234. Energy Sequence of the Lowest Antibonding Orbitals in Symmetrical Didehydro[*n*]annulenes with $n=4N+2$

by **Fabian Gerson**1), **Joanna Jachimowicz**1), **Masazumi Nakagawa**2) and **Masahiko Iyoda**2)

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80,
4056 Basel, Switzerland, and
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

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Summary. A model of a perturbed n-membered perimeter ($n = 4N + 2$) is used to interpret the ESR.-data for the radical anions of symmetrical tetra-*t*-butyl-didehydro[n]annulenes with $n = 14$, 18, 22 and 26 ($N = 3$, 4, 5 and 6). The singly occupied orbital of such radical anions correlates with one of the doubly degenerate, lowest antibonding perimeter MO's which have been classified as symmetric (ψ_S) or antisymmetric (ψ_A) with respect to the mirror plane passing through two opposite centres and perpendicular to the plane of the perimeter. The relevant MO is ψ_S for $n = 14$ ($N = 3$) and 22 ($N = 5$), but ψ_A for $N = 18$ ($N = 4$) and 26 ($N = 6$), in accordance with the prediction of the model. It has been shown that the introduction of two symmetrically placed triple bonds into a ($4N + 2$)-membered perimeter should *stabilize* ψ_S and *destabilize* ψ_A when N is *odd*, whereas the *reverse* should hold when N is *even*.

[n]Annulenes are of considerable interest in theoretical chemistry, since they represent model compounds for the n-membered π-electron perimeters [1]. Owing to the synthetic work of *Sondheimer et al.*, [14]-, [18]- and [22]annulenes, where the number $n = 4N + 2$ obeys the *Hückel* rule of aromaticity, have become available in the last decade [2]3). However, no ESR.-data have yet been reported for the corresponding radical ions, presumably because the conformational flexibility of these large monocyclic compounds [4] affects the relative stability of their radical ions and/or complicates the analysis of the ESR.-spectra4). On the other hand, numerous bridged [10]-, [14]- and [18]annulenes, in which the geometry is fixed by the bridging groups, have also been synthesized [2] and their radical ions successfully studied by ESR.-spectroscopy [6]. Alternatively, a fair amount of rigidity can be imposed on [n]annulenes by the introduction of triple bonds. The first known compound, in which such an alternative has been realized, is the symmetrical didehydro[14]annulene synthesized by *Sondheimer & Gaoni* in 1960 [7]. It readily forms the radical anion by standard procedure and the analysis of the resulting ESR.-spectrum is unproblematic [8]. More recently, *Nakagawa et al.* applied an efficient method [9] to the synthesis

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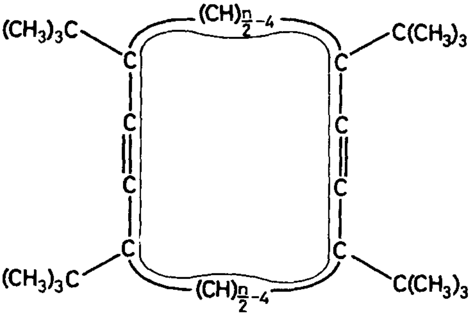
1) Universität Basel.

2) University of Osaka.

3) Two geometrical isomers of the highly unstable [10]annulene have been isolated by *Masamune et al.* [3].

4) An ESR. – spectrum of the [18]annulene radical anion has been reproduced in a paper by *Oth et al.* [5], but no analysis of its hyperfine structure was given. (Note added in proof: the pertinent ESR.-data were cited by Prof. Oth at the 2nd Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, held in Lindau, Germany, 22nd–27th September 1974.)

of symmetrical tetra-*t*-butyl-didehydro[n]annulenes I [9], II [10a], III [10b] and IV [10c] where n = 4N + 2 = 14, 18, 22 and 26, respectively. All these compounds are planar, relatively rigid and have essentially the same geometry, although a progressive loss in 'aromatic character' is indicated by a decreasing 'ring current' with an increasing n.



I: n = 14
II: n = 18
III: n = 22
IV: n = 26

In the present paper, we describe the ESR.-spectra of the radical anions I$^\ominus$ to IV$^\ominus$ and discuss the results in terms of a perimeter model.

Experimental Part. – The syntheses of the symmetrical tetra-*t*-butyl-didehydro[n]annulenes I to IV have been described previously [9] [10]. The corresponding radical anions were prepared by reaction of the respective neutral compounds with potassium in 1,2-dimethoxyethane (DME). At temperatures below – 20°, their half-lives are of the order of hours, with the stability slightly diminishing in the sequence I$^\ominus$ > II$^\ominus$ > III$^\ominus$ > IV$^\ominus$.

