# Nature of Bonding in $\lambda^5$-Phosphorins[1]

**Werner Schäfer,[2a] Armin Schweig,*[2a] Karl Dimroth,[2b] and Hartmut Kanter[2b]**

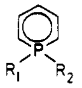
*Contribution from the Fachbereich Physikalische Chemie and the Fachbereich Chemie, Universität Marburg, D 355 Marburg/L., Germany.*

*Received September 8, 1975*

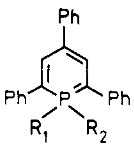
**Abstract**: The $\lambda^5$-phosphorin system is investigated both theoretically and by uv photoelectron spectroscopy. The results reveal that this system is best described as a superimposition of a polar internal salt structure enforced by the pentavalency of the phosphorus atom and a Huckel-"aromatic" structure enabled through participation of the d AO's on phosphorus in the cyclic $\pi$ conjugative process. The question whether this system is to be best described by an "aromatic" (i.e., a Huckel) model, an "antiaromatic" (i.e., a Mobius) model, or a model known in literature as "conjugatively interrupted at phosphorus" is investigated in some detail and on novel lines.

By attaching the substituents $R_1$ and $R_2$ to the tervalent phosphorus atom in $\lambda^3$-phosphorins (**1**), $\lambda^5$-phosphorins (**2**) are generated. These systems possess a pentavalent phosphorus atom and can be viewed as being composed from a five sp$^2$-carbon fragment linked to the $PR_1R_2$ unit through two PC $\sigma$ bonds. As recent review articles[3,4] indicate, the nature of the electronic structure of $\lambda^5$-phosphorins is not well understood. Important questions raised concern: (1) the nature of the subunit interactions, i.e., by $p_\pi p_\pi$, $p_\pi d_\pi$ conjugation, and/or by $\pi/PR_1(R_2)$ hyperconjugation, and (2) the changes in charge distribution and total energy connected with such interactions, i.e., the question whether such systems should be described by an aromatic or antiaromatic model or something else.[5] Starting from an analysis of the photoelectron spectra of $\lambda^5$-phosphorins, we proceed to develop a picture of the electronic structure of these systems from quantum chemical model calculations.

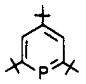

1


2

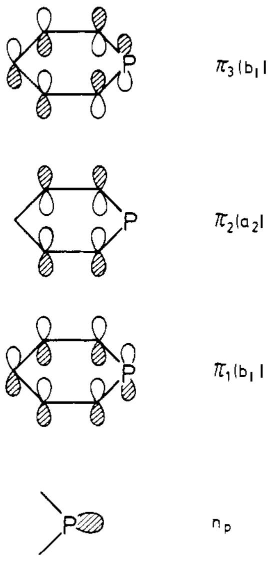
## Results and Discussion



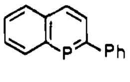
| $R_1$ | $R_2$ | |
|---|---|---|
| – | – | 3 |
| Ph | Ph | 4 |
| Me | Me | 5 |
| OMe | OMe | 6 |
| Cl | Cl | 7 |
| F | F | 8 |
| F | NEt$_2$ | 9 |
| NEt$_2$ | NEt$_2$ | 10 |



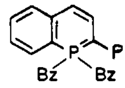
| | | | |
|---|---|---|---|
| $\pi_3$ | ($b_1$) | 8.0 eV | 9.2 eV |
| $\pi_2$ | ($a_2$) | 8.6 eV | 9.8 eV |
| $n_p$ | | 8.6 eV | 10.0 eV |
| | | 11 | 12 |



**Photoelectron Spectra of 2,4,6-Triphenyl-$\lambda^3$-phosphorin (3), 1,1,2,4,6-Pentaphenyl-$\lambda^5$-phosphorin (4), 1,1-Dimethyl-2,4,6-triphenyl-$\lambda^5$-phosphorin (5), 1,1-Dimethoxy-2,4,6-triphenyl-$\lambda^5$-phosphorin (6), 1,1-Dichloro-2,4,6-triphenyl-$\lambda^5$-phosphorin (7), 1,1-Difluoro-2,4,6-triphenyl-$\lambda^5$-phosphorin (8), 1-Fluoro-1-diethylamino-2,4,6-triphenyl-$\lambda^5$-phosphorin (9), and 1,1-Bis(diethylamino)-2,4,6-triphenyl-$\lambda^5$-phosphorin (10).** Figure 1 shows the photoelectron (PE) spectra of the aforementioned compounds **3–10**. All PE spectra exhibit a broad and intense band (band 3) arising from phenyl $\pi$ ionizations (designated by Ph) and additionally, in the case of the $\lambda^3$-phosphorin **3**, from the phosphorus lone-pair orbital (labeled $n_p$). From previous experience with the state sequence of ions produced from 2,4,6-tri-*tert*-butyl-$\lambda^3$-phosphorin[6] and the unsubstituted phosphorin[7] (the corresponding ionization potentials and assignments are given in **11** and **12** below), the first two bands in the PE spectrum of 2,4,6-triphenyl-$\lambda^3$-phosphorin (**3**) have been assigned to ionization from the phosphorin $\pi_3(b_1)$ and $\pi_2(a_2)$ orbitals (these orbitals and the $\pi_1(b_1)$ and $n_p$ orbitals are illustrated below), respectively.[8] *The characteristic feature of the remaining PE spectra of the $\lambda^5$-phosphorins when referenced against the spectrum of the $\lambda^3$-phosphorin is the marked shift to lower ionization potentials that one of the phosphorin ionizations undergoes.* This shift has been previously noted for 1,1-dimethoxy-2,4,6-triphenyl-$\lambda^5$-phosphorin[9] (**6**) and also for 1,1-dibenzyl-2-phenyl-1-phosphanaphthalene (**14**),[10] a derivative of 2-phenyl-


7.65 eV

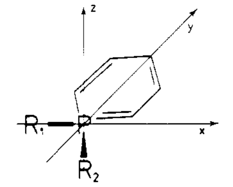
13


6.00 eV

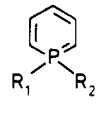
14

1-phosphanaphthalene (**13**) (for the relevant first ionization potentials see below). Irrespective of the nature of interaction responsible for the observed dramatic shift, such a shift can only happen to the $\pi_3(b_1)$ ionization, since the $\pi_3(b_1)$ has no node passing through the $PR_1R_2$ unit and $\pi_2(a_2)$ is nodal there. Therefore, we must assign the first two bands in the spectra of the $\lambda^5$-phosphorins **4–10** to the $\pi_3(b_1)$ and $\pi_2(a_2)$ ionizations in the order of increasing ionization energy. The measured ionization potentials and the ionization correlations for all $\lambda^3$- and $\lambda^5$-phosphorins considered here (**3–10**) are summarized in Figure 2. In case of the Ph ionizations, the measured half-widths of band 3 are given. Again, the tremendous shift of the $\pi_3(b_1)$ ionizations of $\lambda^5$-phosphorins toward lower ionization potentials compared to the same ionization of the $\lambda^3$ counterpart is evident. On the contrary, the $\pi_2(a_2)$ ionizations of the $\lambda^5$ compounds occur not far away from the region where this ionization occurs in the $\lambda^3$ case. It is further noteworthy that the substituent ($R_1$,$R_2$) dependent trends in the shifts of all three relevant ionization regions ($\pi_3(b_1)$, $\pi_2(a_2)$, and Ph) are quite similar.

