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THE NEW PICTORIAL STRUCTURAL COVARIANCE METHOD FOR QUALITATIVE QUANTUM CHEMISTRY. II: ARENES WITH OR WITHOUT POLYENE SIDE CHAINS AND POLYENE BRIDGES

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Abstract

The aromaticity, anti-aromaticity, and two new types of behaviour of pi-hydrocarbons with one or more C_mH_m rings attached by polyene bridges and with or without several polyene side chains are readily obtainable "on the blackboard" directly from the structural formulae using the general pictorial method recently presented. The HOMO-LUMO types, number of non-bonding MOs, and qualitative stability are also deduced. The single pi-rings fall into four homolog classes characterized by their first members C_3H_3, C_4H_4, C_5H_5, and C_6H_6 rather than the two previous Hückel $4n$, $4n+2$ types. A general rule for finding the number of NBMOs for bridged combinations of such ring types is given.

1. Introduction

The present method [1,2] gives qualitative quantum chemical properties such as the number of bonding (n_+), nonbonding (# NBMOs = n_0), and antibonding (n_-) molecular orbitals (MO), that is, the "level pattern indices" (LPI = $\{n_+, n_0, n_-\}$), the HOMO-LUMO types, distortability, etc. of organic or inorganic molecules directly from structural formulae (SF) or ORTEP diagrams (X-ray crystallographic pictures of molecular structures). A series of papers [3,4] laid out the mathematical machinery which leads to the simple pictorial rules of this "structural-electronic formula" (SEF) method. The theory [1–4] involves (i) a dyad-space field living on the ordinary three-dimensional space, the former containing the effective one-electron Hamiltonians of an isomeric assembly of molecules; (ii) a principle of linear covariance; (iii) a resulting non-unitary classification of molecular-electronic structures or Hamiltonians into equivalence classes; (iv) and (v) principles of "structural" and "deformational" covariance resulting in the pictorial rules [1,2]. However, this mathematical background is not required for the use of the rules in day-to-day chemical reasoning on the blackboard, say, in chemical synthesis work.

Paper I [3] demonstrated the rules on diverse organic and inorganic contexts in detail. The present paper (paper II) treats π-rings alone, or as attached to polyene chains, or to each other via such chain bridges. Paper III will deal with π-polycycles (edge-fused multiple rings with or without side chains in large classes).

The Hückel [5] $4n + 2$ rule classified single rings into two types, aromatic for $4n + 2$, anti-aromatic for $4n$ rings (actually, electrons in the Hückel rule, cf. below), with $n = 1, 2, 3, \ldots$. We shall find below that single rings fall into four distinct classes rather than two. The new rules give the MO LPIs not only for monocycles, but also for any other π-system as well, such as styrene, fulvadiene, etc. There is, of course, also the well-known Frost–Musulin [6] algorithm and its Möbius extension by Zimmerman [7], which give the actual MO energy level values, not only the LPIs. However, also these polygon-in-circle algorithms apply only to monocycles, to the regular π-polygons.

2. Summary of the graphical "structural covariance" rules

A structural formula (SF) is first drawn as a more detailed "structural-electronic formula" (SEF), as described in paper I [3]. Each AO is represented by a valency point (VP); a line is drawn between pairs of VPs tentatively or definitely thought to be interacting. In the special case of planar π-systems, this leads to the familiar "molecular diagrams", but for an arbitrary sigma or sigma-pi molecule, one gets the more general SEF which one might also call a "valency-point interaction formula", VIF. The VIF does not depict a wave function as the valence bond (VB) structure did. It depicts the effective one-electron Hamiltonian of the given molecular structure. Thus, VIF yields qualitative HOMO-LUMO reactivity, lowest valence shell excited states as well as the ground-state properties, together with information on anions and cations of the species.

The "structural covariance" (sc) theorem of references [1–4] is:

All VIFs obtainable from each other by the two rules given below (and/or permutations of the VPs) have the same MO LPI. Such VIFs will be said to be structurally covariant (designated "sc"). These sc-VIFs (or actual molecules) are in the same equivalence class [4]. Then, provided the electron occupations, or electron count indices (ECI $= \{N_+, N_0, N_-\}$), in the one-electron levels are also the same, the sc molecules will have very roughly the same "thermicity", i.e. qualitative thermochemical stability (regarding energy alone, to be supplemented by entropy, solvent effects, etc. considerations if need be).

RULE 1

Any VP in a VIF may be multiplied by an arbitrary constant, positive or negative, but nonzero, κ. Multiplying a VP by κ means multiplying the strengths of the lines emanating from that VP by κ. After this kind of multiplication, the resulting and original VIFs have the same LPI.

Multiplication changes or distorts the VIF and its actual molecular structure. Changes in the interatomic β parameters, e.g. those in a Hückel method, can be made, and whether these cause a change in the quality of the MOs, i.e. of the LPI, may be examined by this rule.

RULE 2

Any VP in a VIF may be lifted up and placed onto any other VP′, carrying its lines along to the new VP′. The original lines of the initial VP and that VP itself are retained in the VIF. If two lines superimpose, their strengths add algebraically. The new resulting VIF′ and the initial VIF will have the same LPI and thus be sc with each other.

Below, we take the π-system VIFs (cf. other papers in this series for the inclusion of the sigma parts as well) with standard nearest-neighbour VP–VP′ interaction lines taken to have unit strength ($\beta/\beta_0 = 1$), all self-energies of the VIFs have the same (α) and taken out of the one-electron Hamiltonian, as is customary, so that the VIF here will depict the

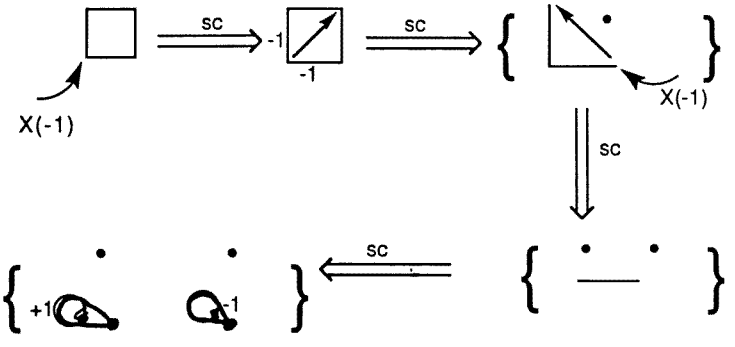
$$\bar{h} = (h - \alpha I)/\beta_0 ,$$

or some such effective Hamiltonian.

