

871. "Island" and Cyclic Delocalisation in $p\pi$ - $d\pi$ Systems

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The "island" model and cyclic delocalisation model for rings of alternating first- and second-row elements with $p\pi$ - $d\pi$ overlapping orbitals are compared for a range of parameters. Calculations are restricted to planar six- and eight-membered rings, the ring angle at the second row element being fixed at 120° , in harmony with many known examples. The basis atomic orbitals for the cyclic model are taken to be $p\pi$, $d(xz)$, and $d(yz)$ without restriction on relative electronegativities and resonance parameters. On this basis the island model is a special case, and its usefulness can be discussed by comparing properties calculated from it with those for unrestricted cyclic delocalisation.

Values of delocalisation energy are calculated in the two models. Where the $d\pi$ -orbitals are equally electronegative, delocalisation over three-centre islands accounts for 85—95% of the total delocalisation energy, depending on the electronegativity compared with that of the p -orbital. The remaining 5—15% is the contribution by cyclic delocalisation over more than three centres. For non-equivalent $d\pi$ -orbitals the island model varies widely in performance, giving less than 50% in some cases which, so far as is known, lie within the range of possible d -orbital electronegativities and resonance parameters for real systems; in special cases within a narrow range of parameters it can give nearly 100% of the delocalisation energy. The comparison of models is extended to the wave functions by a calculation of the projection of one wave function on the other.

The discussion allows general conclusions about $p\pi$ - $d\pi$ delocalisation. No attempt is made to deal with particular molecules in which the $p\pi$ - $d\pi$ term occurs side-by-side with others, such as lone-pair delocalisation, which need to be included with it in a full treatment of the bonds.

IN planar cyclic $(AB)_n$ molecules in which A is an atom of the first row of the Periodic Table providing a $p\pi$ -orbital to a delocalised system, and B a second row atom with $d\pi$ -orbitals, the delocalisation has novel features. These have been described in terms of two models; in one the cyclic character of the delocalisation and the similarities to and differences from benzenoid aromatics are stressed,¹ and in the other the delocalisation is non-cyclic and extends over non-interacting sets of three adjacent atoms, or "islands."² The purpose of this Paper is to analyse the relationship of the two models. It must be emphasised that

¹ D. P. Craig, M. L. Heffernan, R. Mason, and N. L. Paddock, *J.*, 1961, 1376, and references therein.

² M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J.*, 1960, 2423.

$p\pi-d\pi$ delocalisation is only one of several factors in the stability of $(AB)_n$ systems; others are lone-pair delocalisation³ and non-neighbour interactions. We are not, therefore, concerned with the general problem of the bonds in these systems, but only with one of the important energy terms amenable, to a certain degree, to separate treatment.

Atomic Orbital Basis.—To be definite, the discussion will be given for the P–N ring system found in phosphonitrilic ring compounds, $(PNX_2)_n$; it will apply, suitably modified, to other rings made from alternating first- and second-row elements. Each nitrogen atom of the ring system (assumed planar for purposes of classification, although the restriction is not essential) provides one electron in a $p\pi$ -orbital, with Coulomb parameter α . Each phosphorus atom also provides one electron and has two π -orbitals, $d(xz)$ and $d(yz)$ (Figure 1), with Coulomb parameters $\alpha(xz)$ and $\alpha(yz)$, respectively; both are less negative than α on account of the electropositive character of the phosphorus d -orbitals.

The ring angle at phosphorus is always close to 120° , and neither of the two $d\pi$ -orbitals overlaps the $p\pi$ -orbital in the most favourable way. If $\omega(xz)$ and $\omega(yz)$ are the overlap

