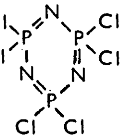
202. *Delocalization in* pπ–dπ *Bonds.*

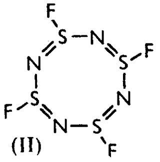
By D. P. Craig.

π-Electron delocalization in cyclic systems of alternating atoms A and B is discussed with reference to the contrast between examples such as borazole in which both atoms use *p*π orbitals, and the phosphonitrilic halides $(NPX_2)_n$ where it is likely that the nitrogen atom contributes a *p*π- and the phosphorus a *d*π-orbital. Certain broad differences depend upon the symmetry properties of the orbitals, supporting the idea that aromaticity is in fact of two types, the phosphonitrilic halides being the first recognized examples of the second of them. Simple molecular-orbital theory is used to examine the major points of distinction.

Delocalization in the organic aromatic compounds is associated with overlapping *p*π-orbitals on neighbouring carbon atoms. Recently another potentially aromatic situation has been recognized[1] possessing distinct features, associated with the overlapping of alternate *p*π- and $d\pi(d_{xz})$-orbitals. Probable examples are the trimeric (I) and tetrameric phosphonitrilic halides, and also the " thiazyl " halides of which the tetrameric fluoride (II) is illustrated. The formulation of the π-electron systems of such molecules which seems the most likely uses *p*π-orbitals on the nitrogen atoms and *d*π-orbitals on the phosphorus or sulphur, and the same alternating pattern applies to many analogous ring systems $(AB)_n$ of first-row atoms A and second-row atoms B. In this paper the features of such plane monocyclic alternating systems will be examined by using simple molecular-orbital theory and compared with those of the familiar *p*π–*p*π aromatic compounds. They will be investigated without reference to particular compounds, the question of how far these expectations are realized in actual molecules being deferred.



(I)



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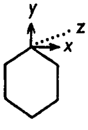

(III)

Symmetry Considerations.—π-Orbitals being defined as those antisymmetric to reflection in the molecular plane there are two *d*π-orbitals, namely, d_{xz} and d_{yz}. The former have their lobes directed tangentially to the ring and the latter radially, the system of axes being that already indicated. Although these *d* orbitals are degenerate in a free atom or

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[1] Craig and Paddock, *Nature*, 1958, **181**, 1052.

in a diatomic molecule they behave differently in the circumstances of our problem, as may readily be seen by symmetry analysis. Regular plane $(AB)_n$ systems belong to groups $\boldsymbol{D}_{nh}$, the cyclic order n being equal to the number of atoms of each species present. If we choose one atom of the ring and select those operations of the appropriate group which map that atom on itself we get a subgroup C_{2v} consisting of the identical operation, a two-fold rotation, and two reflections, one in the ring plane and one in a perpendicular plane containing the principal axis of symmetry. This subgroup is the same for all ring atoms in a molecule and the same for any n, and is characteristic of the atomic environment. It may be called the " site group " by analogy with a corresponding group in the theory of crystals, and with its help the types of aromatic systems can be distinguished. The π-orbital at the chosen centre must transform like an irreducible representation of this group. It is by definition antisymmetric to reflection in the ring plane and as a consequence it can belong to one of only two possible representations of the site group C_{2v}. The first possibility is the one occurring in the well-known $p\pi$-orbitals which are symmetric to reflection in the perpendicular plane and antisymmetric to the two-fold rotation; and the second possibility includes antisymmetric behaviour under reflection in the perpendicular plane and symmetric behaviour under two-fold rotation. It will be observed that, while d_{yz}, like $p\pi$, belongs to the first of these representations, d_{xz} belongs to the second, defined here and throughout in terms of sets of local axes as shown. Fig. 1 illustrates the d_{xz} and $p\pi$ types schematically in a projection perpendicular to the ring plane.