3. π-monocycles (cyclopropenyl radical and anion, cyclobutadiene, cyclopentadienyl, benzene, cycloheptatrienyl, and other π-systems, $C_m H_m$) and their classification

Consider first the examples π-C_4H_4 and π-C_6H_6 for obtaining their LPIs with the rules (although these cases can be obtained by the circle algorithm [6]).

C_4H_4: π-VIF:



(1)

Therefore, LPI = $\{n_+ = 1, n_0 = 2, n_- = 1\}$.

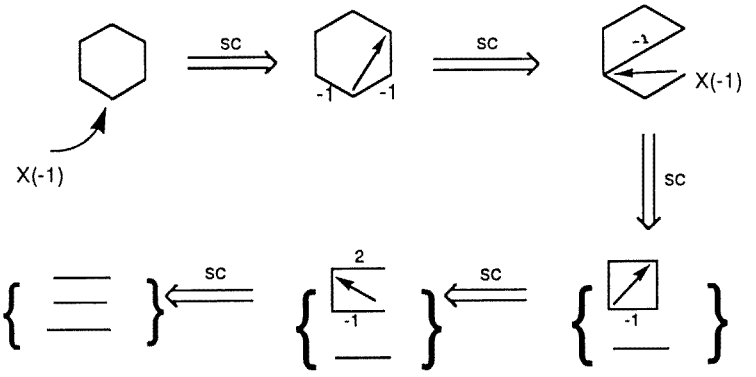
With no strengths shown, the

$$\bar{A}_{ij} = \{|e_i\rangle\langle e_j| + |e_j\rangle\langle e_i|\}$$

lines [2,4] between the AO kets $|e_i\rangle$ and $|e_j\rangle$ are taken to have coefficient unity. Multiplication of one corner with (-1) makes two lines of (-1) strength. Then by rule 2, that corner is taken onto the opposite corner, thereby cancelling out two lines. Proceeding similarly, we obtain two free VPs (hence $n_0 = 2$), and a single segment (•——•) which (as shown in detail in [3]) breaks up into a (-1)- and $(+1)$-strength loop. Thus, the LPI is read off. Along the way, a number of VIFs, all with the same LPI as the square (hence all sc), have also been obtained.

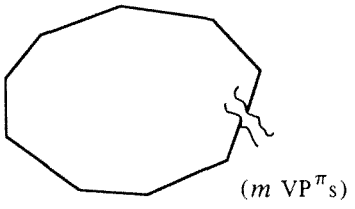
Note that in reducing the VIF of a ring toward the LPI, the strategy is to first open the ring.

Similarly, in eq. (2) benzene yields the familiar $\{n_+ = n_- = 3\}$ result:



(2)

Now, for the general annulene C_mH_m, the π-VIF,

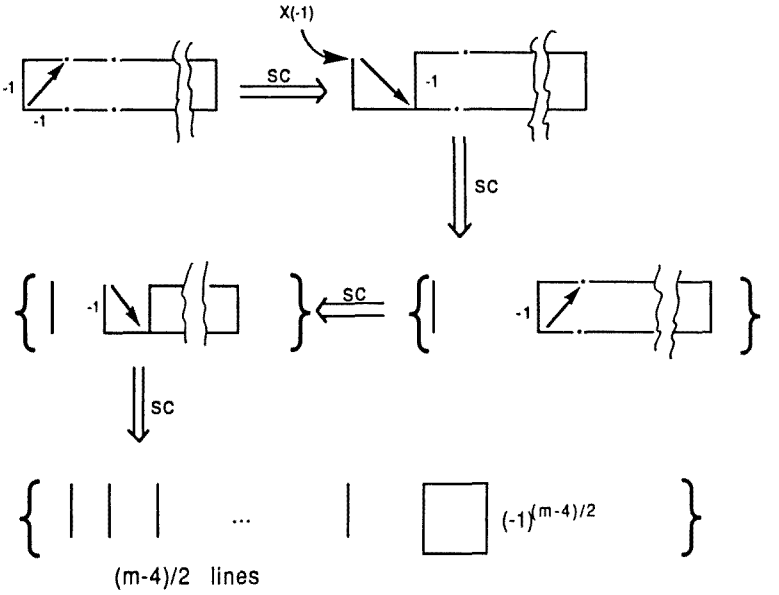


(3)

we have:

(a) The m = even cases (see below for the π-VIF and its reduction).

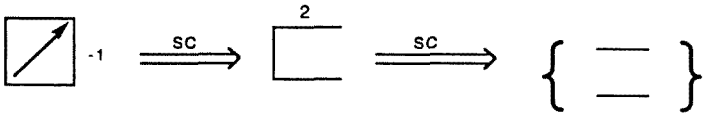
The π-VIF is iso-LPI for m even with $(m - 4)/2$ single line segments and a square with one edge of sign $(-1)^{(m-4)/2}$.



(4)

Thus, for π-C_mH_m with m = even, if

(a1) $(m - 4)/2$ = odd(= $2k + 1$ with $k = 0, 1, 2, \ldots$), then the residual square of eq. (4) will have a minus edge (hence a Möbius square [7]), being thereby of $n_+ = 2$, $n_- = 2$, as seen in eq. (4′):



(4′)

If

(a2) with m = even in C_mH_m, $(m - 4)/2$ = even, then the square is all positive-edged (Hückel square [5]), with the reduction as in eq. (1).