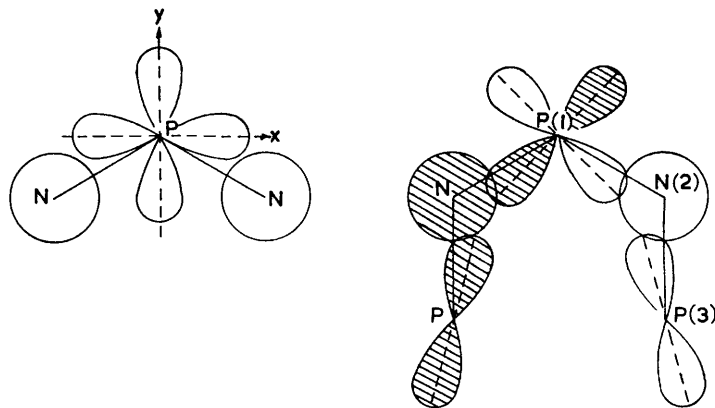


FIGURE 1. π -Orbitals at nitrogen and phosphorus projected on to the local NPN plane. Left-hand diagram; $d\pi$ -orbitals in the $d(xz)$ and $d(yz)$ scheme; right-hand diagram: orbitals rotated by 45° for "island" delocalisation. Shaded atomic orbitals are combined in molecular orbitals

integrals for the two $p\pi-d\pi$ overlaps in optimum orientation, the values $\pm\omega(xz) \cos(\pi/6)$ and $-\omega(yz) \sin(\pi/6)$ apply in structures with the usual 120° bond angle and with the axis convention of Figure 1. Proportionality between resonance integral and overlap is assumed, leading to resonance integrals of $\pm\beta(xz) \cos(\pi/6)$ and $-\beta(yz) \sin(\pi/6)$; each depends upon the Coulomb parameter of the d -orbital.

The molecular orbitals for the system defined by these quantities can be found by solving the secular equation (1) in the Hückel approximation:⁴

$$\begin{vmatrix} \alpha - E & 2i\beta(xz) \cos(\pi/6) \sin(\pi p/n) & 2\beta(yz) \sin(\pi/6) \cos(\pi p/n) \\ -2i\beta(xz) \cos(\pi/6) \sin(\pi p/n) & \alpha(xz) - E & 0 \\ 2\beta(yz) \sin(\pi/6) \cos(\pi p/n) & 0 & \alpha(yz) - E \end{vmatrix} = 0 \quad (1)$$

where $2n$ is the number of ring atoms and p is the ring quantum number, with allowed values of $0, \pm 1, \dots, n/2$, or $0, \pm 1, \dots, \pm(n-1)/2$ for even or odd n . The total energy of the π -electron system can be found from equation (1) by adding the energies of the occupied orbitals; then, by subtracting the energies of electrons in localised π -bonds, each being formed by the overlap of a nitrogen $p\pi$ -orbital with the most stable combination of the

³ D. P. Craig and N. L. Paddock, *J.*, 1962, 4118.

⁴ D. P. Craig, *Chem. Soc. Special Publ.* No. 12, 1958, p. 343.

adjacent $d(xz)$ and $d(yz)$ orbitals, we get the delocalisation energy. The energy of an electron in a localised π -bond is given by the lowest solution of equation (2).

$$\begin{vmatrix} \alpha - E & \beta(xz) \cos(\pi/6) & \beta(yz) \sin(\pi/6) \\ & \alpha(xz) - E & 0 \\ & & \alpha(yz) - E \end{vmatrix} = 0 \quad (2)$$

In the island model the electronegativities $\alpha(xz)$ and $\alpha(yz)$ and the resonance parameters $\beta(xz)$ and $\beta(yz)$ are assumed to be the same for the two orbitals. The two $d\pi$ -orbitals being thus equivalent, any orthogonal linear combinations are equally acceptable as basis orbitals for the valency problem; Dewar *et al.*² proposed the sum and difference combinations (3) as the most convenient. At any phosphorus atom k :

$$\begin{aligned} d^+(k) &= 2^{-\frac{1}{2}} \{ -d(xz, k) - d(yz, k) \} \\ d^-(k) &= 2^{-\frac{1}{2}} \{ d(xz, k) - d(yz, k) \} \end{aligned} \quad (3)$$

These orbitals are rotated clockwise by turns of $\pi/4$ from the first set. They belong to an axis system shown by broken lines in Figure 1 (right-hand side) and point at 15° to the P-N bonds, having overlap integrals with the nitrogen $p\pi$ -orbitals of $\omega \cos 15^\circ$, where ω is the overlap integral for optimum orientation, as already employed. The orbital d^- at atom 1 and d^+ at atom 3 both overlap the nitrogen $p\pi$ -orbital at atom 2 strongly; Dewar's proposal was that the delocalisation properties of the ring system were essentially those of such three-centre islands without delocalisation over the complete cyclic structure as in benzenoid aromaticity.