The proposed assignments are fully confirmed by comparison of the measured (Figure 2) and the calculated (Figures 3 and 4) ionic state correlation diagrams. The calculations are performed by use of the extended CNDO/S method,[11] both in an sp and spd basis and with and without configuration interaction (CI).[12] Where available, experimental geometries[3,4] were used. Otherwise, assumed geometries were taken. The coordinate system chosen in all cases is illustrated in **15**. To save computer time, most of the calculations were carried out for the ring-unsubstituted systems **16–23**. The results, however, were checked in a few fully-substituted cases. Figures 3 and 4 depict, e.g., the Koopmans' ionic states[13] in the spd basis and the corresponding ionic states in the same basis, but now improved by extensive configuration interaction (CI).[12,14] All states are labeled according to the designation of the orbitals which are vacated during the ionization process. The results clearly show that the sequence and spacing of orbital energies (i.e., the negative of the Koopmans' state energies of Figure 3) and ionic state energies (Figure 4) agree. In consequence, the conclusions drawn throughout this paper are actually unaffected by invoking Koopmans' theorem.[13] It is further gratifying to note the good qualitative agreement between the calculated (Figure 4) and measured[7] (**12**) energies for the ionic states of phosphorin.



15



| R₁ | R₂ | |
|---|---|---|
| – | – | 16 |
| Ph | Ph | 17 |
| Me | Me | 18 |
| OMe | OMe | 19 |
| Cl | Cl | 20 |
| F | F | 21 |
| F | NEt₂ | 22 |
| NEt₂ | NEt₂ | 23 |

## Nature of the Electronic Structure of $\lambda^5$-Phosphorins. Deductions from Photoelectron Spectra and Model Calculations

The main point of interest in the foregoing photoelectron

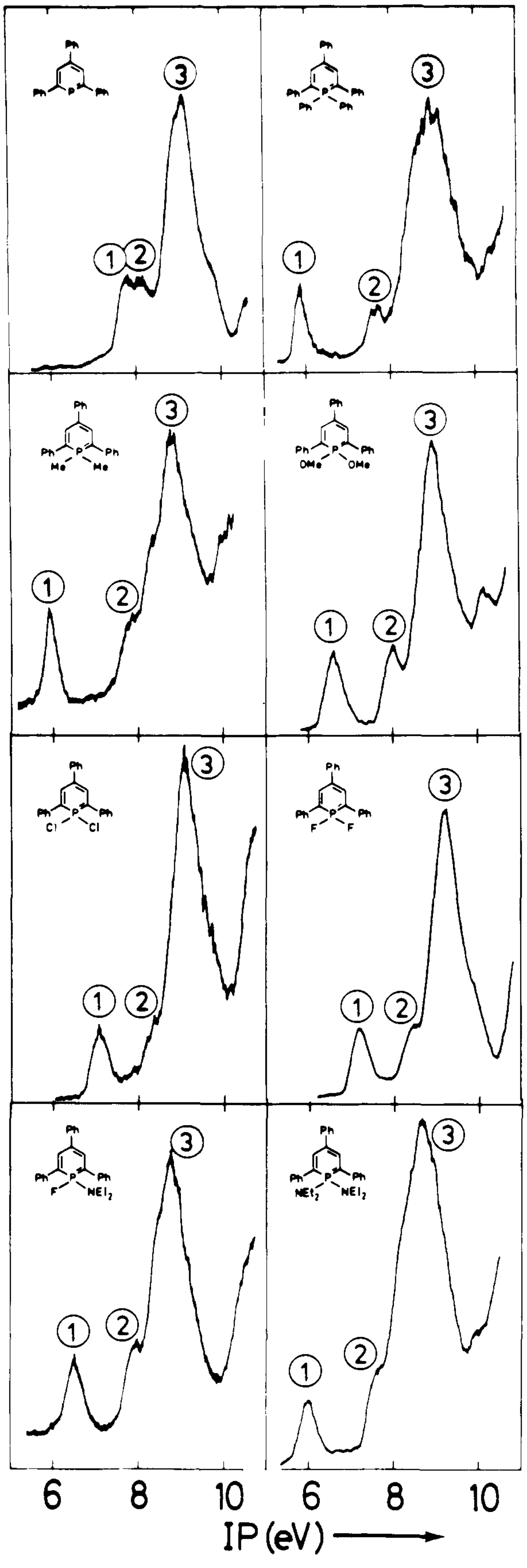


**Figure 1.** Photoelectron spectra of 2,4,6-triphenyl-$\lambda^3$-phosphorin, 1,1,2,4,6-pentaphenyl-$\lambda^5$-phosphorin, 1,1-dimethyl-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1,1-dimethoxy-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1,1-dichloro-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1,1-difluoro-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1-fluoro-1-diethylamino-2,4,6-triphenyl-$\lambda^5$-phosphorin, and 1,1-bis(dimethylamino)-2,4,6-triphenyl-$\lambda^5$-phosphorin. For the assignments and measured vertical ionization potentials, see Figure 2.

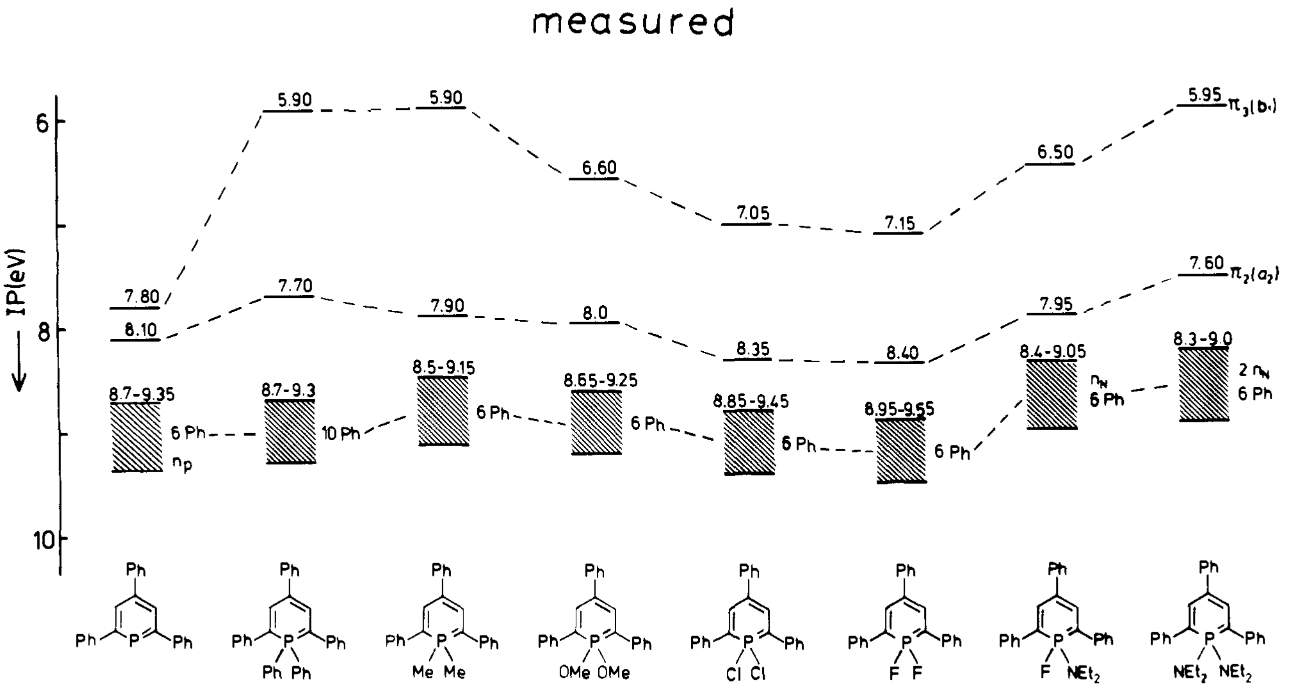
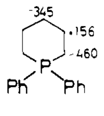


