to large polycyclic systems, to electronically excited states and, more importantly in the present context, to charged conjugated molecules. Typical results of such studies can be found in ref 45.

B. The Structural Aspect. π-Bond Delocalization vs. π-Bond Localization

How can one decide experimentally whether or not π-bond alternation occurs within a neutral or charged monocyclic π-system? While criteria derived from electron absorption spectroscopy have been mentioned in section IXC, NMR and ESR spectroscopic arguments will now be investigated.

The most important piece of evidence, clearly, is the molecular symmetry which can be inferred for diamagnetic species from the number of NMR signals. The simple ^{1}H NMR spectra, e.g., of 7^{2-}[140] and of 17^{2-}[121] readily indicate a D_{4h} and C_{2v} symmetry of the perimeter, respectively, which is only compatible with a π-bond-delocalized system. Such an interpretation is not always straightforward due to complex signal overlap in the ^{1}H NMR spectra (particularly for the corresponding neutral compound). Counting the number of the relevant ^{13}C singlet signals generally leads to convincing results. Thus, the observation of four olefinic resonances in the ^{13}C NMR spectrum of 17^{2-} is in accord with a π-bond-delocalized structure.

The inherent problem with this kind of argument is the occurrence of a rapid π-bond shift. If a π-bond-delocalized structure is only slightly higher in energy than a π-bond-localized one, a π-bond shift might occur. The latter process, if rapid on the NMR time scale, would give rise to deceptively high symmetry. The example of the neutral [12]annulene **17**[118] is revealing. The observation of six olefinic resonances, which is expected for a π-bond-localized structure of C_2 symmetry, can only be made at temperatures below −120 °C. At higher temperatures the peripheral π-bond shift interconverts the isodynamic structures **17** and **17′**. The concomitant exchange of the magnetic sites of related nuclei causes the coalescence of certain signals. Consequently, in the fast-exchange domain (e.g., at room temperature) one observes a ^{13}C spectrum which could also be compatible with a π-bond-delocalized structure.

It is clear that negative evidence for a double-minimum potential (the case of two π-bond-localized isomers) cannot be taken as proving a single-minimum potential (the case of one π-bond-delocalized structure). Thus, the observation of high symmetry in the NMR spectra of, e.g., 7^{2-} and 17^{2-} even at low temperatures does not exclude the occurrence of second-order π-bond fixation.

The necessity arises to invoke additional NMR spectroscopic features which should be related to the peripheral resonance integrals or to the ratio of resonance integrals of consecutive bonds (the term β_1/β_2 would then serve as a measure of the degree of π-bond fixation).

Theory predicts a diatropic ring-current effect to be severely quenched in the presence of π-bond alternation[310,314] (i.e., if β_1/β_2 deviates significantly from unity). From this point of view the well-established diatropic character of dianions and dications derived from [4*n*]annulenes excludes the occurrence of a pronounced first- or second-order double-bond fixation and points toward π-bond-delocalized structures.

It is, therefore, most instructive to extend the above reasoning to an homologous series of [4*n* + 2]annulenes and, if they exist, to their corresponding $(4n + 2)\pi$-tetraanions.

As has been indicated in section I the occurrence of π-bond fixation is also expected for large [4*n* + 2]-annulenes. The decrease of diatropism in the series of neutral [4*n* + 2]annulenes **22**–**25** which is obvious from the ^{1}H NMR analysis in section V[10] can compellingly be ascribed to the existence of π-bond fixation. As already indicated, the diatropism of the tetraanions exceeds that of the neutral annulenes. Obviously, the tendency of the excess charge to be uniformly distributed over the entire π-system strongly reinforces the π-bond delocalization.[10] Further support of this naive view is obtained when comparing the homologous tetraanions. Their diatropism, as measured by the term $(\delta_0 - \delta_i)/S$, decreases in the larger rings—this "quenching effect", however, being much less severe than in the neutral species.

For the dianions and dications of [4*n* + 2]annulenes, (species which constitute $(4n)\pi$-monocycles) a discussion of π-bond fixation is different, since such ions will tend to alternate their bond lengths. We recall that both second-order double-bond fixation and paratropism originate from the admixture of electronically excited states to the electronic ground state of the π-system.[348] The fundamental importance of the HOMO/LUMO gap for interpreting the paratropic behavior of such ions (see section VIII) is, therefore, obvious. The question remains for the paratropic dianions and dications if, in addition to first-order double-bond fixation, a second-order fixation process will occur which lowers the symmetry of the molecular framework. The ^{1}H and ^{13}C NMR spectra of the strongly paratropic dianions **22**$^{2-}$–**25**$^{2-}$ have been measured at temperatures as low as −115 °C[10] (similar experiments have been performed for **27**$^{2-}$) but fail to provide any evidence in favor of distorted structures.

A different situation is encountered in the [18]annulene dianion **8**$^{2-}$ where the exact line-shape analysis of exchange-broadened ^{1}H NMR signals provides evidence for the occurrence of a peripheral π-bond shift. This outcome, on the other hand, implies the existence of π-bond fixation.

Another feature related to the π-bonding situation is the conformational mobility of annulenes. In a formal sense this process implies a rotation of double bonds around the neighboring single bonds. Typical examples are the ring inversion of cyclooctatetraene or the rotation of trans double bonds (e.g., in **5**, **6**, **7**, and **8**) around the adjacent bonds which exchanges the magnetic sites of inner and outer protons. The important point here is that the barrier to rotation around a formal single bond should increase with the relevant π-bond order. The significant decrease in conformational mobility which is observed upon going from neutral [4*n*]annulenes to their dianions, therefore, indicates a tendency toward equalized π-bond orders in the ions.

It has been mentioned before that the cyclooctatetraene radical anion **3**$^{-}\cdot$, like the corresponding dianion, conforms to D_{8h} symmetry. If, according to the above discussion, the reduction of π-bond-localized [4*n*]annulenes produces π-bond-delocalized dianions, a determination of the structure of the intermediate radical anions is of great importance.

The experimental criteria are completely analogous to those applied for the diamagnetic species: the number of independent ESR hyperfine coupling constants reflects the symmetry of the nuclear framework. For a π-bond localized perimeter of the [12]annulene radical anion **17**$^{-}\cdot$ one would expect five different coupling constants each corresponding to two protons (note that a C_2 axis perpendicular to the ring and passing through the bridge would be the only element of symmetry). The observation of only three coupling constants for the ring protons belonging to two groups of four equivalent hydrogens and one group of two equivalent hydrogens[120] not only facilitates the assignment but also indicates the existence of two planes of symmetry. This demonstrates that—in the ESR time scale—the radical anion exists as a π-bond-delocalized species. An inspection of Table I reveals that related arguments hold for other [4*n*]annulene radical anions (e.g., **7**$^{-}\cdot$[140] and **19**$^{-}\cdot$[122]).

