

## Simple Theoretical Considerations of Counterion Effects on Proton Chemical Shifts in Charged Annulenes

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Ring-current contributions to  $^1\text{H}$  chemical shifts of charged annulenes with  $(4m + 2)$  and  $(4m)$   $\pi$ -electrons are investigated by means of simple molecular orbital theory. It is shown that electrostatic and covalent interaction between annulene and counterion reduce the paratropism of  $(4m)$   $\pi$ -electron annulenes but do not affect the diatropism of  $(4m + 2)$   $\pi$ -electron annulenes.

There is great interest in the study of charged  $[n]$ annulenes,<sup>1</sup> since they offer the chance to compare dia- and para-tropic systems<sup>2</sup> which do not differ in the size of the perimeter. In diatropic annulenes the outer protons exhibit shifts to the lower field and inner protons to the higher field in the n.m.r. spectrum whereas the opposite applies to paratropic annulenes. The dia- and para-tropism of neutral annulenes can be rationalized by means of the quantum mechanical ring-current model.<sup>3</sup> Haddon<sup>4</sup> could show that the ring-current model accounts also for the diatropism of doubly charged  $[4m]$ annulenes,  $[4m + 1]$ annulene anions, and  $[4m + 3]$ annulene cations. However, magnetic properties like  $^1\text{H}$  chemical shifts of doubly charged  $[4m + 2]$ annulenes,  $[4m + 1]$ annulene cations, and  $[4m + 3]$ annulene anions have not been studied theoretically. In this communication we will show that the ring-current model can be applied to such annulenes as well if suitable perturbations<sup>5-7</sup> are introduced into the perimeter.

The dia- and para-tropism of charged annulenes is a function of their  $\pi$ -system alone only if annulene and counterion(s) form exclusively free ions (FI). However, there is ample evidence<sup>1</sup> that in solution one has an equilibrium between FIs, solvent-separated ion pairs (SIP), and contact ion pairs (CIP). In the case of a SIP or CIP we cannot assume *a priori* that the interaction between the annulene and the counterion does not have a significant effect on the magnitude of the ring current and hence the  $^1\text{H}$  n.m.r. spectrum. Although one can shift the equilibrium between the different types of ion pairs by varying counterion, temperature, or solvent it is usually impossible to prepare solely FIs. To the best of our knowledge there exists no quantum chemical studies of proton chemical shifts of charged conjugated systems where counterions are explicitly taken into consideration. Therefore we have investigated the effect of counterions on the magnitude of the ring current and hence the extent of dia- and para-tropism in the case of  $[n]$ annulenes with charge  $Q$  where  $n = 4m + 2$  or  $4m$  with  $Q = \pm 2$  and  $n = 4m + 1$  or  $4m + 3$  with  $Q = \pm 1$ . Such annulenes possess either  $(4m' + 2)$  or  $(4m')$   $\pi$ -electrons where  $m' = m$  or  $m \pm 1$ .

**Electronic Structure of Annulenes.**—The  $\pi$  orbitals  $\varphi_j = \sum_{s=1}^n c_{js}\chi_s$  and associated energies  $\varepsilon_j$  of  $[n]$ annulenes are given analytically by equations (1) and (2).<sup>8</sup> If we assume an ideal

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

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

perimeter which is characterized by a single bond length and a single negative resonance integral  $\beta$ . In equations (1) and (2)  $j$