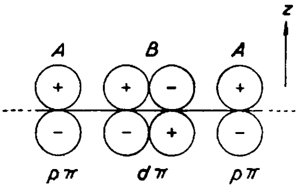


FIG. 1. *$p\pi$-Orbitals at the two centres* A *and a d_{xz} orbital at* B *shown in projection normal to the ring plane. The d_{yz} orbital is obtained from d_{xz} by a* 90° *turn about the z axis.*

The site symmetries restrict the symmetry species of the possible one-electron molecular orbitals. It is convenient to consider separately the symmetry-adapted combinations of the n atomic orbitals at A centres and those at B, leaving the question of how they combine together to form molecular orbitals for the system of A and B together. Table 1 lists the molecular orbital species which can occur in relation to the site species for $n = 3$ and $n = 4$ (six- and eight-membered rings), these being representative of the odd and the even classes, and moreover being the most important practically. The specifying symbol l in the left-hand column of the Table is the ring quantum number to be explained in the next section. The Table shows that for both values of n the combinations may transform differently for different species of atomic orbital and, as will be shown, this leads to a significant cleavage between molecules in which A and B use orbitals of the same site species (homomorphic aromatic) and others (heteromorphic aromatic).

TABLE 1. *Symmetry species of atomic orbital combinations in plane* $(AB)_n$ *molecules.*

	$n = 3$ ($\boldsymbol{D}_{3h}$)		$n = 4$ ($\boldsymbol{D}_{4h}$)	
l	$p\pi$ and d_{yz} *	d_{xz} †	$p\pi$ and d_{yz} *	d_{xz} †
0	a_2''	a_1''	a_{2u}	a_{1u}
± 1	e''	e''	e_g	e_g
2	—	—	b_{2u}	b_{1u}

* Site species b_1. † Site species b_2.

Molecular-orbital Energy Calculations.—The forms of the proper linear combinations of atomic orbitals in cyclic systems are determined by symmetry. We give the atoms of species A indices p running from 1 to n, denote the π orbitals by A_p, and fix their relative signs by supposing each to be generated from A_1 by successive n-fold rotations. The orbitals at B are then denoted by $B_{p+1/2}$. The proper combinations are as follows, defined with the aid of a ring quantum number l:

$$\left.\begin{aligned} \phi_A{}^l &= n^{-1/2}\sum_p \exp(2\pi i l p/n)\,.\,A_p \\ \phi_B{}^l &= n^{-1/2}\sum_p \exp\{(2\pi i l)(p+1/2)/n\}\,.\,B_{p+1/2} \end{aligned}\right\} \quad . \; . \; . \; . \; . \quad (1)$$

These combinations have the symmetry properties listed in Table 1.

As usual, molecular orbitals are found by combining functions (1) of the same l to give stationary values of the energy. If the orbitals at A and B are identical $p\pi$-orbitals our problem is that of the monocyclic aromatic hydrocarbons, and the energies and molecular orbitals may be found from the roots of the secular equation:

$$\begin{vmatrix} \alpha - \varepsilon & 2\beta\cos(\pi l/n) \\ 2\beta\cos(\pi l/n) & \alpha - \varepsilon \end{vmatrix} = 0 \quad . \; . \; . \; . \; . \; . \quad (2)$$

where α and β have the meanings usual in simple molecular-orbital calculations, namely, coulomb and resonance integrals, respectively. The roots $\varepsilon_l = \alpha \pm 2\beta\cos(\pi l/n)$ are the well-known hydrocarbon molecular-orbital energies which can of course be found directly by using the higher symmetry appropriate to a molecule in which A and B are identical. If the orbitals are both of $p\pi$-type, but one is more electronegative than the other by an amount which may be expressed as ρ times the resonance integral β (as in 1 : 3 : 5-triazine, where A is carbon and B nitrogen), the secular equation is derived from (2) by putting $\alpha + \rho\beta - \varepsilon$ for the diagonal entry referring to the more electronegative atom. We find that, for all values of ρ, equation (2) leads to orbital energies which are least for $l = 0$, β being a negative quantity. The situation is no different if one of the orbit types is d_{yz} because according to the Table a d_{yz} orbital in the site group has the same symmetry behaviour as $p\pi$, and the secular equation is of the form of (2) with appropriate allowance for the different electronegativities.