Experience accumulated in the study of the neutral compounds indicates, however, that these results might also be due to a rapid reversible interconversion of π-bond-localized structures. We note that ESR spectroscopy would allow one to detect much faster dynamic processes than NMR spectroscopy. It is therefore significant that at −100 °C, the lowest temperature at which ESR spectra, e.g., of **17**$^{-}\cdot$ have been taken, there is no indication of exchange processes.

Another, even more convincing, argument in favor of π-bond delocalization within the radial anions of [4*n*]annulenes can be obtained from a calculation of the spin densities (see section VIA). Only for a delocalized π-structure does one encounter an alternation of π-centers with high and low AO coefficients. In an analogous treatment of a π-bond-localized perimeter the AO coefficients around the ring turn out to be of comparable magnitude. One can allow for an interconversion of the equivalent localized structures by averaging the relevant spin densities. It turns out, however, that the agreement between the calculated (averaged) and experimental coupling constants becomes much worse than for the π-bond-delocalized structure.

Because of the above-mentioned nodal properties of the nonbonding MO's these arguments are generally valid for the radical anions of [4*n*]annulenes (and can, indeed, be easily verified from the experimental data presented in Table I): if the protons of the $C_{2i}H_{2i}$ ring exhibit a weak and alternatively a strong coupling with the unpaired electron, the radial anion can be assumed to be π-bond delocalized. Thereby, the difference between the rigid bridged annulenes and the flexible annulenes lies in the necessity of determining the unknown configuration of the ring in the ionic system.

C. Stabilization Energies

1. The Dynamic Behavior of Ionic Annulenes and Its Kinetic Analysis

A widely accepted method for determining stabilization energies in annulenes employs the kinetic analysis of the occuring dynamic processes. The rotation of a trans double bond around the adjacent bonds in, e.g., a [14]- or [18]annulene proceeds via an essentially nonplanar transition state in which the cyclic π-bond delocalization is interrupted.[77] It has, therefore, been assumed that the corresponding activation energy represents the delocalization energy of the $(4n + 2)\pi$-system. In a related fashion one may consider the transition states for the conformational interconversion and for the π-bond shift process in [4*n*]annulenes. Thus, the ring inversion of cyclooctatetraene, the most thoroughly studied example, was recognized to imply a progressive flattening of the molecule and passage through a planar structure of D_{4h} symmetry; the same flattening should occur during a π-bond shift, but also accompanied by symmetrical bond-length modifications toward a D_{8h} transition state. The difference between the activation energies of the latter and former process was then identified as the (negative) resonance energy in a π-bond-delocalized form of **3**.[77,105] Similar arguments were invoked during the treatment of the [16]annulene **7** although the transition state of the conformational transformation is not planar.[77]

There are a number of investigations which extend these ideas to the ionic annulenes. Accordingly, the strain accumulated in, e.g., a planar cyclooctatetraene ring (estimated from the activation energy of the ring inversion) was accepted as representing the lower limit of stabilization energy in the planar dianion.[101,104]

The [12]annulene dianion 5^{2-} fails to exhibit any line-broadening effects in its ^{1}H NMR spectra between −90 °C and +30 °C. If there were an isodynamic process bringing about the magnetic equivalence of inner and outer protons its free energy of activation would certainly be higher than 75 kJ/mol.[112] This is about 33 kJ/mol greater than that of the dynamic process responsible for the exchange of inner and outer protons which is observed in the isoelectronic [14]annulene **6**. It was concluded[112] that the resonance energy associated with the 14π-dianion of the [12]annulene **5** is at least 33 kJ/mol greater than that in the neutral [14]-annulene.

Likewise, the observation that the [16]annulene dianion 7^{2-} does not provide any indication of NMR exchange up to 140 °C was taken as evidence that the relevant resonance energy is at least 50 kJ/mol greater than that of the isoelectronic [18]annulene.[140]

It has been noted that simple HMO calculations[140] confirm these findings: one obtains delocalization energies for the [12]annulene and [16]annulene dianions which are by about 1 β-unit (63–75 kJ/mol) greater than those of the isoelectronic [14]- and [18]annulenes. On the other hand, the dynamic behavior of the [18]-annulene dianion 8^{2-} [146] reveals that dianion formation will not necessarily favor a rigid planar ring geometry and that there is, indeed, a difference between the charged $(4n)$- and $(4n + 2)\pi$-systems. Starting out from a reasonable kinetic pathway a thermochemical diagram was established from which one could deduce that the resonance energy of a planar or quasiplanar 18-center 20π-system of 8^{2-} lies between −20 and −33 kJ/mol.

A severe shortcoming of these energetic considerations is the restriction to the properties of the π-system. The results of the following theoretical investigations are revealing.

(1) The cyclobutadiene dication 1^{2+} is predicted from ab-initio calculations to prefer a puckered geometry with D_{2d} symmetry (1^{2+}**a**) instead of the square-planar D_{4h} geometry expected from the HMO treatment of the aromatic 2π-system.[344] The decrease in symmetry, which is shown to allow a greater mixing among the orbitals, can mainly be ascribed to an alleviation of the destabilizing 1,3-interactions within the four-membered ring.


1^{2+}


1^{2+}a


93

(2) The recent prediction of an "open" structure $(1^{2-}/2Li^+)$**a** for the dilitho salt of the cyclobutadiene dianion (see section VII) constitutes another example of an ionic (potentially aromatic) annulene structure not in accord with the HMO picture.

(3) The cyclooctatetraene dianion 3^{2-} is found from ab-initio calculations to prefer a planar, π-bond-delocalized structure with D_{8h} symmetry.[345] Although this is in agreement with the HMO model it becomes obvious that the preference for the D_{8h} over the D_{4h} structure is mainly due to a marked decrease in the bielectronic repulsions.

(4) The cycloheptatrienyl anion **93**, potentially an antiaromatic system with negative resonance energy,[346] is described by MINDO/3 calculations as existing in a planar structure with D_{7h} symmetry.[347]

TABLE VII. Thermodynamic Cycle for the Determination of the Enthalpy of Reaction ($\Delta H°$) between Sodium Metal and the Neutral [16]annulene 7 To Yield the Dianion Salt[54,333,334]

reaction	$\Delta H°$, kJ/M
$7\text{-}H_2(s) + 2NaOH(aq) \rightarrow 2Na^+7^{2-}(s) + 2H_2O(l)$	+45.5
$7(s) + H_2(g) \rightarrow 7\text{-}H_2$	−117.0
$2Na^0(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$	−368.6
$2Na^0(s) + 7(s) \rightarrow 2Na^+7^{2-}(s)$	−438.9 ± 16.7

π-system	$\Delta H°$, kJ/M
3	−338.0
7	−438.9
84	−105.1

When returning to an experimental description of annulene ions and their stability it should be pointed out that a MO theoretical approach can ignore neither the role of the σ-core (see above) nor the one of ion pairing and solvation (see section VII).