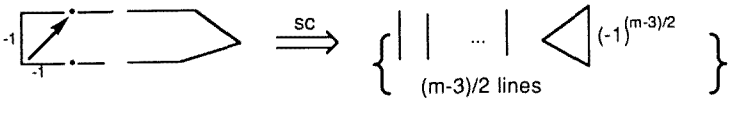
Thus, for m = even, and $(m - 4)/2$ = odd,

$$\text{LPI} = \{n_+ = n_- = m/2\}. \tag{5a1}$$

For m = even, and $(m - 4)/2$ = even,

$$\text{LPI} = \{n_+ = n_- = (m/2) - 1; n_0 = 2\}. \tag{5a2}$$

(b) For π-C_mH_m cases where m = odd, the VIF is



(6)

Thus:

$$m = \text{odd, and } (m-3)/2 = \text{odd},$$

$$\text{LPI} = \{n_+ = [(m-3)/2] + 2,\ n_- = [(m-3)/2] + 1\}, \qquad (6'b1)$$

$$m = \text{odd, and } (m-3)/2 = \text{even},$$

$$\text{LPI} = \{n_+ = [(m-3)/2] + 1,\ n_- = [(m-3)/2] + 2\}. \qquad (6'b2)$$

Thus, we see four types of C_mH_m, depending on the number m. The four series of eqs. (5) and (6) may also be written as:

$$\begin{aligned} C_mH_m: \quad &\text{(i)} \quad m = 4k+3; \qquad k = 0,1,2,3,\ldots \\ &\text{(ii)} \quad m = 4k+5; \qquad k = 0,1,2,3,\ldots \\ &\text{(iii)} \quad m = 4k+4; \qquad k = 0,1,2,3,\ldots \\ &\text{(iv)} \quad m = 4k+6; \qquad k = 0,1,2,3,\ldots \end{aligned} \qquad (7)$$

The smallest prototypes of the modulo-4 series are (i) C_3H_3; (ii) C_5H_5; (iii) C_4H_4; (iv) C_6H_6.

Equations (7) could also have been written as $\{m = 4k' - 1\}$, $\{m = 4k' + 1\}$, $\{m = 4k'\}$, and $\{m = 4k' + 2\}$, with $k' = 1, 2, 3, \ldots$. For the neutral species ($m = N_\pi$ = the number of π-electrons), the Hückel $(4n + 2)$ rule would cover cases (iii) and (iv) of eqs. (7). We see that there are two more classes in eqs. (7). Further, the present rules are based on the number of π-AOs occurring in the VIF (or SEF), and not on the number of π-electrons, as is the case for the Hückel $(4n + 2)$ rule. Thus, eqs. (7) will distinguish between species with the same number of π-electrons, depending also on the size of the polygon frame; for example, with $N_\pi = 6$; $C_7H_7^{+1}$ cation, C_6H_6, and $C_5H_5^{-1}$ anion will have different VIF/LPI electronic features, distortability, etc.

The correspondence between eqs. (7) and eqs. (5), (6) is given in eq. (8):

$$\begin{aligned} &m = \text{even}, (m-4)/2 = \text{odd}, \quad \text{then } m = 4k+6, \\ &m = \text{even}, (m-4)/2 = \text{even}, \quad \text{then } m = 4k+4, \\ &m = \text{odd}, (m-3)/2 = \text{odd}, \quad \text{then } m = 4k+5, \\ &m = \text{odd}, (m-3)/2 = \text{even}, \quad \text{then } m = 4k+3, \\ &\qquad \text{all with } k = 0,1,2,3,\ldots \end{aligned} \qquad (8)$$

The LPI^π of the four classes lead to some qualitative stability properties. For example:

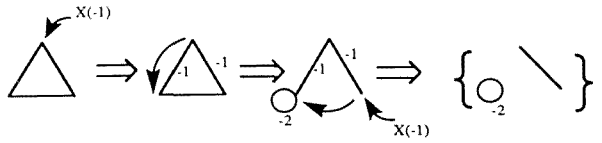
(i) the $m = 4k + 3$, $k = 0, 1, 2, 3, \ldots$ series $\{C_3H_3, C_7H_7, C_{11}H_{11}, \ldots\}$ has the $LPI^{\pi} = \{n_+ = [(m-3)/2] + 1; n_- = [(m-3)/2] + 2\}$. There is an odd number of electrons $N_{\pi} = m$ in the neutral species of this series, so they are radicals*. The highest occupied MO, the HOMO, is antibonding, as is the lowest unoccupied MO, the LUMO. Thus, the anions $C_mH_m^{-1}$ are not favoured, and the cations $C_mH_m^{+1}$ are, because the latter result from the removal of the antibonding electron from the free radical. The radicals should react mainly with electrophiles☆. (For very large rings, however, one should also consider the nonplanarity caused by the sigma frame.)

(ii) The $m = 4k + 5$, $k = 0, 1, 2, 3, \ldots$ series $\{C_5H_5, C_9H_9, C_{13}H_{13}, \ldots\}$ has the $LPI^{\pi} = \{n_+ = [(m-3)/2] + 2; n_- = [(m-3)/2] + 1\}$. The neutral radicals now have bonding HOMOs and bonding LUMOs. Thus, the radicals are more stable than the previous series, and more so than their cations $C_mH_m^{+1}$. The anions $C_mH_m^{-1}$ would also be more stable (caution with the sigma-frame-caused non-planarity of the large rings, however). The radicals should be reactive towards nucleophiles and electron-donating agents.

(iii) The $m = 4k + 4$, $k = 0, 1, 2, 3, \ldots$ series $\{C_4H_4, C_8H_8, C_{12}H_{12}, \ldots\}$ has the $LPI^{\pi} = \{n_+ = n_- = (m/2) - 1; n_0 = 2\}$. The last two electrons of the neutrals are in a degenerate pair of nonbonding MOs. This has been taken as the criterion for anti-aromaticity (Hückel $4n$ systems [5]). A full discussion of aromaticity and anti-aromaticity would, however, require the distortability properties of both the pi and sigma systems, and is deferred. Here, we examine the standard VIF^{π} only. The standard VIF^{π} itself becomes unstable (regardless of the electron occupations) with respect to

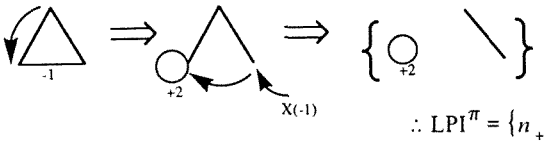
*At the suggestion of one of the referees, we add here the reduction of both a Hückel and a Möbius triangle, as this case also illustrates the use of one of the loop subrules given in paper I [3].