The basis set for the three-centre molecular orbital consists of the nitrogen $p\pi$ -orbital, and the combination $2^{-\frac{1}{2}}\{d^-(k) + d^+(k + 2)\}$ of the new d -orbitals at phosphorus atoms on either side of the nitrogen. The linear combination (4) describes the molecular orbital

$$2^{-\frac{1}{2}} \cos \xi \{d^-(k) + d^+(k + 2)\} + \sin \xi \cdot p\pi(k + 1) \quad (4)$$

formed in this way, where the angle parameter ξ is to be chosen to make the energy a minimum, its value then being given by the expression

$$\tan 2\xi = -2\sqrt{2} \cos 15^\circ / \gamma \quad (5)$$

The energy of the molecular orbital is

$$\alpha + \sqrt{2}\beta \cos 15^\circ \cot \xi \quad (6)$$

$\alpha(xz)$ and $\alpha(yz)$ in equation (5) being taken to be the same, namely $\alpha - \gamma\beta$.

The Case of Equivalent d-Orbitals.—The formulæ (5) and (6) allow the energies of three-centre molecular orbitals to be calculated. The energy of an isolated π -bond molecular orbital is easily obtained from equation (2) which in the case of equally electronegative d -orbitals becomes especially simple; a linear combination of d -orbitals may be taken with axes along, and at right angles to, the P-N bond; the localised π -bond reference structure is formed by overlap of the nitrogen $p\pi$ -orbital with the former d -orbital, the appropriate resonance integral being β . We then have for the double bond molecular orbital the two expressions (7) and (8), analogous to (5) and (6) above. The mixing parameter for the $p\pi$ - and $d\pi$ -orbitals is ξ , defined in equation (7) for minimum energy

$$\tan 2\xi = -2/\gamma \quad (7)$$

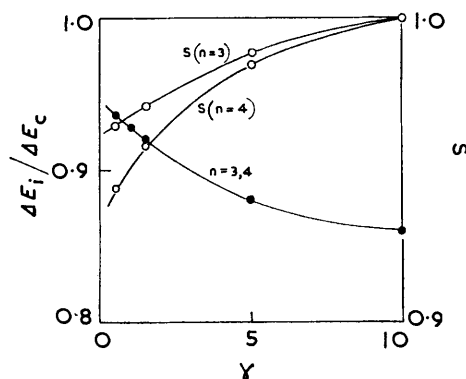
leading to the energy in (8),

$$E_{\min.} = \alpha + \beta \cot \xi \quad (8)$$

By subtracting the energy for isolated double bonds [equation (8)] from that for islands [equation (6)] we get the delocalisation energy ΔE_i in the island model. The same localised π -bond energy subtracted from the energy from equation (1) for equal electronegativities and resonance parameters gives the delocalisation energy ΔE_c in the full cyclic model.

The two calculations are compared in Figure 2 by plotting the ratio $\Delta E_i:\Delta E_c$ over a range of electronegativity difference γ . ΔE_c is greater than ΔE_i but the ratio is always close to unity, confirming the near equivalence of the two models under conditions of equivalent $d(xz)$ and $d(yz)$ orbitals. The small departures from unity occur because the islands are not orthogonal. Thus $d^-(k)$, which overlaps $p\pi(k+1)$ strongly, also weakly overlaps $p\pi(k-1)$ and would do so in all cases in which the bond angle differed from 90° . Since this angle is near 120° in real systems, the islands are not independent units. At large values of γ , where the $p\pi$ -orbital is much more electronegative than the d -orbitals, the π -electrons are increasingly confined to the $p\pi$ -orbitals, and the delocalisation energy approaches zero in both models. Indeed, the wave functions themselves are in the limit

FIGURE 2. Lower curve: ratio of delocalisation energy calculated for the island model to that for cyclic delocalisation in six- and eight-membered plane rings. Upper curves: the overlap S of the wave functions for the two models



identical, having unit overlap calculated in a way to be described later in this Paper. The ratio of delocalisation energies $\Delta E_i:\Delta E_c$ goes to a limit of $\cos(\pi/6)$ as the energies themselves go to zero, as can be seen from the formulæ given.