2. Analysis of Electrochemical and Thermochemical Data

It has been outlined in section IXA that the spacing between the first and second reduction potentials of annulenes in aprotic media $\Delta E = E_2 - E_1$ provides a measure for the disproportionation equilibrium. The significance of the ΔE values is exemplified by elucidating the role of ion pairing: dianions will ion pair more strongly than radical anions so that more effective ion pairing due to smaller cations can be detected by a decreasing ΔE.

On the other hand, the smaller ΔE values measured for $[4n]$annulenes than for $[4n + 2]$annulenes can be ascribed to the fact that the electronic stabilization of the reduction product in the former case (the case of a $(4n + 2)\pi$-product) forces the disproportionation equilibrium toward the dianion. Similar arguments have been applied to the formation of $(4n + 2)\pi$-tetraanions (see above).

It has been deduced from *calorimetric* measurements that the aromatic dianions 3^{2-} and 7^{2-} react much less exothermally with water than, e.g., the anthracene dianion.[334] From the heat of this reaction and from the heat of hydrogenation of the neutral compound one can deduce the thermodynamic cycle which in Table VII is depicted for the example of the [16]annulene **7** and its corresponding hydrogenation product **7**-H_2.

One arrives at the enthalpy of reduction of the neutral π-system with sodium metal to yield the sodium salt of the dianion. The data thus obtained are compiled in Table VII for the examples **3**, **7**, and anthracene (**84**).

The data in Table VII(b) nicely support the conclusions drawn from the electrochemical results. The dianions 3^{2-} and 7^{2-} exhibit a strong stabilization and are, therefore, recognized as having aromatic character. In contrast, the neutral compounds do not exhibit any extra thermodynamic stability with respect to other nonconjugated olefins.

On the other hand, the formation of an aromatic species is not the only driving force for the above reduction processes (note, for example, that the enthalpy of formation of the dianion salts derived from acenes is also negative). An additional factor controlling this reaction is the large crystal lattice energy of the ionic products. A thermochemical cycle has been constructed for the determination of this energy term whereby (calculated) electron–electron repulsion energies[8] and the electron affinities were utilized.[334] The crystal lattice energies for a broad series of π-systems were found to lie in the very narrow range of 1670–1840 kJ/mol.

An interesting case can be made when extending these considerations to the hypothetical dianion salt of benzene (2^{2-}).[334] The heat of the reaction of 2^{2-} with cyclooctatetraene 3 to afford 3^{2-} and 2 is estimated as −740 kJ/mol. In discussing the driving force of this process the authors ascribe a value of +234 kJ/mol to the larger repulsion energy in the (smaller) dianion 1^{2-} and claim "that the concept of aromaticity accounts for about −506 kJ/mol of the enthalpy of generation of two aromatic systems (3^{2-}, 2) from two antiaromatic systems via electron transfer".

In concluding the electrochemical and thermochemical arguments, one might consider two features as relevant for the existence of stable annulene dianions and tetraanions: the achievement of a $(4n + 2)\pi$-system and the effective compensation of electron–electron repulsion.[8]

The importance of the number of π-electrons for the stability of ionic annulenes is, thus, firmly supported by experimental and theoretical evidence. In an empirical approach the role of the electron–electron repulsion energies can be deduced from the following findings:

(1) The greater thermodynamic stability of the [16]annulene dianion 7^{2-} with respect to the cyclooctatetraene dianion 3^{2-} (see thermochemical data) is ascribed to the reduced Coulomb effects in the larger ring.[322]

(2) The failure of **22** to provide a tetraanion (in contrast to the behavior of **23–25**) indicates that there is a minimum ring size for tetraanion formation.

(3) The fact that the [18]annulene **39** forms a trianion radical, but not a tetraanion can be rationalized by the properties of its perimeter which possesses relatively short transannular distances and, thus, strong Coulomb interactions of the relevant π-charges.[108]

(4) Due to the unfavorable electron–electron repulsion within a small ring, stable dianions of cyclobutadiene systems can only be prepared when the greatest portion of the excess charge is accepted by substituents (and stabilized by the interaction with the counterions).

XI. Annulene Character of Homoconjugated and Polycyclic Ions

A. Annulenes as Model Compounds

Because annulenes constitute suitable probes for the evaluation of theoretical predictions, it is not surprising that they have also been invoked as model compounds for more complicated π-species.

The orbital-symmetry control of pericyclic reactions has been reduced to the question of electronic stabilization or destabilization within the cyclic transition state[349] and, thus, to its aromaticity or antiaromaticity.[350]

Another extension of the concept of aromaticity concerns polyenes in which the cyclic conjugation is interrupted by one or more sp^3-hybridized centers. In those instances a cyclic delocalization can only be maintained if there is sufficient ("homoconjugative") overlap of the terminal p_π-orbitals "below" the bridging group.[351]

A third class of compounds with potential annulene character is the unsaturated polycyclic hydrocarbons: when depicting the possible Kekulé formulae of such polycycles one may well raise the question of whether perimeter-type structures significantly contribute to the ground state of the molecules.

From the foregoing treatments of "true" (monocyclic) annulenes the attempts directed toward a meaningful definition of aromaticity invoke (1) theoretical criteria among which Hückel's rule is the most famous example; (2) the ground-state energy as well as the gain in energy achieved by cyclic π-conjugation; (3) experimentally observable properties such as diatropic or paratropic behavior.

Not surprisingly, the well-known difficulties involved in these approaches are further exaggerated when dealing with the above mentioned homoconjugated or polycyclic π-systems. A few examples are revealing:

(1) The significance of homo- or bishomoaromaticity has recently been questioned for neutral and anionic π-systems.[352,353] Concerning the application of experimental criteria, the "thermodynamics of homoaromaticity" has been described[354] while in a more qualitative approach it is asked to what extent a conjugated $(4n + 2)\pi$-polyene can maintain its diatropic character in spite of the interruption by an sp^3 center.[355]

(2) For polycyclic π systems it is clear that Hückel's rule is only valid for monocyclic structures. An early extension of Hückel's rule to polycycles was provided by Platt's perimeter concept.[43] The latter points out that certain polycycles possess a stable "peripheral" shell isolated from an inner moiety by circular nodes. "Inner" π-centers and cross-links can be considered as weak perturbations of the outer annulene skeleton. It was indicated in subsequent approaches toward the aromaticity of polycycles[356] that the number of π-electrons is not the critical factor, but rather their coupling in conjugated circuits. One thereby investigates the Kekulé structures and enumerates the circuits with alternating single and double bonds. Polycyclic systems possessing only conjugated circuits with $(4n + 2)\pi$-electrons are defined as aromatic.

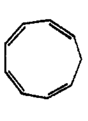
Having firmly established the significance of reduction and oxidation processes in annulene chemistry, one should consider the π-structures of charged homoconjugated and polycyclic species in the light of the above concepts. Thereby, ion formation can play two basically different roles:

(1) Given that a diatropic $[4n + 2]$annulene or a paratropic $[4n]$annulene can be transformed into a paratropic or diatropic dianion, respectively, this criterion may be tentatively extended to polycycles and used to investigate an eventual perimeter structure by going to the corresponding ions. The most prominent example of this approach is constituted by porphyrin molecules (see section XID).

