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THE (N+1)-PHOSPHONIA [N,N] SPIRARENES

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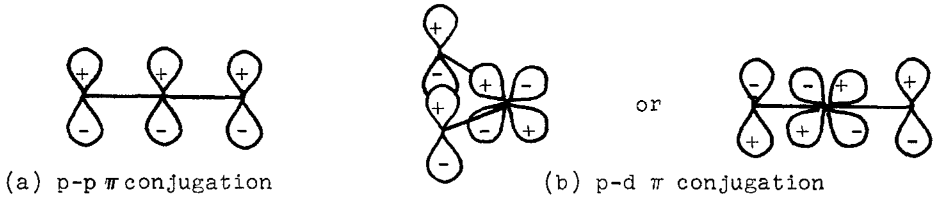
As is well known carbocyclic molecules with p-π bonds can form extensively conjugated "aromatic" systems. The prime symmetry requirement for this conjugation is that the constituent p-orbitals have a common nodal plane. Therefore, these systems must be planar or nearly so. On the other hand d-orbitals can also form π-bonds with carbon p-orbitals. However the symmetry properties of d-orbitals are considerably different from those of p-orbitals and there are several ways in which d-p π conjugation can take place.

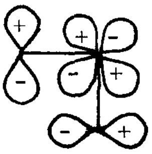
The conjugation of two p-orbitals with a d-orbital in Fig. 1b is very similar to the p-p π interaction in Fig. 1a: the orbitals all have a common nodal place. The interaction of the two p-orbitals with the d-orbital in Figure 1c is considerably different. The nodal plane of each p-orbital is 90° from the other. Therefore the plane of conjugation has been rotated 90° while passing through the d-orbitals.

FIG. 1



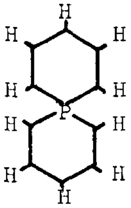
(a) p-p π conjugation

(b) p-d π conjugation

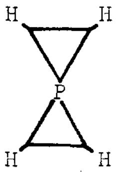


(c) p-d π conjugation

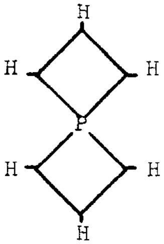
It may then be possible to construct aromatic systems in which two parts of the system are mutually perpendicular to each other yet are fully conjugated through such a d-p π interaction.[1] One possible way to construct such a system is to connect two polyene fragments by spiro-linkage through an atom with accessable d-orbitals such as a tetravalent phosphorus. The purpose of this work is to examine the stability and possible existence of a number of (n+1)-phosphonia [n,n] spirarenes I-V. We will first consider the stability of the most promising member of the series, I and then go on to others, II-V.



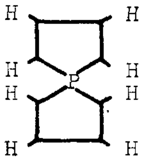
I



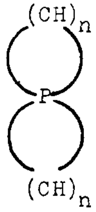
II



III



IV



V

Ignoring the σ-framework of systemI, we must consider the interaction of ten carbon 2p atomic orbitals with five phosphorus 3d orbitals. The molecule belongs to the D_{2d} symmetry froup. If the z-axis is taken to contain the S_4 molecular axis, one ring will lie in the xz plane and the other in the yz plane. Under these symmetry operations the representation of the 2p orbitals is $3E + 2A_2 + 2B_1$, while the d-orbitals fall into $E + A_1 + B_2 + B_1$. These orbitals are shown in Figure 2. Application of the variation method gives a secular determinant, $H_{ij} - S_{ij}E = 0$. For the above molecule we obtain a 2x2 A_2, a 3x3 B_1, and a pair of degenerate 4x4 determinants. Neglecting overlap these determinants can be solved if values for the coulomb integral of a phosphorus 3d orbital, αpp, and the resonance integral of a carbon 2p with a phosphorus 3d orbital are known.