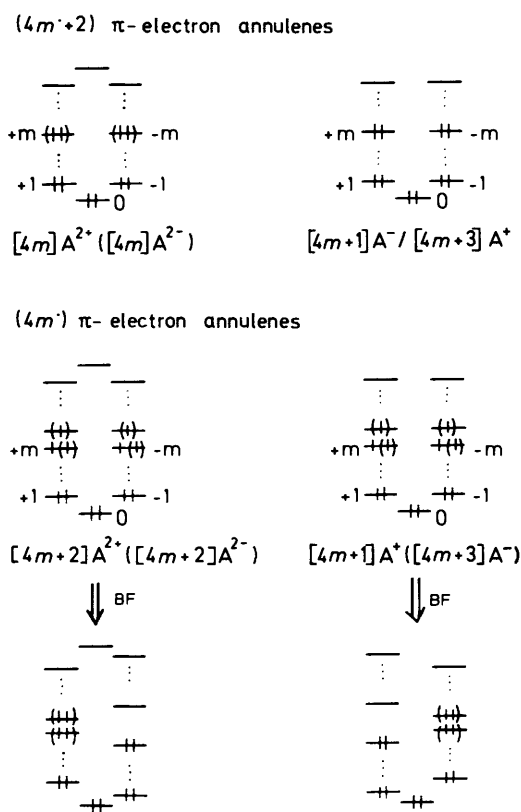


Figure 1. Orbital energy and occupation schemes for charged  $[n]$ annulenes  $[n]\text{A}^Q$  with charge  $Q$

takes the values  $j = 0, \pm 1, \dots, \pm[(n/2) - 1], (n/2)$  if  $n = 4m$  or  $4m + 2$  and  $j = 0, \pm 1, \dots, \pm(n-1)/2$  if  $n = 4m + 1$  or  $4m + 3$ . The resulting orbital scheme is displayed in Figure 1. All  $(4m' + 2)$   $\pi$ -electron systems exhibit closed shells according to the aufbau principle but not the  $(4m')$   $\pi$ -electron annulenes; this prevents a straightforward application of the Hückel approach. The assumption of an ideal perimeter is justified with the  $(4m' + 2)$   $\pi$ -electron annulenes; however, according to theoretical investigations,<sup>5,6,9</sup> perimeters with reduced symmetry are encountered with  $(4m')$   $\pi$ -electron annulenes. This lifts the degeneracy of orbitals so that closed shells are obtained.

Within a Hückel approach perimeters with reduced symmetry can be approximately treated by introduction of bond fixation, *i.e.* a resonance integral  $k\beta$  with  $k \geq 1$  is used between the atom pairs  $m + 1, m + 2$  and  $3m + 2, 3m + 3$  in the case of  $[4m + 2]$ annulenes and 1,2 with  $[4m + 1]$ - or  $[4m + 3]$ -

annulenes. The orbitals of such a system with perturbed perimeter are the same as those given by equation (1) if we neglect the small coupling between different orbitals, but the orbital energies are now given by equation (3) where  $f(k) =$

$$\epsilon_j = \begin{cases} 2\beta\{[1 + f(k)]\cos(2\pi j/n) + (-)^j w_{0j} w_{j(n/2)} f(k)\} & \text{if } n = 4m + 2 \\ 2\beta\{1 + [(1 + w_{0j})/2]f(k)\}\cos(2\pi j/n) & \text{if } n = 4m + 1 \text{ or } 4m + 3 \end{cases} \quad (3)$$

$(2/n)(k - 1)$ ,  $w_{ij} = 0, +1, -1$  if  $i = j, i < j, i > j$ . For  $k = 1$  equation (3) reduces to (2). The orbital energy schemes with bond fixation are displayed in Figure 1. The highest occupied orbital  $\phi_{\text{HOMO}}$ , the lowest unoccupied orbital  $\phi_{\text{LUMO}}$ , and the HOMO - LUMO gap  $g$  for a  $(4m')$   $\pi$ -electron annulene  $[n]A^Q$  with charge  $Q$  are given by equations (4) and (5).