(2) Ion formation, on the other hand, can induce profound changes in the π-structures. A perimeter structure may, thus, only be detectable for a charged polycycle, and not for the corresponding neutral species; likewise, homoaromaticity or bishomoaromaticity may originate only in the ions.

B. Potentially Homoaromatic Anions through Electron-Transfer Processes

Homo- and bishomoaromatic cations have preferentially been prepared by protonation or solvolysis reactions, while the related anions have been obtained mainly from deprotonation procedures. These routes, which have been covered by a recent review,[355] are beyond the scope of this text. However, those examples which are accessible via electron-transfer processes will be discussed.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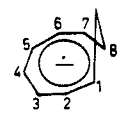

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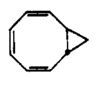
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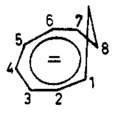

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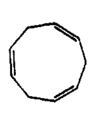
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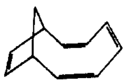
76a


76b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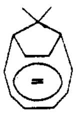
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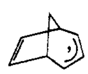
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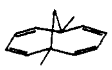
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When *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**76**)[357-359] or *cis*-cyclononatetraene (**94**)[358,360] are reduced with alkali metal one observes the radical anion **95**. The ESR spectrum indicates a large hyperfine coupling constant (ca. 1.7 mT) for one of the hydrogens at C-9 and a small one (ca. 0.2 mT) for the other. A classical structure with a fully formed cyclopropane ring could, therefore, be rejected since it would not accommodate the large coupling. A planar structure with negligible C-1–C-8 interaction is also unlikely since the two hydrogens at C-9 are equivalent in this form. Instead, a nonclassical, monohomocyclooctatetraene radical anion has been suggested as depicted by formula **95**.

It is significant that reduction of the *trans*-bicyclo[6.1.0]nona-2,4,6-triene (**96**) does not lead to a nonclassical structure.[357] This follows from the fact that **96** cannot undergo a symmetry-allowed disrotatory ring opening of the cyclopropane unit without the formation of a highly strained transition state. Instead, the electron accepted upon reduction remains delocalized in the π-hexatriene system which is in a helical arrangement about the trans ring fusion.

Donation of two electrons to **76** gives rise to the dianion **97**[357] (first prepared as the potassium salt, the lithium salt was later shown to possess a much higher solubility in THF). A most revealing outcome is the resonance of the methylene protons at C-9 since the outer one appears at δ 2 and the inner one at δ 0. This diatropic behavior together with other ^{1}H NMR spectroscopic features (e.g., the geminal coupling constant between the methylene protons or the vicinal coupling constants of the ring protons) can best be explained by the assumption of a homoconjugated 10 π-structure **97**. In subsequent studies **97** was shown to be accessible via dimetalation of (*Z*,*Z*,*Z*)-1,3,6-cyclononatriene (**98**) with butyllithium.[361] It could be concluded from an analysis of the vicinal coupling constants of the ring protons that the unsaturated ring adopts a conformation with a similar degree of twisting around all peripheral C–C bonds instead of a tub-shaped arrangement of the C-1–C-8 moiety. The molecule thus maintains optimal π-overlap.

One might deduce from these findings that **97** can be regarded as an analogue of the "aromatic" dianions of cyclooctatetraene or [16]annulene. This appears doubtful, however, when other experimental criteria are invoked.

It appears from the electrochemical reduction of **76** and related species[362] that the electron-transfer processes occur with considerably greater difficulty (half-wave potentials are characteristic of medium-sized triene rings) than in cyclooctatetraene. The obvious noninvolvement of the C-1–C-8 cyclopropane electrons during the reduction has been rationalized by the assumption that the energetically preferred conformation **76a** takes part in the reduction process. Only the folded conformation **76b**, however, allows for sufficient overlap of the C-1–C-8 bond with the adjacent π-orbitals which seems necessary for a facile electron-transfer-induced ring opening.

The monohomocyclooctatetraene dianion also differs from 3^{2-} by its high basicity: when prepared by reduction of **76** in liquid ammonia, **97** undergoes rapid protonation to yield a cyclononatrienyl monoanion.[363] Thermodynamic studies such as those mentioned in section IX were also performed for **97**[354] although, due to its instability in solution, they could be carried out only in the solid state. It was found that the heat of formation of the potassium salt of **97** (which from its diatropism was termed an aromatic homo[8]annulene dianion) is close to 0. The thermodynamic stability of **97** is, thus, low relative to its reference compound, the dianion of cyclooctatetraene.

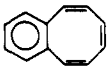
Quite naturally, these electron-transfer studies have also been directed toward the synthesis of a bishomocyclooctatetraene dianion. Reduction of the tetraene **99** does not yield the bishomoconjugated species **100**;[364] instead, one obtains a highly basic product which localizes its negative charge within the triene moiety.

It has been argued that the elusiveness[352,353] of bishomoaromaticity in the monoanion **101**[365-367] can be ascribed to the weak orbital overlap and to the large energy difference of the basis orbitals, i.e., the allyl anion and the ethylene bond. This reasoning also holds for **100**. In view of these arguments the dianion of the tetraene **102**[368] should constitute a more favorable candidate for a bishomoconjugated structure since it possesses two identical butadiene units which are significantly twisted with respect to each other. Reduction of **102** yields a dianionic product (lithium salt) which exists as a strongly diatropic, π-bond-delocalized species of C_{2v} symmetry.[369] Significant NMR spectroscopic features are the chemical shifts of both ring and bridge protons, the number and positions of the ^{13}C signals as well as the vicinal coupling constants of the ring protons. Even more convincing are the results of the electrochemical reduction of **102** (THF, sodium tetraphenylborate as supporting salt) which reveal that the second electron is transferred more easily (i.e., at a more positive potential) than the first.[369] In accordance with what has been said in section IX this finding may be ascribed to some conjugative stabilization in the dianion. Moreover, it follows from the current-potential curves that an ECE mechanism is operative. This can best be explained by the assumption that the initially formed radical anion suffers from a conformational change improving the orbital overlap between the butadiene moieties.

C. Benzannulenes

The large number of known benzannulenes has been described in a recent review.[370] One can conclude from the ^{1}H NMR data that benzannelation reduces the diatropism or paratropism of the parent macrocycle. This can be reconciled with the occurrence of π-bond localization caused by the annelated ring. Particularly interesting examples are [4*n* + 2]annulenes with a fusion of benzene rings in which the resulting Kekulé formulas are symmetrical and identical. In those instances no π-bond localization is induced and the annulenes remain strongly diatropic. It seems promising within this context to investigate the influence of electron-transfer processes upon π-bonding. The largest portion of the published work, however, is restricted to benzannelated cyclooctatetraene.

