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A Theoretical Study of the ^{1}H-Chemical Shifts of [4n]- and [4n+2]-Annulenes and their Di- and Tetraanions

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A simple MO-theoretical and a more sophisticated coupled Hartree-Fock approach are applied to [$4n$]- and [$4n + 2$]annulenes and their di- and tetraanions in order to delineate the relationship between ^{1}H-chemical shifts and ring current, local anisotropic and net charge effects. The theory rationalizes the observed diatropism in neutral and negatively charged [N]annulenes with an even number N and ($4n + 2$) π-electrons and the paratropism in [N]-annulenes with ($4n$) π-electrons.

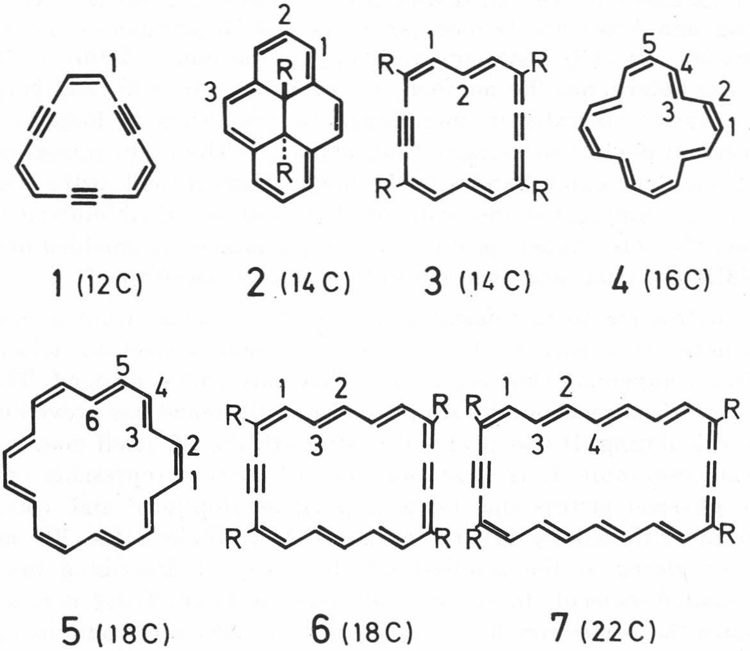
I. INTRODUCTION

[N]Annulenes are carbocyclic conjugated systems with N carbon atoms. For even numbers N we can distinguish $N = 4n + 2$ from $N = 4n$. The corresponding annulenes are termed [$4n + 2$]- and [$4n$]annulenes. These neutral annulenes are (N) π (N) C-systems according to the nomenclature of Winstein[1], since N also determines the number of π-electrons. [$4n + 2$]- and [$4n$]annulenes differ characteristically in their magnetic properties as long as the perimeter does not deviate drastically from planarity. The outer (inner) protons of a [$4n + 2$]annulene exhibit shifts to the lower (higher) field in the NMR spectrum. A cyclic conjugated molecule of this kind is called *diatropic*. On the other hand the outer (inner) protons of a [$4n$]annulene are shielded (deshielded) in the NMR spectrum and this molecule is termed *paratropic*[2].

The diatropism (paratropism) is considered to arise from a diamagnetic (paramagnetic) ring current (RC) due to the cyclic π-electron delocalization[3]. Conjugated compounds showing no RC effect are called *atropic*[4]. The idea of a π-electron RC is conceptually simple and the RC model has proven extremely useful in calculating ^{1}H-chemical shifts, although the RC itself does not present a physical observable. It is clear that the RC concept represents only an incomplete physical picture due to its implicit assumptions[3] and, consequently, it has been criticized by several authors[5]. Nevertheless, the RC model can still be considered as the simplest intuitive way of describing the response of a conjugated molecule to an external magnetic field[6]. There is now evidence that besides the π-electron RC local anisotropic (LA) contributions also determine the magnetic properties of conjugated systems[2c,5–8]. It has been shown[9] that only the combined consideration of RC and LA terms leads to a satisfactory quantitative description of ^{1}H-chemical shifts in neutral annulenes.

The comparison of the ^{1}H-NMR spectra of $[4n+2]$- and $[4n]$annulenes and drawn conclusions on the importance of RC effects is quite often hampered by the fact that such annulenes not only differ in the number of carbon atoms but in their geometrical structures as well. Furthermore, deviations from planarity are frequently encountered due to non-bonded interactions of the inner hydrogens, especially in the case of $[4n]$annulenes. Non-planarity reduces the π-electron delocalization and hence affects greatly the magnitude of the RC.

In recent years several di- and even tetraanions (super charged species[10]) of $[N]$annulenes have been prepared[2d,2e,11,12], representative examples are displayed in Figure 1. On the other hand, only few corresponding dications are known hitherto.[13] The neutral annulenes **1**—**7** are planar or almost planar compounds and we can assume that the same holds true for the anions. Therefore, we obtain series of $[N]$annulenes where N is fixed while the number of π-electrons differs. Thus the annulenes **2**, **3**, **5**—**7** and their di- and tetraanions represent $(4n+2)\,\pi\,(4n+2)$ C-, $(4n')\,\pi\,(4n+2)$ C- or $(4n'+2)\,\pi\,(4n+2)$ C-systems with $n' = n+1$, whereas the annulenes **1**, **4** and their di- and tetraanions are of the $(4n)\,\pi\,(4n)$ C-, $(4n+2)\,\pi\,(4n)$ C- or $(4n')\,\pi\,(4n)$ C-type. All neutral annulenes in Figure 1 are either diatropic (the $(4n+2)\,\pi$-systems **2**, **3**, **5**—**7**) or paratropic (the $(4n)\,\pi$-systems **1** and **4**), *cf.* Table I. With the corresponding dianions all protons at low (high) field are shifted to higher (lower) field and the shifts amount to over 30 ppm in some cases. Obviously diatropic compounds turn into paratropic ones and *vice versa*. The further reduction of the dianions to



1 (12C) 2 (14C) 3 (14C) 4 (16C)

5 (18C) 6 (18C) 7 (22C)

Figure 1. Examples of $[4n]$- and $[4n+2]$annulenes.

