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THE NEW PICTORIAL STRUCTURAL COVARIANCE METHOD FOR QUALITATIVE QUANTUM CHEMISTRY. III: FUSED POLYCYCLICS AND THEIR IONS

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Abstract

The number of non-bonding (NBMOs), bonding, and anti-bonding MOs, the HOMO-LUMO types, reactivity to electro- or nucleophiles, qualitative relative stabilities of the neutral species, their anions or cations, are readily deduced for pi-polycyclics "on the blackboard" directly from the structural formulae utilizing the recently presented pictorial quantum rules. Among others, the bicyclo [$p.q.0$] pi-hydrocarbons are treated extensively and are found to fall into ten distinct homolog classes. In addition to the customary pi-aromatic or pi-anti-aromatic types, classes of compounds with other behaviour (e.g. one here called "anti-Kekulé") are found. When an anti-aromatic ring is fused with another anti-aromatic or with a pi-aromatic ring, the resulting bicyclo-molecule is not anti-aromatic. In another series, the heptalene and other ($4k + 3$), ($4k' + 3$) bicyclics have two electrons in a single NBMO, making them "anti-Kekulé". The method is able to distinguish between the properties of pairs of isomers such as (s-indacene; as-indacene) and (1.2,5.6-dibenzpentalene; 1.2,4.5-dibenzpentalene).

1. Introduction

The new pictorial method [1–3] allows one to deduce qualitative quantum chemical properties, the numbers of bonding, non-bonding (NBMO), antibonding MO levels, distortability, and HOMO-LUMO [4] reactivity of molecules directly from their structural formulae (SF) or ORTEP (X-ray crystallographic structure) diagrams. The mathematical theory that leads to the easy-to-use pictorial rules was given earlier [5]. Paper I [3] then gave examples of the use of the rules on some inorganic and organic molecules. Paper II [6] used the rules to classify single π-ring molecules into what turned out to be four classes. The method gives also the HOMO and LUMO types, and applies at once to the anion and the cation of a neutral species as well. While the Hückel $4n + 2$ rule [7] and the Frost–Musulin circle algorithm [8] applies to single (regular polygon) π-rings only, the present "structural-electronic formula" (SEF) method works for diverse structures, such as rings with polyene side chains, substituted species, polycyclics, etc. and for sigma as well as pi systems.

In this, paper III, we will treat systematically a wide range of fused ring π-polycyclics [9].

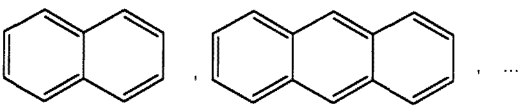
2. Polyacenes

As discussed in papers I [3] and II [6], the first objective is to obtain the MO energy level pattern characterized basically by the "level pattern indices", the LPI $= \{n_+, n_0, n_-\}$, where the three integers $\{n_i\}$ are the numbers of bonding, nonbonding, and antibonding MOs, respectively. The SEF, or with an alternative name we have also used, i.e. the "valency-points interaction formula" (VIF) [1–3], is drawn from the SF and corresponds not to wave function (contrary to the valence-bond picture), but to the effective one-electron Hamiltonian itself. As in paper II [6], the present paper will deal, as a start, with the π-systems, the VIF$^\pi$ alone, the sigma treatment [1,3] being reserved for future papers.

With pi-alternant hydrocarbons (HC), there is of course the well-known alternant HC theorem [10] (or the two-colourability theorem in mathematics), from which it follows that $n_+ = n_-$ (alternants, pi). Longuet-Higgins [11] emphasized the need for a direct way to obtain the n_0, crucial for anti-aromaticity, for finding multi-radicals [12], etc. This author found an inequality for n_0 for certain types of pi-HCs. The present SEF method deduces the actual n_0 (= # NBMO) for any molecule. It also displays the distortability and various reaction pathways [2,5].

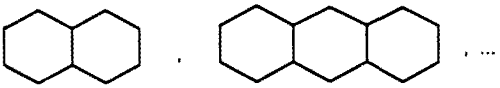
(a) STRAIGHT POLYACENES

SF (Kekulé):



(1)

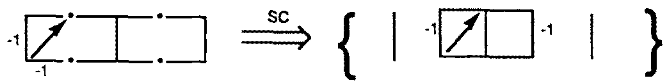
VIF$^\pi$:



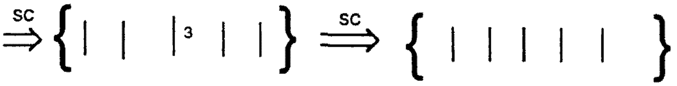
(i) (ii)

(1′)

The homologs in eq. (1′) are "reduced" by the two rules [6] to get the LPI$^\pi$s:



(2)

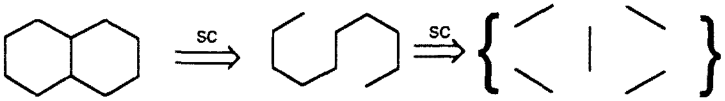


(2′)

For example, for the π-naphtalene, a corner has been multiplied by (-1), then taken over across, giving the second reduced VIF$^\pi$ of eq. (2). Each single line segment [3] at the end of eq. (2′) contributes a pair of bonding and antibonding MO levels; thus, eq. (2′) gives $\{n_+^\pi = n_-^\pi = 5\} = \mathrm{LPI}^\pi$.

