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HETEROAROMATICITY. 4[1]. THE STATUS OF PHOSPHORUS AND ARSENIC AS HETEROATOMS.

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Abstract-Aromaticity indices are reported for a range of phosphorus and arsenic containing heterocycles. Five and six-membered rings with phosphorin-type phosphorus have similar indices to their nitrogen counterparts. The arsenic analogues are less aromatic. 1H-Phospholes show less aromaticity than the corresponding oxygen heterocycles.

Phosphorus and arsenic are relatively new additions to the traditional elements associated with heterocycles. While the relative abilities of oxygen, sulphur and selenium to contribute to the aromaticities of their respective heterocycles are fairly well established, the situation with regard to nitrogen, phosphorus and arsenic is as yet unclear. To date two different theoretical treatments have deduced disparate resonance energies for phosphorin of 64[2] and 109kJ/mol[3], with the latter value being closely comparable to that of 107 kJ/mol obtained for pyridine by the same method. For the five-membered heterocycles thiophene, pyrrole, furan and phosphole ab initio calculations have provided resonance energies of 149, 124, 89 and 54 kJ/mol respectively[4,5]. The current availability of molecular dimensions for a range of phosphacycles and some arsacycles permits an experimentally based assessment using the aromaticity indices introduced in preceding papers[6,7,8] in this series. These indices are based upon a statistical evaluation of the deviations in peripheral bond orders and are provided by the equation $I = 100(1-V)/V_K$ where $V = 100/\bar{N}\sqrt{\Sigma(N-\bar{N})^2/n}$ and $\bar{N}$ is the arithmetic mean of the n various ring bond orders, N. V_K is the value of V for the corresponding non-delocalised Kekulé form with alternating single and double bonds. The especial value of these indices for providing quantitative assessments of aromatic character has been indicated by a recent evaluation[9] of a range of physicochemical criteria commonly used for this purpose.