ESR.-Spectra. – Fig. 1 shows the ESR.-spectra of the radical anions I$^\ominus$, II$^\ominus$ and III$^\ominus$ which exhibit relatively simple hyperfine structures. The more complex spectrum of the radical anion IV$^\ominus$ is presented in Fig. 2, together with the computer-simulated derivative curve.

Fig. 1 and 2 also give the values of the pertinent coupling constants. Their assignment to sets of equivalent ring protons in I$^\ominus$ is straightforward. It is also unambiguous for the proton pairs in II$^\ominus$, III$^\ominus$ and IV$^\ominus$, since such pairs are unique for each radical anion. On the other hand, the assignment of the remaining coupling constants does not directly follow from experiment and has therefore been based on the MO calculations dealt with in the Discussion. This assignment is specified in Fig. 3 where the calculated π-spin populations are given for the proton-bearing centres, in addition to the coupling constants of the corresponding ring protons.

In none of the spectra, the hyperfine splittings from the 36 equivalent *t*-butyl protons could be resolved. As estimated from the line-width, these splittings are about 0.08 gauss[5]) for I$^\ominus$ and decrease even further on passing to the higher members of the series.

In the range of -20 to $-90°$, where the ESR.-studies have been performed, the spectra do not substantially depend on temperature. This finding suggests that the relative rigidity of the compounds I to IV [9] [10] is shared by their radical anions.

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[5]) 1 gauss = 10^{-4} tesla.

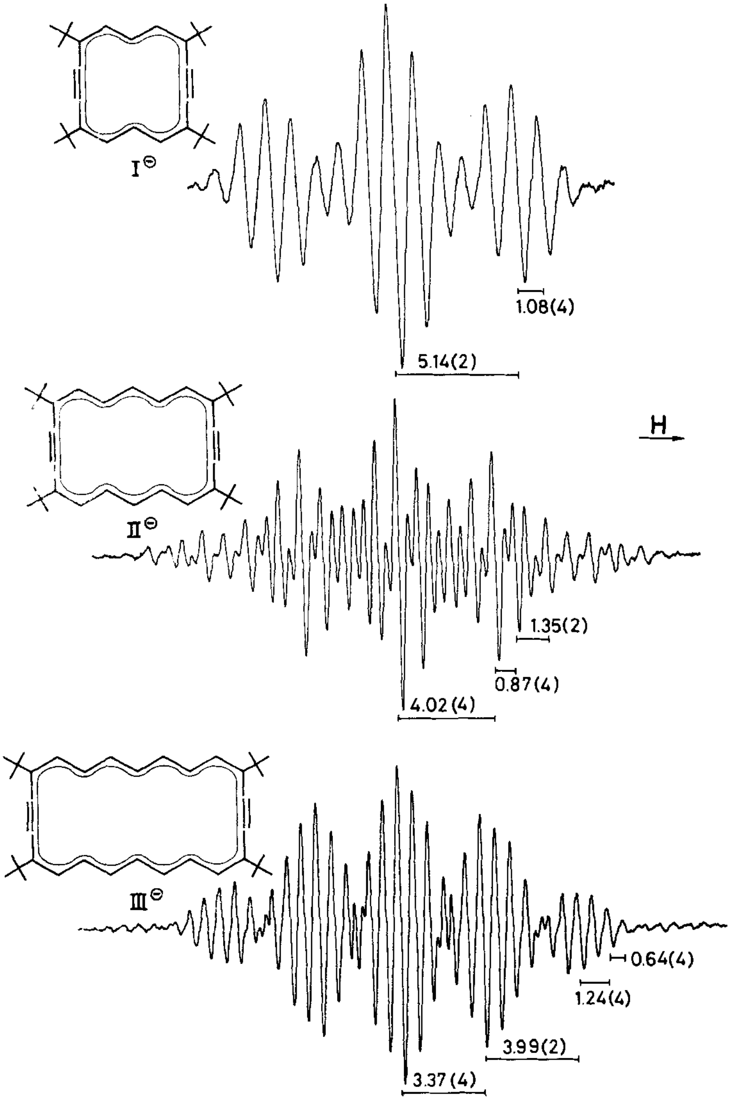

Fig. 1. *ESR.-spectra of the radical anions $I^{\ominus}$, $II^{\ominus}$ and $III^{\ominus}$.* Solvent: DME; counter-ion: $K^{\oplus}$; temp.: − 50°. Below each spectrum, the hyperfine splittings (in gauss[5]) are indicated, along with the numbers (2 or 4) of protons giving rise to them.