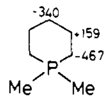
**Figure 2.** Measured correlation diagram for the lowest ionic states of 2,4,6-triphenyl-$\lambda^3$-phosphorin, 1,1,2,4,6-pentaphenyl-$\lambda^5$-phosphorin, 1,1-dimethyl-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1,1-dimethoxy-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1,1-dichloro-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1,1-difluoro-2,4,6-triphenyl-$\lambda^5$-phosphorin, 1-fluoro-1-diethylamino-2,4,6-triphenyl-$\lambda^5$-phosphorin, and 1,1-bis(dimethylamino)-2,4,6-triphenyl-$\lambda^5$-phosphorin. The states are labeled according to the designation of orbitals from which they arise. The numbers shown above the levels are vertical ionization potentials (in eV) for the first two bands (see Figure 1) or define the half-widths of the third band in the spectra of Figure 1. Since it is shown in the present work that Koopmans' theoretical description of ion states considered is valid (see Figures 3 and 4), the present diagram can also be considered as an experimental correlation diagram for the highest occupied orbitals of the respective molecules.

spectroscopic discussion has been the strong shift toward lower ionization potentials that the $\pi_3(b_1)$ ionization experiences in $\lambda^5$-phosphorins relative to the comparable $\lambda^3$-phosphorin. The explanation of this shift, which is also fully reproduced by the CNDO/S calculations, provides the key to a main aspect of the electronic structure of $\lambda^5$-phosphorins, as we will demonstrate below. To this end, we come back to Figures 3 and 4 and corresponding figures (not shown here) based on calculations in the sp basis, which contain an intriguing feature not yet discussed. Comparisons of the latter figures with Figures 3 and 4 show that the ionizations of the $\lambda^5$-phosphorins can be equally well explained in the sp and the spd basis. *This result obviously means that important gross features of the electronic structure of $\lambda^5$-phosphorins can be predicted with complete neglect of the d AO's on the phosphorus atom.*

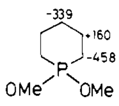
Since phosphorus in these compounds is involved in four $\sigma$ bonds (2 PC bonds and the $PR_1$ and $PR_2$ bonds), the three p orbitals on phosphorus are, disregarding the phosphorus d orbitals, fully employed for making these bonds. By implication, the fifth electron of the phosphorus atom must have left this atom to reside eleswhere. The most probable guess is that this electron has gone into the partially filled highest occupied orbital of the five-carbon radical unit, thus forming a corresponding anion and leaving a positively charged phosphorus behind. This primary internal charge transfer of just one electron between both entities should be substantially facilitated by inductive lowering of the acceptor orbital under the influence of the nearby positive unit charge. These expectations are fully corroborated by the CNDO/S charge density diagrams (shown in **24–37** below; charges in $10^{-3}$ e). **24–30** give the $\pi$ charges alone and **31–37** present the total charges. Accordingly, nearly one electron is transferred to the ring carbon atoms and about one electron has abandoned the phosphorus atom. For the more electronegative substituents $R_1$ and $R_2$, the phosphorus atom becomes even more positive due to additional charge transfer to these groups.



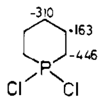
24



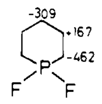
25



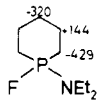
26



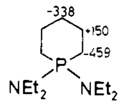
27



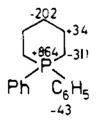
28



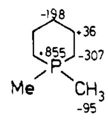
29



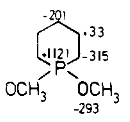
30



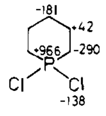
31



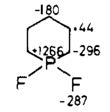
32



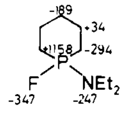
33



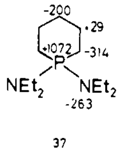
34



35



36



37

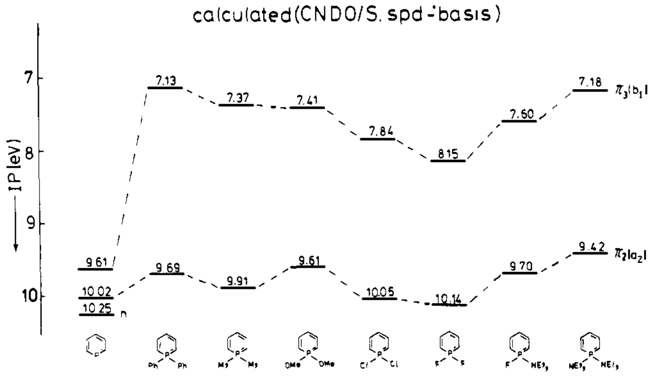


**Figure 3.** Calculated (using the CNDO/S method in conjunction with an spd basis) Koopmans' ionic state correlation diagram (identical with the orbital energy correlation diagram for the highest occupied orbital) of $\lambda^3$-phosphorin, 1,1-diphenyl-$\lambda^5$-phosphorin, 1,1-dimethyl-$\lambda^5$-phosphorin, 1,1-dimethoxy-$\lambda^5$-phosphorin, 1,1-dichloro-$\lambda^5$-phosphorin, 1,1-difluoro-$\lambda^5$-phosphorin, 1-fluoro-1-diethylamino-$\lambda^5$-phosphorin, and 1,1-bis(diethylamino)-$\lambda^5$-phosphorin. The numbers above the levels are vertical ionization potentials (or the negative of orbital energies (in eV)).

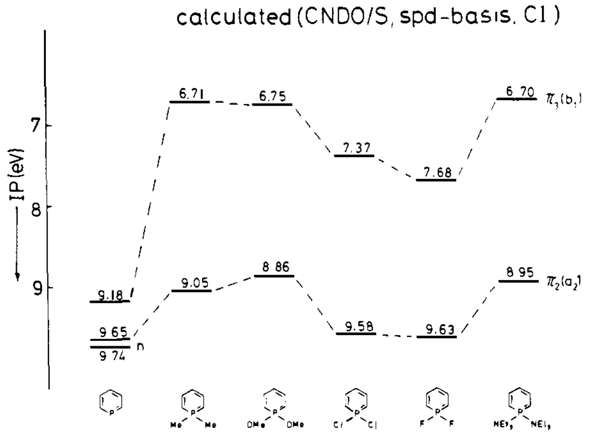
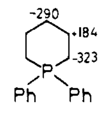
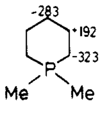


**Figure 4.** Calculated correlation diagram for the lowest ionic states of $\lambda^3$-phosphorin, 1,1-dimethyl-$\lambda^5$-phosphorin, 1,1-dimethoxy-$\lambda^5$-phosphorin, 1,1-dichloro-$\lambda^5$-phosphorin, 1,1-difluoro-$\lambda^5$-phosphorin, and 1,1-diamino-$\lambda^5$-phosphorin. The ionic states are evaluated on the basis of the CNDO/S method (spd basis) and a recent CI approach.[12,14] The ionizations are labeled according to the designation of orbitals from which they arise. The numbers above the levels are vertical ionization potentials in eV.