$$\phi_{\text{HOMO}}/\phi_{\text{LUMO}} \equiv \begin{cases} \phi_{(-)m_m}/\phi_{(-)m_m} & \text{if } n = 4m + 2, Q = +2 \\ \phi_{(-)m(m+1)}/\phi_{(-)m(m+1)} & \text{if } n = 4m + 2, Q = -2 \\ \phi_{+m}/\phi_{-m} & \text{if } n = 4m + 1, Q = +1 \\ \phi_{-(m+1)}/\phi_{+(m+1)} & \text{if } n = 4m + 3, Q = -1 \end{cases} \quad (4)$$

$$g = \begin{cases} -4\beta f(k) & \text{if } n = 4m + 2, Q = \pm 2 \\ -2\beta f(k)\sin(\pi/2n) & \text{if } n = 4m + 1, Q = +1 \\ & \text{or } n = 4m + 3, Q = -1 \end{cases} \quad (5)$$

**Ring-current Effects in Annulenes.**—The reduced ring current<sup>10</sup>  $I = c\chi/S$  constitutes a measure for the mean <sup>1</sup>H chemical shift of the inner and outer protons of an annulene.  $S$ ,  $\chi$ , and  $c$  denote the area enclosed by the perimeter, the magnetic susceptibility of the perimeter, and the velocity of light. A positive  $I$  is tantamount to a diamagnetic ring current which causes diatropism. Conversely, a negative  $I$  corresponds to a paramagnetic ring current leading to paratropism. We fix the origin of the vector potential at the centre of the perimeter. Then the reduced ring current  $I$  (in units of  $[e^2\beta S/3\hbar^2 cn^2]$ ) is calculated by means of the modified HMO method<sup>11</sup> according to formula (6). The matrix elements of the operators  $h'$  and  $h''$

$$I = \beta^{-1} \underbrace{\sum_j^{\text{occ}} \langle \phi_j | h' | \phi_j \rangle}_{I^d} + \beta^{-1} \underbrace{\sum_j^{\text{occ}} \sum_k^{\text{unocc}} (\epsilon_k - \epsilon_j)^{-1} \langle \phi_j | h'' | \phi_k \rangle^2}_{I^p} \quad (6)$$

with respect to the  $\pi$ -basis functions  $\chi_s$  are given as  $h'_{st} = w_{st}^2 h_{st}$  and  $h''_{st} = w_{st} h_{st}$  where  $h_{st}$  are those of the Hückel operator. It is obvious from equation (6) that  $I^d \geq 0$  and  $I^p \leq 0$  so that  $I < 0$  and hence paratropism is possible only if  $|I^p| > I^d$ .

By utilizing equations (1), (2), and (6) we obtain for the charged  $(4m' + 2)$   $\pi$ -electron annulenes, *i.e.* doubly charged  $[4m]$ annulenes,  $[4m + 1]$ annulene anions, and  $[4m + 3]$ -annulene cations, expressions (7) and (8) for the ring-current

$$I^d = \begin{cases} 2\tan^{-1}(\pi/n) & \text{if } n = 4m \\ \sin^{-1}(\pi/2n) & \text{if } n = 4m + 1 \text{ or } 4m + 3 \end{cases} \quad (7)$$

$$I^p = 0 \quad (8)$$

contributions. Consequently we have  $I = I^d > 0$  and these compounds should be diatropic which has indeed been verified experimentally.<sup>1</sup>

For the  $(4m')$   $\pi$ -electron annulenes, *i.e.* doubly charged  $[4m + 2]$ annulenes,  $[4m + 1]$ annulene cations, and

$[4m + 3]$ annulene anions, formulae (9) and (10) for the ring-current contributions are obtained.

$$I^d = \begin{cases} 2\{[1 + f(k)][\sin^{-1}(\pi/n) - \sin(\pi/n)] + f(k)\} & \text{if } n = 4m + 2 \\ [1 + f(k)/2]\sin^{-1}(\pi/2n) - 2\sin(\pi/2n) & \text{if } n = 4m + 1 \text{ or } 4m + 3 \end{cases} \quad (9)$$

$$I^p = \begin{cases} 8\beta^{-1}g^{-1}[1 + f(k)]^2\cos^2(\pi/n) & \text{if } n = 4m + 2 \\ \beta^{-1}g^{-1}[2 + f(k)]^2\cos^2(\pi/2n) & \text{if } n = 4m + 1 \text{ or } 4m + 3 \end{cases} \quad (10)$$