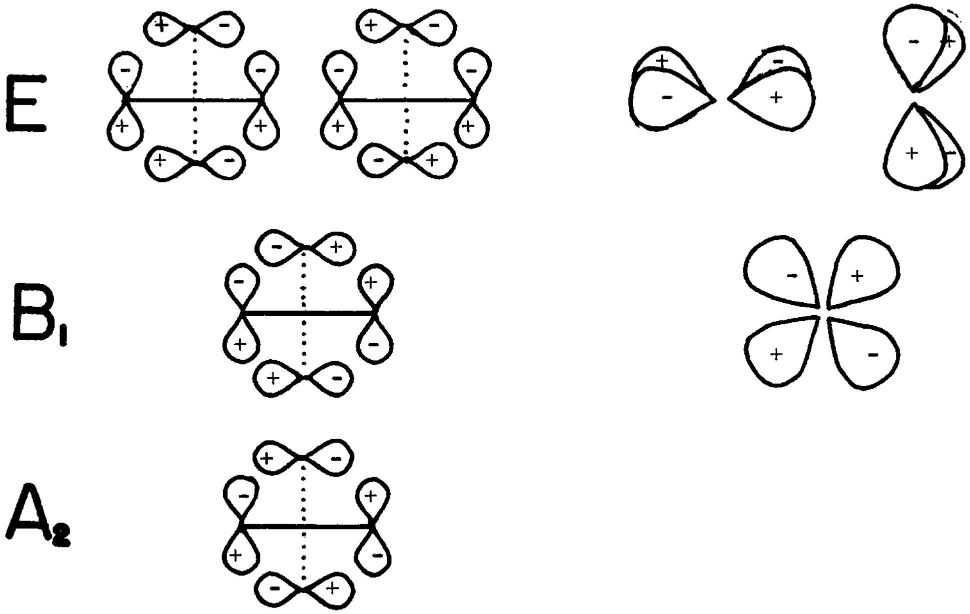
In the usual manner these can be defined in terms of the corresponding carbon parameters:

$$\alpha pp = \alpha cc + a\beta cc$$

$$\beta pc = b\beta cc$$

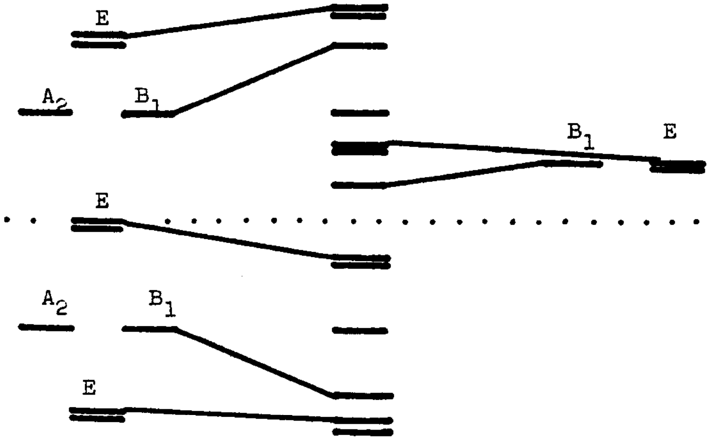
The problem of assigning reasonable values to the parameters a and b has been

FIG. 2



The symmetry of the interacting orbitals of the (n+1)-phosphonia-[n,n] spirarenes. The terminal carbon atoms of the polyene M.O. (left) and the phosphorus 3d orbitals (right) are viewed down the S_4 axis.

FIG. 3

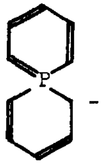


The interaction of two pentadienyl radicals (left) with the phosphorus 3d orbitals (right) forms the M.O.'s of the 6-phosphonia [5,5] spirarene (center).

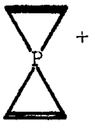
discussed in detail by Brown who took a as -.50 to -.70[3]. No reliable values for b are available although it has been suggested that this interaction may be quite large when phosphorus bears a formal positive charge.[4]

In the absence of this information it seems most reasonable to look at the π-stabilization due to interaction with the phosphorus 3d orbital as a qualitative function of b. When b is zero, the system is a pair of pentadienyl radicals connected by an insulating phosphorus atom. Each pentadienyl system has a non-bonding orbital. As b increases these E orbitals are lowered in energy and become bonding. The B_1 bonding orbital and the other E bonding orbitals are also lowered but of course the A_2 orbital is ineffected. The B_1 interaction, which couples the two rings, is quite strong and accounts for one half of the decrease in π-energy. Thus for reasonable values of a and b there are seen to be six bonding M.O.'s. Filling them with twelve electrons would give anion Ia.

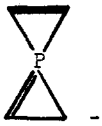
The other molecules of the series can be solved by an extension of the above method. For weak interaction with phosphorus, system II approximates two ethylene molecules. There are two bonding orbitals of symmetry E and two antibonding orbitals of symmetry A_2 and B_1. If the phosphorus interaction were particularly strong, the B_1 orbital might become bonding. Thus for weak interaction cation IIa is predicted to be the stable species while a very strong interaction might favor anion IIb.



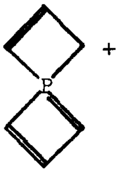
Ia.



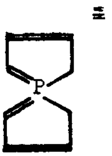
IIa.



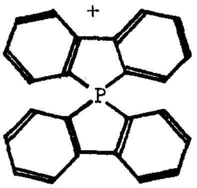
IIb.



IIIa.



IVa.