TABLE I

Experimental ^{1}H-Chemical Shifts δ of the Annulenes 1—7 and their Di- and Tetraanions

Annulene A	Proton[a]	δ (A) ppm	δ (A^{2-}) ppm	δ (A^{4-}) ppm	Ref.
1	1	4.42	6.74		d
2[b]	1	8.63	—3.19 to —3.96		e
	2	8.14			
	3	8.67			
3[c]	1	9.32	1.85		f
	2	—4.44	24.37		
4	1,2	5.11, 5.40	7.45, 8.83		e
	3	10.53	—8.17		
5	1	9.28	—1.13		e
	3	—2.99	29.5		
6[c]	1	9.32	1.0	7.95	f
	2	9.82	1.0	9.85	
	3	—3.64	24.9	—8.97	
7[c]	1	8.76	1.15	9.03	f
	2	9.21	—0.29	10.61	
	3	—0.82	24.80	—10.67	
	4	—0.82	23.23	—9.50	

[a] See Figure 1.

[b] R = Me.

[c] Tetra-*t*-butyl derivative.

[d] G. Schröder, G. Plinke, D. M. Smith, and J. F. M. Oth, *Angew. Chem.* **85** (1973) 350.

[e] See References 2a (**4**), 2d (**4**, **5**), 2e (**2**, **4**, **5**).

[f] See Reference 11.

the tetraanions, which seems to be possible only with large enough N^{11}, causes another reversal of the RC effect.

The observed dia- and paratropism of neutral [4*n*]- and [4*n* + 2]annulenes have been rationalized within the simple RC model[3,14]. The occurence of paratropism in $(4n')\,\pi\,(4n)$ C- or $(4n')\,\pi\,(4n+2)$ C-systems and of diatropism in $(4n+2)\,\pi\,(4n)$ C- or $(4n'+2)\,\pi\,(4n+2)$ C-systems was expected[2e] analogously to the neutral $(4n)\,\pi$- and $(4n+2)\,\pi$-annulenes. However, except for the special case of a $(4n+2)\,\pi\,(4n)$ C-system[15], the RC effects in negatively charged annulenes have not been studied theoretically. Therefore, it is the aim of this paper to investigate if the simple RC model accounts satisfactorily for the magnetic properties of di- and tetraanions of [4*n*]- and [4*n* + 2]annulenes, as they are manifest in their ^{1}H-NMR spectra, and to elucidate the importance of LA contributions, net charge and counterion effects.

II. APPLICATION OF THE SIMPLE RC MODEL

The orbital energy schemes of [4*n* + 2]- and [4*n*]annulenes and their di- and tetraanions are displayed in Figure 2. These schemes are obtained irrespectively of the chosen theoretical method as long as the perimeter possesses a C_n symmetry axis with $n \geqq 3$. The degeneracy of the orbitals ϕ_{+j} and ϕ_{-j} (for $0 < j \leqq n$) is maintained even when bond length alternation (BLA) is introduced into the perimeter[16]. Only in $(4n)$ C-annulenes is the degeneracy of

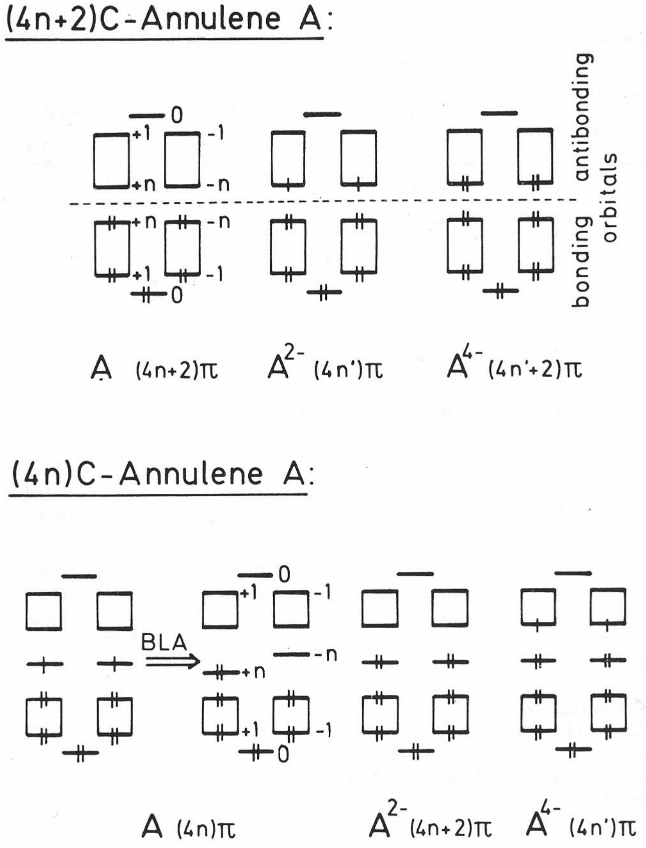


Figure 2. Orbital energy schemes of [4n + 2]- and [4n]annulenes A and their di- and tetraanions A^{2-} and A^{4-}.

ϕ_{+n} and ϕ_{-n} lifted by BLA. Consequently, without BLA the application of any one-determinant approach (Hückel or Hartree-Fock type) is prohibitive for all $(4n)\,\pi$-systems, since total symmetrical closed shells cannot be constructed. With BLA this remains still valid for $(4n')\,\pi\,(4n+2)$ C- and $(4n')\,\pi\,(4n)$ C-annulenes, *i. e.* dianions of $[4n+2]$- and tetraanions of [4*n*]annulenes. Here, further distortions of the perimeter beyond simple BLA have to be present in order to obtain closed shell structures by lifting the degeneracy of the highest occupied orbitals.

Under consideration of BLA the simple RC model[14] can be applied to the neutral $[4n+2]$annulene and its tetraanion, and to the neutral [4*n*]annulene and its dianion. The reduced susceptibility I is a direct measure of the magnitude of the induced RC as long as we compare annulenes which differ only in the number of electrons (otherwise one would have to take into account the areas of the perimeters as well[14,15]). I can be calculated according to the following formula, which represents a trivially generalized version of the one given in Reference 14:

$$I(\lambda) = N^{-2} \sum_{j}^{\mathrm{occ}} v_j F_j(\lambda) \tag{1}$$

where

$$F_j(\lambda) = \lambda^{1/2}\,[\lambda + (1 + \lambda^2)\cos\alpha_j + \lambda\cos^2\alpha_j]\cdot[1 + \lambda^2 + 2\,\lambda\cos\alpha_j]^{-3/2}$$

$$\alpha_j = 4\,\pi j/N.$$

The parameter λ $(0 < \lambda \leqq 1)$ determines the amount of BLA by introducing alternating resonance integrals $\beta_1 = \lambda^{1/2}\,\beta$ and $\beta = \lambda^{-1/2}\,\beta$, where β symbolizes the standard resonance integral. A positive (negative) I indicates a diamagnetic (paramagnetic) RC. The sum in Eq. (1) is taken over all occupied orbitals ϕ_j, the corresponding indices j can be gathered from Figure 2. The factor v_j equals $+\,1$ if ϕ_j is a bonding orbital (ϕ_j^+) and -1 if ϕ_j is an antibonding orbital (ϕ_j^-). Since $\cos\,\alpha_j = \cos\,(-\,\alpha_j)$ we have $F_j(\lambda) = F_{-j}(\lambda)$ and therefore degenerate orbitals ϕ_{+j} and ϕ_{-j} contribute equally to I.

