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Accessory Material

Connection Between Root Signs and Coefficient Signs of Characteristic Polynomials for Even, Fully-π-bonded, Non-alternant Hydrocarbons Which Lack NBMOs

1.   The polynomial coefficient a_n [see equation (1)], is obtained as shown below.

$$a_n = (-r_1)(-r_2)..(-r_i)....(-r_n) \qquad (4)$$

Note that r_i is the ith root of the characteristic polynomial [see equation (1)].

Consecutive polynomial coefficients are obtained in similar ways:

$$a_{n-1} = [(-r_1)(-r_2)...(-r_{n-1})] + [(-r_1)(-r_2)...(-r_{n-2})(-r_n)]$$

$$+ .... + [(-r_2)(-r_3)...(-r_n)] \qquad (5)$$

$$a_{n-2} = [(-r_1)(-r_2)...(-r_{n-2})] + [(-r_1)(-r_2)...(-r_{n-3})(-r_n)]$$

$$+ ... + [(-r_3)(-r_4)...(-r_n)] \qquad (6)$$

2.   Another form can be obtained for each polynomial coefficient, expressing it in terms of a_n. Consider a_{n-1}.

$$a_{n-1} = [(-r_1)(-r_2)...(-r_{n-1})] + [(-r_1)(-r_2)...(-r_{n-2})(-r_n)]$$

$$+ ... + [(-r_2)(-r_3)...(-r_n)]$$

$$= -r_n(-r_n)^{-1}[(-r_1)(-r_2)...(-r_{n-1})] + -r_{n-1}(-r_{n-1})^{-1}[(-r_1)$$

$$(-r_2)...(-r_{n-2})(-r_n)] + ... + -r_1(-r_1)^{-1}[(-r_2)(-r_3)...(-r_n)]$$

$$= (-r_n)^{-1}[(-r_1)...(-r_n)] + (-r_{n-1})^{-1}[(-r_1)...(-r_n)] + ...$$

$$+ (-r_1)^{-1}[(-r_1)...(-r_n)]$$

$$= (-r_n)^{-1}a_n + (-r_{n-1})^{-1}a_n + ... + (-r_1)^{-1}a_n$$

$$= -a_n (r_1^{-1} + r_2^{-1} + ... + r_n^{-1}) \qquad\qquad (7)$$

Similarly, expressions for other coefficients can be obtained in terms of a_n e.g.

$$a_{n-2} = a_n[(r_1r_2)^{-1} + (r_1r_3)^{-1} + ... + (r_{n-1}r_n)^{-1}] \qquad (8)$$

$$a_{n-3} = -a_n[(r_1r_2r_3)^{-1} + (r_1r_2r_4)^{-1} + ... + (r_{n-2}r_{n-1}r_n)^{-1}] \qquad (9)$$

$$a_{n-4} = a_n[(r_1r_2r_3r_4)^{-1} + (r_1r_2r_3r_5)^{-1} + ... + (r_{n-3}r_{n-2}r_{n-1}r_n)^{-1}] \quad (10)$$

and so on. Hence, the sign for a given characteristic polynomial coefficient depends on the signs of a series of terms involving polynomial root reciprocals. The largest reciprocal values are those for the smallest roots. The smallest roots are associated with the frontier orbitals (r_p, r_{p+1}) and their neighbours (r_{p-1}, r_{p+2} etc.). Note $n = 2p$. For non-alternant structures which have $\Delta = 0$ (equal numbers of positive and negative roots), $\text{sign}[(-1)^p] = \text{sign}[a_n]$.

Sign[a_{n-1}] will usually be determined by the frontier orbital eigenvalue which is closest to the non-bonding level [e.g. sign[a_n] = -sign[a_{n-1}] for methylene cyclopropene (low-lying LUMO) and sign[a_n] = sign[a_{n-1}] for methylene cyclopentadiene (high-lying HOMO)].

3.   For non-alternant structures which have $\Delta = 2$, sign[$(-1)^p$] = -sign[a_n]. In such systems, both r_p, r_{p+1} (the small roots) have the same sign and are likely to determine the sign of the sum of root reciprocals shown in equation (7). Structures which have an excess of two positive roots will almost

   certainly have sign[a_n] = -sign[a_{n-1}]. Structures which have

   an excess of two negative roots will almost certainly have sign[a_n] = sign[a_{n-1}].