Transformation of the Energy Matrix to a Basis of Islands.—The island concept may be generalised to describe the case of non-equivalent $d(xz)$ and $d(yz)$ orbitals. d^+ and d^- must still be kept as basis d -orbitals in the three-centre model. They are orthogonal, with equal Coulomb (electronegativity) parameters:

$$(d^+ | \mathbf{h} | d^+) = (d^- | \mathbf{h} | d^-) = \{\alpha(xz) + \alpha(yz)\}/2$$

where \mathbf{h} is the one-electron Hamiltonian. $\alpha(xz)$ and $\alpha(yz)$ are no longer equal, nor are the resonance parameters $\beta(xz)$ and $\beta(yz)$. Scaling in units of $\beta(xz) = \beta$, we write

$$\alpha(xz) = \alpha - \gamma\beta \quad \alpha(yz) = \alpha - \delta\beta \quad \beta(yz) = \sigma\beta(xz)$$

where α is, as before, the electronegativity of the nitrogen $2p\pi$ -orbital. The electronegativities of the d^+ and d^- orbitals are $\alpha - (\gamma + \delta)\beta/2$, and the cross term is $(d^+ | \mathbf{h} | d^-) = (\gamma - \delta)\beta/2$. The resonance parameters for the interactions of $p\pi$ with d^+ and d^- must now be defined. Referred to the phosphorus atom 1 and the nitrogen atom 2 in Figure 1 they are given in expression (9).

$$\begin{aligned} \rho(d^-, p\pi) &= (\beta/\sqrt{2}) (\cos \pi/6 + \sigma \sin \pi/6) \\ \epsilon(d^+, p\pi) &= -(\beta/\sqrt{2}) (\cos \pi/6 - \sigma \sin \pi/6) \end{aligned} \quad (9)$$

The larger resonance parameter ρ applies to atoms in the same island, the smaller, ϵ , applies to the d -orbital of one island interacting with the nitrogen $p\pi$ of another.

We now proceed to the determination of the energy of the island molecular orbitals (4) for the new energy parameters. The energy of the orbital of lowest energy is $\alpha + \sqrt{2}\rho \cot \xi$, where

$$\tan 2\xi = -(4\sqrt{2}\rho/\beta)/(\gamma + \delta) \quad (10)$$

This result, after subtraction of the localised π -bond energy in equation (2), allows the calculation of the island delocalisation energy ΔE_i for any combination of energy parameters.

The energy ΔE_c , namely the best value obtainable with the basis atomic orbitals $d(xz)$, $d(yz)$, and $p\pi$, can be calculated by solving equation (1), summing the energies of the occupied molecular orbitals specified by the ring quantum number p , and subtracting the energy of localised bonds. The plots of $\Delta E_i/\Delta E_c$ in Figure 3 can then be constructed.

Comparison of the Wave Functions.—A useful insight into the differences between the island and cyclic models may be gained by comparing the wave functions themselves, instead of the delocalisation energies in Figure 3. The comparison is made by calculating the projection of one function on the other. In the extremes, a projection (overlap) of unity means that the functions are identical, and one of zero that they are orthogonal.

Let us denote by ϕ_k^1 the expression (4) for the molecular orbital occupied by two electrons in the island model. There is a second molecular orbital of higher energy ϕ_k^2 formed from the same atomic orbitals given in the expression:

$$\phi_k^2 = -2^{-\frac{1}{2}} \sin \xi \{d^-(k) + d^+(k+2)\} + \cos \xi \cdot p\pi(k+1) \quad (11)$$

and a third molecular orbital ϕ_k^3 in expression (12) formed by antisymmetric combination of the d -orbitals,

$$\phi_k^3 = 2^{-\frac{1}{2}} \{d^-(k) - d^+(k+2)\} \quad (12)$$

The set of functions ϕ^1 , ϕ^2 , and ϕ^3 for each of the phosphorus atoms is a complete basis equivalent to the original set $d(xz)$, $d(yz)$, and $p\pi$ used in equation (1).