The polarographic reduction of benzocyclooctatetraene (**103**) and *sym*-dibenzocyclooctatetraene (**104**) (THF, tetra-*n*-butylammonium perchlorate)[371] gave only a single one-electron wave exhibiting Nernstian characteristics. It was concluded that the eight-membered rings of the radical anions possess a puckered arrangement similar to the neutral compounds. The inability of the reduction products to aromatize was ascribed to the benzene-induced minimization of π-electron delocalization in the planar conformation and to the increased structural rigidity. This interpretation was questioned by later studies.[372]



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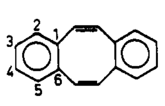

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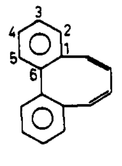

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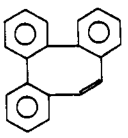

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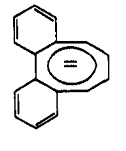
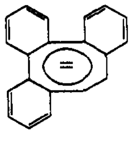
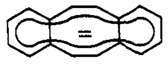


105^{2-}a



106^{2-}a



104^{2-}b

Interestingly, two alternative views of the structure of the radical anion $\mathbf{104}^{-}\cdot$ were also advocated by ESR studies. The anion $\mathbf{104}^{-}\cdot$ was either treated as consisting of four weakly coupled π-moieties[373] or as a system with substantial π-delocalization over the eight-membered ring.[374] A later ESR investigation provided evidence for the latter alternative by indicating a planar geometry for $\mathbf{104}^{-}\cdot$.[375] The similar behavior of **104** and the parent cyclooctatetraene (**3**) also becomes obvious from reduction experiments with potassium in methyltetrahydrofuran (MTHF).[375] Thereby, both species fail to yield the ESR spectra of the radical anions, but pass directly into their dianions. Obviously, the stronger ion pairing in both cases forces the disproportionation equilibrium toward the dianion.

TABLE VIII. ^{1}H NMR Chemical Shifts (δ_H) of Zinc Octaethylporphyrin (109), Its Dianion (109^{2-}/2Li$^+$), and Related Annulene Species[382,383]

	outer	inner
δ_H (**8**)	9.33	−3.17
δ_H (7^{2-}/2K$^+$)	8.83; 7.45	−8.17
δ_H (**109**)	1.95 (CH_3); 4.13 (CH_2); 10.10 (CH)	
δ_H (109^{2-}/2Li$^+$)	−0.64 (CH_3); −1.60 (CH_2); −4.17 (CH)	

The dianion $\mathbf{104}^{2-}$ was characterized by ^{1}H NMR data to be strongly diatropic; a finding which suggests a planar, π-bond-delocalized structure.

A very significant criterion for the π-bonding of a benzannelated monocycle (neutral or ionic) is provided by the ratio of the vicinal coupling constants $^3J_{23}/^3J_{34} = Q$ within the attached benzene ring.[376] The neutral dibenzocyclooctatetraenes **104** and **105** possess Q values close to 1 and are, therefore, identified as olefinic molecules without π-bond delocalization in the boat-shaped eight-membered ring.[377] The significantly larger Q values of the corresponding dianions point toward the formation of π-bond-delocalized structures which is in accord with the ^{1}H chemical shifts.[377] Nonetheless, it cannot be excluded from the NMR data that, due to the steric interaction of the "biphenyl" hydrogens, the dianion $\mathbf{105}^{2-}$ adopts a nonplanar structure with only C_2 symmetry.

The ^{13}C chemical shifts of $\mathbf{105}^{2-}$ and $\mathbf{106}^{2-}$[408] demonstrate that the excess π-charge is essentially localized in the eight-membered ring so that structures $\mathbf{105a}^{2-}$ and $\mathbf{106a}^{2-}$ do not seem remote. Alternatively, one might consider the dianions, e.g., $\mathbf{104}^{2-}$, as de facto monocycles with a 16-center 18 π-perimeter. This bonding situation which may be represented by formula $\mathbf{104}^{2-}\mathbf{b}$ is not born out by the ^{13}C chemical shifts and by the significantly different coupling constants J_{23} and J_{34}. It should be noted, however, that the characterization of the dication $\mathbf{104}^{2+}$, obtained by SbF_5 oxidation of the neutral compound, led to a somewhat different conclusion.[103] The ^{13}C resonances of C-2 and C-3 in $\mathbf{104}^{2+}$ (at considerably lower field than in the neutral molecule) reveal the donation of π-electron density from these positions into the eight-membered ring. This seems to indicate a delocalization of all 14π-electrons over the 16-carbon periphery so that there is a structural similarity between $\mathbf{104}^{2+}$ and the [16]annulene dication $\mathbf{7}^{2+}$.

D. Porphyrins

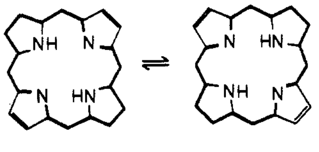
The appreciable diamagnetic ring-current effect associated with the aromatic porphyrin macrocycle is considered as a significant feature of the ^{1}H NMR investigations of porphyrins.[378,379] The π-system can formally be regarded as a bridged diaza[18]annulene (**107**) with two remaining isolated double bonds or as the dianion of a tetraaza[16]annulene (**108**) with four isolated double bonds. For the sake of clarity, Table VIII shows the ^{1}H NMR chemical shifts of some porphyrin systems as well as of the reference systems **8** and

TABLE IX. ^1H and ^{13}C NMR Chemical Shifts (δ_H, δ_C) of Dianions Derived from Pyrene (110) and Its Isomers 58 and 111

	1	2	3	4	5	11	12	15	16	ref
δ_H (110^{2-},$2Li^+$)[a]	0.02	2.20			0.93					152, 401, 402
δ_C (110^{2-},$2Li^+$)	92.0	139.8		147.6	107.3			160.1		
δ_H (58^{2-},$2Li^+$)[b]	7.27		6.93	7.27				92.7		152, 404
δ_C (58^{2-},$2Li^+$)	121.7		124.1	100.5	114.8					
δ_H (111^{2-},$2Li^+$)[a]	−0.33	1.26		−2.05			1.53			159, 401, 402
δ_C (111^{2-},$2Li^+$)	98.6	131.0	121.4	155.8	127.6	132.1	86.8	146.1	173.2	

[a] THF-d_8, −40 °C. [b] THF-d_8, 0 °C.

7^{2-} whose properties have been described in the preceding sections. Indeed, all compounds exhibit strongly shielded inner and deshielded outer protons, so that, according to the ring-current effects, the porphyrins can adequately be described as bridged heteroannulenes incorporating an 18π-perimeter.