Discussion. – The simplest model which can be used to interpret the ESR.-spectra of the radical anions $I^{\ominus}$ to $IV^{\ominus}$ is that of a perturbed π-electron perimeter. Fig. 4 depicts the two lowest antibonding MO's of the 14-, 18-, 22- and 26-membered perimeters which are drawn to reflect the geometry of the corresponding didehydro-[n]annulenes. For each perimeter, the two orbitals have been classified as symmetric (ψ_S) or antisymmetric (ψ_A) with respect to the mirror plane (m) passing through two

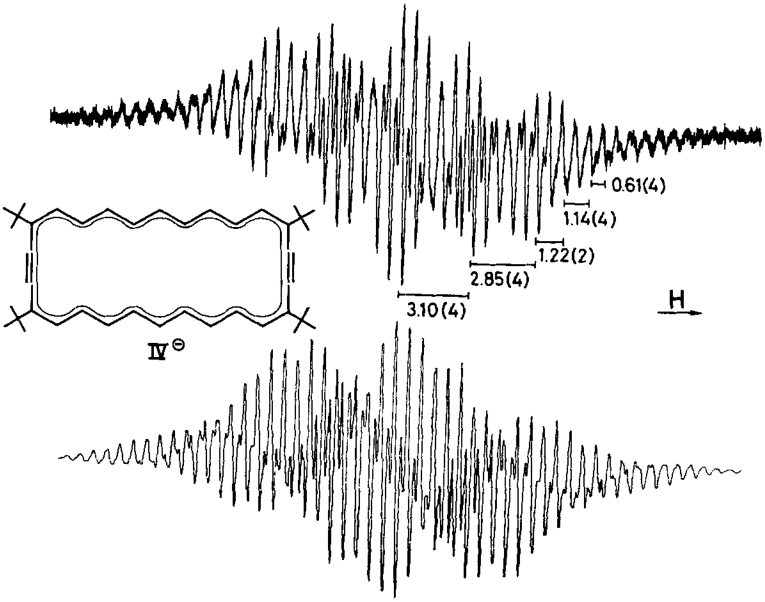

Fig. 2. *ESR.-spectra of the radical anion $IV^{\ominus}$.* Top: Experimental spectrum. Solvent: DME; counter-ion: $K^{\oplus}$; temp.: – 50°. Below the spectrum, the hyperfine splittings (in gauss[5]) are indicated, along with the numbers (2 or 4) of protons giving rise to them.
Bottom: Computer simulated spectrum. Coupling constants as shown in the Figure; line-shape: Lorentzian; line-width: 0.15 gauss[5]).

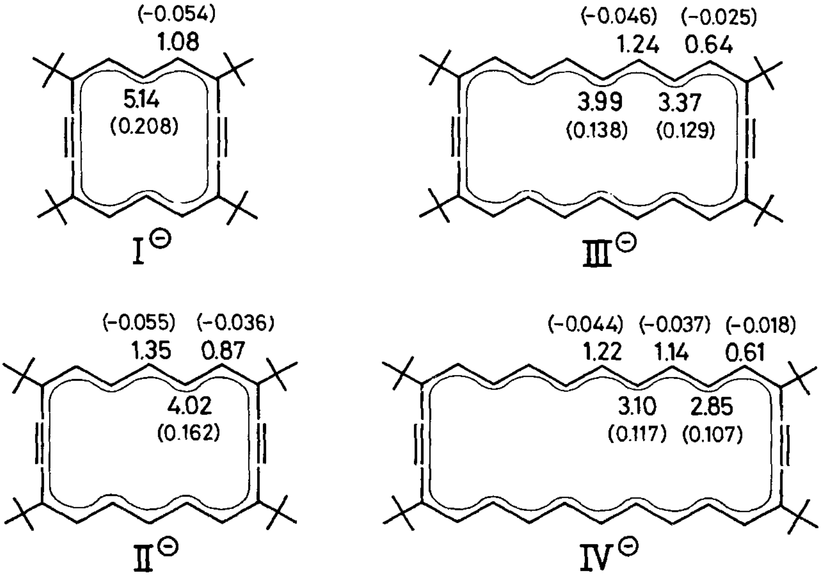

Fig. 3. *Coupling constants* (in gauss[5])) *of the ring protons in the radical anions $I^{\ominus}$ to $IV^{\ominus}$, and the calculated π-spin populations at the corresponding proton-bearing carbon centres* (numbers in parentheses). Experimental error: ±0.5% for larger (> 3 gauss) and ±1% for smaller coupling constants (< 1.5 gauss). Spin populations calculated according to the *McLachlan* procedure [12] with $\beta_{\mu\nu} = 1.5\beta$ for the triple bonds and $\lambda = 1.2$ (*cf.* text)