4.   For non-alternant structures which have $\Delta = 4$, sign[$(-1)^p$] = sign[a_n]. In such systems, r_{p-1}, r_p, r_{p+1}, r_{p+2} (the small roots) have the same sign and are very likely to determine the sign of the sums of root reciprocal terms shown in equations (7) and (8). Structures which have an excess of four positive roots will almost certainly have sign[a_n] = -sign[a_{n-1}] = sign[a_{n-2}]. Structures which have an excess of four negative roots will almost certainly have sign[a_n] = sign[a_{n-1}] = sign[a_{n-2}].

5. Each time that Δ increases by 2, another coefficient sign is likely to join the growing pattern of coefficient signs in accord with the expectations arising from equations (9), (10) and so on. In general $(\Delta/2)+1$ adjacent polynomial coefficients (beginning with a_n) will have signs that don't match/do match when the larger of the subset of polynomial roots is positive/negative i.e. (if s is one sign and o the other) excess π-antibonding orbitals will be associated with

the coefficient sign pattern s,s,s,s... and excess π-bonding orbitals will be associated with the coefficient sign pattern s,o,s,o,s...

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6.   From equation (4), when a polynomial root is zero (one   eigenfunction with eigenvalue α), then $a_n = 0$.

7.   From equation (5), a_{n-1} is obtained as the sum of terms in which all of the roots save one have been multiplied together. If only one root, say r_f, is zero, then all of the terms for a_{n-1} vanish, except the one lacking the zero root, r_f. Hence,

$$a_{n-1} = (-r_1)(-r_2)...(-r_{f-1})(-r_{f+1})...(-r_n) \qquad (11)$$

Thus when $a_n = 0$, a_{n-1} has a definition analogous to the definition for a_n when $a_n \neq 0$. Argumentation analogous to that advanced earlier for $a_n \neq 0$ systems leads to the following conclusion: for $a_n = 0$ systems (one NBMO only), Δ, the difference in the numbers of π-bonding and π-antibonding orbitals will be equal to the difference in the numbers of 4J+3 and 4J+1 circuits in dominant (n-1)-site Sachs' subgraphs. Surplus 4J+3 circuits imply an excess of π-antibonding orbitals and surplus 4J+1 circuits imply an excess of π-bonding orbitals.

Theorem

8. If any neutral hydrocarbon has unequal numbers of π-bonding and π-antibonding MOs, where the difference between the numbers is Δ and that same structure has U NBMOs, then no NBMO can be a frontier orbital if $\Delta > U$.

9. Suppose such a structure has n vertices in its π system and an excess of Δ π-bonding orbitals. It will have T_B bonding orbitals.

$$T_B = \Delta + (n - \Delta - U)(2^{-1})$$
$$= 2\Delta(2^{-1}) + (n - \Delta - U)(2^{-1})$$
$$= (n + \Delta - U)(2^{-1}) \tag{12}$$

In general, such a structure will have n/2 occupied orbitals. If $\Delta > U$, $T_B > n/2$ so that the number of π-bonding orbitals will exceed the number of occupied orbitals. Thus, both the HOMO and the LUMO will be π-bonding orbitals and no NBMO can be a frontier orbital.

10. Suppose such a structure has n vertices in its π system and an excess of Δ π-antibonding orbitals. It will have a total of T_{B+NB} π-bonding and non-bonding orbitals.

$$T_{B+NB} = U + (n - \Delta - U)(2^{-1})$$
$$= 2U(2^{-1}) + (n - \Delta - U)(2^{-1})$$
$$= (n - \Delta + U)(2^{-1}) \tag{13}$$

In general, such a structure will have n/2 occupied orbitals. If $\Delta > U$, $T_{B+NB} < n/2$ so that the number of occupied orbitals will exceed the total number of π-bonding and NBMOs and at least one π-antibonding orbital will be occupied. Thus, both the HOMO and the LUMO will be π-antibonding orbitals and no NBMO can be a frontier orbital. Ergo, no NBMO can be a frontier orbital when $\Delta > U$.