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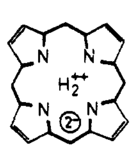

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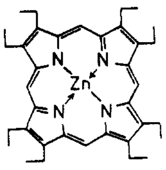


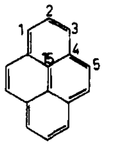
109

More general aspects of the ring-current model as applied to porphyrins and of the use of annulenes and annulene ions have been extensively discussed in the literature.[378,379] It should be mentioned here that structural effects exerted upon ring-current phenomena in porphyrins are in full accord with the experience accumulated in the annulene field.[378,380,381] A few typical aspects are (1) the opposite shift effects suffered by "inner" and "outer" protons upon structural changes, (2) the decrease of ring-current effects when a distortion of the macrocycle reduces the π,π-overlap, and (3) the large upfield shifts experienced by the protons of ligands coordinated to the central metal ion.[380]

Additional information comes from the properties of the zinc octaethylporphyrin (**109**) and its corresponding dianion. If the diatropic neutral compound exists as a true [4*n* + 2] perimeter, the corresponding (4*n*)π-dianion which can be prepared by reduction with alkali metal should exhibit strongly paratropic properties. This is, indeed, born out by the extreme high-field resonances of the methine (δ −4.17)[382] as well as of the ethyl protons in 109^2 (δ_{CH_2} −1.59; δ_{CH_3} −0.65).[383]

E. Pyrene and "Isopyrenes"

A different situation is encountered in the case of pyrene (**110**) as well as its isomers acepleiadylene (**111**) and dicyclopenta[*ef*,*hl*]heptalene (**58**); molecules which can all be reduced the corresponding dianions.[152,159] The LUMO of **110** and **111** can be shown from simple MO arguments to possess a nodal plane through the central ethylene units. One would, therefore, predict for the corresponding radical anions and dianions a vanishing probability for the excess charge to reside on the inner carbons. Convincing evidence in favor of this description is obtained from ^{13}C NMR measurements of 110^{2-} and 111^{2-}, as it appears that the carbons of the inner ethylene units resonate at very low field (downfield from the neutral absorptions, see Table IX). One concludes that the excess π-charge is largely localized within the periphery.



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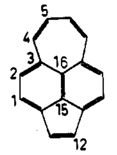

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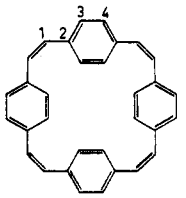


112

The isomer **58** adopts a completely different orbital scheme.[152] When following the interaction of the antibonding perimeter MO's with the π-orbital for the bridge, one realizes that the LUMO of **58** possesses large AO coefficients at the bridge. This is nicely born out by the ESR hyperfine coupling constants of the radical anion $58^{-}\cdot$ as well as by the ^{13}C resonances of 58^{2-}. In the latter the resonances of the bridge carbons suffer from a very large charge-induced upfield shift indicating a high local π-charge.

Upon going from **58** to 58^{2-} the average proton signal is shifted upfield by $\Delta\delta_H$ = −1.3 ppm which is close to the value predicted from the well-established proportionality constant K_H ~10 ppm/e (see section VIB). There is, thus, no indication of an anisotropic ring-current effect being exerted upon the hydrogens. The dianions 110^{2-} and 111^{2-} have been described via ^{13}C NMR data to exist as (14 + 2 = 16 = 4*n*)π-perimeters with an inner ethylene moiety. The predicted paratropic behavior of these (4*n*)π-perimeters is clearly evidenced by the extreme upfield resonances of the dianion protons (see Table IX).[401,402]

Two findings are worth noting which are in complete agreement with this assignment. As expected from the pairing properties of the MO's within the alternant π-system **110** the description of the π-charge distribution in 110^{2-} should also be valid for the corresponding dication 110^{2+}. In particular, the positive charge is expected to remain in the periphery, thus, giving rise to a (12 = 4*n*)π-perimeter. The paratropic character of the latter is again witnessed by the ^1H resonance of 110^{2+}:[152] the charge-induced deshielding of the protons is largely compensated by the ring-current-induced shielding.

The following piece of evidence, again, reveals the useful correlation with the annulene field. The paratropic (4*n*)π-dianions 23^{2-}–25^{2-} have been shown to afford diatropic (4*n* + 2)π-tetraanions upon reduction. Similarly, the paratropic dianion 111^{2-} can be further reduced to a tetraanion which, according to the ^{13}C

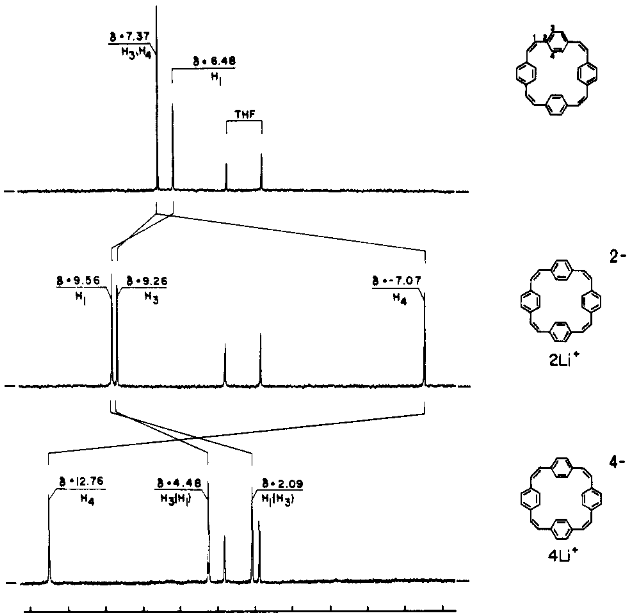


Figure 5. ^{1}H NMR spectra of the paracyclophane tetraene 112 and its corresponding dianion and tetraanion.[195]

chemical shifts, builds up a "normal", i.e., more uniform π-charge distribution and which can also be recognized as a diatropic species.[159] The latter finding follows from the fact that the proton signals of the tetraanion 111^{4-} appear ca. 4 ppm downfield from those of the dianion, although on the basis of the charge effect one would have predicted the reverse effect.[158]

F. Cyclophanes

When investigating the charge-induced formation of perimeter-type structures in polycyclic π-systems, the following case is even more spectacular. The paracyclophane tetraene 112 exhibits "ordinary" behavior in that its ^{1}H NMR spectrum shows typical benzene and olefin resonances without any indication of peripheral ring-current effects. Electrochemical evidence as well as quenching experiments leave no doubt that 112 affords a dianionic derivative.[195] Surprisingly enough, the ^{1}H NMR resonances of 112^{2-} exhibit tremendous shielding effects: protons outside the macrocyclic ring absorb at very low field while the benzene protons inside the ring give rise to a signal at δ −7. Upon further reduction to the tetraanion the signals of the inner protons are shifted to extremely low field again, while those of outer protons appear at high field (see Figure 5). In rationalizing these shielding effects one is compelled to invoke peripheral ring-current effects: while the neutral compound 112, in a formal sense, can be regarded as incorporating a $(24 = 4n)\pi$-perimeter, the corresponding dianion and tetraanion constitute a true diatropic $(4n + 2 = 26)\pi$-perimeter and a paratropic $(4n = 28)\pi$-perimeter, respectively.