Let us first consider the $(4n + 2)$ C-annulenes A and A^{4-}. Without BLA $(\lambda = 1)$ Eq. (1) can be reduced after some trigonometric transformations to the formulae

$$I_A(1) = [2\,N^2\,\sin(\pi/N)]^{-1} \tag{2}$$

$$I_{A^{4-}}(1) = I_A(1) - N^{-2}\,\sin(\pi/N) \tag{3}$$

Eq. (2) has already been derived by Haddon[15]. From Eq. (3) follows that the tetraanion A^{4-} exhibits a diamagnetic RC similar to the neutral A. The magnitude of the RC in A^{4-} should be smaller than in A, however, the difference becomes smaller with increasing N. The respective orbital contributions to I are displayed in Figure 3a. The smaller $I_{A^{4-}}(1)$ with respect to $I_A(1)$ follows from the different sign of contributions v_jF_j of the orbitals $\phi^{+}_{\pm n}$ and $\phi^{-}_{\pm n}$ where the latter are occupied only in the tetraanion A^{4-}. The RC of A is reduced by BLA $(\lambda < 1)$ due to the decrease and even change of sign of the contribution of the highest occupied orbitals $\phi^{+}_{\pm n}$. This was already recognized by Baer *et al.*[17] within a free-electron model approach. The effect of BLA on the magnitude of the RC is smaller for the tetraanion A^{4-} than for A, as long as λ does not reach unrealistic low values since BLA affects mostly the orbitals $\phi^{+}_{\pm n}$ and $\phi^{-}_{\pm n}$, whose contributions cancel each other out.

Now we shall treat the $[4n]$annulene A and its dianion A^{2-}. Figure 3b reveals that the paramagnetic RC in the neutral A results from the contribution $+\,F_n(\lambda)$ of the highest occupied orbital ϕ_n^+. This is in agreement with findings in Reference 17. We can write $F_n(\lambda) = -\,\lambda^{1/2}\,(1 - \lambda)^{-1}$ which depends drastically on the amount of BLA. The Fermi gap between the highest occupied and lowest virtual orbital ϕ_n^+ and ϕ_n^- is given as $\varepsilon_n^- - \varepsilon_n^+ = -\,2\,\beta\lambda^{-1/2}\,(1 - \lambda)$. Consequently, $F_n(\lambda)$ is inversely proportional to the Fermi gap. Similarly to the tetraanion of a $[4n + 2]$annulene, the orbital contributions of the two highest occupied orbitals ϕ_n^+ and ϕ_n^- in the dianion A^{2-} cancel each other out, so that a diamagnetic RC emerges and its magnitude does not depend very much on BLA as in the case of the neutral A. Without BLA $(\lambda = 1)$ the reduced suceptibility of A^{2-} can be written as

$$I_{A^{2-}}(1) = [2\,N^2\,\tan(\pi/N)]^{-1}.$$

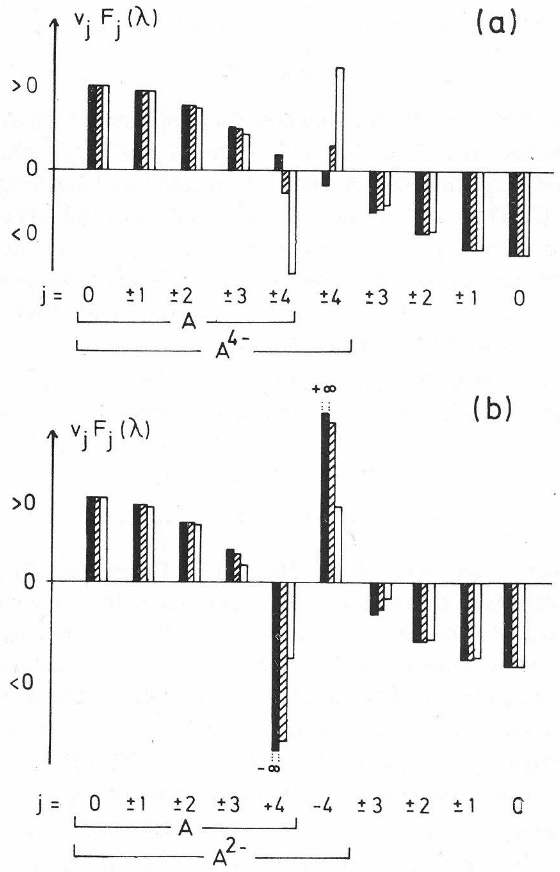


Figure 3. Orbital contributions v_jF_j (λ) (in arbitrary units) to the reduced susceptibility $I(\lambda)$ for $\lambda = 1$ (black beams), 0.9 (hatched beams) and 0.8 (white beams) for a (a) $[4n + 2]$annulene A and its tetraanion A^{4-} and a (b) $[4n]$annulene A and its dianion A^{2-} with $n = 4$. In (b) the lengths of the beams for $j = \pm 4$ and $\lambda < 1$ have been reduced by a factor of 10.

III. COUPLED HARTREE-FOCK APPROACH TO THE ^{1}H-CHEMICAL SHIFTS OF [16]- AND [18]ANNULENE AND THEIR DI- AND TETRAANIONS

A. Geometries of Neutral and Negatively Charged [16]- and [18]annulenes

Solid state geometries of the neutral [16]- and [18]-annulene **4** and **5** are known[18,19], however the solid state geometries of the corresponding di- and tetraanions are not. [18]Annulene **5** possesses D_{6h} symmetry with almost negligible BLA both in the crystal and in solution, and only such a geometrical structure accounts satisfactorily for the ^{1}H-chemical shifts[9] and other molecular properties[20]. On the other hand, [16]annulene **4** is characterized by important BLA in the solid state and exhibits considerable distortions from planarity[18] presumably due to the non-bonded interaction of the inner hydrogens. However, it should be stressed that we do not know if the geometrical structure of **4** in solution matches closely the one in the crystal.