Hückel case:



$\therefore LPI^{\pi} = \{n_+ = 1, n_- = 2\}$

Möbius case:



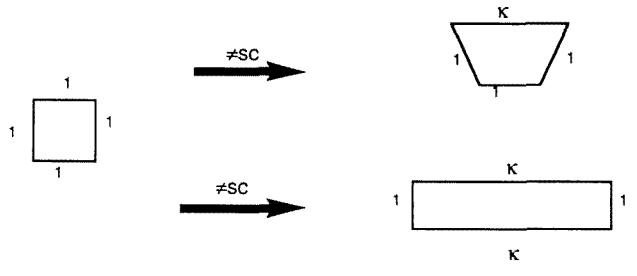
$\therefore LPI^{\pi} = \{n_+ = 2, n_- = 1\}$

☆For the experimental properties of cyclopropenyl radical, its anion, and cation with various substituents, as well as the properties of some $4k + 5$ species (see text), we refer to A. Streitweiser, Jr., *Molecular Orbital Theory for Organic Chemists* (Wiley, 1961), and for some early MO considerations on some of the species related to those in the present papers II and III to J.D. Roberts et al. J. Amer. Chem. Soc. 74(1952)4579.

some distotions, if those distortions are physically permitted or reinforced by the distortion requirements of the sigma frames.

As an example, the C_4H_4 VIF^{π} is unstable, for example, with respect to the distortions shown in eq. (9). Such distortions stabilize the π-system of C_4H_4. The resulting VIF^{π}s with more favourable LPI^{π}s, turning the HOMO from an NBMO, nonbonding, into a bonding one, are not structurally covariant ($\neq$ sc) with the initial square. They cannot be obtained by the two rules.

C_4H_4, VIF^{π}:

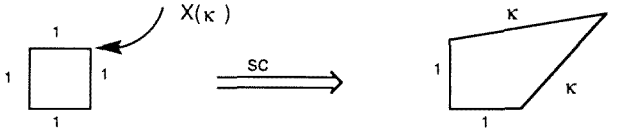


(9)

$(n_+^{\pi} = n_-^{\pi} = 1; n_0^{\pi} = 2)$ $(n_+^{\pi} = n_-^{\pi} = 2)$

$(N_+^{\pi} = 2; N_0^{\pi} = 1 + 1')$ $(N_+^{\pi} = 4)$.

On the other hand, a distortion, eq. (10), results from the multiplication of a corner by any $\kappa \neq 0$ and is sc, not stabilizing.



(10)

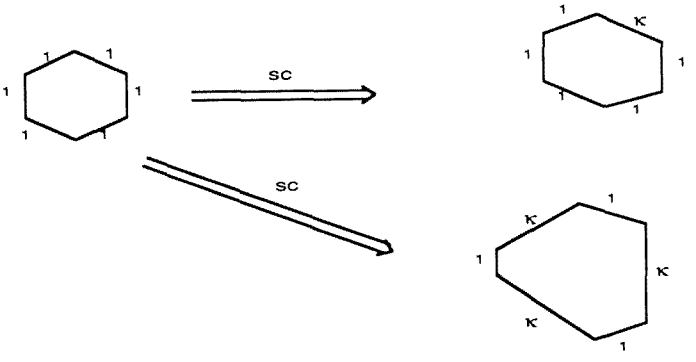
The C_4H_4 π-potential energy surface has a maximum at the perfect square shape, the distortions of, for example, eq. (9) leading rapidly downhill, while those of eq. (10) going more or less flat. So, the square is more like on a ridge, rather than a sharp cone of a hill in all directions.

(iv) The $m = 4k + 6$, $k = 0, 1, 2, 3, \ldots$ series $\{C_6H_6, C_{10}H_{10}, C_{14}H_{14}, \ldots\}$ has the $LPI^{\pi} = \{n_+ = n_- = m/2\}$. With $N_+^{\pi} = m = 2n_+^{\pi}$, all the π-electrons in the neutrals are in bonding MOs, with the LUMO antibonding. This makes the π-ring unreactive towards both electrophiles and nucleophiles. This has been taken as the criterion for aromaticity (Hückel $4n + 2$ systems, $m = 4k + 6 = 4k' + 2$). Dewar and others [9] have given a more extended criterion. They compare the stability of a cyclic π-system with that of the cut-open chain [10].

A qualitative criterion for aromaticity, anti-aromaticity, and the other two above types, is obtained from the present method.

Compare the VIF^{π}s and their LPI^{π}s of the given π-system with that of the cut-open version *and* with the LPI^{π} of a Kekulé structure from the initial structural formula (SF). If all these have the same LPI^{π} and all electrons can be assigned to bonding MOs, i.e. to n_{+}^{π}, then the system is aromatic. However, we again note that a more complete treatment of aromaticity will require the examination of the distortability modes of the π-system, as well as the VIF properties of the sigma frames.

Returning to the C_6H_6, $C_{10}H_{10}$, . . . ($m = 4k + 6$) series, the above LPI^{π} shows that the neutral π-rings are more stable than either the cations or the anions. If we now examine the π-ring distortions with the two rules, we see that the distortions analogous to those in eq. (9) now do not change the LPI^{π}. Thus, for example those of eq. (11), are smooth distortions on a plateau, with the MO levels changing, not in LPI type, but only slowly for $\kappa \neq 0$.



(11)

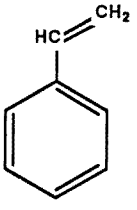
Thus, there is no major stability to be gained by such distortions of the π-hexagon, unlike in the π-square, and the average π-structure VIF^{π} remains at the regular hexagon. However, while these π-distortions are smooth, the sigma distortions are "hard" and sharper (for some modes), giving a stiff sigma frame to C_6H_6 (the sigma part deferred to other papers). The special stability of the actual benzene molecule (sigma and pi both) appears to involve both these aspects. This is reasonable since chemically, aromaticity involves a lack of tendency to add to the π-system, but it also involves substitutional reaction properties, which again involves mostly a sigma effect.