In the sequence of eq. (1), each VIF$^\pi$ is *iso-LPI*$^\pi$ with the corresponding SF Kekulé structure and with the VIF$^\pi$ of a cut-open straight π-chain. For example:

VIF$^\pi$:



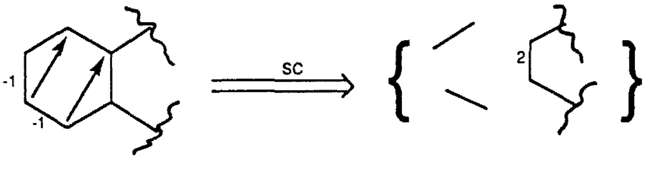
(3)

and in all three $\mathrm{LPI}^\pi = \{n_+^\pi = n_-^\pi = n/2;\ n_0 = 0\}$. In the neutrals, all the N_π electrons occupy the n_+^π bonding MOs. Thus, $N_+^\pi = 2n_+^\pi = N_\pi$ satisfies the qualitative criterion [6] for π-aromaticity (see also Dewar et al., refs. in [6]).

A full treatment of actual aromaticity should, however, involve distortion properties of the VIFs as well as the sigma VIFs, this paper being restricted to pi alone.

(b) PHENANTHRENE, PENTALENES, . . .

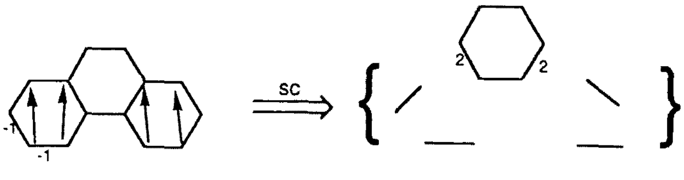
The VIF-piece reduction of eq. (4) is useful in obtaining the LPIs of multiple fused benzene rings:



(4)

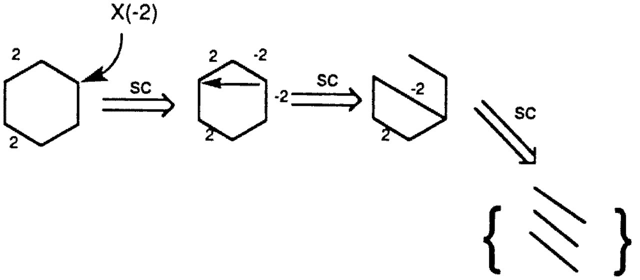
Thus, pi-phenanthrene becomes

VIF$^\pi$:



(5)

The distorted hexagon with two edges of strength 2 is reduced by first multiplying some corners by (−2):



(6)

From eqs. (6) and (5), LPI$^\pi$ = $\{n_+^\pi = n_-^\pi = 7\}$, iso-LPI$^\pi$ with the Kekulé structure.

The above applies for other non-straight polyacenes. Rule 1 [3,6] (multiplication of a corner by a $\kappa \neq 0$) indicates which distortions of the VIF$^\pi$ preserve the LPI$^\pi$, these modes being the smooth, soft ones.

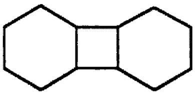
3. Biphenylene and other fused even-membered rings containing cyclobutadienes

The π-C_4H_4 itself has $n_0^\pi = 2$, which would give an $N_0^\pi = 2$ pi-biradical which, however, can stabilize by, e.g., a rectangular distortion if the sigma frame permits it [6]. However, what happens when such an anti-aromatic ring is fused with some otherwise aromatic rings? Will the polycyclic be anti-atomatic?

Take, for example,

BIPHENYLENE:

VIF$^\pi$:

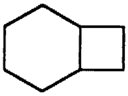


(7)

or

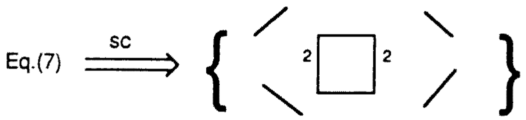
BENZ-CYCLOBUTADIENE:

VIF$^\pi$:



(8)

The π-biphenylene reduces by eq. (4) as:



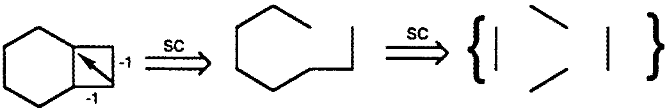
(9)

The flanking benz-rings cause the central square-like piece to come out sc-equivalent to a rectangle, with two of the sides of strength 2 (relative to the standard sides [6] of $1 = \beta/\beta_0$). The rectangle has $n_0 = 0$, with the overall π-biphenylene coming out with the $\mathrm{LPI}^\pi = \{n_+^\pi = n_-^\pi = 6\}$. Thus, this π-system is iso-LPI^π with the Kekulé structure of biphenylene,

(9′)

and is π-aromatic even though it appeared in the SF to contain a π-anti-aromatic cyclobutadiene portion. (Actually, a full aromaticity treatment will include the sigma portion and distortability properties.)