The new basis functions are now combined according to representations of the appropriate cyclic group in (13),

$$\psi_p^m = n^{-1} \sum_{k \in \mathbb{P}} e^{2\pi i p k / 2n} \phi_k^m, \quad m = 1, 2, 3 \quad (13)$$

the summation being over k 's applying to phosphorus atoms. Finally, the molecular orbitals are given by the expression:

$$\Psi_p = \sum_{m=1}^3 a_p^m \psi_p^m \quad (14)$$

For example, in the six-membered ring system, with real coefficients

$$\begin{aligned} \psi_0^m &= 3^{-\frac{1}{2}} \{\phi_1^m + \phi_3^m + \phi_5^m\} \\ \psi_+^m &= 6^{-\frac{1}{2}} \{-\phi_1^m - \phi_3^m + 2\phi_5^m\} \\ \psi_-^m &= 2^{-\frac{1}{2}} \{\phi_1^m - \phi_3^m\} \end{aligned} \quad m = 1, 2, \text{ or } 3.$$

By solving secular equations (given on a separate page) with these basis functions we obtain eigenvalues identical with those of equation (1), and can evaluate coefficients a in the new molecular orbitals (15),

$$\left. \begin{aligned} \Psi_0 &= a_1 \psi_0^1 + a_2 \psi_0^2 + a_3 \psi_0^3 \\ \Psi_\alpha &= a_4 \psi_+^1 + a_5 \psi_+^2 + a_6 \psi_-^3 \\ \Psi_\beta &= a_4 \psi_-^1 + a_5 \psi_-^2 - a_6 \psi_+^3 \end{aligned} \right\} \quad (15)$$

there being three of each type. The most stable orbital is the lowest of the Ψ_0 triad, followed by the lowest of the degenerate Ψ_α , Ψ_β sets; the molecular wave function for cyclic delocalisation may thus be written as in the expression:

$$\Phi_c = (6!)^{-\frac{1}{2}} \det\{\Psi_0(1) \overline{\Psi_0(2)} \Psi_\alpha(3) \overline{\Psi_\alpha(4)} \Psi_\beta(5) \overline{\Psi_\beta(6)}\} \quad (16)$$

where the bars denote spin β .

On the other hand, the complete molecular wave function for the island model with pairs of electrons assigned to individual wave functions ϕ_k^1 , is

$$\Phi_i = 2^{-\frac{3}{2}} \det\{\phi_1^1(1) \overline{\phi_1^1(2)}\} \det\{\phi_3^1(3) \overline{\phi_3^1(4)}\} \det\{\phi_5^1(5) \overline{\phi_5^1(6)}\} \quad (17)$$

Equally good wave functions may be set down by assigning electrons in other ways to the independent islands. A measure of the degree to which the properties of the correct molecular orbital wave function are contained in the island model (17) is given by the projection (overlap) $(\Phi_c|\Phi_i) = 90^{-1/2}a_1^2a_4^4$ obtained by taking the product of (16) and (17) and integrating over the electron co-ordinates. However, even if a_1 and a_4 take their maximum values of unity, this overlap is still small, reflecting the artificial restriction in (17) to occupancy of the island orbitals by named electron pairs. A better procedure