Bond lengths of conjugated compounds can be calculated iteratively by using bond order — bond length — resonance integral relationships (SC-β procedures) provided that the carbon skeleton can be built up without severe angle strain and that non-bonded interactions are unimportant. However, in molecules like **4** such a SC-β method is not sensible, since the geometry will be determined predominantly by angle strain and non-bonded interaction of the inner hydrogens. Therefore, we utilize a modified[21] molecular mechanics (MM) procedure of Lindner[22] which yields, for example, a D_{6h} geometrical structure in contrast to the original version[22] or other MM methods[23].

Experimental and calculated bond lengths for **4** and **5** and their di- and tetraanions are collected in Table II. In the case of **4**, MM yields a nonplanar structure **4a** (see Figure 4) with S_4 symmetry in agreement with the solid state geometry[18]. The calculated bond lengths are longer by about 2 pm with respect to the experimental ones. The same was encountered with another MM approach[23]. The distortions from planarity turn out to be less severe than those observed in the crystal. This may be due to the larger calculated bond lengths, which reduce in effect the non-bonded interactions of the inner hydrogens. Furthermore, the correlation energy, which is partly taken into account in the parametrization of our modified MM method[21], seems to stabilize a (nearly) planar structure with BLA more than a highly non-planar one[24]. For $\mathbf{4}^{2-}$, we obtain a geometry **4b** without significant BLA and with smaller distortions of the perimeter from planarity. A geometry **4c** with D_2 symmetry is predicted for the tetraanion $\mathbf{4}^{4-}$ where only some parts of the molecule are characterized by strong BLA.

TABLE II

Calculated and Experimental Bond Lengths of [16]- and [18]- Annulene ***4*** *and* ***5*** *and their Di- and Tetraanions*

Compound	Bond[a]	Bond length/pm Calc.	Exptl.
4	1—2	136.6	132.6[b]
	2—3	146.4	145.2
	3—4	136.2	134.0
	4—5	146.8	145.4
$\mathbf{4}^{2-}$	1—2	141.6	
	2—3	141.0	
$\mathbf{4}^{4-}$	1—2	140.7	
	2—3	145.5	
	3—4	138.2	
	4—5	144.1	
5	1—2	141.3	141.9[c]
	2—3	141.1	138.2
$\mathbf{5}^{2-}$	1—2	137.6	
	2—3	145.6	
	3—4	138.2	
	4—5	144.0	
	5—6	140.7	
$\mathbf{5}^{4-}$	1—2	142.9	
	2—3	141.4	

[a] See Figure 1.

[b] Average values[18] accoding to S_4 symmetry.

[c] Reference 19.

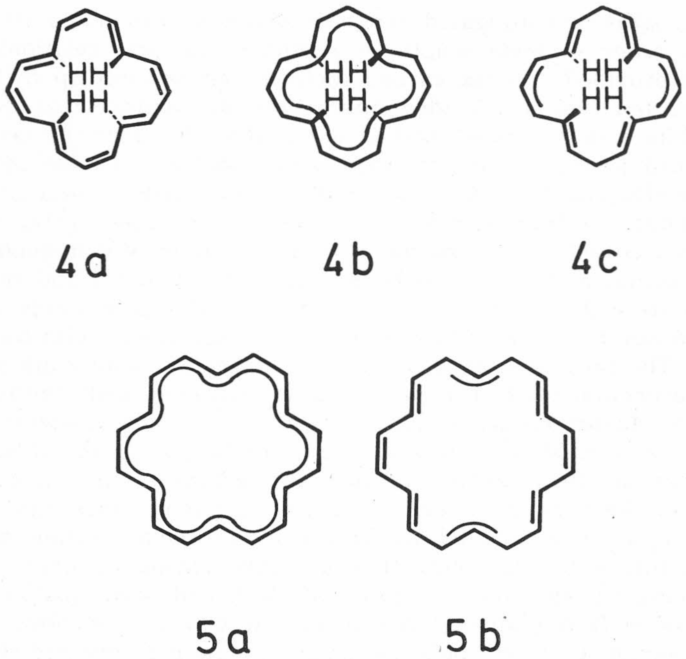


Figure 4. Geometrical structures for **4**, **5**, $\mathbf{4}^q$ and $\mathbf{5}^q$ with $q = -2$ and -4 as obtained with the modified MM procedure.

The MM geometry optimization of **5** yields a planar structure **5a** without significant BLA in agreement with experimental solid state and solution data[19,20]. A similar structure **5a** is calculated also for $\mathbf{5}^{4-}$. On the other hand, we obtain a geometry **5b** for the dianion $\mathbf{5}^{2-}$ which is characterized by significant BLA in parts of the molecule as in the case of the tetraanion $\mathbf{4}^{4-}$.

The geometrical structures **4c** and **5b** for $\mathbf{4}^{4-}$ and $\mathbf{5}^{2-}$ no longer possess a symmetry axis C_n with $n > 2$. Therefore, all degeneracies of orbitals are lifted and this results in a closed shell structure for these compounds, so that chemical shifts can be calculated straigtforwardly. In the case of the dianions of the annulenes **3**, **6** and **7**, such a symmetry reduction is no prerequisite for a closed shell electronic structure due to the lower symmetry of the perimeter with respect to that of **4** and **5**.

B. Calculation of ¹H-Chemical Shifts

The MM geometries for [16]- and [18]annulene **4** and **5** and their di- and tetraanions allow the calculation of ¹H-chemical shifts δ by using a π-theoretical coupled Hartree-Fock approach[8] which goes beyond the simple RC model and has been successfully applied to a large number of neutral hydrocarbons[9,25]. The shift δ can be written as a sum

$$\delta = \delta^{\mathrm{RC}} + \delta^{\mathrm{LA}} + \delta^{q} + \delta^{0} \tag{4}$$

of the RC contribution δ^{RC}, the LA term δ^{LA} and the effect on δ of the net π-charge q ($q < 0$ for excess electron density) on the carbon atom which is bound to the proton in question. δ^0 defines the zero of the δ-scale.