4. Arenes linked to polyenes

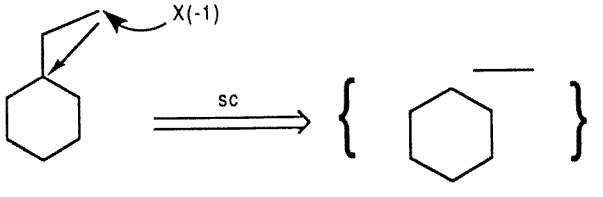
The VIF method allows one to examine the qualitative properties such as aromaticity, reactivity, and distortions of molecules not confined to single rings. The numbers of NBMOs, the LPI^{π}s, etc. of arbitrary molecules are readily obtained by the two rules on the VIF. Take, for example,

(a) STYRENE AND OTHER PHENYL POLYENES

Styrene, the SF:



The VIF^{π} (planar SF case):



(12)

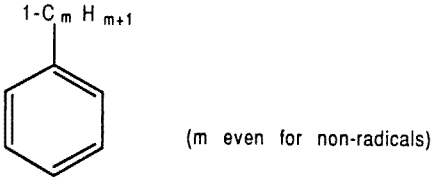
Therefore,

$$LPI^{\pi} = \{n_+ = n_- = 4\},$$

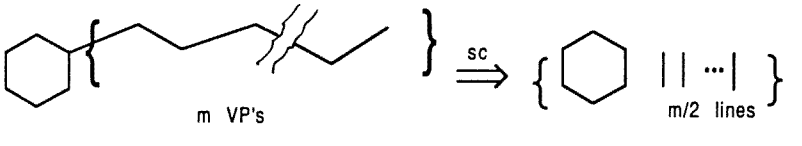
$$ECI^{\pi} = \{N_+ = 8; N_- = N_0 = 0\}.$$

Or, more generally:

1-phenyl polyenes, the SF (planar):



VIF^{π}: (13)

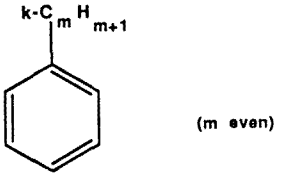


Therefore,

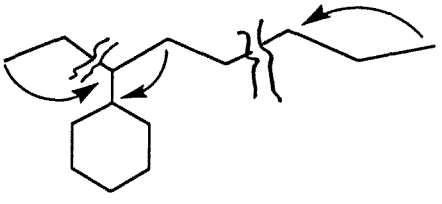
$$LPI^{\pi} = \{n_+ = n_- = (m/2) + 3\},$$

or k-phenyl-polyenes attached at the kth carbon of the chain (see below).

k-phenyl polyenes, the SF, m even:



VIF$^{\pi}$: (14)

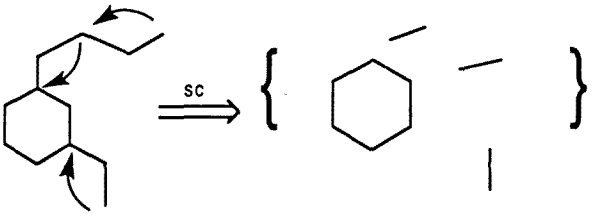


$$LPI^{\pi} = \{n_+ = n_- = (m/2) + 3\}.$$

Thus, the homologs in eqs. (13) and (14) have the same LPI$^{\pi}$.

SF, {o-, m-, or p-} dipolyene substituted benzene

VIF$^{\pi}$, e.g.:



(15)

and so on.

For any non-radical (m = even) polyenes-substituted benzene, the VIF$^{\pi}$ reduces into a benzene VIF$^{\pi}$ and $m/2$ single π-line segments, each π-line indicating by the principle of linear covariance [2,4] a pair of overall MOs over the entire π-system, the pair being one bonding, one antibonding, delocalized MO.

Thus, for any polyenes-substituted benzene, including several chains, the LPI$^{\pi}$ is the sum(union) of the LPI$^{\pi}$ of the ring plus the LPI$^{\pi}$ of each polyene itself, for the

case of the overall system remaining essentially planar so as not to introduce additional lines in the VIF^{π}. The ring π-system is then *qualitatively* not affected, i.e. it remains aromatic.

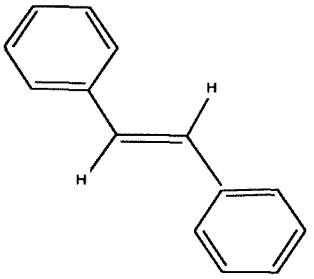
(b) OTHER SINGLE PI-RINGS WITH POLYENE SIDE CHAINS

The above general rule applies to any other π-ring C_qH_q with one or more even m polyenyl substituents (C_mH_{m+1}, m even) at any carbon (but overall planar, or planar VIF^{π} preserving shapes). If C_qH_q were anti-aromatic, it would remain so with the even polyenes attached, and so on. The reactivities of the side chains and the ring would retain their individual qualities when mutually attached.

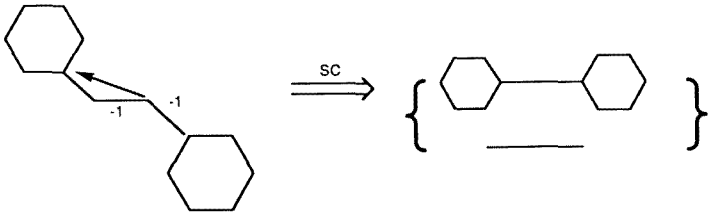
(c) STILBENE AND OTHER POLYENE-BRIDGED RINGS

We now examine the VIF^{π} of stilbene and other polyene-bridged rings, keeping in mind, however, that a full treatment would involve the sigma part as well. We restrict ourselves to planar or quasi-planar (same VIF^{π}) cases (although the planar molecules may not be the stable forms due to the ring hydrogens; cf. the biphenyl discussion below).

