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RING CURRENT EFFECTS IN [4m+2]ANNULENES AND THEIR DI- AND TETRAANIONS

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Abstract—Simple MO theory of induced ring currents is used in order to rationalise the observed diatropism of neutral $[4m+2]$annulenes and their tetraanions and the paratropism of the corresponding dianions.

The outer protons of $[n]$annulenes with $n = 4m+2$ exhibit shifts to the lower field, the inner protons, however, exhibit shifts to the higher field in the ^{1}H-NMR spectrum. Such a cyclic conjugated molecule is called diatropic.[1] Recently[2] dianions of the $[4m+2]$-annulenes **1**–**4**[3] (Fig. 1) have been prepared and for $n \geq 18$ even tetraanions (supercharged species[4]) are accessible.[2] Therefore one obtains a series of $[n]$annulenes where n is fixed while the number of π-electrons differs. According to the nomenclature of Winstein[5] the neutral annulene and its di- and tetraanion constitute $(4m+2)C(k)\pi$-systems where $k = 4m+2$, $4m'$ and $4m'+2$ with $m' = m+1$. Consequently it is possible to compare ^{1}H-chemical shifts of $(4m+2)\pi$- with those of $(4m)\pi$-systems without changing the perimeter which is impossible with neutral annulenes alone.

The outer protons of the $[4m+2]$annulene dianions $\mathbf{1}^{2-}$–$\mathbf{4}^{2-}$ are shifted towards the higher field with respect to the neutral compounds whereas the opposite applies to the inner protons. Thus the diatropic neutral annulenes turn to paratropic[1] ones. The further reduction of the dianions to the tetraanions in case of **2**–**4** causes another reversal from para- to diatropism. The shifts amount to over 30 ppm which is exemplified in Fig. 2 with **2**, $\mathbf{2}^{2-}$ and $\mathbf{2}^{4-}$.

The diatropism of neutral $[4m+2]$annulenes has been rationalised by assuming a diamagnetic ring current (RC) due to the cyclic π-electron delocalisation.[6] Such an RC model is conceptually simple and has proven extremely useful in calculating ^{1}H-chemical shifts although the RC itself is not physically observable. It is clear that the RC concept represents only an incomplete physical picture due to its implicit assumptions.[6] Consequently it has been criticised by several authors.[7] 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.[8] The diatropism of $[4m+2]$annulenes and the paratropism of $[4m]$annulenes is mainly determined by RC effects,[9] although there is now evidence that besides the π-electron RC local anisotropic contributions also have to be taken into account for a satisfactory quantitative description of proton chemical shifts.[7,8,10,11]

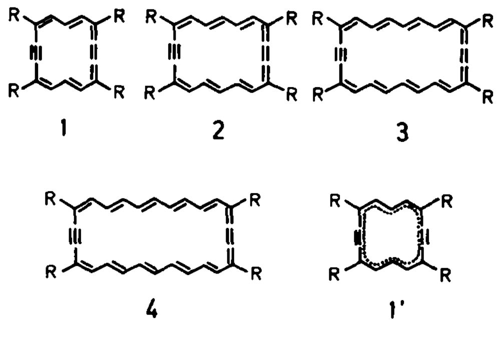

Fig. 1. Bisdehydro$[4m+2]$annulenes with m = 3–6 (R = t-Bu).

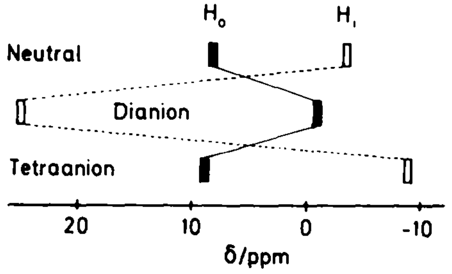

Fig. 2. Observed[2] average ^{1}H-chemical shifts for inner (H_i) and outer (H_o) protons of **2** and its di- and tetraanions $\mathbf{2}^{2-}$ and $\mathbf{2}^{4-}$ (R = t-Bu).