The RC and LA terms δ^{RC} and δ^{LA} contribute almost equally to the low field shift experienced by protons in benzenoid hydrocarbons with respect to those in olefinic compounds[8]. Consequently, in the case of benzenoid hydrocarbons δ can be calculated by the simpler formula

$$\delta' = \delta^{RC} + \delta^{q} + \delta^{o} \tag{5}$$

if a different scalling factor is used in δ^{RC} and another value is chosen for δ^0. For annulenes Eq. (5) is, however, an insufficient approximation for a proper description of the ^{1}H-chemical shifts, since here δ^{RC} and δ^{LA} are of different sign either for inner or outer protons[9] .

Neutral annulenes are characterized by a uniform charge distribution but in the corresponding di- and tetraanions we have necessarily significant net charges q on the carbon atoms. It was shown[26] that δ^q and q are approximately related by

$$\delta^q = aq.$$

Clearly a net charge q will also have a long range effect on the ^{1}H-chemical shifts, however, this should be small[27] and is neglected here. The proportionality constant a was estimated[26,28] to be about 10 ppm *per* electron by comparison of net charges in $C_5H_5^-$,C_6H_6 and $C_7H_7^+$ with ^{1}H-chemical shifts. The inclusion of $C_3H_3^+$, $C_9H_9^+$ and $C_8H_8^{2-}$ in this analysis does not lead to a significantly different value for a. Only a slightly smaller a value is obtained if the RC contribution or even the LA term is explicitly taken into account in these cyclic compounds since the signs of δ^{RC} and δ^{LA} (both taken with respect to the corresponding benzene values) and δ^q are the same. The charged annulenes which have been used for the determination of a exhibit bond angles which deviate considerably from 120^0. Therefore, the carbon atoms are no longer sp^2-hybridized which will affect the LA contributions. However, such hybridization effects are not taken into consideration in our δ^{LA} values. Furthermore, the rôle of the counterion was neglected in the determination of a. This would be justified if only solvent-separated ion pairs were present. In such a case nothing but the electrostatic field of the counterion is effective. This does not significantly influence the ^{1}H-chemical shift as we have checked[21] for $C_5H_5^-$ and $C_7H_7^+$ by simulating the counterion by a pseudo-proton. However, the existence of an equilibrium between solvent-separated and contact ion pair affects both δ^{RC} and δ^q. In order to study the influence of the counterion in a contact ion pair, we calculated δ^{RC} and q for $C_5H_5^- \ldots Li^+$ in the energetically most favourable half-sandwich arrangement[30]. The counterion reduces slightly the magnitude of the net charges in $C_5H_5^-$ whereas δ^{RC} increases. Here we assume that the Li^+ is complexed on one side with solvent molecules so that it can interact with the π-system of $C_5H_5^-$ only with its 2s-orbital or a hybrid of the same symmetry. Consequently a should become sligthly larger. Obviously there is some uncertainty concerning the exact magnitude of a. Therefore, we consider our calculated δ^q values only as rough estimates.

The RC contributions in non-planar compounds are calculated as the mean value of the δ^{RC} terms for the planes xy, xz and yz. The LA contributions, however, have been derived[8] only for planar conjugated system. Therefore, we calculate δ^{LA} for [16]annulene **4** and its ions $\mathbf{4}^{2-}$ and $\mathbf{4}^{4-}$ by using their MM geometries which have been obtained under the restriction of planarity. Since the bond lengths of optimal (non-planar) and planar geometries are similar, we expect that our calculated LA values for the non-planar molecules have roughly the correct order of magnitude.

C. Numerical Results

The calculated and experimental ^{1}H-chemical shifts of [16]- and [18]annulene **4** and **5** and their di- and tetraanions are collected in Table III. The RC contribution δ^{RC} is negative (positive) with the outer (inner) protons of **4**, $\mathbf{4}^{4-}$ and $\mathbf{5}^{2-}$ and the inner (outer) protons of $\mathbf{4}^{2-}$, **5** and $\mathbf{5}^{4-}$. Thus the $(4n + 2)$ π-systems $\mathbf{4}^{2-}$, **5** and $\mathbf{5}^{4-}$ exhibit a diamagnetic and the $(4n)$ π-systems **4**, $\mathbf{4}^{4-}$ and $\mathbf{5}^{2-}$ a paramagnetic RC.

TABLE III

*Calculated ^{1}H-Chemical Shifts δ^{RC}, δ^{LA}, δ^q, δ and δ' and Corresponding Experimental Values δ_{exp} of [16]- and [18]Annulene **4** and **5** and their Di- and Tetraanions*

Compound	Proton[a]	δ^{RC} ppm	δ^{LA} ppm	δ^q ppm	δ ppm	δ' ppm	δ_{exp}[c] ppm
4	1	−1.80	1.32		4.72	4.92	5.11, 5.40
	2	−2.09	1.29		4.40	4.47	
	4	−2.05	1.27		4.42	4.51	
	3[d]	7.07	1.58		14.2	18.6	10.53
$\mathbf{4}^{2-}$	1	2.68	1.11	−1.4	7.59	9.90	7.45, 8.83
	2	3.06	1.16	−1.3	8.12	10.6	
	3[d]	−10.5	1.43	−1.0	−4.49	−8.35	−8.17
$\mathbf{4}^{4-}$	1	−20.1	0.97	−1.6	−15.5	−23.9	
	2	−22.5	0.52	−3.5	−20.3	−29.8	
	4	−22.4	0.91	−1.8	−18.1	−27.6	
	5	−19.9	0.33	−4.3	−18.7	−27.0	
	3[d]	77.4	0.95	−1.8	82.1	120.	
5	2	3.34	1.40		9.94	12.6	9.28
	3[d]	−11.8	1.63		−4.59	−9.50	−2.99
$\mathbf{5}^{2-}$	2	−16.5	1.14	−0.8	−11.0	−17.7	−1.1
	4	−16.8	1.26	−0.5	−10.8	−17.7	
	5	−16.6	0.94	−2.3	−12.8	−19.6	
	3[d]	58.8	1.24	−1.3	64.3	93.0	29.5
	6[d]	58.8	1.48	−0.1	65.8	94.5	
$\mathbf{5}^{4-}$	2	3.11	0.84	−2.4	6.75	9.26	
	3[d]	−10.9	1.10	−1.7	−5.95	−10.0	

[a] See Figure 1.

[b] Calculated with the scaling factor for δ. In the case of δ', δ^{RC} has to be multiplied with 1.47.

[c] Taken from Table I.

[d] Sterically overcrowded protons, δ° includes a van der Waals correction, see Reference 8.