Stilbene(trans), the SF:



VIF^{π} (quasi-planar π-system, cf. the biphenyl discussion in the text):



(16)

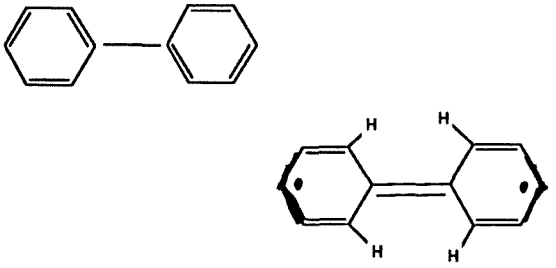
The negative sign in the biphenyl-like piece can be replaced by a plus sign, the piece remaining structurally covariant as can be seen by the multiplication of the

successive vertices of one of the hexagons by (-1). (The minus sign does not occur in biphenyl itself in the next section, and therefore does not affect its deformational properties either.)

Thus, the LPI^{π} is that of the sum(union) of the LPI^{π}s of ethylene and of biphenyl for the planar case (this also applies to the alkyne-bridged case).

For *biphenyl* itself, which has the SF resonance structures, eq. (17) in a planar structure is readily reduced in eq. (18) into two benzene π-rings, with the total $\mathrm{LPI}^{\pi} = \{n_{+}^{\pi} = 6; n_{-}^{\pi} = 6\}$, stable and aromatic, with $N_{+}^{\pi} = 12$.

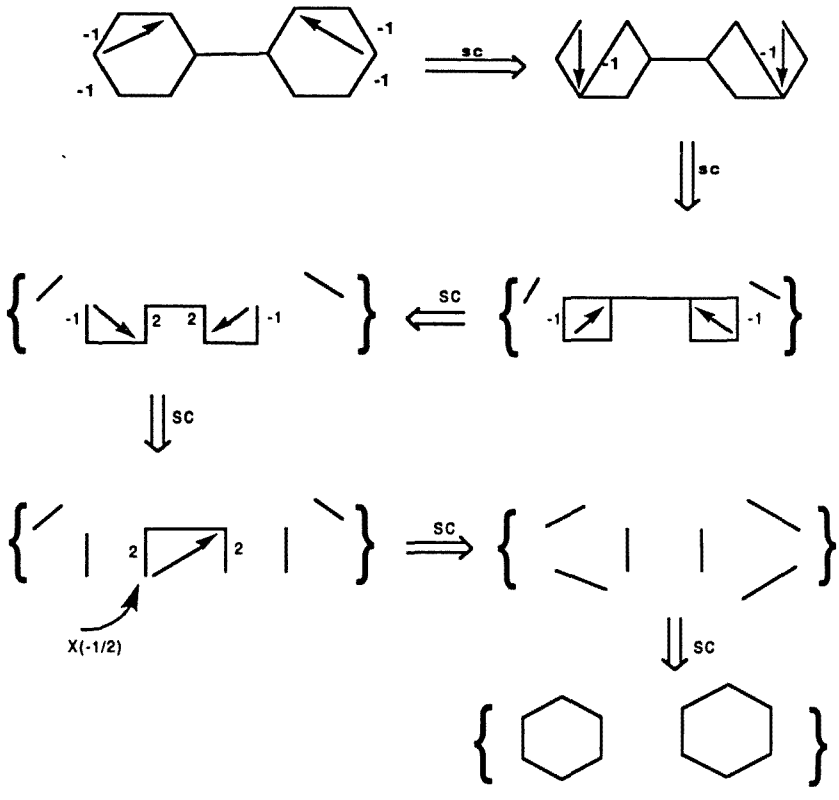
Biphenyl, the resonance structures:



(17)

(planar; has steric effects. cf. text)

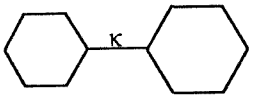
VIF^{π}:



(18)

Further, we see from eq. (18) that, had the π-bridging interaction line between the two π-rings been stretched out by a $\kappa \neq 1$, the reduction would have proceeded just the same all the way from $\kappa = 1$ (π-biphenyl) to $\kappa = 0$ (two π-benzenes). Thus, the biphenyl VIF^{π} is not only structurally covariant (sc) with the final VIF^{π} (two π-benzenes) in eq. (18), i.e. with the same LPI^{π} in the initial and final VIF^{π}s, but also these two end VIF^{π}s are deformationally covariant (dc) [4]. That is, the LPI^{π} remains the same during the full deformation from the initial to the final VIF^{π} along the entire bridge stretch path ($\kappa = 1$ to $\kappa = 0$) in eq. (19):

VIF^{π}s:



(19)

$$0 \leqslant \kappa \leqslant 1$$

$$LPI^{\pi}(0 \leqslant \kappa \leqslant 1) = \{n_{+}^{\pi} = 6; n_{-}^{\pi} = 6\}.$$

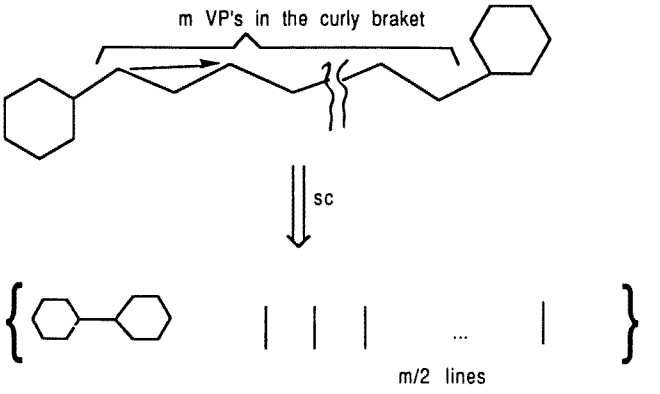
The π-system will not, therefore, have a qualitatively large barrier over this path, only some loss of delocalization. (In the actual molecule and bridge stretch reaction path, the sigma frame VIF^{σ} will be the barrier-determining factor.)