Where A and B provide π-orbitals of different site symmetries, one d_{xz} and the other $p\pi$, we may take B to be the $p\pi$ centre and again write for the coulomb integral $\alpha_B = \alpha_A + \rho\beta$, allowing the parameter ρ to vary according to the different electronegativities of the orbitals. The Table shows that the orbitals $l = 0$ belong to different species and cannot interact. Accordingly the energies ε_0 must be α_A and $\alpha_A + \rho\beta$. For other values of l the secular equation must be solved:

$$\begin{vmatrix} \alpha_A - \varepsilon & 2i\beta\sin(\pi l/n) \\ -2i\beta\sin(\pi l/n) & \alpha_A + \rho\beta - \varepsilon \end{vmatrix} = 0 \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

The appearance of the sine in the off-diagonal element of (3) leads to important differences from the normal aromatic secular equation (2). First, the most stable orbital is that for $l = n/2$ or $(n - 1)/2$ for n even or odd instead of $l = 0$; and, secondly, the energies of the molecular orbitals are either different from the normal aromatic case (odd n) or the same in magnitude but inverted with respect to their associated l values (even n). Typical energy level schemes are illustrated in Fig. 2.

Proceeding conventionally we may exhibit the features of the systems in a convenient way by assigning electrons to the orbitals and calculating the total energy and from it the delocalization energy per electron. We consider six- and eight-membered rings for $p\pi$–$p\pi$ and $p\pi$–d_{xz} systems and allow the electronegativity difference between atoms A and B to vary between zero and 2β. The results are shown in Fig. 3.

There are three types of behaviour. The centre curve applies to eight-membered ring systems of both aromatic types. The top curve, recording larger values of delocalization energy per electron, applies to $p\pi$–$p\pi$ six-membered rings and the lower curve, with smaller delocalization energy values, to $p\pi$–$d\pi$ six-membered rings. When A and B are equally electronegative the conditions are those of the aromatic hydrocarbons and, as is well known, benzene has a substantially more stable π-electron system than a hypothetical planar *cyclo*octatetraene would have, a situation which is aggravated in the actual molecule by strain in the σ-bonds. However, in the $p\pi$–$d\pi$ case the eight-membered ring has a more stable π-system than the six-membered ring, so that even allowing that σ-bond strain is greater for the larger ring we might expect six- and eight-rings to be of comparable stability under conditions of equally electronegative atoms A and B. These features persist qualitatively when the electronegativities are allowed to differ. The three curves all tend to zero at larger values of ρ, because the π-electrons then tend to be localized on the more electronegative centre, but in approaching the common limit the curves do not cross, so that delocalization, if it occurs at all, follows a fundamentally different pattern according to whether it is of the $p\pi$–$p\pi$ or $p\pi$–d_{xz} type.

FIG. 2. *π-Electron energy level patterns for* (AB)$_n$ *regular plane rings. The upper diagram refers to* $n = 3$ *and the lower to* $n = 4$. *The labels are the* l *values used in equation* (1). *The energy scale is in units of the resonance integral appropriate to each case and may be expected to vary, in absolute terms, from case to case.*

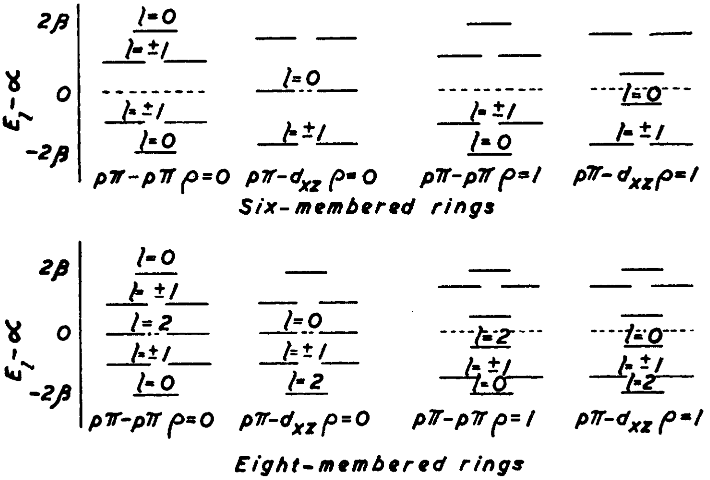


FIG. 3.