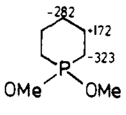
We turn now to the role played by the phosphorus d orbitals, which is best exemplified by looking at the corresponding charge density diagrams (shown in **38–51**; charges in $10^{-3}$ e)



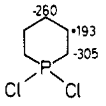
38



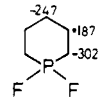
39



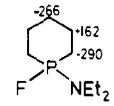
40



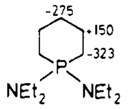
41



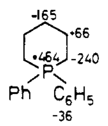
42



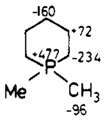
43



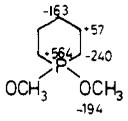
44



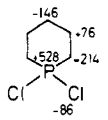
45



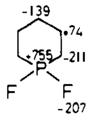
46



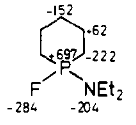
47



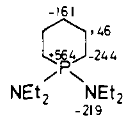
48



49



50



51

calculated in the spd basis. **38–44** show the $\pi$ charges at the carbon ring positions and **45–51** the total charges. Diagrams **38–44** and **45–51**, when referenced against diagrams **24–30** and **31–37**, respectively, at once reveal that the d orbitals on phosphorus accept $\pi$ charge back from the ring, thus somewhat remedying the electron deficiency of the depopulated phosphorus atom.

To get some support for the calculated CNDO/S charge densities, the densities at the carbon ring positions of pyridine, phosphorin, and the $\lambda^5$-phosphorin **6** are plotted vs. the corresponding $^{13}$C chemical shift data published recently[15] (Figure 5). The density data used pertain to the spd basis and include also ab initio results[16] where available. Both the CNDO/S and the ab initio densities correlate equally well with the chemical shift data with the exception of the densities at the C(2) position in phosphorin, where both sorts of calculations seem to be drastically in error. We believe here that this observed departure from the linear correlation between the calculated charge densities and the determined chemical shifts is not due to erroneous densities but points to some special influence of the adjacent tervalent phosphorus atom, the mechanism of which is presently not understood.

To summarize, $\lambda^5$-phosphorins are primarily composed of a pentadienyl anion (i.e., the negatively charged five-carbon subunit) and a highly positively charged phosphorus atom. The resulting internal zwitterionic structure, as far as the ring atoms are concerned, is made somewhat less pronounced by back-donation of charge from the anionic part to the phosphorus d AOs, owing to anion/d back-bonding. Nonetheless, it is important to recognize that, in dealing with properties of $\lambda^5$-phosphorins, we primarily deal with properties of the pentadienyl anionic part contained in these systems, modified somewhat under the inductive influence of the highly positive charge on the adjacent phosphorus atom. In this context, it is in order now to come back to the characteristic feature of the photoelectron spectra of $\lambda^5$-phosphorins, namely the low-energy first ionic state of these compounds mentioned above. In the light of the present discussion, this observation can be regarded as direct evidence for the supposition that a *$\pi$ anion (i.e., the pentadienyl anion) is involved in the ionization process.* To support this argument further we invented and investigated the following model case. We first calculated the Koopmans ionic states for the pentadienyl anion, using the same geometry as this entity possesses in the $\lambda^5$-phosphorins. Owing to the missing positive charge on phosphorus in the direct neighborhood of the anionic part, the predicted ionizations came out much too low (Figure 6). To improve the situation, we decided to place a positive unit charge at the same position where the positive phosphorus atom in the $\lambda^5$-phos-

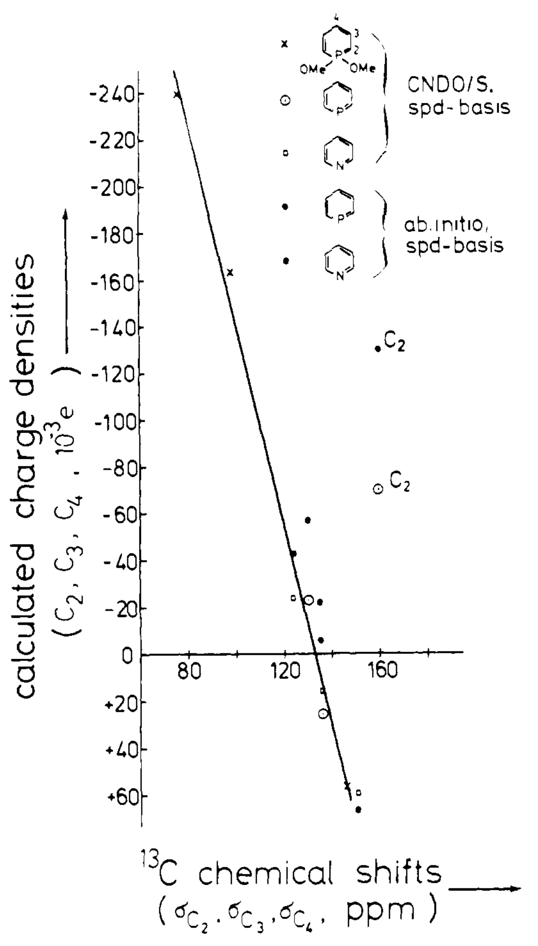
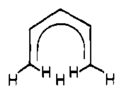


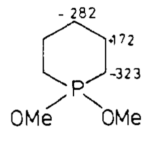
**Figure 5.** Plot of the calculated (using the CNDO/S and ab initio[16] methods and in both cases an spd basis) charge densities at the ring positions C(2), C(3), and C(4) vs. the corresponding experimentally derived $^{13}$C chemical shifts for pyridine, $\lambda^3$-phosphorin, and 1,1-dimethoxy-$\lambda^5$-phosphorin.

phorins is located. In practice, this was accomplished by using a hydrogen atom (the studied arrangement is shown in **52** below) instead of the $PR_1R_2$ grouping as an electron donor to

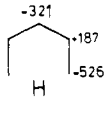


52

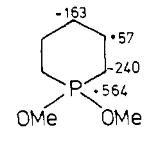
the pentadienyl radical fragment. The Koopmans ionic states now obtained are very close to those predicted for the $\lambda^5$-phosphorin **19** when using the spd basis (Figure 6). These results get support from inspection of the charge density diagrams (shown in **53–56** below, charges in $10^{-3}$ e). Both the $\pi$ (**53** and **54**) and the total (**55** and **56**) charges for the $\lambda^5$-phosphorin (treated in the spd basis) and the model system are very similar. The results suggest that the $P(OMe)_2$ unit, including d AO's on phosphorus, exerts a very similar influence on the adjacent five-carbon entity as a hydrogen atom at the same location does.



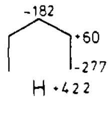
53



54



55



56

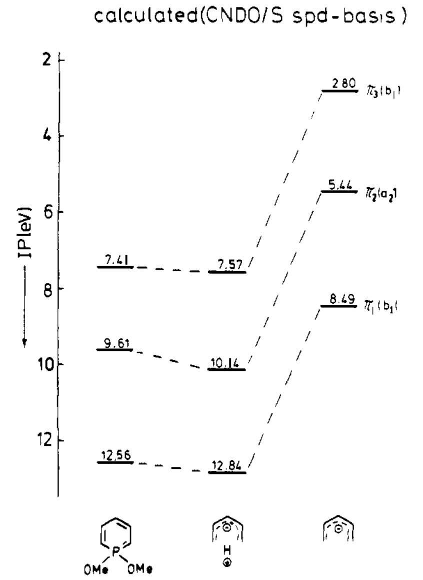


**Figure 6.** Calculated (using the CNDO/S method and an spd basis) Koopmans' ionic state correlation diagram (identical with the orbital energy correlation diagram for the occupied $\pi$ orbitals) of 1,1-dimethoxy-$\lambda^5$-phosphorin, of system **52** (see text, the electronic structure of **52** is suitably referred to as an inner salt between a pentadienyl anion and a proton located at the same position as the phosphorus atom in $\lambda^5$-phosphorins), and of pentadienyl anion with the geometrical structure as shown.

