RING CURRENT EFFECTS IN DOUBLY AND
QUADRUPLY CHARGED ANNULENES

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Abstract. Ring current contributions to [1]H-chemical shifts of [4m+2]- and [4m]annulenes and their doubly and quadruply charged ions have been investigated by means of simple molecular orbital theory. Either bond length alternation or double bond fixation has been introduced in the perimeter in order to achieve closed shell systems. A diamagnetic ring current is obtained for all annulenes with (4m+2) π-electrons and a paramagnetic one for those with (4m) π-electrons.

1. Introduction

The diatropism [1] of neutral [n]annulenes with n = 4m+2 and the para-
tropism [1] of those with n = 4m have been rationalized by assuming a dia-
magnetic (n = 4m+2) and paramagnetic (n = 4m) ring current (RC) [2]. The
RC model can be considered as the conceptual simplest way of describing the
response of a conjugated molecule to an external magnetic field [3]. In re-
cent years di- and even tetraanions of [4m+2]- and [4m]annulenes have been
prepared [1,4,5] whereas only few corresponding dications are known hither-
to [6]. Such annulenes are either (4m'+2) or (4m') π-electron systems with
m' = m or m' = m±1. Although the observed [1,4-6] dia- and paratropism of
the charged (4m'+2) and (4m') π-annulenes was expected [5] the RC effects
in doubly or quadruply charged annulenes have not been studied theoreti-
cally except for the special case of doubly charged [4m]annulenes [7].
Therefore we present in this communication an investigation of the RC con-
tribution to proton chemical shifts in neutral, double and quadruple nega-
tively or positively charged [n]annulenes with even n.

2. Electronic Structures of [n]Annulenes

An ideal perimeter is characterized by a single bond length and reso-
nance integral with negative standard value β. The orbitals $\phi_j = \Sigma_{s=1}^{n} c_{js} \chi_s$
and the associated energies ε_j are given analytically as [8]

$$c_{js} = \begin{cases} [(2-\delta_{j0}-\delta_{j\frac{n}{2}})/n]^{1/2} \cos[2\pi j(s-1)/n] & \text{if } j \geq 0 \\ (2/n)^{1/2} \sin[2\pi j(s-1)/n] & \text{if } j < 0 \end{cases} \quad (1)$$

$$\varepsilon_j = 2\beta \cos(2\pi j/n) \quad (2)$$

where j takes the values 0,±1,...,±2m,2m+1 if n = 4m+2 and 0,±1,...,
±(2m-1),2m if n = 4m. The resulting orbital scheme is displayed in Fig. 1.
Doubly charged [4m+2]annulenes and neutral and quadruply charged [4m]annu-
lenes, i.e. all (4m') π-systems, exhibit open shell structures due to or-
bital degeneracy. Clearly this prevents the straightforward application of
Hückel type theory.

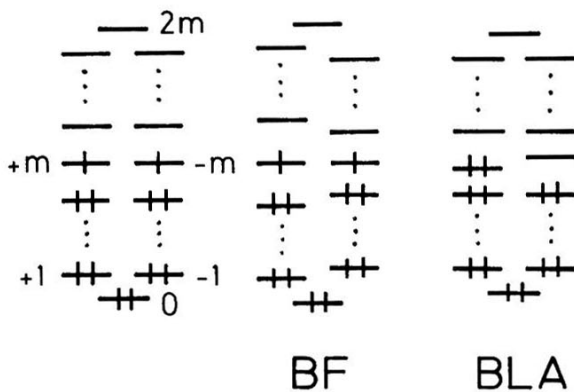# [4m+2]Annulenes:

BF

[4m]Annulenes:

BF   BLA
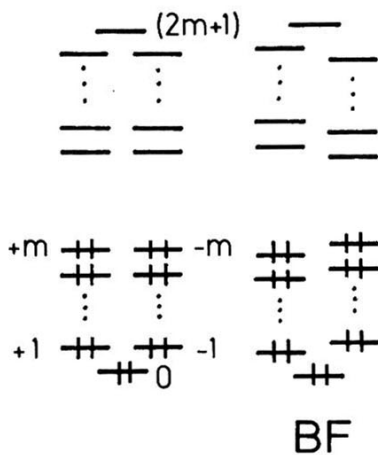
Fig. 1. Orbital energy schemes for annulenes with (4m+2) and (4m) carbon atoms. The orbital occupations are given for the neutral compounds.