The RC contribution δ^{RC} is a sum of the two terms $E_{11}{}^n$ and $E_{011}{}^n$, see Reference 8. $E_{11}{}^n$ depends on the wave function not being perturbed by the magnetic field, whereas (in the notion of perturbation theory) $E_{011}{}^n$ results from the field induced admixture of singly excited configurations into the Hartree-

-Fock ground state function. $E_{11}{}^{n}$ and $E_{011}{}^{n}$ correspond to the diamagnetic and paramagnetic part of the magnetic susceptibility. The magnitude and sign of $E_{11}{}^{n}$ and $E_{011}{}^{n}$ depend on the special choice of the coordinate origin for the vector potential and only their sum is gauge invariant. However, if we choose the centre of the annulene perimeter as coordinate origin for the vector potential, $|E_{011}{}^{n}|$ reaches its minimum value so that it is possible to discuss the relative importance of $E_{11}{}^{n}$ and $E_{011}{}^{n}$ for δ^{RC}.

All outer protons of **4**, $\mathbf{4}^{q}$, **5** and $\mathbf{5}^{q}$ with $q = -2$ and -4 show negative $E_{11}{}^{n}$ values, whereas they are positive for the inner protons. Thus the signs are the same for $(4n)\,\pi$- and $(4n + 2)\,\pi$-systems. For inner protons $E_{11}{}^{n}$ is numerically, at least, three times larger than that for the outer protons. Numerically small values are encountered for $E_{011}{}^{n}$ of all $(4n + 2)\,\pi$-systems $\mathbf{4}^{2-}$, **5** and $\mathbf{5}^{4-}$ that $E_{11}{}^{n}$ determines sign and magnitude of δ^{RC}. On the other hand, the $(4n)\,\pi$-systems **4**, $\mathbf{4}^{4-}$ and $\mathbf{5}^{2-}$ exhibit $E_{011}{}^{n}$ values which differ in sign from $E_{11}{}^{n}$ and are numerically larger by at least a factor of two. Thus the sign and size of δ^{RC} for the $(4n)\,\pi$-annulenes is governed by $E_{011}{}^{n}$.

The LA contribution δ^{LA} is positive for all protons so that shifts to lower field caused by the RC effect are increased, whereas those to higher field are reduced. This applies especially to inner protons since these exhibit generally the largest δ^{LA} values due to the small distances to the perimeter carbon atoms. Without consideration of LA terms the differences between the ¹H-chemical shifts of inner and outer protons would be considerably larger, *cf.* δ and δ' in Table III.

In the charged annulenes $\mathbf{4}^{2-}$, $\mathbf{5}^{2-}$, $\mathbf{4}^{4-}$ and $\mathbf{5}^{4-}$, one would expect $\delta^{q} \cong -1.3$, -1.1, -2.5 and -2.2 ppm if the negative charge would be distributed uniformly over the perimeter. However, this is not true and we find in Table III quite significant differences up to over 2 ppm between δ^{q} for individual protons.

The calculated ¹H-chemical shifts δ *and* δ' for inner and outer protons of **4** and **5** and their dianions predict shifts either to lower or higher field in agreement with the experimental shifts. Consequently, the directions of the shifts are determined predominantly by the RC effect. The agreement between calculated (δ) and experimental shifts is satisfactory for the neutral annulenes **4** and **5** and the dianion $\mathbf{4}^{2-}$. The shifts of the inner protons of **4** and **5** are numerically too large, which indicates a slight overestimation of the RC effect. This is probably due to small inadequacies in our MM geometries which first of all affect the RC term of the inner protons. On the other hand, the calculated δ for the inner protons of the charged $(4n + 2)\,\pi$-annulene $\mathbf{4}^{2-}$ is numerically too small. Although part of the error may be due to a slight underestimation of the RC term, in this case the neglected long range effects of the net charges which cause high field shifts my also be important, since the inner protons are in unusual close contact to other perimeter carbon atoms.

In contrast to the $(4n + 2)\,\pi$-annulene $\mathbf{4}^{2-}$ the calculated shifts for the $(4n)\,\pi$-annulene $\mathbf{5}^{2-}$ are numerically much larger than the experimental ones. Obviously the RC is greatly overestimated and as yet not considered factors must be responsible for the reduction of $|\delta^{\mathrm{RC}}|$ or $|E_{011}{}^{n}|$, since δ^{RC} is dominated by $E_{011}{}^{n}$. $E_{011}{}^{n}$ is inversely proportional to the Fermi gap which is for one thing smaller in the charged $(4n)\,\pi$-systems than in the $(4n + 2)\,\pi$- or neutral $(4n)\,\pi$-annulenes[31], and for another depends critically on the chosen numerical procedure as well as on details of the geometry. With decreasing the Fermi gap electron correlation, processes which are not treated in the Hartree-Fock approach, become more important. Preliminary investigations[21] of these correlation effects have shown that they indeed lead to a reduction of the magnitude of the RC effect. Clearly, the counterions will also significantly influence the ^{1}H-chemical shifts of the charged annulenes, above all with $(4n)$ π-systems, if besides solvent-separated ion pairs contact ion pairs are present as well in solution. The existence of an equilibrium between these different types of ion pairs has been proven[11] in the case of the dehydroannulenes **3**, **6** and **7**. From the electrostatic potentials[32] above the annulenes, we can conclude that in a contact ion pair the counterions should be arranged mainly over the inner side of the perimeter. Some test calculations with explicit inclusion of Li^+ ions demonstrate that the RC term can be considerably altered depending on the mutual arrangement of counterions and annulene and on the availability of the Li^+ ions, *i. e.* if they interact with the π-system *via* all valence shell orbitals or only with an *s*-type orbital. In most cases the RC terms are strongly reduced in magnitude.

IV. CONCLUSION

In this paper we have shown that the simple RC model of Pople and Untch[14] allows qualitative conclusions on the RC effect in $[4n + 2]$annulenes and their tetraanions and $[4n]$annulenes as well as their dianions. Even with the inclusion of BLA, this RC model cannot be applied to dianions of $[4n + 2]$- or tetraanions of $[4n]$annulenes due to the degeneracy of the orbitals. For such compounds, it is indispensible to determine realistic geometries. This was done for [16]- and [18]-annulene **4** and **5** and their di- and tetraanions by using a modified MM procedure[21,22]. For $\mathbf{4}^{4-}$ and $\mathbf{5}^{2-}$, we obtained geometries which are characterized by a reduction in symmetry, *i. e.* the loss of any C_n symmetry axis with $n > 2$, so that all orbital degeneracies are lifted and the ground state is described by a closed shell configuration for which ^{1}H-chemical shifts can be calculated within a coupled Hartree-Fock approach[8].