The various aspects of the electronic structure of $\lambda^5$-phosphorins discussed so far and several new aspects can be examined and elucidated by applying a method[17-26] developed in recent years, which allows one to interrupt the conjugation of selected parts of a molecule from the rest of the system. This method, meanwhile exemplified in many cases, has proved to be very useful with respect to several fundamental problems in theoretical organic chemistry Thus, it has become possible to calculate orbital interaction diagrams between orbitals localized on two different parts of the molecule.[20,21] The so quantified interactions are of particular interest in the rationalization of photoelectron spectroscopic results[19-21] or with regard to rationalizing destabilizations or stabilizations connected with switching on conjugation between molecular subunits.[22-25] Thus, eventually the degree of "aromaticity" of some particular system may be read out from such diagrams.[25] It is further possible to distinguish inductive from conjugative effects and to evaluate such interactions.[19,23] Moreover, the method is very useful for elucidating the nature of bonding in stable molecular conformations[18,24] and for putting the "aromaticity" concept on a new, more quantitative footing.[26]

Figure 7 (spd basis) summarizes the predicted ionization potentials for the conjugatively decoupled molecules **17–23.** The positions of conjugative interruption are indicated by dashes (see the ring C–P bonds). Comparison with the corresponding coupled results of Figure 3 at once indicates that both the locations of the ionic states and the gross trends of their shifts within the series of molecules shown stay nearly unchanged under the decoupling process. In particular, the result means that the characteristic low first ionization potential of $\lambda^5$-phosphorins is not due to conjugative interactions[27] between the coupled subunits but is, as argued above, a feature of the pentadienyl anionic subunit. The result is further to be interpreted as an indication that the individual shifts of ionization

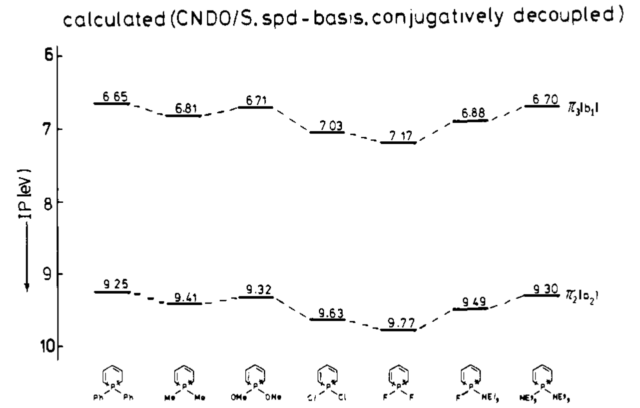


**Figure 7.** Calculated (using the CNDO/S method and an spd basis) Koopmans' ionic state correlation diagram (identical with the orbital energy correlation diagram for the $\pi_3(b_1)$ and $\pi_2(a_2)$ orbitals) of 1,1-diphenyl-$\lambda^5$-phosphorin, 1,1-dimethyl-$\lambda^5$-phosphorin, 1,1-dimethoxy-$\lambda^5$-phosphorin, 1,1-dichloro-$\lambda^5$-phosphorin, 1,1-difluoro-$\lambda^5$-phosphorin, 1-fluoro-1-diethylamino-$\lambda^5$-phosphorin, and 1,1-bis(diethylamino)-$\lambda^5$-phosphorin. The ionic states (orbital energies) shown are those obtained when the $\pi$ conjugation between the pentadienyl and $PR_1R_2$ subunits is interrupted.

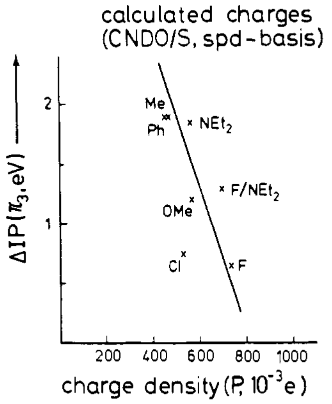
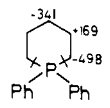
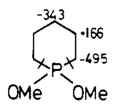


**Figure 8.** Plot of the measured shifts of the lowest ionization potential of $\lambda^5$-phosphorins (marked by their substituents at phosphorus: Ph = 1,1,2,4,6-pentaphenyl-$\lambda^5$-phosphorin, Me = 1,1-dimethyl-2,4,6-triphenyl-$\lambda^5$-phosphorin, OMe = 1,1-dimethoxy-2,4,6-triphenyl-$\lambda^5$-phosphorin, Cl = 1,1-dichloro-2,4,6-triphenyl-$\lambda^5$-phosphorin, F = 1,1-difluoro-2,4,6-triphenyl-$\lambda^5$-phosphorin, F/NEt$_2$ = 1-fluoro-1(diethylamino)-2,4,6-triphenyl-$\lambda^5$-phosphorin, and NEt$_2$ = 1,1-bis(diethylamino)-2,4,6-triphenyl-$\lambda^5$-phosphorin) relative to 2,4,6-triphenyl-$\lambda^3$-phosphorin vs. the calculated (by use of the CNDO/S method and an spd basis) charge density on phosphorus.

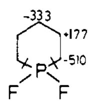
potentials in the $\lambda^5$ series are mainly caused by the varying positive charge on the phosphorus atom and not by the also differing hyperconjugative bonding abilities of the various exocyclic P-X (X = C, O, Cl, F, N) bonds. The latter conclusion is further supported by the plot of Figure 8, where the change in the first ionization potential ($\Delta$IP) of the $\lambda^5$-phosphorins **4** to **10** is represented as a function of the charge on phosphorus. The role of the phosphorus d orbitals discussed above is fully reflected in the charge diagrams (charges in $10^{-3}$ e) shown below for three representative interrupted cases. **57–59** and **60–62** give the $\pi$ charges in the sp and spd basis, respectively, and **63–65** and **66–68** gather the corresponding total charges. Comparison with the corresponding coupled cases (i.e., **57–59** with **24**, **26**, and **28**, **60–62** with **38**, **40**, and **42**, **63–65** with **31**, **33**, and **35**, and **66–68** with **45**, **47**, and **49**) confirms that the hyperconjugative coupling process leads only to minor changes in the charge densities. It is only by addition of the d orbitals that the picture changes appreciably, as a consequence of their $\pi$-charge withdrawal from the ring atoms.



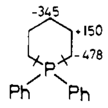
57



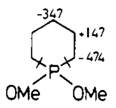
58



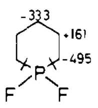
59



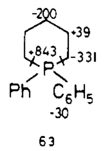
60



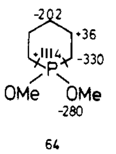
61



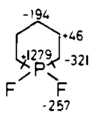
62



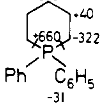
63



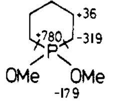
64



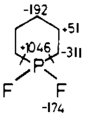
65



66

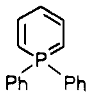


67



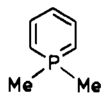
68

Because of the close correspondence between subunit charge transfer and the stabilization to be expected on the subunit coupling process, we must anticipate low stabilization energy on hyperconjugative coupling (i.e., coupling introduced in the sp calculations) and higher stabilization energy on allowing d orbitals to partake in conjugation (i.e., coupling introduced in the spd calculations). These expectations are met as shown below in **69–75** (stabilization energies in kcal/mol, the upper values refer to sp and the lower ones to spd calculations). It might be interesting to quote here the corresponding stabilization (conjugation) energies in phosphorin (**16**), which amount to 129 (sp) and 154 (spd) kcal/mol, respectively.[28] Though it is difficult at present to assess the exact quantitative meaning of these values, there is some indication that they are somewhat too high (the MINDO/2 conjugation energies amount to about 70% of the CNDO/S ones[25]). In view of these