The occurrence of paratropism in the $(4m')\pi$- and of diatropism in the $(4m'+2)\pi$-systems of the di- and tetraanions of $[4m+2]$annulenes was expected[12] in analogy to the neutral $[4m]$- and $[4m+2]$annulenes. However, the RC effects in negatively charged $[4m+2]$-annulenes have not been studied theoretically. Therefore it is the aim of this communication to investigate if the simple RC model accounts satisfactorily for the dia- and paratropism of the $[4m+2]$annulenes **1**–**4** and their di- and tetraanions.

Electronic structure of [4m+2]*annulenes*

The annulenes **1**–**4** possess besides sp^2-hybridised carbon atoms also sp-hybridised ones which form a π'-electron system orthogonal to the ordinary π-system.[11] However, in this communication only the π-system is taken into consideration since the π'-system does not contribute to the RC but leads only to local anisotropic effects which should be roughly the same for neutral and charged annulenes.[13]

All bond lengths of an ideal perimeter are the same and hence all resonance integrals are given by the negative standard value β. The matrix elements of the Hückel operator h are given with respect to the π-basis functions χ_s as $h_{st} = \delta_{s+1,t}\beta$ if we number the n perimeter atoms consecutively and equate $n+1 \equiv 1$. The orbitals

$$\phi_j = \sum_{s=1}^{n} c_{js}\chi_s$$

and the associated energies ε_j are given analytically as[14]

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

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

where j takes the values $0, \pm 1, \ldots, \pm 2m, 2m+1$. The resulting orbital scheme is displayed in Fig. 3. The degeneracy of the orbitals with $0 < |j| < 2m+1$ which persists even with bond length alternation[15] leads to an open shell structure in case of a $[4m+2]$annulene dianion so that conclusions on RC effects are impossible.

Experimental data[2,3,16,17] and more elaborate theoretical studies[18] demonstrate that annulenes **1**–**4** and their di- and tetraanions are adequately represented by structures **1'** (Fig. 1) exhibiting two C_{sp}—C_{sp} bonds which are considerably shorter than all other bonds. Thus these annulenes are characterised by bond fixation (BF) which lifts the degeneracy of all orbitals, see Fig. 3. Consequently also dianions of the $[4m+2]$annulenes form closed shell systems and RC effects can be studied.

A simple theoretical description of the π-system of annulenes **1**–**4** is obtained by introducing BF by means of a resonance integral $\eta\beta$ with $\eta > 1$ between sp-hybridised atoms $m+1/m+2$ and $3m+2/3m+3$. The parameter η is estimated to be $\eta \cong 1.9$ if we take the mean of the calculated bond lengths[18] for **2**, $\mathbf{2}^{2-}$ and $\mathbf{2}^{4-}$ and utilise the formula given in Stollenwerk *et al.*[19] which relates bond length and resonance integral. BF causes a perturbation V of h leading to a new Hückel operator $H = h+V$. V has non-vanishing matrix elements $(\eta-1)\beta$ only with respect to the C_{sp}—C_{sp} bonds. Unfortunately orbitals and associated energies of H are not known analytically. However, in our context it is a sufficient approximation to use the restricted Hückel operator

$$H' = h + \sum_{j \geqslant 0} |\phi_{\pm j}\rangle\langle\phi_{\pm j}|V|\phi_{\pm j}\rangle\langle\phi_{\pm j}|$$

whose orbitals agree with those of h (Eq. 1) but exhibit different energies

$$\varepsilon_j = \beta[2f(\eta)\cos(2\pi j/n) + (-)^j v_{0j} v_{j(n/2)} g(\eta)] \quad (3)$$