Similar conlusions are drawn from eq. (8):



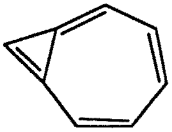
(10)

With two separately pi-anti-aromatic rings fused together ($4k$, $4k'$ ring combinations [6] ; $k, k' = 1, 2, 3, \ldots$), the pi-instabilities are again seen to be lost without any need of structural distortions. For example, the π-bicyclo [6.2.0] decapentalene, a combination of a π-eight ring with a π-four ring has the $\mathrm{LPI}^\pi = \{n_+^\pi = n_-^\pi = 5;\, n_0 = 0\}$ and $N_\pi = N_+^\pi = 10$. Combinations of $4k$-rings with $4k + 6$ rings [6] are also pi-stabilized.

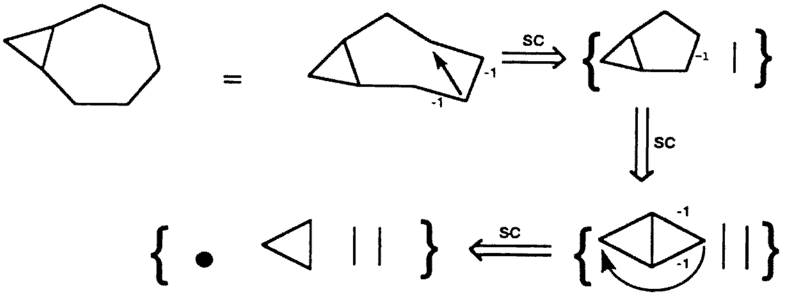
4. Other classes of π-bicyclo $[p.q.0]$ hydrocarbons also containing odd-membered rings

In paper II [6], we found that the single C_mH_m π-rings fell into four classes: (i) $m = 4k + 6$; $k = 0, 1, 2, 3, \ldots$, (ii) $m = 4k'$; $k' = 1, 2, 3$, (iii) $m = 4k + 3$; $k = 0, 1, 2, 3, \ldots$, and (iv) $m = 4k + 5$; $k = 0, 1, 2, \ldots$. Above, we have already looked at some π-cyclo $[p.q.0]$ systems, which are combinations of $4k'$ and $4k''$, of $4k'$ and $4k + 6$, and of $4k + 6$, $4k + 6$. Consider now the other types:

(a) HEPTALENE AND OTHER $4k + 3$, $4k' + 3$ FUSED RINGS



(bicyclo[5.1.0]...)



(11)

Therefore,

$$\mathrm{LPI}^{\pi} = \{n_+^{\pi} = 3,\ n_0^{\pi} = 1,\ n_-^{\pi} = 4\}$$

and

$$\mathrm{ECI}^{\pi}(N_\pi = 8) = \{N_+^{\pi} = 6;\ N_0^{\pi} = 2\},$$

where ECI^{π} are the "electron count indices", i.e. the electron occupations in the three MO types.

Thus, with the VIF rules we find the π-heptalene to have one NBMO. Without the bridge, we would have had two NBMOs. Another molecule with the same octagonal outer ring, i.e. bicyclo[4.2.0] in eq. (10), had no NBMOs.

From the LPI^{π} of π-heptalene (eq. (11)), we expect the anion to be unstable, the cation about the same as the neutral, and both less stable than the neutral Kekulé structure. Therefore, here we have a novel kind of "anti-aromaticity": the pi-energy is higher than the Kekulé sum of separate pi-bond energies, yet the last two electrons are not in a degenerate pair of NBMOs, which would be typical of the conventional or "Hückel anti-aromaticity" [7]. Perhaps we should call the (π-)heptalene an *"anti-Kekulé" molecule.*

More generally, with the π-bicyclo[$p.q.0$] HCs, which are fusions of two $4k + 3$ type π-rings, we have

$$4k + 3 = p + 2$$

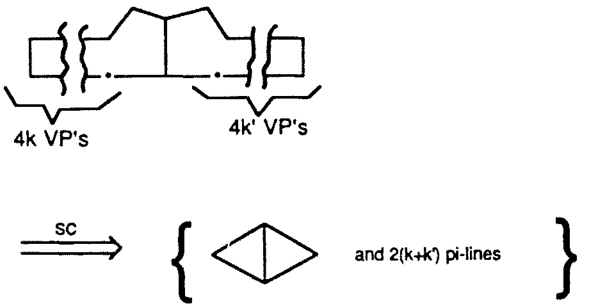
$$4k' + 3 = q + 2, \quad k, k' = 0, 1, 2, \ldots, \qquad (12)$$

giving

$p = 4k + 1$ and $q = 4k' + 1$.

Thus, $[p.q.0] = \{[1.1.0], [5.1.0], [5.5.0], [9.1.0], [9.9.0], \ldots\}$.

The general LPI^{π} is obtained with the rules [1–3] from the VIF^{π}:



(13)

Therefore:

$$\mathrm{LPI}^{\pi}(4k+3;4k'+3) = \{n_{+}^{\pi} = 2(k+k')+1;\, n_{0}^{\pi} = 1;\, n_{-}^{\pi} = 2(k+k')+2\}, \quad (14a)$$

or, from eq. (12):

$$\mathrm{LPI}^{\pi}(\text{bicyclo}\,[p.q.0] \text{ with } p = 4k+1,\, q = 4k'+1,\, k, k' = 0, 1, 2, 3, \ldots)$$

$$= \{n_{+}^{\pi} = (p+q)/2;\, n_{0}^{\pi} = 1;\, n_{-}^{\pi} = [(p+q)/2] + 1\}. \quad (14b)$$

In the neutral species, $N_{\pi} = p + q + 2$. Therefore, the N_{π} electron occupations (ECI) are:

$$\mathrm{ECI}^{\pi} = \{N_{+}^{\pi} = p + q;\, N_{0}^{\pi} = 2 \text{ (non-degenerate)}\}.$$

In the cut-open pi chain of m pi VPs, with $m = n = p + q + 2$, we would have had $n_{+}^{\pi} = n_{-}^{\pi} = [(p+q)/2] + 1$, as would the Kekulé SF^{π}-leading VIF^{π} of $[(p+q)/2] + 1$ isolated pi line segments with $N_{+}^{\pi} = p + q + 2$.