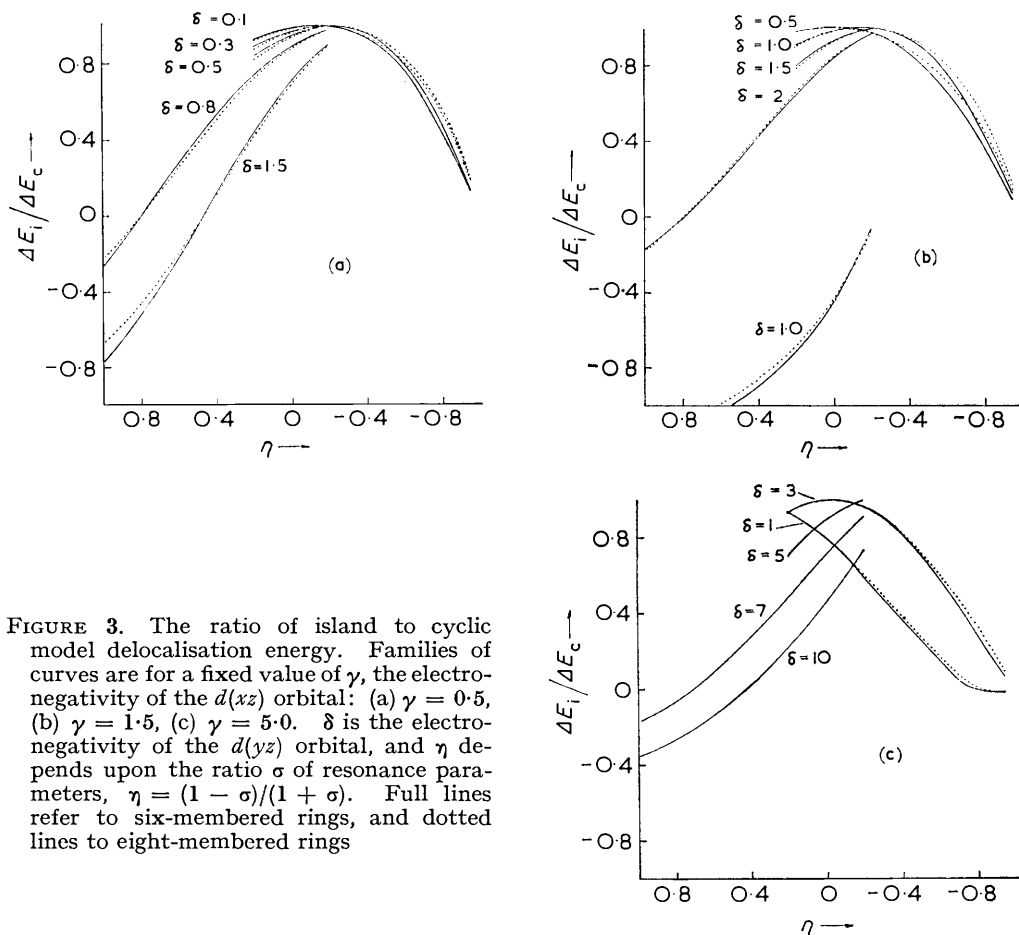


FIGURE 3. The ratio of island to cyclic model delocalisation energy. Families of curves are for a fixed value of γ , the electronegativity of the $d(xz)$ orbital: (a) $\gamma = 0.5$, (b) $\gamma = 1.5$, (c) $\gamma = 5.0$. δ is the electronegativity of the $d(yz)$ orbital, and η depends upon the ratio σ of resonance parameters, $\eta = (1 - \sigma)/(1 + \sigma)$. Full lines refer to six-membered rings, and dotted lines to eight-membered rings

is suggested by noting that if $a_1 = a_4 = 1$, and other a 's zero, the complete wave function (1) goes into the expression:

$$\Phi_i^1 = (6!)^{-1/2} \det\{\phi_1^1(1) \overline{\phi_1^1(2)} \phi_3^1(3) \overline{\phi_3^1(4)} \phi_5^1(5) \overline{\phi_5^1(6)}\} \quad (18)$$

or, in other words, the overlap of (18) and (16) is given by $a_1^2 a_4^4$, being unity in the special case just mentioned. The important difference between the function (18) and that for independent islands (17) is that the energy of the totally antisymmetric (18) contains terms for the interaction of different islands which do not appear in the formally correct (17).

The overlap of wave functions (16) and (18) in Figure 4 effectively measures the usefulness of the Dewar island orbitals as basis orbitals for the π -electron problem. Unit overlap implies that the correct molecular wave function contains only the basis orbitals ϕ_1^1 ,

The secular equations for the energies of the state Ψ_0 , and for Ψ_α , Ψ_β , in expressions (15) are, respectively:

$$\left| \begin{array}{ccc} \alpha - \delta \cos^2 \xi + \sqrt{2}(\rho + \epsilon) \sin 2\xi - E & \sqrt{2}(\rho + \epsilon) \cos 2\xi + (\delta/2) \sin 2\xi & 0 \\ \alpha - \delta \sin^2 \xi - \sqrt{2}\rho + \epsilon \sin 2\xi - E & \alpha - \gamma - E & 0 \end{array} \right| = 0$$