The π-biphenyl of eq. (17) has actually been for a *planar* conformation which, in reality, is opposed by the sigma and VSEPR (i.e. steric) effects of the hydrogens of adjacent rings. The non-planarity twist of one ring against the other breaks up the VIF^{π} into two separate benzene VIF^{π}s. The twist away from planarity also affects the VIF^{π} by changing the π-bridge line κ from one towards zero, as in eq. (19). Thus, the π-system still does not provide a qualitative barrier for this mode as the LPI^{π} remains the same during the dc twist all the way to the two end π-benzenes in going from a planar into the twisted biphenyl conformation or the reverse path. Therefore, any actual qualitative effect should arise mainly from the sigma frame, including the hydrogens' VSEPR ("valence shell electron pair repulsion", the same thing as "steric") effects. The π-part would actually lower the barrier due to π-delocalization over both rings in the planar conformation within the iso-LPI^{π} situation.

1, *m*-DIPHENYLPOLYENES (*m* EVEN)

The steric effect between the nearest ring hydrogen and the first one of the chain hydrogens again favours the ring-twisted, non-planar structures. However, in the planar state between twists (and in the alkyne-bridged cases), the planar-originated VIF^{π} is as follows.

VIF^{π} (m even):



(20)

Therefore,

$$LPI^{\pi}\,(\text{planar}) = \{n_{+}^{\pi} = n_{-}^{\pi} = (m/2) + 12\}.$$

This is the same LPI^{π} as the actual rings-twisted molecule, m-polyene (m even). Thus, the π-system itself does not provide a barrier as compared to sigma and hydrogens in the paths between opposite twists passing through the planar to the final state of eq. (20). In fact, the planar case is favoured somewhat, by the π-delocalization energy (albeit within the same LPI^{π} context).

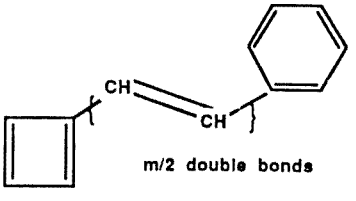
The m = odd cases lead to one NBMO, $n_0^{\pi} = 1$, but the same arguments about non-planarity apply, and twisting from a planar conformation could occur.

In the *1, 1-diphenylethylene,* in *tri-* and *tetra-phenylethylenes,* the situation is similar to the above ethylene-bridged cases. In all, the VIF^{π}s for the planar conformations reduce into the LPI^{π}s of separated benzene π-rings and a π-ethylene. Thus, the full VIF^{π}s favour planarity, while twists of rings away from planarity may be caused by the sigma frames including the hydrogens.

5. Cyclobutadiene or other $4k'$-rings ($k' = 1, 2, \ldots$) with or without $4k + 6$ rings ($k = 0, 1, 2, \ldots$) on an m-polyene backbone or bridge

Take, for example, the planar form of the following.

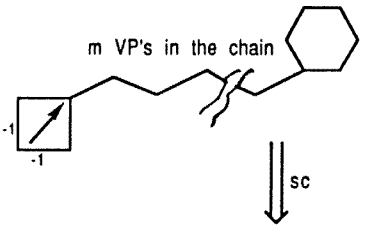
SF (m even):



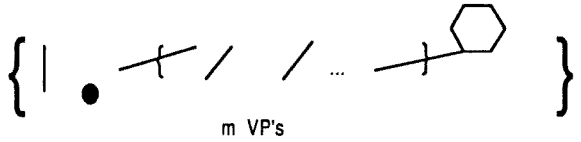
(21)

before any distortions of the $4k'$ ring. Then, the VIF^{π} is as follows.

VIF^{π} (m even):

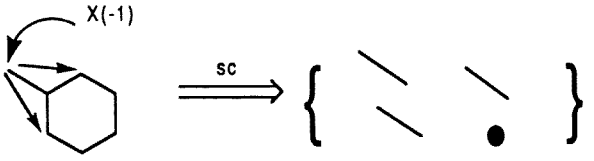


(21′)



(21″)

Then, since



(22)

we get from eqs. (21″) and (22) that

$$LPI^{\pi}\ (m \text{ even}) = \{n_+ = n_- = [(m + 10)/2] - 2;\ n_0 = 2\}$$

for eq. (21′).

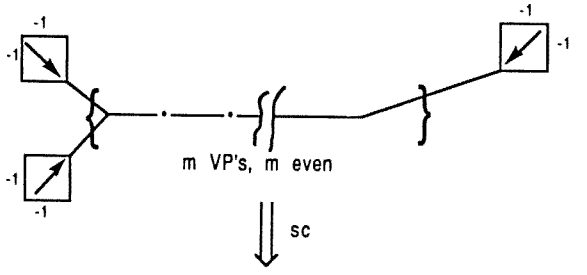
The last two electrons of the $N_{\pi} = m + 10$ (m even) would occupy two degenerate and nonbonding overall MOs (NBMOs), with the resulting singlet and triplet very close to each other in energy because the two NBMO electron spins here have a chance to stay apart (cf. eqs. (21″) and (22), which refer not only to overall MOs, but also alternately to the localized pieces by the principle of linear covariance [4]). However, if the cyclobutadiene ring were to distort, say into a rectangular VIF^{π} (which does not necessarily imply a rectangular SF: the SF could pucker and cause such a change in the VIF^{π}), one would get the $(LPI^{\pi})' = \{n'_+ = n'_- = (m + 10)/2;\ n'_0 = 0\}$. This would stabilize the new structure and remove the di-radical nature of the full molecule.

In this example of eq. (21), the number of NBMOs (n_0) turned out the same ($n_0 = 2$) as that of the square ring piece (undistorted, planar case). *With several $4k'$-rings, multi-radicals with n_0 different than the number of $4k'$-rings or than the*

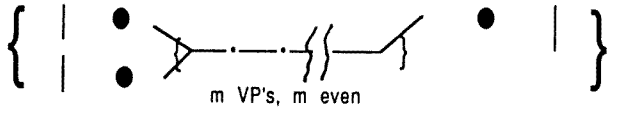
sum of the number of the separate $4k'$-rings can result. This depends on where the $4k'$-rings are attached on the m(even)-polyene chain.