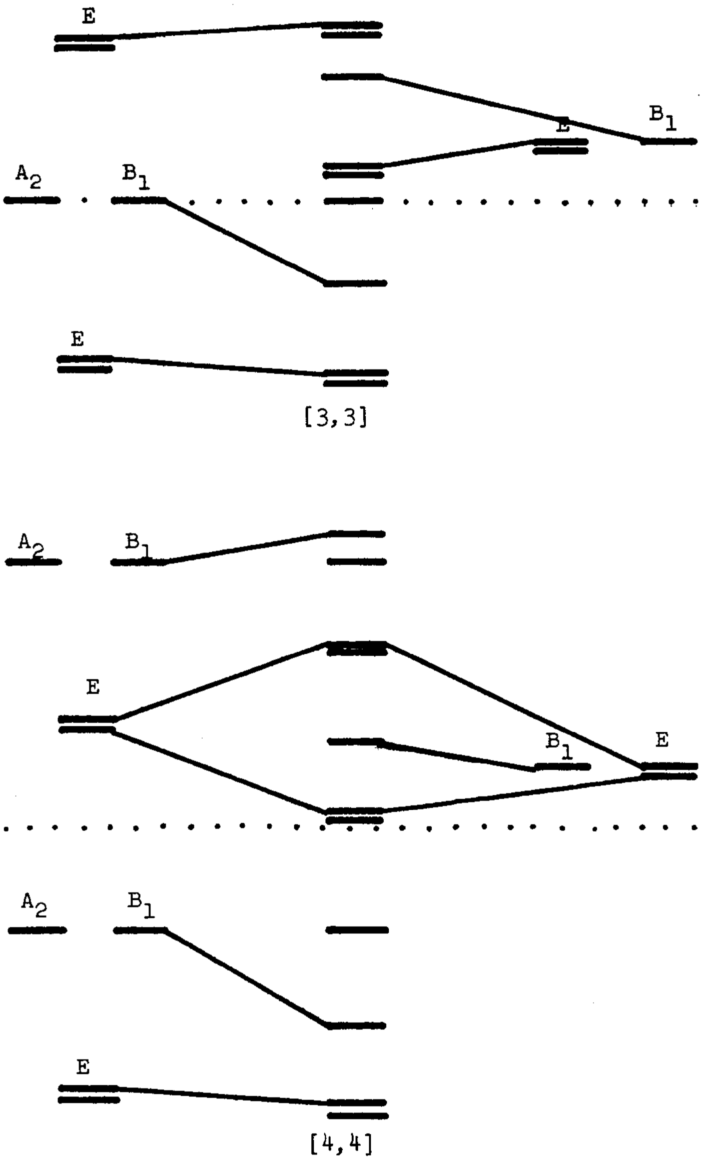


VI.

System III can be approximated as two allyl radicals bridged by a phosphorus atom. The two allyl non-bonding orbitals have symmetry A_2 and B_1. Any interaction will lower the B_1 orbital so it will become bonding (Fig. 4), filling these three bonding orbitals gives cation IIIa.

For weak interaction system IV appears to be two butadiene fragments. A strong interaction may allow the lowest antibonding E orbitals to become

FIG. 4



The interaction diagram of the 4-phosphonia [3,3] spirarene (above) and the 5-phosphonia [4,4] spirarene (below). Polyene orbitals (left) interact with the phosphorus 3d orbitals (right) to form the M.O.'s of the spirarenes (center).

bonding. Filling them all would give the trianion IVa, a rather unlikely species. A derivative of system IV, the cation VI, has been synthesized by Hellwinkel.[5] In this case the benzo groups are probably less likely to interact strongly with the phosphorus atom than would the unsubstituted system.

The (n+1) - phosphonia [n,n] spirarenes of any size can be solved by extension of the methods already discussed. In conclusion one might note that: (1) the interaction of the phosphorus atom always lowers some energy level. Therefore the effect is always a stabilization; (2) the strongest stabilization may occur for the cations such as IIIa since the positive charge will increase the parameters a and b,[4] and (3) although only phosphorus has been used in this paper, other atoms with accessible d-orbitals could be used as well. Indeed the present treatment is equally valid if P is replaced by S^+.

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REFERENCES

(1) H. P. Koch and W. E. Moffitt, Trans. Faraday Soc., 47, 7 (1951).

(2) It is also necessary to take into account the different directional character of the E and B_1 P-C interactions.

(3) D. A. Brown, J. Chem. Soc., 929 (1962).

(4) D. P. Craig, A. Maccoll, R. S. Nyholm L. E. Orgel, and L. E. Sutton, Ibid., 332 (1954); H. H. Jaffee, J. Phys. Chem., 58, 185 (1954); D. P. Craig and Magnusson, J. Chem. Soc., 4895 (1956).

(5) D. Hellwinkel, Ber., 98, 576 (1965).