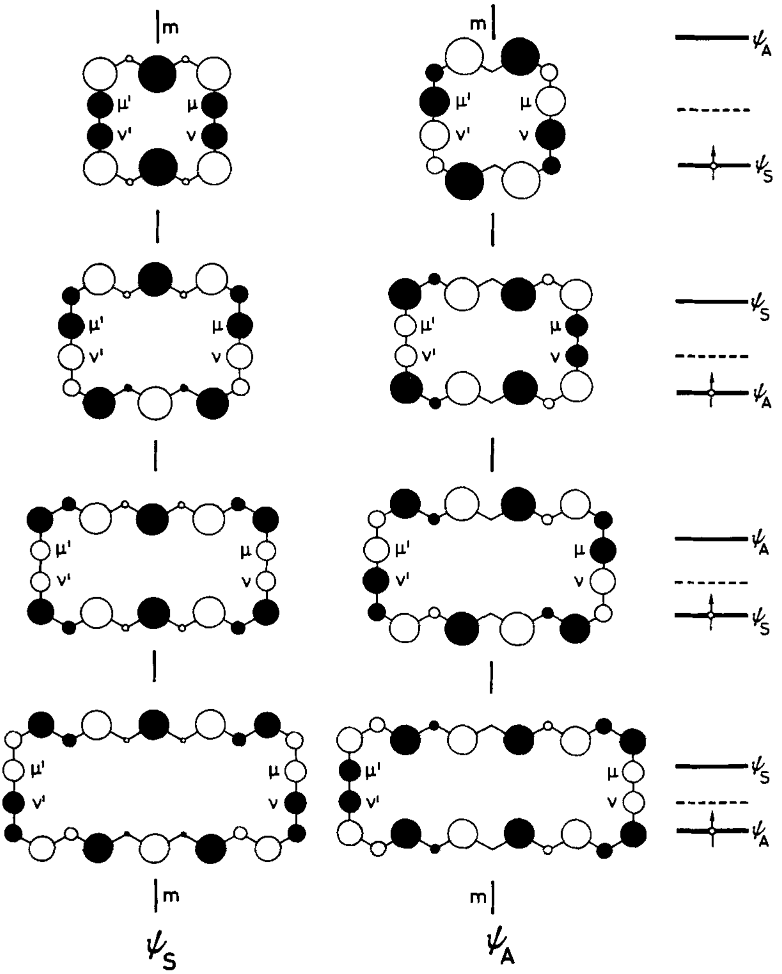

Fig. 4. *The lowest antibonding MO's ψ_S and ψ_A of 14-, 18-, 22-, and 26-membered perimeters.* The radii of the circles are proportional to the absolute values of the LCAO coefficients. Blank and filled areas symbolize different signs. The letter m denotes the trace of the mirror plane used for the classification of ψ_S and ψ_A (see text), while μ—ν and μ'—ν' represent the centres which are triply bound in the didehydro[n]annulenes. The levels on the right indicate the energies of ψ_S and ψ_A in the perturbed perimeters (solid lines) relative to their energies in the absence of perturbation (dashed lines). The arrows mark the orbital occupancy in the radical anions.

opposite centres and perpendicular to the plane of the perimeter. The MO's ψ_S and ψ_A are degenerate for an unperturbed n-membered perimeter of symmetry D_{nh} but their degeneracy is removed in the didehydro[n]annulenes. Clearly, the relative energies of ψ_S and ψ_A will be determined by the perturbation arising from the introduction of the two triple bonds into the π-system of the perimeter. In a MO formalism, such a perturbation is simulated by a change $d\beta_{\mu\nu}$ in the integral $\beta_{\mu\nu}$ of the triply bound centres μ—ν and μ'—ν'. The corresponding changes dE_S and dE_A in the energies of ψ_S and ψ_A are expressed – to the first order – as

$$dE_S = 2\, d\beta_{\mu\nu} \left(c_{S_\mu} c_{S_\nu} + c_{S_{\mu'}} c_{S_{\nu'}}\right) \tag{1}$$

and

$$dE_A = 2\, d\beta_{\mu\nu} \left(c_{A_\mu} c_{A_\nu} + c_{A_{\mu'}} c_{A_{\nu'}}\right) \tag{2}$$

where $c_{S_{\mu'}} \ldots c_{A_{\nu'}}$ denote the LCAO coefficients at the centres $\mu, \ldots \nu'$.