Equations (12) and on display the "anti-Kekulé" nature defined above (with two electrons in only one NBMO) of all the $(4k+3)$, $(4k'+3)$ bicyclo's.

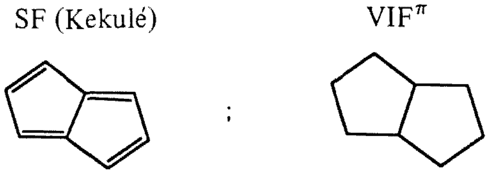
(b) PENTALENE AND OTHER $(4k+5)$, $(4k'+5)$ RING FUSIONS

Since $p + 2 = 4k + 5$ and $q + 2 = 4k' + 5$, with $k, k' = 0, 1, 2, \ldots$, this bicyclo $[p.q.0]$ sequence is $[p.q.0] = \{[3.3.0], [7.3.0], [7.7.0], \ldots\}$. The number n_{π} of pi-VPs is

$$n_\pi = p + q + 2 = 4k'' ,$$
$$\text{for } k'' = k + k' + 2 \ \text{ so that } \ k'' = 2, 3, 4, \ldots \, . \tag{15}$$

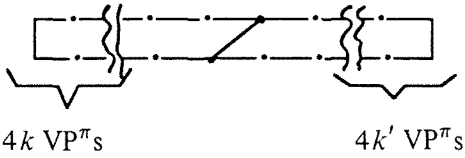
Were it not for the bridge, one would have the peripheral ring, which is of $4k''$ valency points. Again, the question arises whether the neutral ($N_\pi = n_\pi = 4k''$) species will loose the peripheral ring anti-aromaticity.

The prototype member ($k'' = 2$) is pentalene:



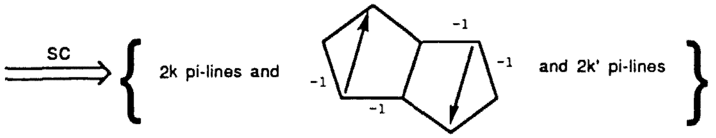
(16)

The general VIF$^\pi$ for the sequence is:

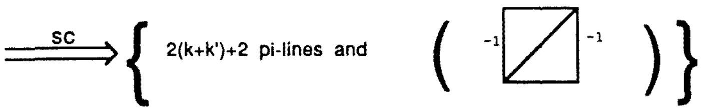


(17)

which reduces by the two rules into

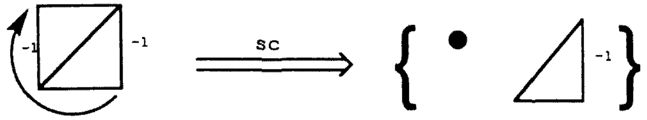


(17′)



(17″)

Then,



(18)

yielding an NBMO and a Möbius triangle which has $n_+^\Delta = 2$, $n_-^\Delta = 1$.

The overall LPI^π of the pentalene sequence is

$$\mathrm{LPI}^\pi(\text{bicyclo}\,[p.q.0],\ \text{with}\ p = 4k + 3,\ q = 4k' + 3,\ k,\ k' = 0, 1, 2, \ldots)$$

$$= \{n_+^\pi = [(p+q)/2] + 1;\ n_0^\pi = 1;\ n_-^\pi = (p+q)/2\}. \qquad (19)$$

Neutrals have $N_\pi = n_\pi$ electrons, so that

$$\mathrm{ECI}^\pi = \{N_+^\pi = 2n_+^\pi = p + q + 2;\ N_0^\pi = 0;\ N_-^\pi = 0\},$$

and the HOMO is bonding, LUMO nonbonding. Thus, the anions will be quite stable (about the same as the neutrals in the simple MO picture, but less stable due to electron repulsions and correlations [13]). Cations, too, will be close in stability to neutrals (small IP, EA). Note how different these properties are from the previous heptalene series.

(c) AZULENE AND OTHER $(4k + 3)$, $(4k' + 5)$ FUSED π-RINGS:

There are

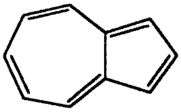
$$n_\pi = (4k + 3) + (4k' + 5) - 2 = 4k'' - 2, \qquad k'' = 2, 3, 4, \ldots \qquad (20)$$

pi-centers. The neutrals ($N_\pi = n_\pi$) would have the unbridged periphery $4N + 2$ Hückel π-aromatic. Is this property preserved once the bridge is formed?

The first members are:

SF:

,

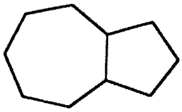


, ...