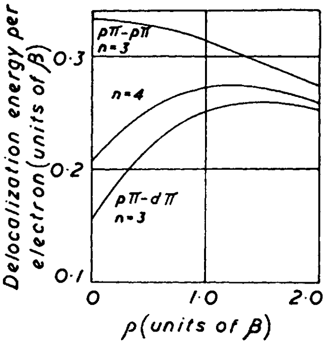
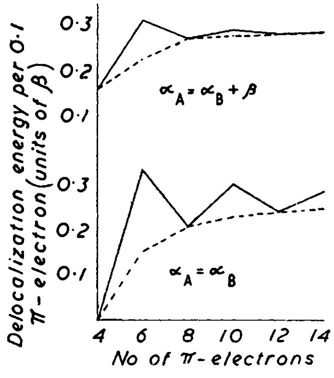


FIG. 4. *Delocalization energies per π-electron in plane* (AB)$_n$ *systems as a function of* n. *Upper diagram*: *coulomb integrals differing by* β; *lower diagram*: *equal coulomb parameters. Full lines refer to* $p\pi$–$p\pi$ *and broken lines to* $p\pi$–d_{xz}.



Another useful way of bringing out the difference is to compare behaviour of the

π-systems as a function of ring size, again overlooking problems connected with strain. Fig. 4 illustrates the delocalization energies per π-electron calculated from equations (2) and (3) for values of n from 2 to 7 for two cases: for equally electronegative atoms A and B, and for electronegativities differing by one unit of the resonance integral β.

The curves for $p\pi$–$p\pi$ delocalization illustrate Hückel's rule that special stability occurs in systems of $4n + 2$, not of $4n$, electrons, a result which holds even when the atoms are dissimilar. In $p\pi$–d_{xz} delocalization the variation with n is smooth, showing no equivalent of Hückel's rule, and leading in the limit of large rings to the same energy per π-electron as in the $p\pi$–$p\pi$ type.

It is clear that the primary distinction lies in the symmetry restrictions which different atomic orbitals place on delocalization, and a simple theory such as the molecular-orbital considerations used in this paper cannot be expected to do much more than to give formalized expression to the symmetry arguments. To make even semi-quantitative deductions from the results in the Figures we should note that the common unit β, as well as being different in absolute magnitude in the two cases, is also a function of the electronegativity parameter ρ: to be sure, it is easy to show that it varies only slowly in the range of ρ plotted, but comparisons should ideally be confined to particular ρ values.

Refinements to the theory described must of course include the possibility that the second-row element uses π-orbitals of both types in one and the same molecule as discussed elsewhere.[2] Refinements can more usefully be taken up in relation to the performance of the theory in particular examples which will be examined in a later paper.

Conclusions.—Some conclusions from this discussion, applying to plane cyclic arrangements of the atoms, are the following:

(i) In plane systems of alternating atoms A and B each providing one π-electron there are only two symmetry-distinguishable types of delocalization, represented as examples by neighbour $p\pi$–$p\pi$ interactions and $p\pi$–d_{xz}, the former being the type familiar in aromatic hydrocarbons and the latter not hitherto recognized.

(ii) In the familiar type of aromaticity the sextet is of dominating importance. The lower stability of π-electrons in a four- or an eight-membered ring than in a six-membered ring is well known in its relation to the *cyclo*butadiene–benzene–*cyclo*octatetraene problem.

(iii) In $p\pi$–d_{xz} delocalization the dominance of the sextet is lost. The delocalization energy per electron increases steadily with the number of π-electrons, leading to the expectation that on the basis of π-electrons alone an eight-membered ring would be more stable than a six-membered one. It can be shown that the energy per electron increases to a limiting value with increasing ring size, so that still larger rings are feasible, insofar as σ-bond strain permits them.

Finally, anticipating application to particular molecules, we note that in case the ring is non-planar conditions of π-bonding are differently affected in the two cases. A $2p_z$ orbital of a first-row element has its orientation fixed relative to the σ-bonds: that is, its axis of symmetry, the z-axis, is always normal to the plane of the three σ-bonds, leading to a rapid loss of overlapping power with at least one of its neighbours as the ring puckers. In the actual configuration of *cyclo*octatetraene, for example, each π-orbital overlaps effectively with one neighbour only, its axis being approximately perpendicular to that of the other neighbour. A $d\pi$ orbital of P or S in compounds such as (I) and (II) is in a higher quantum level than the σ-valence shell and its axis of quantization is not so rigidly fixed but may accommodate itself to give the best compromise binding with its two neighbours. Generally speaking this means that $p\pi$–$d\pi$ binding is less sensitive to non-planarity, and also that the particular distortion from the plane which is energetically favoured may not be the same as in the $p\pi$–$p\pi$ analogue.

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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[2] Craig, *Chem. Soc. Special Publ.*, 1958, No. 12, p. 343.