Again looking at the VIF$^{\pi}$s of the standard (undistorted and planar) structures, we have, e.g.,

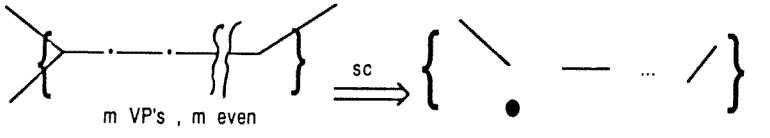
VIF$^{\pi}$ (standard):



(23)



One π-NBMO is contributed by each square (not *two*). However, in addition, the m(even) chain gives one more NBMO in this particular case, as seen in eq. (24) below:



(24)

Hence, for eq. (23) we have:

$$\text{LPI}^{\pi}\ (\text{standard SF};\ m\ \text{even}) = \{n_{+} = n_{-} = [(m+2)/2] + 3,\ n_0 = 4\},$$

with the number of NBMO$^{\pi}$s being one more than the number of square rings.

A general rule for the number of NBMO$^{\pi}$s is readily derived for any number of $4k'$- and $(4k+6)$-rings (standard SFs, undistorted and planar).

Rule: The even m-VP$^{\pi}$ chain is extended by one more VP$^{\pi}$ for each $4k'$-ring at its juncture, but not for $(4k+6)$-rings. The new straight or branched VP$^{\pi}$ chain has $m + R_{(4k')}$ points with $R_{(4k')}$ = the number of $4k'$-rings. On this chain, the sc rules give:

$$\Delta n_0^{\pi} = R_{(4k')} - 2 \quad \text{for } R_{(4k')} = \text{odd}$$
$$R_{(4k')} - 1 \quad \text{for } R_{(4k')} = \text{even}. \tag{25}$$

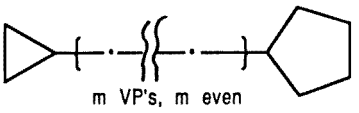
Each $4k'$-ring contributes one NBMO (as in eq. (23)). Thus, the total number of NBMOs is

$$n_0^{\pi} \text{ (standard VIF}^{\pi} \text{ and } m \text{ even)}$$
$$= 2R_{(4k')} - 1 \quad \text{for } R_{(4k')} = \text{even}$$
$$= 2R_{(4k')} - 2 \quad \text{for } R_{(4k')} = \text{odd}. \tag{26}$$

6. Fulvadiene, heptafulvadiene, and other m (even)-polyene-bridged C_qH_q odd rings, $q = 4k + 3$ or $q' = 4k' + 5$, $k, k' = 0, 1, 2, 3, \ldots$

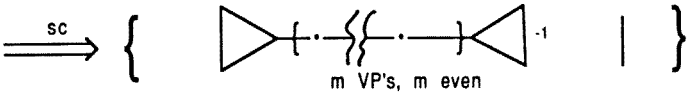
The planar configurations give the full VIF$^{\pi}$, e.g.,

VIF$^{\pi}$:

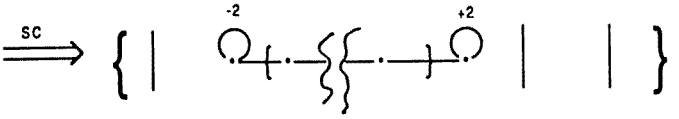


(27)

The individual ring VIF$^{\pi}$s are reduced as in sect. 3. We obtain straight or branched (depending on where each of the several rings is attached to the polyene) m-polyenic π-VIF chains, with some Hückel [5] or Möbius–Zimmerman [7] triangles remaining (the latter arise from $4k' + 5$ rings). For eq. (27), we obtain:



(27′)



The VIF$^{\pi}$ chains with positive or negative strength loops are also easily reduced by the sc rules 1 and 2. Loop cases were demonstrated in paper I [3]. We omit the details, but mention the result that the effect of an odd, $(4k + 3)$-ring substituent on

the polyene is analogous to the effect of an (-OH) substituent on an alkane sigma chain. Two similar VIFs, both with (± 2) loops, arise in these two chemically distinct problems. The loops come about in the (-OH) case from the oxygen lone pairs not counting the electronegativity effect.

The π-VIF effect of a $(4k + 5)$-ring on the polyene is analogous (VIF-wise) to the π-VIF effect of a pure electronegative (not the lone pair effect) substituent, as this introduces a positive strength loop on an alkane chain, the more electronegative VP (relative to carbon or hydrogen) having a lower self-energy.

In our odd-odd′ rings plus polyenes cases, after the electron count assignments, the π-electron density would be found to be pulled from the $(4k + 3)$-rings towards the $(4k' + 5)$-rings.

In sects. 4 to 6, we frequently considered the planar conformations which occasionally are not the actual stable ones for the sigma-pi molecules. These yield extended VIF$^{\pi}$s, which we demonstrated by reducing them to their LPI$^{\pi}$s. When non-planarity, ring twist-outs, etc. occur, smaller or piecemeal VIF$^{\pi}$s result if some π-VPs can no longer interact. The LPI$^{\pi}$ or sc reductions of these are simpler. As in sect. 4, the structural and deformational covariance rules [2,4] roughly indicate what the π-system does to the barriers to such conformation changes. The full treatment involves the very similar VIF$^{\sigma}$ manipulations on the sigma parts as well (cf. for example, [3] and forthcoming papers). Another interesting matter concerns working out some pairs of co-spectral graphs (discussed by Herndon and other authors) using the present VIF methods. We hope to do this in a separate, brief publication.

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(d) J. Aihara, Chem. Phys. Lett. 73(1980)404.

[10] Other important works on aromaticity and numbers of NBMOs using the characteristic equation with graph methods and other approaches by Trinajstić, by Gutman, Croavac, by Randić, and by Hosoya are in the references of our earlier papers (refs. [1–3] above); cf. also N. Trinajstić, in: *Semiempirical Methods of Electronic Structure Calculation,* Part A: *Techniques,* Vol. 7, ed. S.A. Segal (Plenum, 1977); I. Gutman and N. Trinajstić, Naturwissenschaften 60(1973)475. See also papers by the above-mentioned authors and by W. Herndon in the proceedings (1983) volume in ref. [2].