(21)

VIF^π:

,



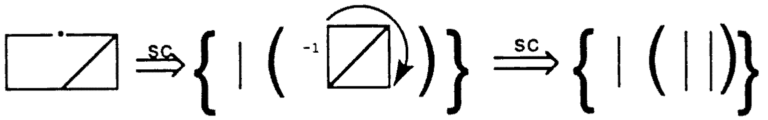
, ...

where bicyclo $[p.q.0]$ . . . , $p = 4k + 3$, $q = 4k' + 1$, k, $k' = 0, 1, 2, 3, \ldots$.

The general reduction is:

$\xrightarrow{\text{SC}} \Big\{$ 2k' pi-lines and $\Big($  $\Big)$ and 2k pi-lines $\Big\}$ (22)

where



(22′)

Thus, the "azulene sequence" is without any NBMOs:

$$\mathrm{LPI}^{\pi}(\text{bicyclo}[p.q.0],\ p = 4k' + 3,\ q = 4k + 1,\ k,\ k' = 0, 1, 2, \ldots)$$

$$= \{n_{+}^{\pi} = n_{-}^{\pi} = 2(k + k') + 3\}. \tag{23}$$

In the neutrals, all π-electrons are in n_{+}^{π} bonding MOs. The HOMO is bonding, LUMO antibonding. So the neutrals are poor electron acceptors and donors. Further, since the VIF^{π} is iso-LPI^{π} with the cut-open chain and with the Kekulé structure, the molecules of this sequence are π-aromatic (for full aromaticity, see also distortions and sigma VIF properties).

Note that although the azulene sequence is non-alternant [11], we nevertheless have $n_{+}^{\pi} = n_{-}^{\pi}$ (but not MO levels symmetrically disposed around the zero energy).

(d) BENZ-CYCLOPROPENYL AND OTHER $(4k + 6)$, $(4k' + 3)$ RADICALS

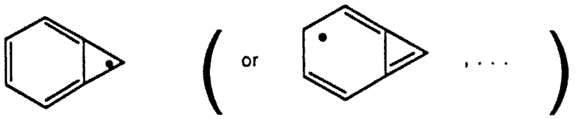
The number n_{π} of pi valency points (VP^{π}) is

$$n_{\pi} = (4k + 6) + (4k' + 3) - 2 = 4k'' - 1, \qquad k'' = 2, 3, 4, \ldots . \tag{24}$$

The neutral species are radicals. Anions ($N_{\pi} = n_{\pi} + 1$), if they were not bicyclo bridged, would have been $4N$-Hückel anti-aromatic systems. Similarly, the cations ($N_{\pi} = n_{\pi} - 1$), if unbridged, would have been the $4N + 2$ aromatic. However, what about the π-aromaticity/anti-aromaticity of the bridged species?

For the

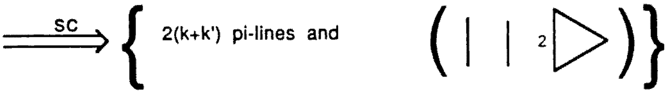
SF:



(25)

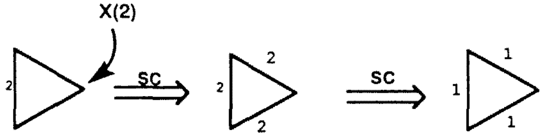
and higher ($k'' > 2$) members, the VIF^{π}s reduce into

VIF^{π}:



(26)

The flattened triangle reduces by rule 1 [3] into an equilateral triangle iso-LPI$^\pi$ with:



(27)

Therefore, the overall LPI$^\pi$s are:

$$\mathrm{LPI}^\pi(\text{bicyclo}[p.q.0], \{p, q\} = \{4(k+1), 4k'+1\}, k, k' = 0, 1, 2, \ldots)$$

$$= \{n_+^\pi = 2(k+k') + 3; n_-^\pi = 2(k+k') + 4\}, \tag{28}$$

and for the neutrals:

$$\mathrm{ECI}^\pi = \{N_+^\pi = 4(k+k') + 6; N_-^\pi = 1\}. \tag{29}$$

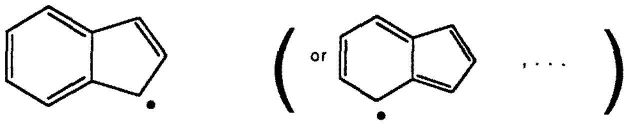
Both the HOMO and LUMO are antibonding. This makes it easier to form the cations, but not the anions.

(c) BENZ-CYCLOPENTADIENYL RADICAL (ITS CATION AND ANION) AND HIGHER $(4k+6)$, $(4k'+5)$ FUSED PI-RINGS

Here,

$$n_\pi = (4k+6) + (4k'+5) - 2 = 4k'' + 1, \quad k'' = 2, 3, 4, \ldots \tag{30}$$

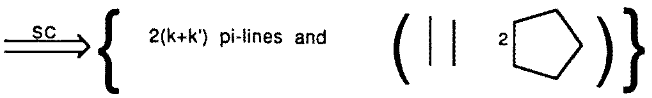
SF:



(31)

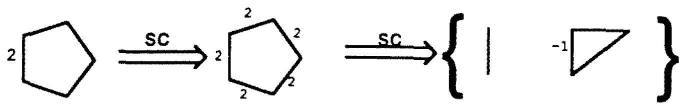
and higher members with the sc-reductions:

VIF$^\pi$:



(32)

with



(33)