Without strong non-bonded interactions [4m+2]annulenes show almost ideal perimeters [9], see for example 1a and 2a in Fig. 2, whereas [4m]annulenes exhibit bond length alternation (BLA) [10], see 3a. Experimental structures are unknown for doubly and quadruply charged annulenes with larger n. Calculations with a π-SCF force field approach [11,12] demonstrate that also charged annulenes with (4m'+2) π-electrons should be characterized by almost ideal perimeters (e.g. $2a^{4\pm}$ and $3b^{2\pm}$). On the other hand the charged (4m') π-electron annulenes possess perimeters with lower symmetry, see for example $1b^{2-}$, $1c^{2+}$, $2b^{2\pm}$ and $3c^{4+}$, which can be approximately treated simply by introducing bond fixation (BF). Thus we can study all (4m'+2) π-species by assuming ideal perimeters whereas BLA must be taken into account with neutral [4m]annulenes and BF with all charged (4m') π-compounds. Neutral and charged [4m+2]annulenes of type 4a (cf. Fig. 2) can also be studied by means of the BF approach since their perimeters are adequately described by structures 4b [12,13] which exhibit two very short bonds between the sp-hybridized carbon atoms.

In the BF model for [n]annulenes we associate a resonance integral $k\beta$ with $k \geq 1$ with atom pairs m+1/m+2 and 3m+2/3m+3 if n = 4m+2 respectively 1/2 and 2m+1/2m+2 if n = 4m. It is a sufficient approximation in our context to neglect all mixing between different orbitals which then turn out to be identical to those given by eq. (1). The associated energies are given as follows:

$$\epsilon_j = \begin{cases} 2\beta[g(k)\cos(2\pi j/n)+(-)^j v_{oj} v_{j\frac{n}{2}} f(k)] & \text{if } n = 4m+2 \\ 2\beta[1+(v_{oj} v_{j\frac{n}{2}}+1) f(k)]\cos(2\pi j/n) & \text{if } n = 4m \ . \end{cases} \tag{3}$$

Here we use the symbols $f(k) = (2/n)(k-1)$, $g(k) = 1+f(k)$, and $v_{ij} = 0, +1, -1$ if $i = j$, $i < j$, $i > j$. The energy gap between the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) is given as

$$\epsilon_{LUMO}-\epsilon_{HOMO} = \begin{cases} -4\beta f(k) & \text{if } n = 4m+2, \ q = \pm 2 \\ -4\beta f(k)\sin(2\pi/n) & \text{if } n = 4m, \ q = \pm 4 \end{cases} \tag{4}$$