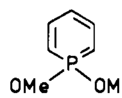
35.8
96.0

69



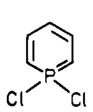
18.3
82.1

70



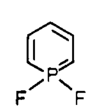
16.5
78.3

71



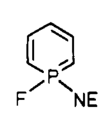
27.4
92.5

72



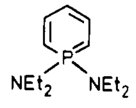
27.7
97.5

73



16.5
87.4

74



20.2
79.1

75

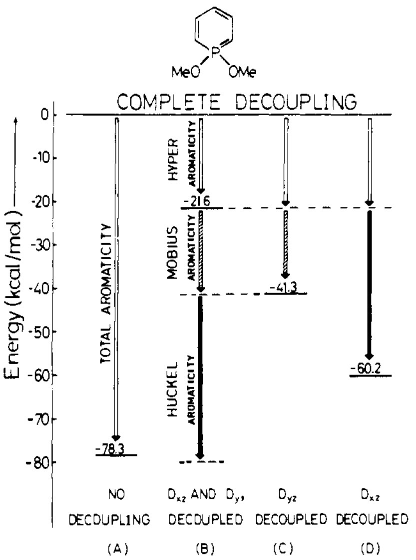
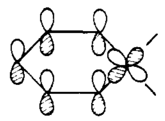


**Figure 9.** Graphical representation of the various energetic effects evaluated on successive individual decoupling processes between d orbitals on phosphorus and the $\pi$ orbitals of the pentadienyl unit. Case A represents the total conjugative effect between the pentadienyl and $PR_1R_2$ subunits. Cases C and D reproduce the conjugative energetic contributions of the $d_{xz}$ and $d_{yz}$ orbitals, respectively, and case B shows at first the gain in energy if both d orbitals are excluded from conjugation (shown as solid level) and secondly the total conjugative effect obtained on summing up the three individual contributions from B, C, and D. Using current notation the three effects are referred to as "hyperaromaticity", Möbius "aromaticity", and Hückel "aromaticity". The three individual effects are symbolized in B, C, and D as open, shaded, or black arrows, respectively. All calculations are based on the CNDO/S method.

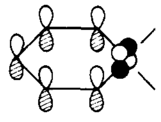
results, the $\lambda^5$-phosphorins might be referred to as "aromatic" systems. However, because of the problems and possible pitfalls connected with the "aromaticity" concept and in the face of some previous[5] attempts to distinguish between "aromatic", "antiaromatic", and "conjugatively interrupted" models for $\lambda^5$-phosphorins, we decided to seek further insight into the above obtained stabilization energies on the following novel lines.

The terms "aromatic", "antiaromatic", and "conjugatively interrupted at phosphorus" in connection with the $\lambda^5$-phosphorins were utilized with respect to the possible involvement of the d orbitals on phosphorus in a cyclic conjugation process.[5] Supposing the $d_{yz}$ orbital exclusively contributes to the $\pi$ atomic orbital basis, then we deal with a Hückel-type basis.[29,30] If, on the other hand, phosphorus uses its $d_{xz}$ orbital only, the resulting atomic orbital basis is of the Möbius type.[29-31] Finally, if the $d_{xz}$ and $d_{yz}$ orbitals are thought to contribute with exactly equal weights, then we refer here to this type as Dewar type[32] (for a pictorial representation of the various types, see below). In the first instance (Hückel type) "aromatic" stabilization, in the second instance (Möbius type) "antiaromatic" destabilization, and in the last example (Dewar type) some intermediate energetic effects are to be anticipated. Whatever destabilization might be believed to mean, we understand it here to be synonymous with less stabilization than in the aromatic case and "conjugatively interrupted at phosphorus" with some intermediate gain in energy, in between both (the aromatic and antiaromatic) limiting cases.

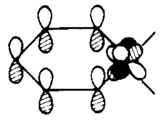
Our method for analyzing conjugative interactions and energetic effects connected therewith is ideally suited for looking into the three different models proposed for $\lambda^5$-phosphorins. For the procedure and results obtained, see Figure 9. First, we exclude conjugation between the five $p_\pi$ orbitals on the carbon atoms and both d orbitals (model B), then we exclude conjugation with the $d_{yz}$ orbital alone (model C), and



Hückel-type



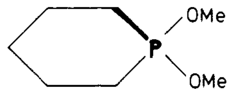
Möbius-type



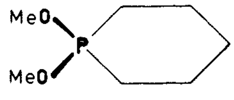
Dewar-type

subsequently with the $d_{xz}$ orbital alone (model D). In each case the total energies are calculated, referenced against the completely decoupled case, and compared with the stabilization energy (−78.3 kcal/mol) of the all-coupled case (model A). All calculations are performed in the spd parametrization scheme and made for the $\lambda^5$-phosphorin **19.** The stabilization according to model B amounts to −21.6 kcal/mol and is the energetic gain due to hyperconjugation with the exocyclic P-O bonds. Switching on conjugation with the $d_{xz}$ orbital (model C) increases the stabilization to −41.3 kcal/mol. Thus, the extra stabilization due to the $d_{xz}$ orbital is about (−41.3) − (−21.6) kcal/mol and is represented by a shaded arrow. In analogy, conjugation with the $d_{yz}$ orbital leads to (−60.2) − (−21.6) kcal/mol, $d_{yz}$ stabilization represented by a heavy black arrow. On these lines the total stabilization ("aromaticity") effect (−78.3 kal/mol) can be traced back to the "hyperaromaticity", Möbius "aromaticity", and the leading Hückel "aromaticity". Several conclusions can be drawn from these results: *$\lambda^5$-phosphorins may be classified* (if one likes to adhere to the "aromaticity" concept for these molecules and its subdivisions as "aromaticity", "antiaromaticity", and "hyperaromaticity" that we are faced with here) *as Hückel "aromatic" systems.* Nonetheless, the "hyperaromaticity" and Möbius "aromaticity" account for about half of the total stabilization in the studied molecule. In this connection it is important to be clearly aware of the fact that the Möbius-type interaction is stabilizing, though considerably less than the Hückel type, and not destabilizing relative to the complete decoupling case as one might have guessed, at first brush, on some wrongly biased understanding of the process.