Therefore,

$$\mathrm{LPI}^{\pi}(\text{bicyclo}[p.q.0], \{p, q\} = \{4(k+1), 4k'+3\},\ k,\ k' = 0, 1, 2, 3, \ldots)$$
$$= \{n_{+}^{\pi} = 2(k+k') + 5;\ n_{-}^{\pi} = 2(k+k') + 4\}. \tag{34}$$

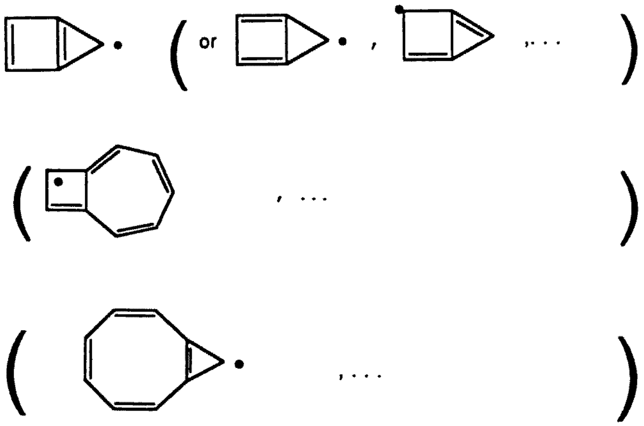
In the neutrals (radicals),

$$\mathrm{ECI}^{\pi} = \{N_{+}^{\pi} = 4(k+k') + 9;\ N_{0}^{\pi} = N_{-}^{\pi} = 0\}. \tag{35}$$

Both the HOMO and LUMO are now bonding. Thus, the anions would tend to be stable, but not the cations. Note that this is the reverse of the case in section (d).

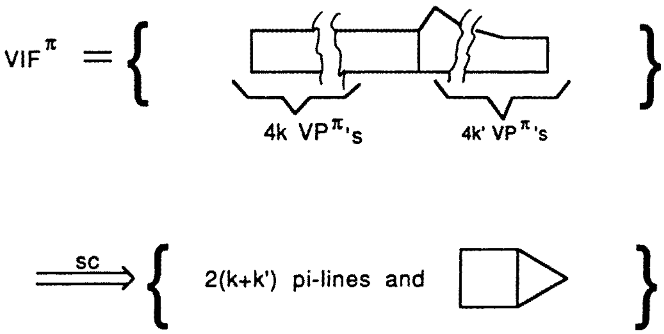
(f) BICYCLIC, FUSED $(4k+4)$, $(4k'+3)$ PI-RING SYSTEMS

SF:



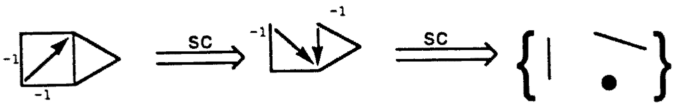
(36′)

and higher members, all with the



(36)

with



Thus,

$$\mathrm{LPI}^{\pi}(\text{bicyclo}[p.q.0], \{p, q\} = \{4k+2, 4k'+1\}, k, k' = 0, 1, 2, \ldots)$$
$$= \{n_+^{\pi} = 2(k+k') + 2;\ n_0^{\pi} = 1;\ n_-^{\pi} = 2(k+k') + 2\}. \tag{37}$$

As the last part of eq. (36) shows, the full VIF$^{\pi}$s are iso-LPI$^{\pi}$ with the Kekulé structure VIF$^{\pi}$s, e.g.

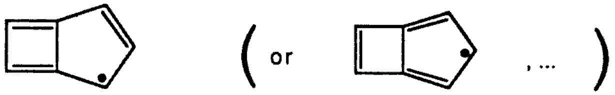
For the neutrals (radicals),

$$\mathrm{ECI}^{\pi} = \{N_+^{\pi} = 4(k+k') + 4;\ N_0^{\pi} = 1\}. \tag{38}$$

The anions, cations, and the radicals are iso-stable (at the qualitative LPI$^{\pi}$ level only, of course).

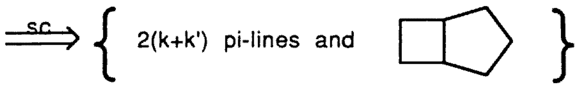
(g) THE $(4k+4)$, $(4k'+5)$ FUSED RINGS

SF:



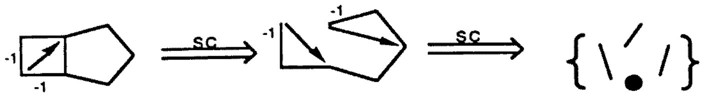
and higher members, with

VIF$^{\pi}$:



(39)

where



(40)

Hence:

$$\mathrm{LPI}^{\pi}(\text{bicyclo}[p.q.0], \{p, q\} = \{4k+2, 4k'+3\}, k, k' = 0, 1, 2, \ldots)$$

$$= \{n_{+}^{\pi} = 2(k+k') + 3; n_{0}^{\pi} = 1; n_{-}^{\pi} = 2(k+k') + 3\}. \tag{41}$$

The neutrals have $N_0^{\pi} = 1$. They are iso-stable (in the LPI$^{\pi}$ sense only) to their anions and cations, as well as being iso-LPI$^{\pi}$ with their cut-open polyenyl chains and with their Kekulé SFs VIF$^{\pi}$s.