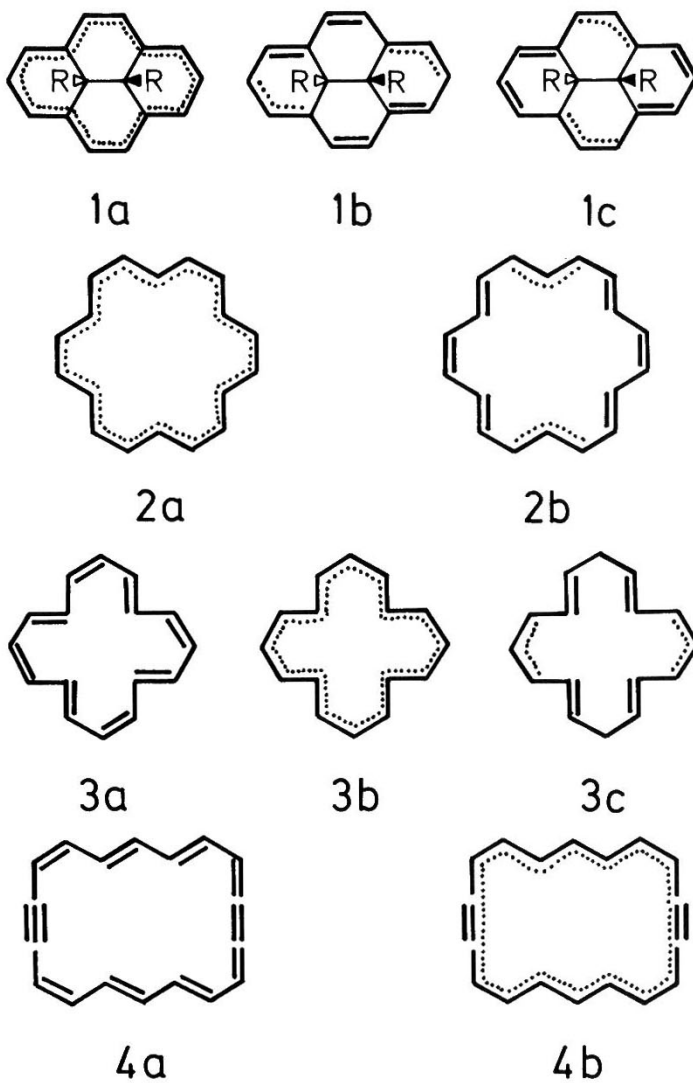where q is the charge. BF lifts the degeneracy of all orbitals except of

Fig. 2. Perimeter structures of some representative annulenes.

ϕ_{+m} if n = 4m so that closed shell systems are obtained for all (4m'+2) and charged (4m') π-electron annulenes, see Fig. 1.

In the BLA model for neutral [4m]annulenes we use alternating resonance integrals kβ and β with k $\leq$ 1 [14]. The exact orbitals and associated energies for this model have been given [14,15], however, they lead to a rather complicated formula for the RC. Therefore we neglect the interaction between orbitals ϕ_j and ϕ_k if $|j| \neq |k|$. Then the orbitals are given by eq. (1) except for

$$\phi_{HOMO} = 2^{-1/2}(\phi_{+m}-\phi_{-m}) \quad , \quad \phi_{LUMO} = 2^{-1/2}(\phi_{+m}+\phi_{-m}) \quad . \tag{5}$$

The orbital energies are given as

$$\varepsilon_j = \begin{cases} 2\beta h(k)\cos(2\pi j/n) & \text{if } |j| \neq m \\ (m/|m|)(1-k)\beta & \text{if } |j| = m \end{cases} \tag{6}$$

where h(k) = (1+k)/2. The HOMO/LUMO gap

$$\varepsilon_{LUMO}-\varepsilon_{HOMO} = -2\beta(1-k) \tag{7}$$

agrees with that of the exact model [14,15]. BLA lifts the degeneracy of HOMO and LUMO leading to a closed shell structure. All other orbitals ϕ_j with $0 < |j| < m$ and $m < |j| < 2m$ remain degenerate, see Fig. 1.

3. RC Effects in Annulenes

The reduced RC I = cχ/S [16] constitutes a measure for the mean ^{1}H-chemical shift of inner or outer protons of an annulene. S denotes the area of the perimeter. The magnetic susceptibility χ can be calculated within the modified HMO approach [17]. By choosing the centre of the perimeter as origin of the vector potential the reduced RC I (in units of $(e^2\beta/3\hbar^2 c)(S/n^2)$) is calculated by means of the formula

$$I = \beta^{-1} \sum_j^{occ} [\varepsilon_j + \sum_k^{unocc} (\varepsilon_k-\varepsilon_j)^{-1}<\phi_j|h'|\phi_k>^2] \tag{8}$$

where the summations extend over all *occ*upied respectively *unocc*upied orbitals. The operator h' has matrix elements $h'_{st} = h_{st}v_{st}$ with respect to the