Applying equation (5) for the HOMO - LUMO gaps  $g$  equation (10) can be written as (11). By inspection of equation

$$I^p = \begin{cases} -f^{-1}(k)[1 + f(k)]^2\cos^2(\pi/n) & \text{if } n = 4m + 2 \\ -(1/2)f^{-1}(k)[2 + f(k)]^2\sin^{-1}(\pi/2n)\cos^2(\pi/2n) & \text{if } n = 4m + 1 \text{ or } 4m + 3 \end{cases} \quad (11)$$

(11) it is clear that for not too extreme bond fixation, *i.e.* no very large  $k$  values,  $|I^p| > I^d$  so that  $I < 0$  and one has paratropism. The magnitude of the paratropism varies drastically with the extent of bond fixation<sup>7</sup> (see Figure 2) due to the inverse dependence on the HOMO - LUMO gap, see equation (10). For doubly charged  $[4m + 2]$ annulenes the paratropism has been confirmed experimentally,<sup>1</sup> however, it seems<sup>5</sup> that calculated high- and low-field shifts for outer and inner protons are exaggerated.

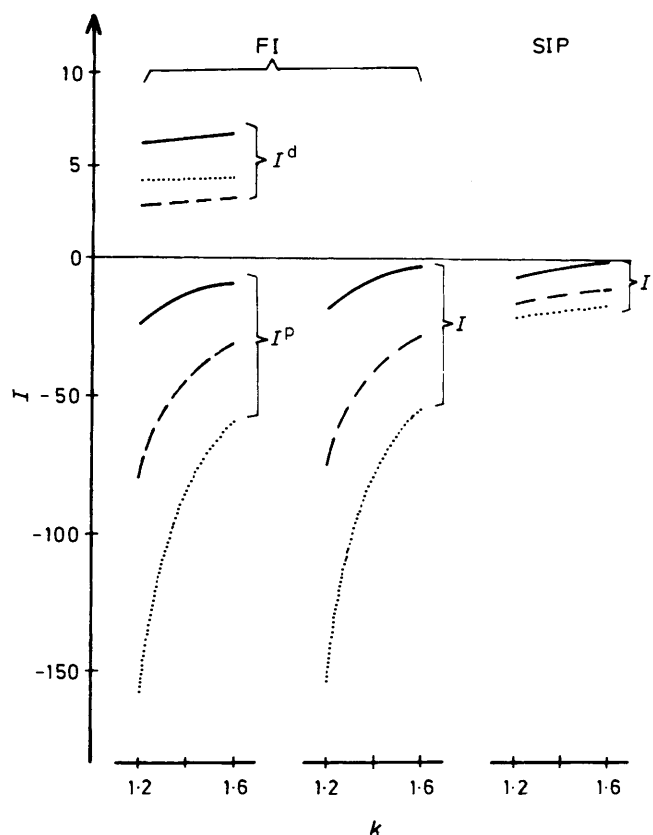


Figure 2. Reduced ring current  $I^d$ ,  $I^p$ , and  $I$  for  $(4m')$   $\pi$ -electron  $[n]$ annulenes with  $n = 10$ , charge  $Q = \pm 2$  (—);  $n = 5$ ,  $Q = +1$  (---); and  $n = 7$ ,  $Q = -1$  (····) for an FI and an SIP