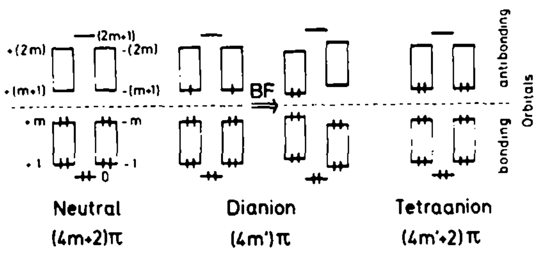

Fig. 3. Orbital energy and occupation scheme of a $[4m+2]$-annulene and its di- and tetraanion.

where $f(\eta) = 1+(2/n)(\eta-1)$, $g(\eta) = (4/n)(\eta-1)$ and $v_{ij} = 0, +1, -1$ if $i = j, i < j, i > j$.

By utilising Eq. (3) we obtain

$$\varepsilon_l - \varepsilon_h = -2\beta g(\eta) \quad (4)$$

for the gap between the highest occupied orbital (HOMO) ϕ_h ($h \equiv -(-)^m(m+1)$) and the lowest virtual orbital (LUMO) ϕ_l ($l \equiv (-)^m(m+1)$) of the dianion of a $[4m+2]$annulene. But we have to use a somewhat smaller $\eta \cong 1.6$ in Eqs (3) and (4) in order to reproduce the HOMO/LUMO gap obtained with the Hückel operator H.

RC effects in [4m + 2]*annulenes*

The reduced RC[20] $I = c\chi/S$ constitutes a measure for the mean ^{1}H-chemical shifts of inner and outer protons of an annulene. S denotes the area of the perimeter. The magnetic susceptibility χ can be calculated within the modified HMO approach[21] according to $\chi = \lambda(\chi^d + \chi^p)$ where $\lambda \cong 0.5$ and χ^d and χ^p represent the dia- and paramagnetic RC contribution:

$$\chi^d = (4/3)\sum_{i}^{\text{occ}} \langle\phi_i|H^{20}|\phi_i\rangle$$

$$\chi^p = (4/3)\sum_{i}^{\text{occ}}\sum_{k}^{\text{virt}} (\varepsilon_k-\varepsilon_i)^{-1}\langle\phi_i|H^{10}|\phi_k\rangle^2.$$

By choosing the centre of the perimeter as the origin of the vector potential the matrix elements of the operators H^{20} and H^{10} are given as follows:

$$H^{20}_{st} = (1/2)(\alpha S/n)^2 H'_{st},$$

$$H^{10}_{st} = (\alpha S/n)H'_{st}v_{st}$$

where $\alpha = e/\hbar c$. The reduced RC I (in units of $(2c\alpha^2\lambda\beta/3)(S/n^2)$) can now be calculated by means of the formula:

$$I = I^d + I^p = \sum_{j}^{\text{occ}} (I^d_j + I^p_j).$$

A positive (negative) I is tantamount to dia(para)-tropism. By applying Eqs (1) and (3) it is straightforward to show that

$$I^d_j = 2f(\eta)\cos(2\pi j/n) + v_{0j}(-)^j g(\eta) \quad (5)$$

$$I^d = 2[\sin^{-1}(\pi/n) + (q/2)\sin(\pi/n)]f(\eta) + \delta_{q-2}g(\eta) \quad (6)$$

where q is the charge. A paramagnetic RC contribution is encountered only with the dianion:

$$I^p = I^p_h = 8\beta(\varepsilon_1-\varepsilon_h)^{-1}f^2(\eta)\cos^2(\pi/n) \quad (7)$$

which reduces to

$$I^p = -(\eta-1)^{-1}nf^2(\eta)\cos^2(\pi/n) \quad (8)$$

due to Eq. (4). An exact calculation of I^p employing the Hückel operator H and its orbitals and orbital energies yields non-vanishing values also in the case of the neutral annulene and its tetraanion if $\eta \neq 1$. However, I^p is numerically not larger than 15% of I^d and is unimportant in the context of our qualitative considerations.