In line with the picture of the electronic structure of $\lambda^5$-phosphorins developed in preceding paragraphs, we would expect little or no phosphorus $p_\pi$-orbital contribution to the $\pi$ MO's and instead its full contribution to the $PR_1(R_2)$ bonds. The expectations are fully met, as orbital and total $\pi$-density plots[33-40] demonstrate. In Figures 10 and 11 the electron density contours are plotted along the $C_{ring}$-P bond in a plane perpendicular to the molecular plane (for illustration of the respective molecular part in 1,1-dimethoxy-$\lambda^5$-phosphorin, see **76,** below). Figure 10 shows the contours without inclusion of d orbitals and Figure 11 with their inclusion. The analogous sorts of representations have been drawn in the OPO plane (for an illustration of this region in the same molecule see **77** below)



76



77

but are not shown here. Figure 10 at once clarifies that there is practically no $p_\pi p_\pi$ density contribution to the $C_{ring}$-P bond,

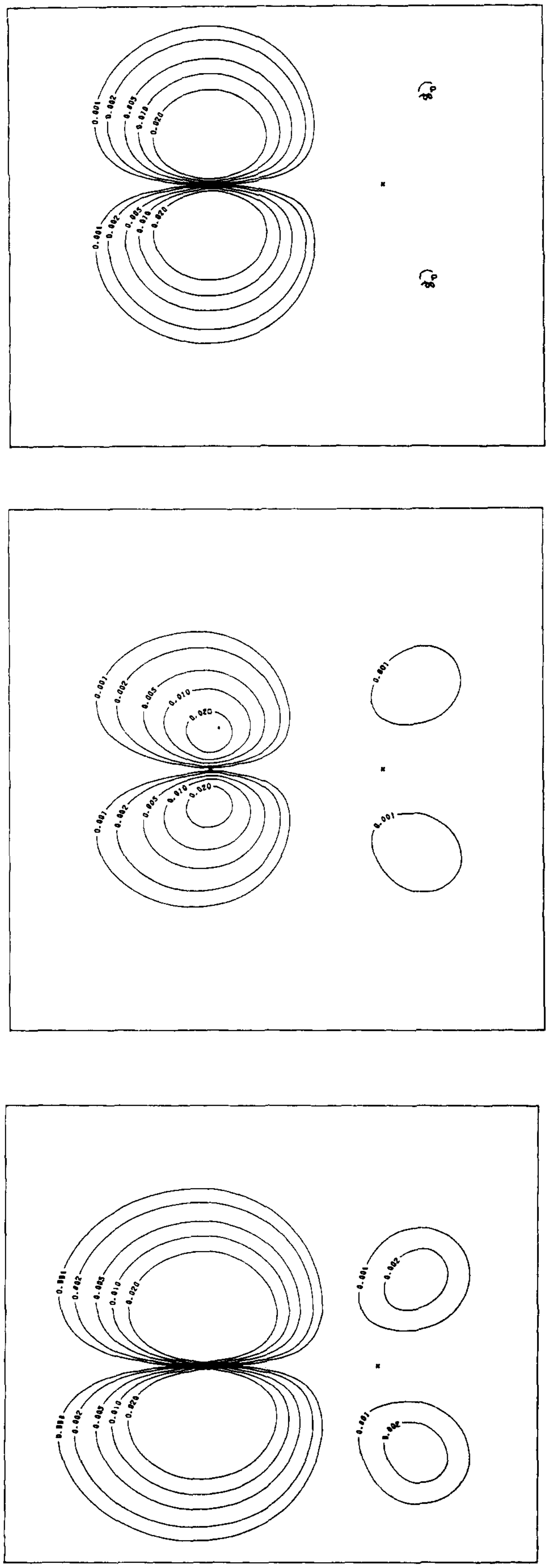


Figure 10. Contour plot of sections of the $\pi_3(b_1)$ orbital (top), the $\pi_1(b_1)$ orbital (center), and the total $\pi$ density (bottom) in a plane perpendicular to the molecular plane along the $C_{ring}$–P bond ($C_{ring}$ is on the left and P on the right). In order to get a correct representation of orbital properties,[39] the Löwdin transformed[34] CNDO/S orbital (sp basis) was used to draw the density contours.

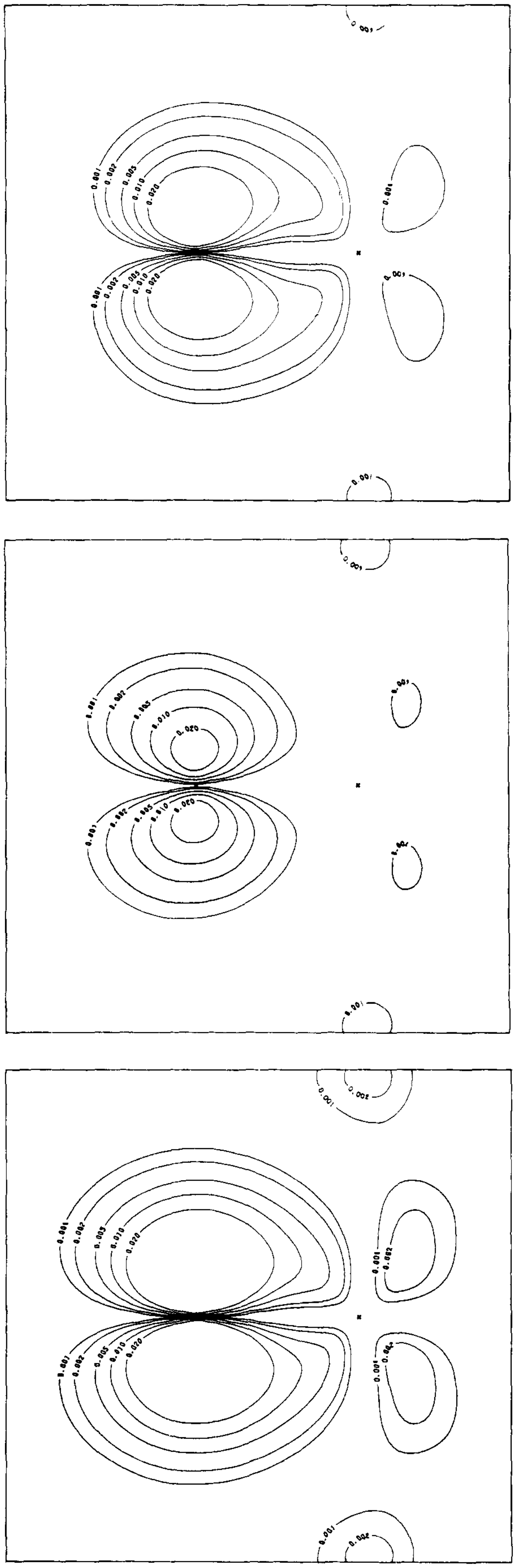
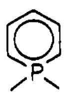


Figure 11. Contour plot of sections of the $\pi_3(b_1)$ orbital (top), the $\pi_1(b_1)$ orbital (center), and the total $\pi$ density (bottom), in a plane perpendicular to the molecular plane and along the $C_{ring}$–P bond ($C_{ring}$ left and P right). The densities shown are those resulting from Löwdin transformed[34] CNDO/S orbitals (determined in the spd basis). The sizable buildup of density in the $C_{ring}$–P bonds due to d-orbital inclusion is clearly seen.

*meaning that the $PR_1R_2$ entity is entirely $\pi$-disconnected from the five-carbon entity.* Instead, the phosphorus $p_\pi$ orbital is wholly involved in the exocyclic P–O bonding. As Figure 11 illustrates, it is the $d_\pi$ AOs that are responsible for phosphorus-ring $\pi$ bonding in full harmony with the charge transfer and stabilization energy analyses presented above.[41–43]

In conclusion, the foregoing analysis has shown that the nature of the $\pi$-electronic structure of $\lambda^5$-phosphorins is best described as a superimposition of structures symbolized as **78** and **79** below. Here **78** stands for the internal salt structure enforced by the pentavalency of phosphorus in these compounds and **79** takes care of the additional dominant presence of Hückel "aromaticity", enabled through participation of the $d_{yz}$ orbital on phosphorus in the cyclic conjugation process. The relevancy of **79** is in our opinion well documented experimentally, by the observation that the $C_{ring}$–P bond distances in **5** and **6** are 1.75[44] and 1.72 Å,[45] respectively, nearly the same as in 2,6-dimethyl-4-phenyl-$\lambda^3$-phosphorin (1.74 Å[46]), and are thus significantly less than the length of a pure C–P single bond (1.88 Å[47]). In this paper we have been able to add similar clear-cut evidence for the relevancy of **78** from our analysis of the photoelectron spectra of $\lambda^5$-phosphorins. Thus, in explaining properties of this class of compounds one should always bear in mind their ambivalent electronic structure (expressed in short-hand notation by **78** and **79**) and, in particular, one should not forget that both structural features do not exclude each other.