π-basis functions χ_s where h_{st} are those of the Hückel operator. Without BLA or BF or when using the same approximations as in the derivation of orbitals and associated energies in the BLA and BF models eq. (8) reduces to

$$I = \beta^{-1} \left[\Sigma_j^{occ} \varepsilon_j + w(\varepsilon_{LUMO}-\varepsilon_{HOMO})^{-1} <\phi_{HOMO}|h'|\phi_{LUMO}>^2 \right] \tag{9}$$

where $w = 1$ if we have a (4m') π-electron system and $w = 0$ otherwise.

By using eqs. (1,3,9) it is straightforward to show that the reduced RC I for all neutral and doubly or quadruply charged [n]annulenes except neutral [4m]annulenes is given as follows:

$$I = \begin{cases} 2\{g(k)[\sin^{-1}(\pi/n)-(|q|/2)\sin(\pi/n)]+ \\[2mm] \quad \delta_{|q|}2[f(k)+4\beta(\varepsilon_{LUMO}-\varepsilon_{HOMO})^{-1}g^2(k)\cos^2(\pi/n)]\} & \text{if } n = 4m+2 \\[4mm] 2\{g(k)\tan^{-1}(\pi/n)-\delta_{|q|}4\sin(2\pi/n)[1- \\[2mm] \quad 4\beta^{-1}(\varepsilon_{LUMO}-\varepsilon_{HOMO})^{-1}g^2(k)\tan^{-2}(2\pi/n)\sin(2\pi/n)]\} & \text{if } n = 4m \,. \end{cases} \tag{10}$$

For neutral [4m]annulenes with BLA I is obtained as

$$I = (1+k)\tan^{-1}(\pi/n) + (1-k) + 2\beta(1+k^2)(\varepsilon_{LUMO}-\varepsilon_{HOMO})^{-1} \tag{11}$$

from eqs. (1,5,6). By utilizing eqs. (4,7) for the HOMO/LUMO gaps eq. (10) reads

$$I = \begin{cases} 2\{g(k)[\sin^{-1}(\pi/n)-(|q|/2)\sin(\pi/n)]+ \\[2mm] \quad \delta_{|q|}2[f(k)-f^{-1}(k)g^2(k)\cos^2(\pi/n)]\} & \text{if } n = 4m+2 \\[4mm] 2\{g(k)\tan^{-1}(\pi/n)-\delta_{|q|}4\sin(2\pi/n)[1+ \\[2mm] \quad f^{-1}(k)g^2(k)\tan^{-2}(2\pi/n)]\} & \text{if } n = 4m \end{cases} \tag{12}$$

and eq. (11) for neutral [4m]annulenes reduces to

$$I = (1+k)\tan^{-1}(\pi/n) + (1-k) - (1-k)^{-1}(1+k)^2 \,. \tag{13}$$

4. Discussion

Eqs. (10-13) constitute simple analytical expressions for the reduced RC
in [4m+2]- and [4m]annulenes and their doubly or quadruply charged ions
which possess either (almost) ideal perimeters or are characterized by BF
or BLA. A positive (negative) I is tantamount to a dia(para)magnetic RC
which causes dia(para)tropism in the proton NMR spectrum. All neutral and
charged annulenes with $(4m'+2)$ π-electrons, i.e. neutral and quadruply
charged [4m+2]- and doubly charged [4m]annulenes, exhibit a positive I cor-
responding to a diamagnetic RC. Consequently they are diatropic compounds.
BF increases slightly the magnitude of I, see Fig. 3. On the other hand
all systems with $(4m')$ π-electrons, i.e. neutral and quadruply charged
[4m]- and doubly charged [4m+2]annulenes, include in I a negative term
which depends inversely on the size of the HOMO/LUMO gap. Without BF or BLA
(i.e. $k \rightarrow 1$) this gap vanishes and consequently we have then $I \rightarrow -\infty$. Due to
this inverse dependency of the RC on the HOMO/LUMO gap the reduced RC I de-
creases drastically in magnitude if BF or BLA is enhanced. Dications and
-anions respectively tetracations and -anions exhibit the same RC I. This
was already observed in the case of [4m]annulene dications and -anions [7].
However, the [1]H-chemical shifts need not to be the same since the shifts
due to charge densities will necessarily be of opposite sign for cations
and anions.