For reasons of symmetry (*cf.* Fig. 4)

$$c_{S_{\mu'}} = c_{S_\mu}; \quad c_{S_{\nu'}} = c_{S_\nu} \tag{3}$$

and

$$c_{A_{\mu'}} = -\, c_{A_\mu}; \quad c_{A_{\nu'}} = -\, c_{A_\nu} \tag{4}$$

so that

$$c_{S_{\mu'}} c_{S_{\nu'}} = c_{S_\mu} c_{S_\nu} \tag{5}$$

and

$$c_{A_{\mu'}} c_{A_{\nu'}} = c_{A_\mu} c_{A_\nu} \tag{6}$$

Consequently, eq. (1) and (2) can be reduced to

$$dE_S = 4\, d\beta_{\mu\nu}\, c_{S_\mu} c_{S_\nu} \tag{7}$$

and

$$dE_A = 4\, d\beta_{\mu\nu}\, c_{A_\mu} c_{A_\nu} \tag{8}$$

Since $d\beta_{\mu\nu}$ is undoubtedly a negative quantity (shortening of the μ—ν and μ'—ν' linkages, due to the introduction of the triple bonds), dE_S will be *negative* when the coefficients c_{S_μ} and c_{S_ν} have the *same* sign (stabilization), but *positive* when their signs are *opposite* (destabilization). An analogous statement holds for dE_A with respect to c_{A_μ} and c_{A_ν}.

It is evident from Fig. 4 that c_{S_μ} and c_{S_ν} have the *same* sign for didehydro[n]annulenes with n = 14 (N = 3) and n = 22 (N = 5), but opposite sign for those with n = 18 (N = 4) and n = 26 (N = 6). The reverse is true for c_{A_μ} and c_{A_ν}. Relative to their levels in the corresponding unperturbed perimeters, the energies of ψ_S should therefore be *lowered* ($dE_S < 0$) when N = 3 or 5, and *raised* ($dE_S > 0$) when N = 4 or 6, whereas the energies of ψ_A should be *raised* ($dE_A > 0$) when N = 3 or 5, and *lowered* ($dE_A < 0$) when N = 4 or 6. An energetic sequence which *alternates* with N is thus predicted for the orbitals ψ_S and ψ_A in the four didehydro[n]annulenes. A generalization of this prediction, which will be proved in the Appendix, can be formulated as follows:

Introduction of two symmetrically placed triple bonds into a (4N + 2)-membered perimeter affects the energies of the degenerate lowest antibonding orbitals in such a way that the *'symmetric'* orbital ψ_S is *stabilized* when N is *odd*, and *destabilized* when N is *even*, whereas the *opposite* holds for its *'antisymmetric'* counterpart ψ_A.

Fig. 4 also presents the relative energies of ψ_S and ψ_A in didehydro[14]-, [18]-, [22]- and [26]annulenes, as predicted by the simple model of a perturbed perimeter. The occupancy, which should result therefrom for the two orbitals in the corresponding radical anions, is likewise indicated. Inspection of the ESR.-data for $I^\ominus$ to $IV^\ominus$ in Fig. 3 makes clear that the expected occupancy has been fully borne out by experiment. Most informative in this context are the coupling constants which have been found for the pairs of equivalent ring protons at the two centres situated in the mirror planes m. For all four radical anions, these coupling constants can be directly assigned from the ESR.-spectra and their magnitude allows an unequivocal characterization of the singly occupied orbital. Thus, in the case of $I^\ominus$ (n = 14; N = 3) and $III^\ominus$ (n = 22; N = 5) where such magnitude is large (5.14 and 3.99 gauss[5]), respectively), the relevant orbital is *symmetric* (ψ_S) relative to m. For $II^\ominus$ (n = 18; N = 4) and $IV^\ominus$ (n = 26; N = 6), on the other hand, the rather small magnitude of the analogous values (1.35 and 1.22 gauss[5]), respectively) points to a single occupancy of an orbital which is *antisymmetric* (ψ_A) relative to m.