78



79

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were carried out using the TR4 computer at the Rechenzentrum der Universitat Marburg and the IBM 370/168 computer at the Rechenzentrum der TU Darmstadt.

## References and Notes

(1) Part 65 of "Theory and Application of Photoelectron Spectroscopy"; part 64: A. Schweig and N. Thon, *Chem. Phys. Lett.*, **38**, 482 (1976).

(2) (a) Fachbereich Physikalische Chemie; (b) Fachbereich Chemie.

(3) G. Märkl, *Heterocycl. Chem.*, **1**, S-69 (1972).

(4) K. Dimroth, *Top. Curr. Chem.*, **38**, 1 (1973).

(5) R. Vilceanu, A. Balint, and Z. Simon, *Nature (London)*, **207**, 61 (1968), and references cited therein.

(6) H. Oehling, W. Schäfer, and A. Schweig, *Angew. Chem.*, **83**, 723 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 656 (1971).

(7) C. Batich, E. Heilbronner, V. Hornig, A. J. Ashe, III, D. T. Clark, U. T. Cobley, D. Kilcast, and I. Scanlan, *J. Am. Chem. Soc.*, **95**, 928 (1973).

(8) For the purpose of $\pi$-orbital classification, all molecules treated (**3–10** and **17–23**) are regarded to have $C_{2v}$ symmetry.

(9) A. Schweig, W. Schäfer, and K. Dimroth, *Angew. Chem.*, **84**, 636 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 631 (1972).

(10) W. Schäfer, A. Schweig, G. Märkl, and K.-H. Heier, *Tetrahedron Lett.*, 3743 (1973).

(11) K. W. Schulte and A. Schweig, *Theor. Chim. Acta*, **33**, 19 (1974). All calculations are performed using the PSS1 parametrization scheme.

(12) G. Lauer, K.-W. Schulte, and A. Schweig, *Chem. Phys. Lett.*, **32**, 163 (1975).

(13) Ionic states calculated on the base of Koopmans' theorem: T. Koopmans, *Physica*, **1**, 104 (1934).

(14) G. Lauer, W. Schäfer, and A. Schweig, *Chem. Phys. Lett.*, **33**, 312 (1975).

(15) T. Buntgaard, H. J. Jakobsen, K. Dimroth, and H. H. Pohl, *Tetrahedron Lett.*, 3179 (1974).

(16) D. T. Clark and I. W. Scanlan, *J. Chem. Soc., Faraday Trans. 2*, 1222 (1974).

(17) N. C. Baird, *Theor. Chim. Acta*, **16**, 239 (1970).

(18) H. L. Hase and A. Schweig, *Tetrahedron*, **29**, 1759 (1973).

(19) C. Müller, A. Schweig, and H. Vermeer, *Angew. Chem.*, **86**, 275 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 273 (1974).

(20) H. Schmidt, A. Schweig, R. W. Hoffmann, and H. Kurz, *Tetrahedron Lett.*, 1953 (1974).

(21) H. Schmidt, A. Schweig, and A. Krebs, *Tetrahedron Lett.*, 1471 (1974).

(22) W. Schäfer, A. Schweig, G. Maier, T. Sayrac, and K. J. Crandall, *Tetrahedron Lett.*, 1213 (1974).

(23) C. Müller, A. Schweig, and H. Vermeer, *J. Am. Chem. Soc.*, **97**, 982 (1975).

(24) H. Schmidt, A. Schweig, F. Mathey, and G. Müller, *Tetrahedron*, **31**, 1287 (1975).

(25) W. Schäfer, A. Schweig, and F. Mathey, *J. Am. Chem. Soc.*, **98**, 407 (1976).

(26) H. L. Hase, C. Müller, and A. Schweig, manuscript in preparation.

(27) The results do not confirm our previous[9] ad hoc assumption on the origin of the unusually low first ionization potential (namely that it is caused by the hyperconjugative interaction of the $\pi_3(b_1)$ orbital and an orbital of the $PR_1R_2$ grouping). Of course, this effect is operating, too, but is of minor importance compared to the effect resulting from the anionic nature of the five-carbon unit itself.

(28) It is interesting to note here that in the case of $\lambda^3$-phosphorins (that possess a tervalent phosphorus atom), the decoupling process results in a pentadienyl cation and a negatively charged (just carrying one extra electron) phosphorus atom.

(29) See e.g.: H. E. Zimmermann, *Acc. Chem. Res.*, **4**, 272 (1971).

(30) See e.g.: M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(31) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).

(32) This model of two orthogonal $d_\pi$ atomic orbitals that interrupts conjugation at the phosphorus atom was put forward by M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960), for the electronic structure of phosphonitrilic halides. Later on, the model was adapted to $\lambda^5$-phosphorins by others.[5]

(33) The orbital plots show the CNDO/S density after renormalization by the Löwdin transformation (including diatomic overlap).[34] This ZDO orbital renormalization procedure was previously used on the CNDO/2 (INDO) level by several authors.[35–38] As previously shown, only the renormalized orbitals produce electron densities with correct nodal properties.

(34) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

(35) C. Giesner-Prettre and A. Pullman, *Theor. Chim. Acta*, **11**, 159 (1968).

(36) D. D. Shillady, F. P. Billingsley, and J. E. Bloor, *Theor. Chim. Acta*, **21**, 1 (1971).

(37) D. B. Boyd, *J. Am. Chem. Soc.*, **94**, 64 (1972).

(38) J. W. McIver, P. Coppens, and D. Nowak, *Chem. Phys. Lett.*, **11**, 82 (1971).

(39) H. L. Hase, H. Meyer, and A. Schweig, *Z. Naturforsch. A*, **28**, 361 (1974).

(40) For the plot program used, see: (a) H. Hahn and J. Radloff, *Electron. Rechenanl.*, **14**, 128 (1972); (b) H. L. Hase, A. Schweig, H. Hahn, and J. Radloff, *Tetrahedron*, **29**, 475 (1973); (c) *ibid.*, **29**, 469 (1973).

(41) As it must be emphasized, these results are not fully independent of the valence electron method used in the calculations. The CNDO/2 method[42] in its original parametrization and with inclusion of d orbitals on phosphorus yields an appreciable contribution of the phosphorus $p_\pi$ orbital to the $\pi$ orbitals partially replacing the $p_\pi$ orbital in the $\sigma$ bonds by the $d_\pi$ orbitals.[42] Since it is rather certain that the CNDO/2 method overemphasizes the degree of d-orbital participation,[16] and that, according to our experience, the extended CNDO/S method[11] behaves much more realistically in this respect, the results of the latter method must be considered to have much more weight. Though all these effects are of minor importance and do not change anything on the gross features of the electronic structure of $\lambda^5$-phosphorins elucidated here ab initio calculations[43] have been started in the hope that further insight into the problem outlined above can be provided.

(42) H. Oehling and A. Schweig, *Tetrahedron Lett.*, 4941 (1970).

(43) Work by H. L. Hase and A. Schweig.

(44) J. J. Daly and G. Märkl, *Chem. Commun.*, 1057 (1969).

(45) U. Thewalt, *Angew. Chem.*, **81**, 783 (1969).

(46) J. C. J. Bart and J. J. Daly, *Angew. Chem.*, **74**, 60 (1962).

(47) L. Maier in *Prog. Inorg. Chem.*, **5**, 27 (1963).