Tetrahedron Letters No.56, pp. 4941-4944, 1970. Pergamon Press. Printed in Great Britain.

A CNDO/2 APPROACH TO THE ELECTRONIC STRUCTURE OF PHOSPHABENZENES

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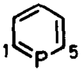
(Received in UK 9 October 1970; accepted for publication 5 November 1970)

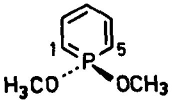
Dedicated to Professor Dimroth on the occasion of his 60th birthday

Introduction

In this letter the phosphabenzenes I[1] and II[2] are investigated theoretically.



I



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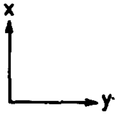


As has been shown on derivatives of these molecules[3] the heterocyclic rings of both I and II are planar with PC bond lengths intermediate between single and double bond lengths and CC bond lengths practically the same as in benzene. From these data one must conclude that in both compounds the phosphorus atom takes part in the ring conjugation. In this context interesting questions remain for theoretical investigation, namely: (1) what orbitals on the phosphorus atom participate in π bonding and, in particular, to what extent they do?, (2) what hybrids on the phosphorus atom are involved in the PC σ bonds?, (3) what is the nature of the phosphorus lone pair?, and (4) what is the direction of the molecular dipole moment?

Results and Discussion

To explore these problems we used the CNDO/2[4] method. Both molecules have C_{2v} symmetry. Thus in the coordinate system used all MOs must be either symmetric or antisymmetric to the σ_{xy} and σ_{xz} planes. MOs antisymmetric to σ_{xy}

(the molecular plane) are called π MOs. On the phosphorus atom the $3p_z$, $3d_{xz}$, and $3d_{yz}$ AOs are available for π bonding with the $2p_z$ carbon AOs. Since the $3d_{xz}$AO is symmetric, the $3d_{yz}$ AO antisymmetric to σ_{xz}, no canonical π MO can be found with $3d_{xz}$ and $3d_{yz}$ contributing simultaneously.Thus, within the canonical set of MOs at least, one would predict that πelectron conjugation is continuous through phosphorus not only by the $3p_z$ AO but also by the $3d_{xz}$ and $3d_{yz}$ AOs.

The extent to which these AOs contribute to the three π MOs occupied in the ground state, may be seen from Table 1. In this Table the expansion coefficients of the π AOs on phosphorus and the adjacent carbon atoms are listed.

Table 1 π AO Expansion coefficients on phosphorus and the adjacent carbon atoms for the occupied π MOs of I and II

Molecule	Wavefunction	P			C_1	C_5
		$3p_z$	$3d_{xz}$	$3d_{yz}$	$2p_z$	$2p_z$
I	ψ_1	0.217	0.140	—	0.342	0.342
	ψ_2	—	—	-0.273	0.514	-0.514
	ψ_3	0.599	0.200	—	0.379	0.379
II	ψ_1	0.019	0.168	—	0.275	0.275
	ψ_2	—	—	-0.032	0.409	-0.409
	ψ_3	0.320	0.312	—	0.445	0.445

For I the major contribution to ring conjugation comes from the $3p_z$ AO, but there are also significant contributions from the d_{π} AOs. But most interestingly, in II there is an appreciable contribution from the $3p_z$ AO, too. This is contrary to previously made model assumptions$^{5)}$ in the case of similar tetracoordinate pentacovalent phosphorus heterocycles. According to these assumptions the $3p_z$ AO should be involved in a sp^3 hybridization on phosphorus and should thus not be taken into account for π bonding.