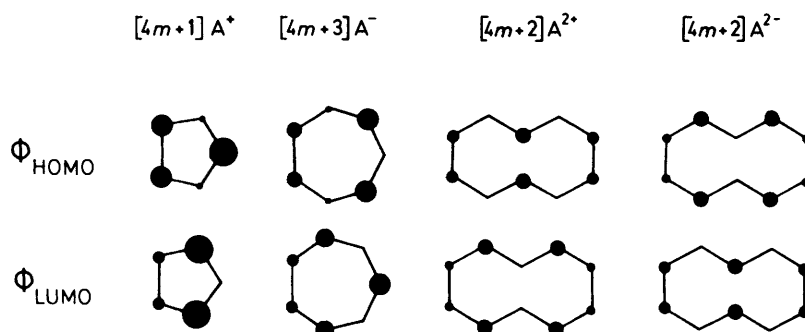


Figure 3. Values for  $c_{\text{HOMO}s}^2$  and  $c_{\text{LUMO}s}^2$  of HOMO and LUMO of  $(4m')$   $\pi$ -electron  $[n]$ annulenes  $[n]A^Q$  ( $m = 1$  if  $n = 4m + 1$  or  $4m + 3$ ,  $m = 2$  if  $n = 4m + 2$ )

**Counterion Effects.**—The reduced ring current has been derived without taking into account the counterion. Thus our formulae (7)–(11) are valid only for FIs which are less likely than SIPs or CIPs in solutions of charged annulenes. In an SIP annulene and counterion X with charge  $q$  interact mainly electrostatically. In the framework of Hartree–Fock theory a charge  $q$  on X causes a change of the diagonal element  $F_{ss}$  of the Fock matrix  $F$  by  $F_{ss} = -q\gamma_s$  where  $\gamma_s = e^2 \int \chi_s^2(1) \chi_X^2(2) r_{12}^{-1} d\tau_1 d\tau_2$  is the Coulombic integral between a  $\pi$ -basis function  $\chi_s$  and an orbital  $\chi_X$  describing the charge distribution on X, e.g. an  $s$ -type orbital.<sup>12</sup> The effect of several counterions is additive. Within the Hückel approach we modify similarly the diagonal matrix element  $h_{ss}$  of the Hückel operator by  $h_{ss} = -q\gamma_s$ . This leads to a change of orbital energies by equation (12) whereas

$$\Delta\epsilon_j = -q \sum_s c_{js}^2 \gamma_s \quad (12)$$

the orbitals are not affected.

Since only the diagonal part of the Hückel operator is altered in an SIP the operators  $h'$  and  $h''$  are also not affected by the interaction with the counterion. Consequently  $I^d$  also remains unchanged due to equation (6) and the magnitude of the diamagnetic ring current in charged annulenes with  $(4m' + 2)$   $\pi$ -electrons should be the same for an FI and an SIP.

The  $(4m')$   $\pi$ -electron annulenes are paratropic because of a non-vanishing  $I^p$ . However,  $I^p$  will be changed by the electrostatic interaction since it depends on the HOMO – LUMO gap  $g$  [equation (10)] which changes by equation (13)

$$\Delta g = -q \sum_s (c_{\text{LUMO}s}^2 - c_{\text{HOMO}s}^2) \gamma_s \quad (13)$$

due to (12). If the counterion is situated over the centre of the perimeter all  $\gamma_s$  have (at least approximately) a common value. Then it follows immediately from equation (13) that  $\Delta g = 0$  and the counterion does not change the ring current  $I$ . However, such an arrangement of the ion pair is energetically unfavourable since there is no uniform charge distribution on the perimeter. The net charge  $q_s$  ( $q_s < 0$  indicates excess of electron density) at atom  $s$  is given by equation (14) where  $Q$  is the

$$q_s = [(2 + Q)/n] - 2c_{\text{HOMO}s}^2 \quad (14)$$

charge on the annulene. Utilizing equations (12) and (14) we arrive at expression (15) for the energy change due to the

$$\Delta E = \sum_j^{\text{occ}} \Delta\epsilon_j = -(q/2)[1 - (2 + Q)/n] \sum_s \gamma_s - q \sum_s \gamma_s c_{\text{HOMO}s}^2 \quad (15)$$