In an HMO-*McLachlan*-type calculation [12] of the π-spin distribution in $I^\ominus$ to $IV^\ominus$, the integral $\beta_{\mu\nu}$ of the triple bonds μ—ν and μ'—ν' was set equal to 1.5 β, whereas all the remaining HMO parameters retained their standard values of α and β. In particular, no allowance was made for the substitutent effect of the *t*-butyl groups, in view of the nearly identical coupling constants observed for the corresponding ring protons in $I^\ominus$ (5.14 and 1.08 gauss[5]); this work) and the unsubstituted radical anion (5.15 and 1.15 gauss[5]) [8]). As shown in Fig. 3, the π-spin populations (*McLachlan* parameter λ = 1.2 [12]), resulting for the proton-bearing centres of $I^\ominus$ to $IV^\ominus$, correlate well with the observed coupling constants of the ring protons. It is therefore justified to use this correlation for the assignment of those ESR.-data which cannot be assigned by experiment alone.

Appendix. – For a n-membered perimeter (n = 4N + 2), which is perturbed by the introduction of two symmetrically placed triple bonds μ—ν and μ'—ν', the first order changes in the energies of the lowest antibonding MO's ψ_S and ψ_A (Fig. 4) have been shown to depend on the products $c_{S_\mu}c_{S_\nu}$ ($= c_{S_{\mu'}}c_{S_{\nu'}}$) and $c_{A_\mu}c_{A_\nu}$ ($= c_{A_{\mu'}}c_{A_{\nu'}}$) of the corresponding LCAO coefficients.

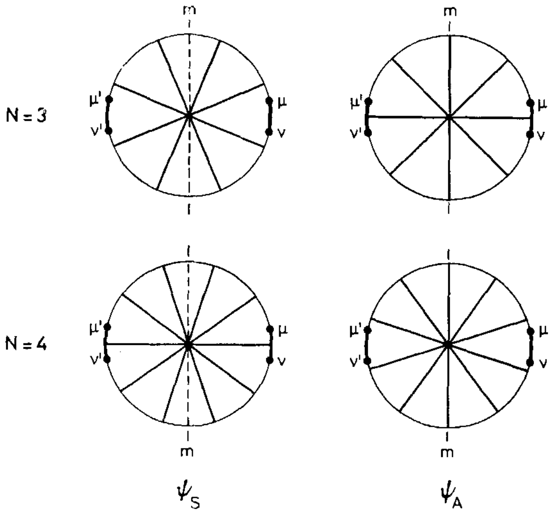

Fig. 5. *Traces of the N + 1 vertical nodal planes* (solid lines) *for the lowest antibonding perimeter MO's* ψ_S *and* ψ_A. Numbers of centres n = 4N + 2 = 14 and 18 or N = 3 and 4. The letter m denotes the trace of the mirror plane (dashed line) used for the classification of the degenerate orbitals, while μ—ν and μ'—ν' represent the centres which are triply bound in the didehydro[n]-annulenes

Stabilization of ψ_S or ψ_A (dE_S or $dE_A < 0$) results when the two coefficients involved in the pertinent product have the *same* sign, whereas *destabilization* (dE_S or $dE_A > 0$) is obtained when their signs are *opposite*. To derive the relative signs of the two relevant coefficients in a general case of N being any integer, one considers the nodal planes perpendicular to the plane of the perimeter [1] [11]. For ψ_S and ψ_A the number of such vertical nodal planes is $N + 1$, and two successive planes form a dihedral angle of $\pi/(N + 1)$. In Figure 5, which depicts the situation for $N = 3$ and 4, the $N + 1$ nodal planes and the mirror plane m (used for the classification of ψ_S and ψ_A) are indicated. From inspection of Figure 5 it is obvious that, when N is *odd*, ψ_A exhibits a vertical nodal plane at right angle to m, whereas ψ_S does not. The reverse holds when N is *even*. The implications of this result for the relative signs of the coefficients at the triply bound centers μ——ν and μ'——ν' and for the changes in energies of ψ_S and ψ_A are specified below. They can be identified with the statement made in the Discussion on the stabilization or destabilization of ψ_S and ψ_A as a function of parity of N.

	relative signs of		signs of	
N	c_{S_μ} and c_{S_ν} ($c_{S_{\mu'}}$ and $c_{S_{\nu'}}$)	c_{A_μ} and c_{A_ν} ($c_{A_{\mu'}}$ and $c_{A_{\nu'}}$)	dE_S	dE_A
odd	same	opposite	negative	positive
even	opposite	same	positive	negative

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