Although other contributions to chemical shifts [18] and a consideration
of counterion effects [12,19] in the case of charged annulenes are impor-
tant for a quantitative assessment of [1]H-chemical shifts of annulenes the
proton shifts are governed by RC effects as long as sufficient planarity
of the perimeter is maintained. Hence our approach represents the first
quantum mechanical rationalization of the transmutation of dia(para)- into
para(dia)tropic species and vice versa if neutral [4m+2]([4m])annulenes are
reduced or oxidized to doubly and quadruply charged ions. A quantitative
theoretical study of [1]H-chemical shifts of neutral and charged annulenes
with an explicit consideration of RC, local anisotropic, charge density,
and counterion effects is in progress.
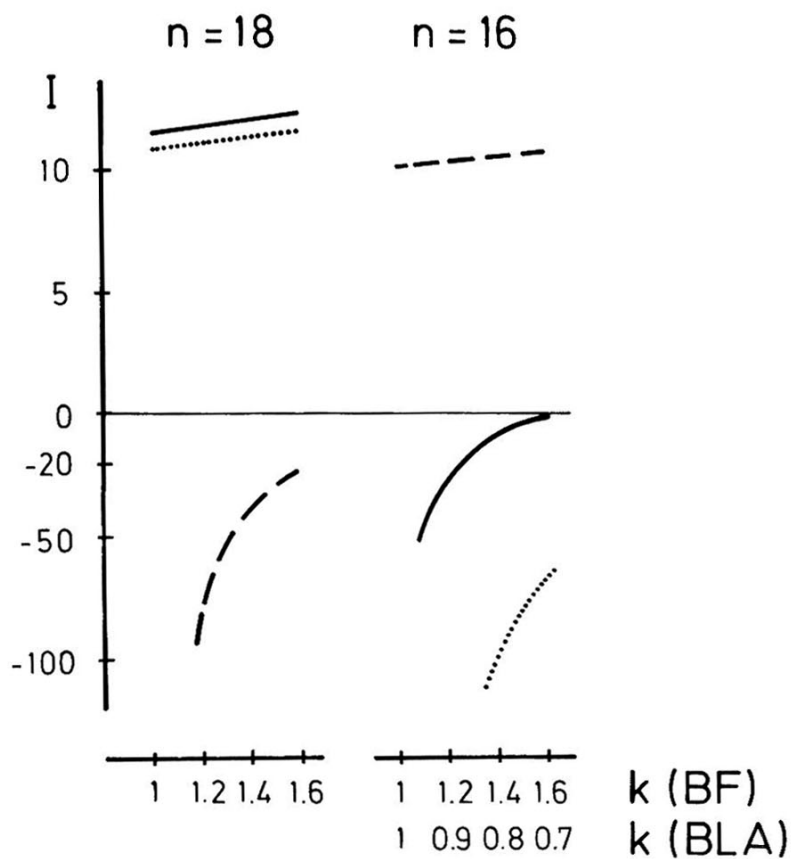
Fig. 3. Reduced RC intensity I for [n]annulenes with n = 18 (4m+2) and n = 16 (4m) with charge q = 0 (———), ±2 (— —) and ±4 (••••••••) as a function of k (degree of BF or BLA).

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