Equations (5)–(8) constitute analytical expressions for the reduced RC in a $[4m+2]$annulene and its di- and tetraanion which are characterised by BF as in **1**–**4**. According to Eq. (6) the diamagnetic part I^d increases linearly with η. On the other hand I^d abates with higher negative charge since the orbital contributions I^d_j (Eq. 5)

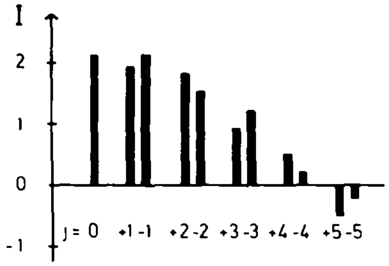

Fig. 4. Diamagnetic orbital contributions I_j^d for a [18]annulene ($\eta = 1.6$).

decrease with enlarged $|j|$ and change even sign between $|j| = m$ (HOMO of the neutral annulene, see Fig. 3) and $|j| = m+1$ (HOMO of the charged annulenes, see Fig. 4), so that certain contributions cancel each other in the di- and tetraanion.

Within our model a paramagnetic term I^p appears only for the dianion. I^p is inversely proportional to the magnitude of the HOMO/LUMO gap ε_l–ε_h (Eq. 7) which depends on $(\eta - 1)$ due to Eq. (8). For vanishing BF, i.e. $\eta \to 1$, we obtain the correct limit $I^p \to -\infty$.

The total RC of the neutral annulene and its tetraanion is determined by I^d which explains their diatropism. In the case of the dianions the paramagnetic term I^p is numerically larger than I^d thus leading to a negative I (only for unrealistic extremely large η values this is no longer valid) which rationalises the observed paratropism.

CONCLUDING REMARKS

In this communication we have studied the RC effects in [4m + 2]annulenes and their di- and tetraanions which are characterised by BF due to short C_{sp}—C_{sp} bonds. BF lifts the degeneracy of orbitals so that a finite HOMO/LUMO gap is encountered not only with neutral and quadruply negatively charged species but also with the dianion. Furthermore we could derive analytical expressions for the reduced RC whose sign and magnitude is crucial for the proton spectra of annulenes. Only a diamagnetic RC term occurs for the $(4m + 2)\pi$-systems whereas a paramagnetic and diamagnetic term is observed for the $(4m)\pi$-systems. The paramagnetic term depends inversely on the magnitude of the HOMO/LUMO gap and turns out to be numerically much larger than the diamagnetic RC contribution. This finding rationalises the observed[2] diatropism of the neutral [4m + 2]annulenes **1**–**4** and their tetraanions and the paratropism of the corresponding dianions. The importance of the HOMO/LUMO gap in the case of the paratropic [4m + 2]annulene dianions was postulated recently[16] and is also encountered with neutral [4m]annulenes.[9,20,22]

Our theoretical model accounts also for the dia- and paratropism of neutral or quadruply and doubly negatively charged [4m + 2]annulenes with sp^2-hybridised carbon atoms only. The $(4m+2)C(4m+2)\pi$- or $(4m+2)C(4m'+2)\pi$-systems seem to be characterised by almost ideal perimeters[9] unless this is prevented by severe non-bonded interactions. Thus we have to put $\eta \cong 1$ in our model which then becomes identical with that of lit.[9,20,23,24] without bond length alternation. On the other hand the $(4m+2)C(4m')\pi$-systems exhibit perimeters[9,18] with two-fold symmetry axes similar to **1**–**4** and their π-electronic structure is approximated by $\eta > 1$.

Although local anisotropic and excess charge contributions are important for a quantitative assessment of ^1H-chemical shifts of annulenes[9] 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 rationalisation of the transmutation of dia- into paratropic species and *vice versa* if neutral [4m + 2]annulenes are reduced to di- and tetraanions. A quantitative theoretical study of the ^1H-chemical shifts of neutral and charged annulenes **1**–**4** with an explicit consideration of RC, local anisotropic, charge density, and counterion effects is in progress.

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