electrostatic interaction. It is obvious that the mutual orientation of the ions is determined by the second term in equation (15) and hence by the values of  $c_{\text{HOMO}s}^2$ . The minimum of  $\Delta E$  is

obtained if the counterions are localized near to those atoms  $s$  with largest  $c_{\text{HOMO}s}^2$  in the case of the negatively charged  $[4m + 2]$ - and  $[4m + 3]$ -annulenes respectively, with smallest  $c_{\text{HOMO}s}^2$  in the case of the positively charged  $[4m + 2]$ - and  $[4m + 1]$ -annulenes.

According to equation (4)  $\phi_{-j}$  constitutes the LUMO if  $\phi_j$  is the HOMO. Consequently the largest values of  $c_{js}^2$  are connected with minimal  $c_{js}^2$  values and *vice versa* due to equation (1) and the numerical properties of sine and cosine functions. This is demonstrated in Figure 3 with some representative examples. Assuming the most favourable energetical arrangement of the ion pair it follows that  $(c_{\text{LUMO}s}^2 - c_{\text{HOMO}s}^2) < 0$  for a negatively charged  $(4m')$   $\pi$ -electron annulene ( $Q < 0$ ,  $q > 0$ ) and hence we obtain from equation (13)  $\Delta g > 0$ . On the other hand, we have  $(c_{\text{LUMO}s}^2 - c_{\text{HOMO}s}^2) > 0$  for the positively charged annulenes ( $Q > 0$ ,  $q < 0$ ) which yields  $\Delta g > 0$  as well.

An estimate of the influence of the counterion X in an SIP on the ring current can be obtained if we use the parameters of ref. 13 for the  $\pi$ -system and a one-centre repulsion integral  $\gamma_X = 20.4$  eV corresponding to a hydrogen  $1s$  charge distribution on X. We assume a distance of 400 pm between the two ions and obtain  $\gamma_s \cong -0.5\beta$  if  $\gamma_s$  is estimated simply by using the Mataga–Nishimoto formula.<sup>14</sup> Now it is straightforward to calculate  $\Delta g$  from equation (13) and the reduced ring current  $I$  from equations (9) and (10) for an SIP. The comparison of  $I$  for an FI with that for the SIP in Figure 2 reveals that the electrostatic interaction between the ion pairs causes a considerable reduction of the paramagnetic ring current with all charged  $(4m')$   $\pi$ -electron annulenes.

In a CIP we have to take into account not only the electrostatic but also the covalent interaction which causes a mixing of  $\pi$ -orbitals with those available from the counterion. This will lead to a charge transfer from the annulene to the counterion so that the effective charges on the ions are smaller than in an FI or SIP. Nevertheless the electrostatic effect alone in a CIP reduces the paramagnetic ring current in  $(4m')$   $\pi$ -electron annulenes similarly as in an SIP. The reduction might even be larger than in an SIP since the distance between the ion pairs is necessarily much shorter in the CIP.

It is difficult to describe completely the covalent interaction between the ions in a CIP within our simple approach. However, some test calculations with semi-empirical all-valence methods on charged annulene-counterion pairs with different mutual orientation of the ions showed that the annulene orbitals are not altered to a considerable degree. Consequently we can assume that the covalent interaction affects mainly the paramagnetic ring current of  $(4m')$   $\pi$ -electron annulenes through a change of the HOMO – LUMO gap. In such negatively charged annulenes the counterion possesses unoccupied orbitals  $\chi_X$  with energies which are higher than