$$\left| \begin{array}{ccc} \alpha - (3\gamma/4 + \delta/4) \cos^2 \xi + \sqrt{2}(\rho - \epsilon/2) \sin 2\xi - E & (3\gamma/8 + \delta/8) \sin 2\xi + \sqrt{2}(\rho + \epsilon/2) \cos 2\xi & (\sqrt{3}/4)(\gamma - \delta) \cos \xi + (\sqrt{6}/2)\epsilon \sin \xi \\ \alpha - (3\gamma/4 + \delta/4) \sin^2 \xi - \sqrt{2}(\rho - \epsilon/2) \sin 2\xi - E & \alpha - \gamma/4 - 3\delta/4 - E & -(\sqrt{3}/4)(\gamma - \delta) \sin \xi + (\sqrt{6}/2)\epsilon \cos \xi \end{array} \right| = 0$$

For the eight-membered rings the procedure is similar. The three-centre orbitals are now grouped as in the expression:

$$\begin{aligned} \psi_0^m &= (\phi_1^m + \phi_2^m + \phi_3^m + \phi_4^m + \phi_5^m + \phi_6^m)/2 \\ \psi_4^m &= (\phi_1^m + \phi_3^m - \phi_5^m - \phi_7^m)/2 \\ \psi_{-m} &= (\phi_1^m - \phi_3^m - \phi_5^m + \phi_7^m)/2 \\ \psi_2^m &= (\phi_1^m - \phi_2^m + \phi_3^m - \phi_4^m)/2 \end{aligned} \quad m = 1, 2, \text{ or } 3$$

Leading to molecular orbitals:

$$\begin{aligned} \Psi_0 &= a_1\psi_0^1 + a_2\psi_0^2 + a_3\psi_0^3 \\ \Psi_\alpha &= a_4\psi_4^1 + a_5\psi_4^2 - a_6\psi_4^3 \\ \Psi_\beta &= a_4\psi_{-1}^1 + a_5\psi_{-1}^2 + a_6\psi_{-1}^3 \\ \Psi_2 &= a_7\psi_2^1 + a_8\psi_2^2 + a_9\psi_2^3 \end{aligned}$$

The corresponding secular equations are as follows:

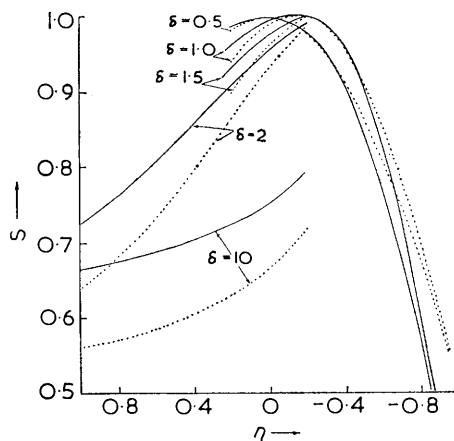
$$\left| \begin{array}{ccc} \alpha + \sqrt{2}(\rho + \epsilon) \sin 2\xi - \delta \cos^2 \xi - E & \sqrt{2}(\rho + \epsilon) \cos 2\xi + (\delta/2) \sin 2\xi & 0 \\ \alpha - \sqrt{2}(\rho + \epsilon) \sin 2\xi - \delta \sin^2 \xi - E & \alpha - \gamma - E & 0 \end{array} \right| = 0$$

$$\left| \begin{array}{ccc} \alpha + \sqrt{2}\rho \sin 2\xi - (\gamma/2 + \delta/2) \cos^2 \xi - E & \sqrt{2}\rho \cos 2\xi + (\gamma/4 + \delta/4) \sin 2\xi & (\gamma/2 - \delta/2) \cos \xi + \sqrt{2}\epsilon \sin \xi \\ \alpha - \sqrt{2}\rho \sin 2\xi - (\gamma/2 + \delta/2) \sin^2 \xi - E & \alpha - \sqrt{2}(\rho - \epsilon) \sin 2\xi - \gamma \sin^2 \xi - E & -(\gamma/2 - \delta/2) \sin \xi + \sqrt{2}\epsilon \cos \xi \end{array} \right| = 0$$

$$\left| \begin{array}{ccc} \alpha + \sqrt{2}(\rho - \epsilon) \sin 2\xi - \gamma \cos^2 \xi - E & \sqrt{2}(\rho - \epsilon) \cos 2\xi + (\gamma/2) \sin 2\xi & 0 \\ \alpha - \sqrt{2}(\rho - \epsilon) \sin 2\xi - \gamma \sin^2 \xi - E & \alpha - \delta - E & 0 \end{array} \right| = 0$$