The perimeter can be constructed via the inner or outer loop of the benzene rings. In each case a butadiene unit is incorporated into the perimeter, leaving an ethylene unit as the bridging group. As can be demonstrated via an analysis of the local π-charges the perimeter strongly favors the outer loop.[195]

As a simple explanation the occurrence of a macrocyclic π-periphery can be ascribed to a partial equilibration of the π-bond orders of formal single and double bonds, the latter behavior being associated with the delocalization of the π-charge. It is, therefore, significant that the rotation of the benzene units around the neighboring single bonds is very much slowed down upon going from the neutral compound to its dianion. The larger rotational barrier is due to the increased π-bond order of the single bonds.

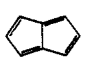
It should be noted without going into further detail that the synthesis of the parent compound 112 can easily be modified to achieve derivatives incorporating larger π-peripheries, heteroatoms, aromatic moieties other than benzene, as well as peripheries deviating severely from planarity.

The corresponding dianions are perceived from their pronounced ring-current effects to exist as "annulene-like" species.[384] One is, therefore, in a position to systematically study the structural dependence of peripheral ring current effects.

G. Pentalene and Heptalene

The bicyclic 8π-, 12π-, and 14π-systems pentalene (113), heptalene (114), and octalene (115) can formally be derived from the isoelectronic [8]-, [12], and [14]-annulenes by the introduction of an additional σ-linkage between opposite centers of the perimeters. The description of 113, 114, and 115 as "de facto annulenes" on the basis of the underlying π-bonding situation is not inaccurate as will become obvious from the corresponding radical anions and dianions.

It follows from an inspection of heptalene (114) and the [12]annulene 17 that both 12π-systems have the same perimeter (cis, cis, trans, cis, cis, trans, i.e., [12]-9-annulene in the coded notation). In both compounds the bridge (a methylene group or a σ-bond) connects two perimeter atoms of the same parity.[141,151] Therefore, according to PMO considerations no first-order changes in π-bonding energy are expected upon going from the hypothetical [12]-9-annulene to 17 or 114.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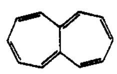
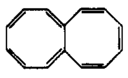
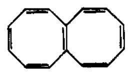

114


115b


115a

^{13}C NMR measurements at very low temperatures indicate that both 17 and 114 exist as π-bond-localized species, but undergo a rapid π-bond shift.[118,385] Not surprisingly in view of the above PMO model, the first reduction potential of heptalene is practically identical with that of 1,7-methano[12]annulene (17). The corresponding value of the 1,6-methano[12]annulene (18) is slightly more negative (see Table VI), an outcome which can be rationalized by the fact that the perimeter of the latter possesses a different configuration and is much more distorted from planarity. The second reduction potential of 114 is more negative than that of 17. This could be explained by the different geometries of the two radical anions: the radical anion of 114 can be planar while that of 17 cannot.

The radical anion of heptalene appears from ESR spectroscopic evidence to possess a π-bond-delocalized ground state.[120] The analogy with $17^{-}\cdot$ is, again, obvious, and it should be mentioned that the arguments of the structural assignment are the same as those applied for radical anions of [$4n$]annulenes (see section VIA): the

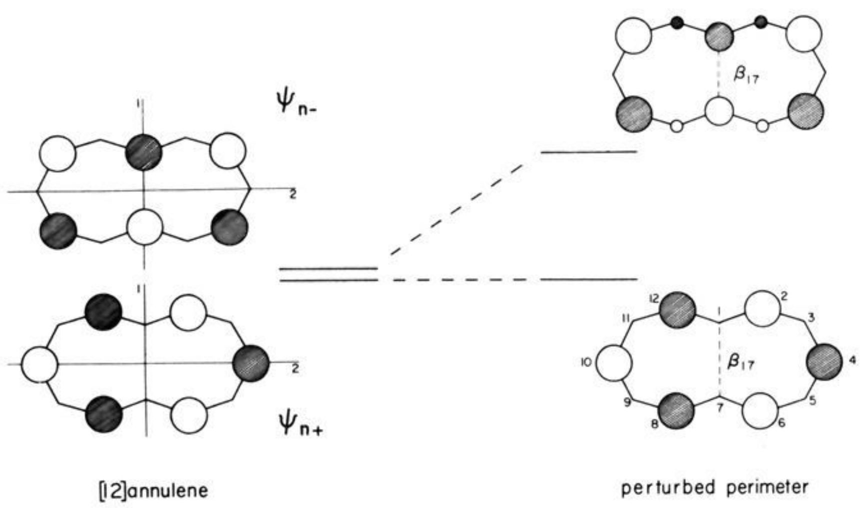


Figure 6. π-Orbital scheme describing the frontier orbitals in a [12]annulene (e.g., compound **17**) and in the isoelectronic heptalene.

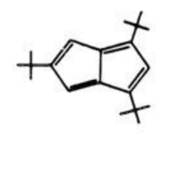
number of experimental ESR coupling constants is only compatible with C_{2v} or D_{2h} symmetry.

The lowest antibonding Hückel MO of **114** is schematically depicted in Figure 6. The existence of a nodal plane through C-4 and C-10 and of a high spin density at C-3 readily explain the experimental detection of a large (4 H) and two small (2 H, 4 H) hyperfine coupling constants. The assignment of the former coupling is, thus, straightforward, while the assignment of the others follows from the number of equivalent nuclei in each group. The coupling constants which have been calculated from the McLachlan procedure and the McConnell relation are in perfect accord with the experimental values. It is, therefore, reasonable to assume that the heptalene radical anion ($\mathbf{114}^{-}\cdot$) is planar.[125]

Toward an understanding of the radical anion structure, one may refer to an idealized [12]annulene whose nonbonding π-orbitals are also given in Figure 6 (note that the deformation of the perimeter does not remove the degeneracy of these MO's). The "bridging" effect can be accounted for by an additional resonance integral. While—to a first approximation—the MO Ψ_{n+} remains unaffected by this perturbation, the MO Ψ_{n-} is destabilized and, thus, accepts the unpaired electron. The above spin-density distribution finds a straightforward explanation. Moreover, the antibonding interaction between the bridgehead centers in the singly occupied MO of $\mathbf{114}^{-}\cdot$ leads to the following conclusions: if the neutral heptalene can adequately be described as a perturbed [12]annulene this is a fortiori valid for the reduction products.

An analogous perturbational treatment can be performed for the lower homologue of **114**, the 8π-system pentalene (**113**). The parent compound **113** is too labile to allow a conventional reduction experiment. The tri-*tert*-butylpentalene (**113a**) is much more stable so that it may be submitted to a low-temperature NMR study[386] and also to the above electron-transfer process.[387,388] The observation of a very large coupling for two equivalent ring protons of $\mathbf{113a}^{-}\cdot$ is in full agreement with the MO model.

The pentalene dianion $\mathbf{113a}^{2-}$ is accessible via deprotonation of the dihydropentalene precursor.[389] Not unexpectedly (from the experience with the reduction of [4*n*]annulenes) the dianion $\mathbf{113}^{2-}$ is much more stable than the corresponding neutral compound. The ^{1}H NMR spectrum of the 10π-system $\mathbf{113}^{2-}$ points toward a pronounced diatropic ring-current effect and, thereby, indicates a close analogy with the isoelectronic annulene system $\mathbf{3}^{2-}$. In contrast to $\mathbf{113}^{2-}$, the heptalene dianion ($\mathbf{114}^{2-}$) cannot be prepared by deprotonation of **117**, but forms smoothly upon reduction of **114** with lithium.