We see that the last two classes of sections (f) and (g) are similar in their properties.

In the above sections, we have covered the bicyclo$[p.q.0]$ π-systems formed by the fusion of the four single π-ring classes [6], i.e. $(4k+4)$, $(4k+6)$, $(4k+3)$, and $(4k+5)$ membered rings. There are ten possible classes of planar bicyclo$[p.q.0]$ compounds, ten being the number of binary combinations of the four distinct single pi-ring classes. Table 1 summarizes the qualitative properties of the ten classes of bicyclo$[p.q.0]$ compounds that result. We see that each of the ten classes has quite distinct properties. Table 1 thus indicates that the ring classifications are phenomenologically relevant.

Table 1

The VIF predictions on pi-bicyclos

Bicyclos	HOMO	LUMO	LPI-stability[†]		
			Cations	Neutrals	Anions
$(4k+6) - (4k'+6)$	bonding	antibonding	unstable[†]	aromatic[†]	unstable
$(4k+6) - (4k'+4)$	bonding	antibonding	unstable	aromatic	unstable
$(4k+6) - (4k'+5)$	bonding	bonding	unstable	quasi-stable[*]	stable[†]
$(4k+6) - (4k'+3)$	antibonding	antibonding	stable	marginal	unstable
$(4k+4) - (4k'+4)$	bonding	antibonding	unstable	aromatic	unstable
$(4k+4) - (4k'+5)$	nonbonding	nonbonding	quasi-stable	quasi-stable	quasi-stable
$(4k+4) - (4k'+3)$	nonbonding	nonbonding	quasi-stable	quasi-stable	quasi-stable
$(4k+5) - (4k'+5)$	bonding	nonbonding	unstable	quasi-stable	quasi-stable
$(4k+5) - (4k'+3)$	bonding	antibonding	unstable	atomatic	unstable
$(4k+3) - (4k'+3)$	nonbonding	antibonding	quasi-stable	"anti-Kekulé"[§]	unstable

[†] Note that these refer only to the π-parts of the molecules (cf. text) and in the relative and qualitative sense only.

[*] "Quasi-stable" is used to distinguish these states from the "stable", where the HOMO is bonding while LUMO is antibonding, and from the "marginal", where the HOMO is antibonding. A quasi-stable molecule can accept or donate an electron without changing dramatically its energetic state.

[§] Cf. text.

We now proceed to the fused-ring systems involving more than two single rings.

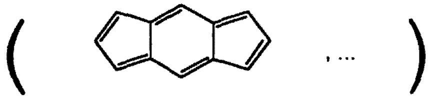
5. Larger polycyclic pi-systems: Methods and some examples

There are quite a few classes of compounds beyond the bicyclics. We therefore treat only some of them here, to indicate the general methods which involve, as in the bicyclics, reductions of the VIF$^{\pi}$s to a number of pi-line segments and a remaining bridging region, the 4k-VP removals, etc.

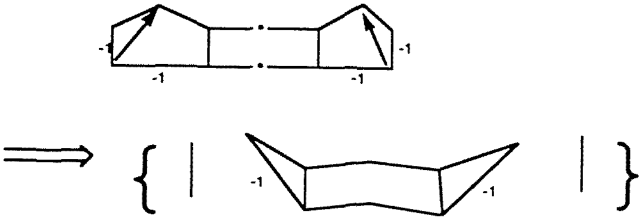
INDACENES

s-indacene:

SF:

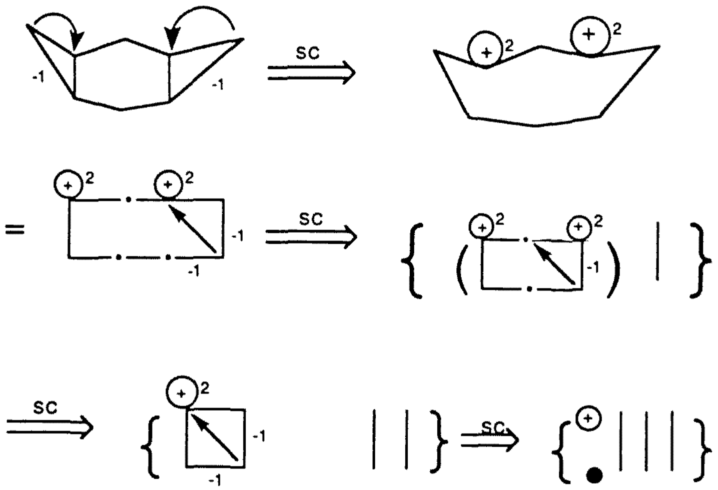


VIF$^{\pi}$:



(42)

and further reductions:



Hence:

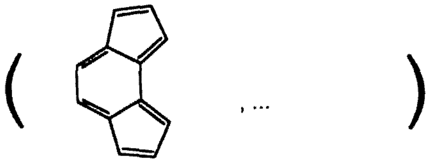
$$\mathrm{LPI}^{\pi} = \{n_{+}^{\pi} = 6, n_{0}^{\pi} = 1, n_{-}^{\pi} = 5\},$$

$$\text{(neutral) } \mathrm{ECI}^{\pi} = \{N_{+}^{\pi} = 12\}. \qquad (43)$$

The HOMO is bonding, LUMO nonbonding.