The simple RC model, together with our exemplary calculations on [16]- and [18]annulenes, demonstrates that with double and quadruple charged $(4n)$ C- and $(4n + 2)$-C-annulenes the nature of the RC effect also depends only on the number of the π-electrons as in the case of the neutral annulenes, *i. e.* $(4n + 2)$ π-systems exhibit a diamagnetic RC whereas $(4n)$ π- a paramagnetic one. BLA reduces the RC contribution to the ^{1}H-chemical shift. However, our results suggest that significant BLA is not present in charged $(4n + 2)$ π-annulenes as in neutral $[4n + 2]$-annulenes as long as BLA or severe distortions of the carbon skeleton are not enforced by non-bonded interactions. On the other hand, in $[4n]$annulenes the magnitude of the RC depends crucially on the extent of BLA.[14,15,33] This carries over to the negatively charged $(4n)$ π-annulenes, *i. e.* the tetraanions of $[4n]$- and dianions of $[4n + 2]$annulenes. In these compounds the actual size of δ^{RC} is very sensitive to details of the geometries or the numerical procedure.[34] Furthermore, correlation and counterion effects lead to a reduction of $|\delta^{RC}|$.

Our calculations reveal the importance of RC effects in the ^{1}H-NMR spectra of di- and tetraanions of $[N]$annulenes. By defining the mean value δ_o (δ_i) of all shifts of the outer (inner) protons, we can call a compound diatropic if $\delta_o - \delta_i > 0$ and paratropic if $\delta_o - \delta_i < 0$. From eq. (4) follows $\delta_o - \delta_i = (\delta_o^{RC} - \delta_i^{RC}) + (\delta_o^{LA} - \delta_i^{LA}) + (\delta_o^{q} - \delta_i^{q}) + (\delta_o^{0} - \delta_i^{0})$, where δ_o^{RC} *etc.* are the correspondent averaged values. Consequently, diatropism (paratropism) is tantamount to a diamagnetic (paramagnetic) RC effect only if $\delta_o - \delta_i \left(\overset{>}{<}\right) (\delta_o^{\mathrm{LA}} - \delta_i^{\mathrm{LA}}) + (\delta_o^q - \delta_i^q) + (\delta_o^0 - \delta_i^0)$ and $|\delta_o - \delta_i| \leqq |\delta_o^{\mathrm{LA}} - \delta_i^{\mathrm{LA}} + \delta_o^q - \delta^q_i + \delta_o^0 - \delta_i^0|$ defines atropic compounds. Generally, the inner protons of annulenes are sterically overcrowded in contrast to the outer protons which means[8] that $\delta_o^0 - \delta_i^0 \cong -0.4$ ppm. In neutral annulenes $\delta_o^q - \delta_i^q$ vanishes and the same applies to charged annulenes only if the charge is rather uniformly distributed over the perimeter. However, this was not true with the di- and tetraanions of the [16]- and [18]annulenes **4** and **5**. Here we have $\delta_o^q < \delta_i^q$, since the negative charge is mainly localized in the outward parts of the perimeter. On the other hand, we have[21] $\delta_o^q > \delta_i^q$ in the case of the tetraanions of **3**, **6** and **7**. Obviously the sign of $\delta_o^q - \delta_i^q$ depends on the annulene of interest but one can estimate that $|\delta_o^q - \delta_i^q| < 1.5$ ppm. The neutral and negatively charged [16]- and [18]annulenes exhibit negative $\delta_o^{\mathrm{LA}} - \delta_i^{\mathrm{LA}}$ values which do not depend significantly on the charge although δ_o^{LA} and δ_i^{LA} decrease with increasing charge (*cf.* Table III). On the other hand, positive $\delta_o^{\mathrm{LA}} - \delta_i^{\mathrm{LA}}$ differences are encountered[21] for the neutral and negatively charged dehydroannulenes **3**, **6** and **7**. Thus, the sign of $\delta_o^{\mathrm{LA}} - \delta_i^{\mathrm{LA}}$ is uncertain as well and we can only give an estimate $|\delta_o^{\mathrm{LA}} - \delta_i^{\mathrm{LA}}| < 1$ ppm. Consequently, diatropism (paratropism) is necessarily connected with a diamagnetic (paramagnetic) RC effect only if $|\delta_o - \delta_i| > 1.5$ ppm for neutral and $|\delta_o - \delta_i| > 3$ ppm for charged annulenes. These limiting values separating atropic from dia- or paratropic cyclic compounds are considerably exceeded by the $\delta_o - \delta_i$ values, which can be obtained from the experimental ^{1}H-chemical shifts of the annulenes **3**—**7** and their di- and tetraanions (*cf.* Table I). Therefore, we can safely conclude that the diatropism of the $(4n + 2)$ π- or the paratropism of the $(4n)$ π-annulenes is connected with a dia- or paramagnetic RC effect and *vice versa.*

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REFERENCES AND NOTES

1. *Aromaticity,* S. Winstein, Special Publication No. 21, The Chemical Society: London, 1967; p. 5.
2. (a) *Aromaticity,* F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society: London, 1967; p. 75. (b) F. Sondheimer, *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research,* **12** (1968) 125. (c) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch. Top. Curr. Chem.* **16** (1971) 103. (d) F. Sondheimer, *Acc. Chem. Res.* **5** (1972) 81. (e) F. Sondheimer, *Chimia* **28** (1974) 163.
3. C. W. Haigh and R. B. Mallion, *Progr. Nucl. Magn. Resonan. Spectrosc.* **13** (1980) 303 and references therein.
4. S. W. Staley and G. M. Cramer, *J. Amer. Chem. Soc.* **95** (1973) 5051.
5. J. I. Musher, *Adv. Magn. Reson.* **2** (1966) 177; P H. Blustin, *Mol. Phys.* **39** (1980) 565; P. Lazzeretti and R. Zanasi, *J. Chem. Phys.* **75** (1981) 5019; P. Lazzereti, E. Rossi, and R. Zanasi, *J. Chem. Phys.* **77** (1982) 3129, *Nuovo Cimento* **1D** (1982) 70; P. Lazzeretti and R. Zanasi, *Chem. Phys. Lett.* **100** (1983) 67.