ϕ_3^1 , and ϕ_5^1 , and, in terms of the Hückel method, the islands are non-interacting. However, this result depends on the one-electron form of the Hamiltonian. When electron repulsions are included the energies of wave function (17) and (18) are no longer the same; indeed, the function (17) is inconsistent with this Hamiltonian unless the islands are infinitely separated. In summary, when $a_1^2 a_4^4$ equals unity the correct molecular wave function is (18) which is not identical with the function (17) for the *independent* island model, although its energy is the same in the Hückel method. Nevertheless, the approach of $a_1^2 a_4^4$ to unity does indicate the conditions for the island model to be a useful description

FIGURE 4. Overlap of island and cyclic delocalisation wave functions for $d(xz)$ electronegativity $\gamma = 1.5$ and a range of $d(yz)$ electronegativities. $\eta = (1 - \sigma)/(1 + \sigma)$, σ being the ratio of resonance parameters. Full lines refer to six-membered rings, and dotted lines to eight-membered rings



of the electron delocalisation in this type of molecule, even though strictly the islands cannot be independent.

Discussion.—Both the cyclic and island models have been presented in this Paper in a more general form than in previous discussions. The purpose of this is to include the wider range of examples now recognised as potential $p\pi-d\pi$ systems.⁵ The change in the cyclic model is the allowance for different d -orbital resonance parameters as well as different electronegativities, and in the island model it is the extension of the basis to examples where the two $d\pi$ -orbitals are not equivalent. The comparison of the two models can then be made quantitative by comparing the delocalisation energy in the full cyclic model with that of islands for the same parameters. The island model is a special case of the cyclic model, and its delocalisation energy is always less, but the differences disclosed in Figure 3 can under special conditions be small. The results in Figures 3 and 4 depend upon the electronegativities of the two d -orbitals relative to the p -orbitals and upon σ the ratio of the resonance parameters. Clearly, the electronegativities are related to the resonance parameters, and a single point on each curve would, if the relationship were known, give the unique result for each pair of d -orbital electronegativities. However, the appropriate values are not known for P-N rings or for any other $d\pi-p\pi$ system, and certainly are different from case to case; it is also not known how to find σ for given electronegativities. It is thus useful to survey a wide range of possible situations. Each family of curves applies to a single value of $d(xz)$ electronegativity, and to a fixed $\beta(xz)$ which determines the energy scale. For $d(yz)$ less electronegative ($\delta > \gamma$) only the positive values of η are relevant, and for $d(yz)$ more electronegative only negative values. For $\gamma = \delta$, $\eta = 0$.

Since the $p\pi-d\pi$ resonance parameter β is a small energy unit, and the electronegativity difference between p - and d -orbitals perhaps large, it may well be that the curves for $\gamma = 5$ are the most realistic. Then, if, as is likely, differences between the two d -orbitals are confined to a range in η of about ± 0.3 units about zero we see that both in the energies and overlap with the complete wave function the island model is most nearly correct for

⁵ N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.

$d(yz)$ slightly more electronegative than $d(xz)$. Otherwise it quickly ceases to be satisfactory. The range of optimum performance centres on small negative values of η , for which the $d(yz)$ orbital is the more electronegative. Here the less favourable orientation of the $d(yz)$ orbital (Figure 1) is offset by its better intrinsic overlapping power, and the result is a more or less equal participation by $d(xz)$ and $d(yz)$. To the right of this region the $d(yz)$ orbital is dominant, giving delocalisation behaviour progressively more homomorphic (benzenoid) in character until, at $\eta = -1$, the $d(yz)$ orbital alone participates. In Figure 3(a) (including $\eta = 0$) the $d(xz)$ orbital increasingly predominates, being favoured both by its increased electronegativity and its better orientation, giving heteromorphic character to the delocalisation.

The overlap of the wave functions, in Figure 4, gives essentially the same account of the relationship of the two models. The overlap approaches unity under conditions that lead to agreement in delocalisation energy, decreasing to much smaller values where the d -orbitals differ in electronegativity and overlapping power.

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