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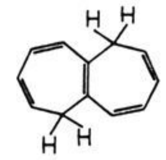


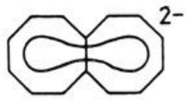
117

H. Octalene and Annulenoannulenes

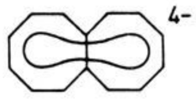
Octalene (**115**) may be considered as a higher homologue of pentalene and heptalene. One realizes, on the other hand, that the molecule consists of two annelated annulene moieties. Such compounds have been termed annulenoannulenes.[390] Depending on the size (*M*,*N*) of each subunit one arrives at three classes of annulenoannulenes

	M	*N*	*M* + *N*
1	4*n* + 2	4*n* + 2	4*n* + 2
2	4*n*	4*n* + 2	4*n*
3	4*n*	4*n*	4*n* + 2

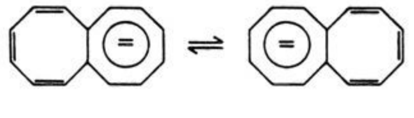
Naphthalene ([6]annuleno[6]annulene), benzocyclooctatetraene (**103**, [8]annuleno[6]annulene), and octalene (**115**, [8]annuleno[8]annulene) are examples of class 1, 2, and 3, respectively.



$\mathbf{115}^{2-}\mathbf{a}$



$\mathbf{115}^{4-}\mathbf{a}$



$\mathbf{115}^{2-}\mathbf{b}$

The question arises whether the properties of such bicyclic species are controlled by those of one subunit or of the overall π-periphery. A detailed discussion of the underlying structural aspects is beyond the scope of this work. However, one concludes from the profound changes of π-bonding and geometry which are observed upon the reduction of monocyclic annulenes that annulenoannulenes constitute promising subjects of electron-transfer experiments: localization of the excess π-charge in one or the other ring or, alternatively, delocalization over the whole molecule should allow for a great variety of π-structures.

In fact, the dianion of naphthalene (similar to those of anthracene and phenanthrene) can adequately be described as a 12π-perimeter with strong paratropic character.[403] In contrast, the behavior of dianions derived from benzo- and dibenzocyclooctatetraene (see section XIC) is dominated by the eight-membered ring which accepts the greatest portion of the excess charge.

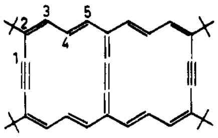
The neutral 14π-bicyclic compound octalene can be shown from its ^{13}C NMR spectrum at −150 °C to exist in the double-bond configuration **115b** with localized π-bonds.[391] Octalene is not planar and does not possess any element of symmetry. Moreover, temperature-dependent NMR measurements allow the detection of two rapid isodynamic processes: an inversion of the cyclooctatetraene and/or cyclooctatriene moiety as well as a π-bond shift. The olefinic character of this potentially aromatic 14π-system can be rationalized by the assumption that the delocalization energy is not sufficient to overcome the strain of flattening the perimeter. Analogous conclusions have been drawn for nonplanar [14]annulenes.

Electrochemical measurements suggested that **115** should form a radical anion, a dianion, a radical trianion, and a tetraanion, and, indeed, one can prepare and spectroscopically characterize all of these species.[156] The identification of the single products follows from the same arguments that have been discussed in section II.

The ^{13}C NMR spectrum of the dianion points toward a D_{2h} symmetry as in structure **115^{2-}a**. For such a perimeter-type structure with $(4n = 16)\pi$-electrons one would predict a strongly paratropic behavior which, however, is not born out by the ^1H NMR chemical shifts. An alternative suggestion might, therefore, invoke structure **115^{2-}b** with a fast π-bond shift. Recent ^{13}C NMR measurements indicate that the latter dynamic process must be rapid on the NMR time scale at temperatures as low as −150 °C.

The novel tetraanionic $(4n + 2)\pi$-species **115^{4-}** which is clearly diatropic can be regarded as an analogue of naphthalene; like the latter, it possesses a $(4n + 2)\pi$-perimeter with π-bond delocalization and consists formally of two annelated $(4n + 2)\pi$-moieties.

Compound **116** constitutes an example of a [14]-annuleno[14]annulene and, thus, belongs to group 1 (naphthalene type).[392] The successful preparation[393] of the dianion **116^{2-}** and the tetraanion **116^{4-}** (lithium salts) allows for similar arguments as in the octalene case. The reference compounds, clearly, are the [14]-annulene **22**, the [22]annulene **24** as well as their corresponding anions.



116

The neutral system **116** is strongly diatropic. Accepting, as has been done in previous sections, the chemical-shift differences of "outer" and "inner" ring protons as a measure of the relevant ring-current effects,[10] one arrives at the following conclusions:

116	22	24	116^{2-}
13.32 (12.68)	13.76	10.03 (9.58)	28.07 (26.53)
116^{4-}	22^{2-}	24^{2-}	24^{4-}
18.87 (17.39)	22.52	25.09 (23.65)	21.28 (19.70)

the $\Delta\delta$ value of **116** is similar to that of **22**, but differs largely from the one for **24**. Consequently, the magnetic properties of **116** are best described as those of an annelated system with two independent 14π-subrings. This is supported by X-ray and ^{13}C NMR evidence.[394]

Similar reasoning is less valid for the ionic species since (see section VIII) the ^1H chemical shifts, before being interpreted in terms of ring-current effects, should be corrected for the influence of the π-charge. Nonetheless, the $\Delta\delta$ values of **116^{2-}** and **116^{4-}**, on the one hand, as well as of **24^{2-}** and **24^{4-}**, on the other hand, provide strong evidence that the dianion and tetraanion of the annulenoannulene **116** must be considered as a 22-center perimeter system.

XII. Conclusion

The recent literature[1] has convincingly demonstrated that the study of electron-transfer processes is of utmost chemical, physical, and biological importance. It is fascinating to modify the properties of an unsaturated compound in a controlled fashion by changing the π-electron configuration or the nature of the frontier orbitals. The annulenes, thereby, demand a crucial role since the consequences of redox reactions can be monitored experimentally and interpreted theoretically in a very straightforward way. With his compounds being "alive" in their relevance, the annulene chemist is somehow like the husband who, only with the passing of years, begins to appreciate the beauty and virtue of his neglected wife.

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(2) A great variety of nomenclature is used in the literature for ionic π-systems. A radical anion of an annulene is termed annulene radical anion or annulenide. Likewise, the corresponding dianion is called annulene dianion or annulenediide (or less common annulenyl dianion). We will use, although not quite correct according to IUPAC rules, the most preponderant names,[3] annulene radical anion (cation) and annulene dianion (dication).
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