6. J. A. N. F. Gomes, *Mol. Phys.* **40** (1980) 765, *J. Chem. Phys.* **78** (1983) 3133.
7. J. A. Pople, *J. Chem. Phys.* **41** (1964) 2559; M. Barfield, D. M. Grant, and D. Ikenberry, *J. Amer. Chem. Soc.* **97** (1975) 6956.
8. H. Vogler, *J. Amer. Chem. Soc.* **100** (1978) 7464.
9. H. Vogler, *J. Mol. Struct.* **51** (1979) 289.
10. M. Rabinovitz, I. Willner, and A. Minsky, *Acc. Chem. Res.* **16** (1983) 298.
11. K. Müllen, W. Huber, T. Meul, M. Nakagawa, and M. Iyoda, *J. Amer. Chem. Soc.* **104** (1982) 5403, *Tetrahedron* **39** (1983) 1575.
12. P. J. Garratt, N. E. Rowland, and F. Sondheimer, *Tetrahedron* **27** (1971) 3157.
13. G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega, and M. J. Carmody, *J. Amer. Chem. Soc.* **99** (1977) 3349; J. F. M. Oth, D. M. Smith, U. Prange, and G. Schröder, *Angew. Chem.* **85** (1973) 352.
14. J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.* **88** (1966) 4811.
15. R. C. Haddon, *J. Amer. Chem. Soc.* **101** (1979) 1722. See also R. C. Haddon, *Tetrahedron* **28** (1972) 3613, 3635, where ^{1}H-chemical shifts have been calculated for neutral annulenes and strong evidence is provided for the existence of para- and diamagnetic ring current effects in $\mathbf{2}^{2-}$ and $\mathbf{4}^{2-}$.
16. P. Karadakov, O. Castaño, F. Fratev, and V. Enchev, *Chem. Phys. Lett.* **78** (1981) 560.
17. F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch. Teil A* **22** (1967) 103.
18. S. M. Johnson and I. C. Paul, *J. Amer. Chem. Soc.* **90** (1968) 6555; S. M. Johnson, I. C. Paul, and G. S. D. King, *J Chem. Soc. B* (1970) 643.
19. J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Crystallogr.* **19** (1965) 227; F. L. Hirshfeld and D. Rabinovich, *Acta Crystallogr.* **10** (1965) 235.
20. H. Baumann and J. F. M. Oth, *Helv. Chim. Acta* **65** (1982) 1885.
21. H. Vogler, in preparation.
22. H. J. Lindner, *Tetrahedron* **30** (1974) 1127.
23. N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.* **95** (1973) 3893; U. Burkert and N. L. Allinger, *Molecular Mechanics,* ACS Monograph 177: Washington, 1982.
24. H. Baumann, *J. Amer. Chem. Soc.* **100** (1978) 7196.
25. H. Vogler, *Tetrahedron* **35** (1979) 657, *Org. Magn. Reson.* **12** (1979) 306, *Tetrahedron Lett.* (1979) 229.
26. G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.* **82** (1960) 5846; J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron. Suppl. 2* **19** (1963) 65.
27. Long range effects of net charges on ^{1}H-chemical shifts have been investigated for example in: T. B. Cobb and J. D. Memory, *J. Chem. Phys.* **50** (1969) 4262; H. W. Vos, C. MacLean, and N. H. Velthorst, *Mol. Phys.* **35** (1978) 329; U. Ehrhardt, B. Deppisch, and H. Musso, *Chem. Ber.* **116** (1983) 119.
28. H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.* (1961) 468; T. Schaefer, and W. G. Schneider, *Can. J. Chem.* **41** (1963) 966; P. J. Black, R. D. Brown, and M. L. Heffernan, *Aust. J. Chem.* **20** (1967) 1305.
29. R. N. Young, *Progr. Nucl. Magn. Resonan. Spectrosc.* **12** (1979) 261.
30. E. D. Jemmis and P. v. R. Schleyer, *J. Amer. Chem. Soc.* **104** (1982) 4781.
31. The Fermi gap in the $(4n)\pi$-annulenes $\mathbf{4}^{4-}$ and $\mathbf{5}^{2-}$ is only 2.6 eV. Nevertheless the Hartree-Fock one-determinant solution constitutes a sufficient approximation for the ground state of these molecules. This has been checked by an investigation of the Thouless Hartree-Fock stability conditions: *The Quantum Mechanics of Many-Body Systems,* D. J. Thouless, Academic Press: New York, 1961.
32. C. Giessner-Prettre and A. Pullman, *Theor. Chim. Acta* **25** (1972) 83. The computation of the electrostatic potentials was done with a modified version of the program of C. Giessner-Prettre, *QCPE* **10** (1974) 249.

33. T. Nakajima and S. Kohda, *Bull. Chem. Soc. Jpn.* **39** (1966) 804.

34. The importance of realistic geometries has been studied also in the case of such neutral and charged polycyclic conjugated hydrocarbons which are characterized by paramagnetic π-electron (sub)structures, see for example: Ref. 33; H. Yamaguchi and T. Nakajima, *Bull. Chem. Soc. Jpn.* **44** (1971) 682; T. Nakajima, *Pure Appl. Chem.* **28** (1971) 219; G. Ege and H. Vogler, *Mol. Phys.* **30** (1975) 1511; C. A. Coulson and R. B. Mallion, *J. Amer. Chem. Soc.* **98** (1976) 592; R. B. Mallion, *Pure Appl. Chem.* **52** (1980) 1541; J. A. N. F. Gomes and R. B. Mallion, *J. Org. Chem.* **46** (1981) 719.

SAŽETAK

Teorijski studij kemijskih pomaka protona kod [4n]- i [4n + 2]-anulena i njihovih di- i tetraaniona

Da bi se odredio odnos između kemijskog pomaka protona kod [4n]- i [4n + 2]-anulena s jedne strane i prstenastih struja s druge strane, te procijenili iznosi efekata lokalne anizotropije i formalnog naboja atoma, izvedeni su MO računi dva stupnja složenosti. Pored najjednostavnijih MO računa primijenjena je i rigorozna spregnuta Hartree-Fockova metoda. Teorijski rezultati racionaliziraju opaženi dijatropizam neutralnih i negativno nabijenih [n]anulena koji imaju parni n i (4n + 2) π-elektrona kao i paratropizam [n]anulena s (4n) π-elektrona.