$\epsilon_{\text{HOMO}}$  of the  $\pi$ -system. The most important interaction will then be that between  $\chi_X$  and  $\phi_{\text{HOMO}}$  which is given by equation (16)

$$\langle \phi_{\text{HOMO}} | W | \chi_X \rangle = \sum_s c_{\text{HOMO}s} \langle \chi_s | W | \chi_X \rangle \quad (16)$$

where the operator  $W$  describes the covalent interaction between the  $\pi$ -system and X. Necessarily this interaction leads to a stabilization of the HOMO of the annulene. It will be largest if the counterion prefers sites near to those perimeter atoms  $s$  with maximum  $|c_{\text{HOMO}s}|$  coefficients. Thus covalent interaction between the ion pair directs the mutual orientation of the ions in an analogous manner to the electrostatic interaction. Maximum stabilization of the HOMO means that the LUMO is not shifted significantly in energy due to the nodal properties of these frontier orbitals in the  $(4m')$   $\pi$ -electron annulenes [see equation (4)]. Therefore the HOMO – LUMO gap is increased, which leads to another reduction of the paratropism. The same applies to positively charged  $(4m')$   $\pi$ -electron annulenes where the increase of the HOMO – LUMO gap is caused by the interaction of low lying occupied orbitals of the counterion with the LUMO of the  $\pi$ -system. The most favourable energetic covalent interaction emerges if the counterion is situated in the proximity of those perimeter atoms  $s$  with smallest  $|c_{\text{LUMO}s}|$  coefficients and due to the related shapes of HOMO and LUMO with largest  $|c_{\text{HOMO}s}|$  values. Thus in the case of positively charged annulenes electrostatic and covalent interactions likewise determine the ion pair arrangement.

**Conclusions.**—In this communication we studied the reduced ring current  $I$  in charged  $[n]$ annulenes. The sign and magnitude of  $I$  is crucial for the  $^1\text{H}$  n.m.r. spectra of such compounds. In addition to the results of Haddon<sup>4</sup> for annulenes with  $(4m' + 2)$   $\pi$ -electrons we could derive formulae for charged annulenes with  $(4m')$   $\pi$ -electrons by introducing bond fixation into the perimeter. The annulenes with  $(4m' + 2)$   $\pi$ -electrons are characterized by a vanishing paramagnetic term  $I^p$  so that only a diamagnetic ring current is encountered leading to diatropism. On the other hand we have a paramagnetic ring current  $I$  in the  $(4m')$   $\pi$ -electron annulenes since here the paramagnetic term  $I^p$  exceeds numerically the diamagnetic one  $I^d$ .  $I^p$  depends inversely on the size of the HOMO – LUMO gap and hence on the extent of bond fixation.

Our theoretical considerations revealed that the electrostatic or covalent interaction between annulene and counterion in an SIP or CIP should not significantly affect the proton chemical shifts in those annulenes which exhibit  $(4m' + 2)$   $\pi$ -electrons. Only the decrease of the effective charge on the annulene by covalent interaction between the ion pair in an CIP should lead to quite small changes in the n.m.r. spectrum. Indeed one finds experimentally only minor alterations of  $^1\text{H}$  chemical shifts ( $<0.5$  p.p.m.) in diatropic, charged annulenes if counterion, temperature, or solvent is varied.<sup>1-15</sup> Thus it is a sufficient approximation to treat diatropic charged annulenes simply as

FIs. On the other hand both electrostatic and covalent interaction between the ion pair lead to an increase of the HOMO – LUMO gap and hence to a considerable reduction of the paramagnetic ring-current effect in the case of charged annulenes with  $(4m')$   $\pi$ -electrons. The reduction will most probably be greater in an CIP than in an SIP since in the former both interactions are effective in the same sense. Indeed an increase of paratropism is found experimentally with paratropic doubly charged  $[4m + 2]$ annulenes when the equilibrium is shifted from CIPs to more SIPs by a convenient variation of counterion, temperature, or solvent.<sup>16</sup> According to our qualitative theoretical results it is obvious that a quantitative assessment of  $^1\text{H}$  chemical shifts in paratropic charged annulenes is only possible if the interaction between the  $\pi$ -system of the annulene and the counterion(s) is explicitly taken into consideration.

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