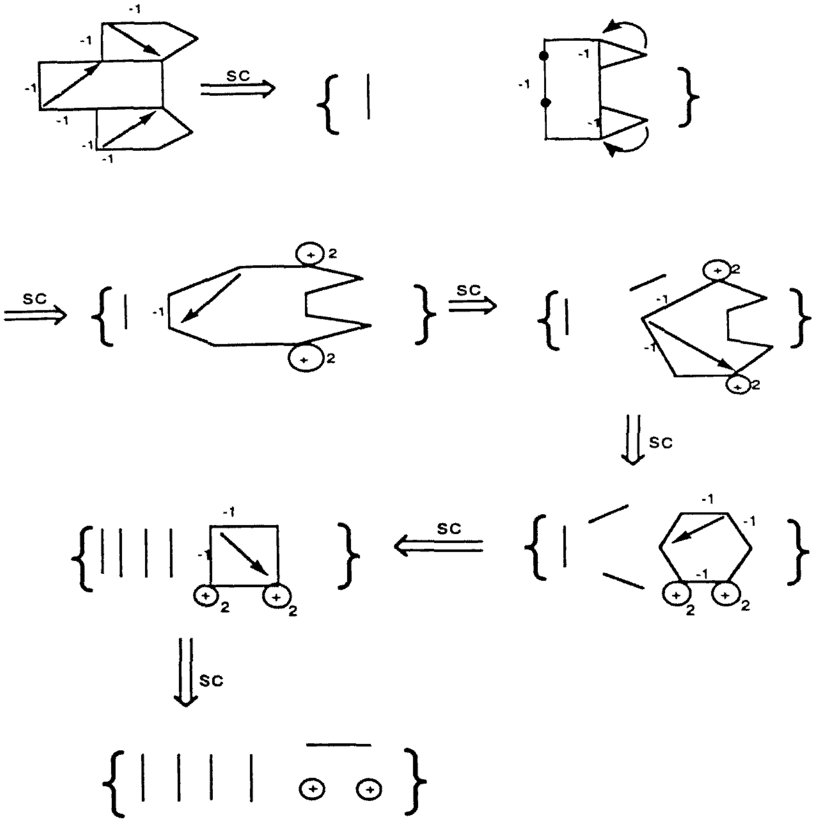
as-indacene:

SF:



(44)

VIF$^{\pi}$:



(45)

(cf. the loop subrules [3], derived from the two basic sc-rules).

Hence:

$$\mathrm{LPI}^{\pi} = \{n_{+}^{\pi} = 7,\, n_{0}^{\pi} = 0,\, n_{-}^{\pi} = 5\},$$

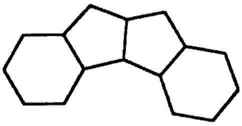
$$\text{(neutral) } \mathrm{ECI}^{\pi} = \{N_{+}^{\pi} = 12\}. \tag{46}$$

Now both the HOMO *and* LUMO are bonding. Thus, the anion of as-indacene should be more stable than that of s-indacene.

Dibenz-pentalenes:

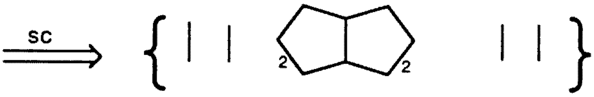
Take, for example, the 1.2, 5.6 isomer:

VIF^{π}:



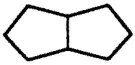
(47)

Reducing out $(4k)$ from each benz, we obtain



(48)

The central portion is like a distorted ($k = 2$ sides) pentalene, which is iso-LPI with the regular ($k = 1$) pentalene (to see this, multiply each VP by a number 2, then LPI is preserved). Thus,

$\mathrm{LPI}^{\pi} = \Big($ LPI of  $\Big)$

$+ \; (n_{+}^{\pi} = n_{-}^{\pi} = 4),$ (49)

or, since pentalene had $\{n_{+}^{\pi} = 4,\, n_{0}^{\pi} = 1,\, n_{-}^{\pi} = 3\}$, we get the LPI^{π} of eq. (47):

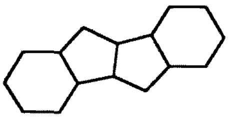
LPI^{π}(1.2, 5.6 dibenz-pentalene)

$$= \{n_{+}^{\pi} = 8,\, n_{0}^{\pi} = 1,\, n_{-}^{\pi} = 7\}. \tag{49'}$$

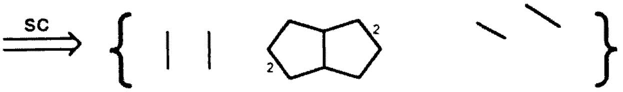
In the neutral molecule, $\mathrm{ECI}^{\pi} = \{N_{+}^{\pi} = 16\}$. The HOMO is bonding, LUMO nonbonding.

Let us compare this with the 1.2, 4.5 dibenz-pentalene isomer:

VIF$^{\pi}$:



(50)



(51)

The central portion is iso-LPI (by rule 1) [6] to a single-edge-distorted pentalene:

which differs in its LPI from the regular pentalene, the LUMO of the latter going from nonbonding to antibonding. Thus, the anion of 1.2, 4.5 dibenz-pentalene will be less stable than that of the C_{2v}-symmetric 1.2, 5.6 dibenz-pentalene isomer.

Any other pi-system, individually or in classes, can be treated with the two sc rules, as exemplified above.

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