To get further insight into the PC σ-bonds we studied therefore the hybridization on the phosphorus atom by a previously described method[6)]. In the case of I phosphorus hybrids $s^{o.1o}p^{o.71}d^{o.2o}$ for each σ-PC bond were obtained. These hybrids overlap with practically pure sp^2 hybrids on the adjacent carbon atoms. There is only a small s contribution to the phosphorus hybrids. This may help to explain the small CPC bond angle which is found to be 1o3°. The corresponding phosphorus hybrids involved in the PC bonds of II were found to be $s^{o.3o}p^{o.48}d^{o.22}$. There is more s contribution to this hybrid in II than in I. This compares favourably with the greater angle of 1o7° in II than in I. The PO bonds cannot be considered as localized because of $\pi\sigma$-AO mixing in these bonds. Therefore, the phosphorus σ- hybrids for these bonds cannot be derived in the same simple manner.

Contrary to pyridine[7)] the highest occupied MOs in I and II are π MOs. The next lower MO in I is 6o % localized on phosphorus and thus may be regarded as a delocalized phosphorus lone pair. The expansion coefficients of the phosphorus AOs in I and for comparison for the nitrogen AOs in pyridine are shown for the "lone pair" MOs in Table 2.

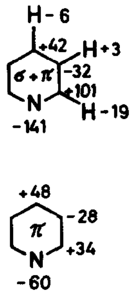
Table 2 AO Expansion coefficients on nitrogen and phosphorus for the "lone pair" MOs in I and pyridine

Atom	s	p_x	d_z2	$d_x2 - y2$
N	o.248	- o.582	—	—
P	o.416	- o.626	o.136	o.155

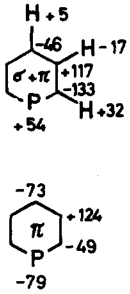
As one sees from this Table the phosphorus "lone pair" has more s participation than the nitrogen lone pair. This agrees with the finding of smaller s contribution to the σ-ring hybrids on phosphorus than on nitrogen. The d_z2 and $d_x2{-}_y2$ contributions tend to enlarge the free electron pair in the xz plane. Thus for phosphorus a more diffuse and less directed lone pair than for nitrogen in pyridine is predicted.

The electron distribution in I and II and for comparison in pyridine (units of

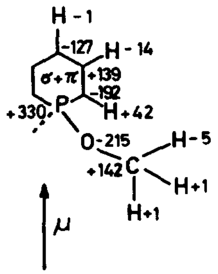
1o^{-3} electrons) are shown in the following molecular diagrams.



pyridine



I



II

As one sees the charge distributions in I and II are dramatically different from that in pyridine. In particular, it is not possible to explain the π charge distributions in I and II as in pyridine by simple π resonance theory. Phosphorus withdraws nearly the same amount of π charge from the rest of the ring as nitrogen in pyridine does, but curiously from the m ring position. Whereas as expected σ charge, too is shifted from the rest of the ring to nitrogen, phosphorus donates σ charge back to the ring.

The dipole moments[2], measured for derivatives of I and II are lower than for pyridine. The directions, however, as these calculations show remain the same.

Acknowledgements

The authors wish to thank the Deutsche Rechenzentrum for providing QCPE 91, 136 and 141 and for performing the calculations. This work was supported by the Deutsche Forschungsgemeinschaft.

References

1) G.Märkl, Angew.Chem.,78,9o7 (1966), K.Dimroth and W.Mach, Angew.Chem.,8o, 489 (1968), 2) K.Dimroth and W.Städe, Angew.Chem.,8o,966 (1968), 3) J.C.J.Bart and J.J.Daly, Angew.Chem., 8o,843 (1968), U.Thewalt, Angew.Chem.,81,783 (1969), 4)J.A.Pople and G.A.Segal, J.Chem.Phys.,43,S129 (1965), D.P.Santry and G.A.Segal, J.Chem.Phys.,47,158 (1967), 5) M.J.S.Dewar, E.A.C.Lucken and M.A.Whitehead, J.Chem.Soc.,196o,2423, G. Märkl, Angew.Chem.,75, 1121 (1963), 6) K.B.Wiberg, Tetrahedron, 24,1o83 (1968), C.Trindle and O.Sinanoglu, J.Am.Chem.Soc.,91,853 (1969), 7)J.E.Bloor and D.L.Breen, J.Am.Chem.Soc.,89,6835 (1967).