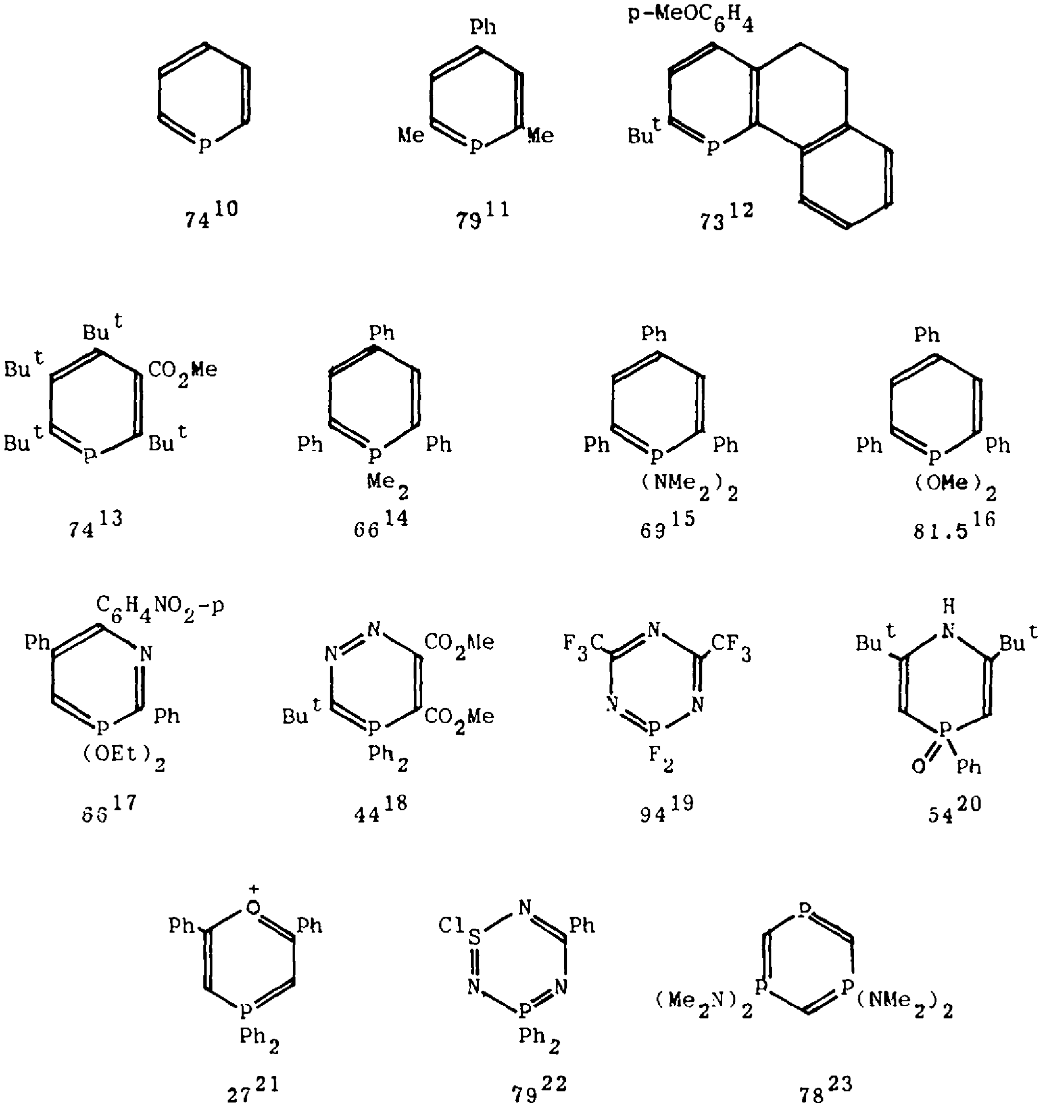


FIGURE 1 Aromaticity indices (I_6) for six-membered ring phosphacycles. (The references are to the source of bond lengths used for their calculation.)

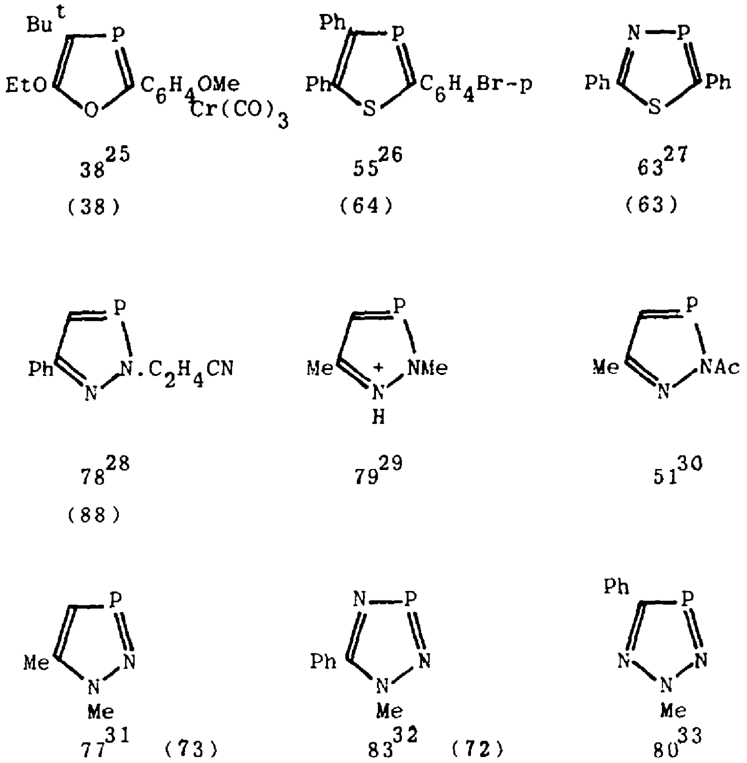
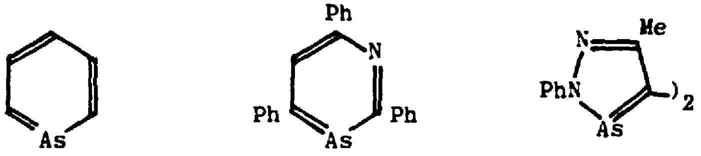


FIGURE 2 Aromaticity indices (I_5) for five-membered ring phosphacycles. The figures in parentheses are the I_5 values for the corresponding aza-analogues taken from reference 6. (The references are to the sources of molecular dimensions.)

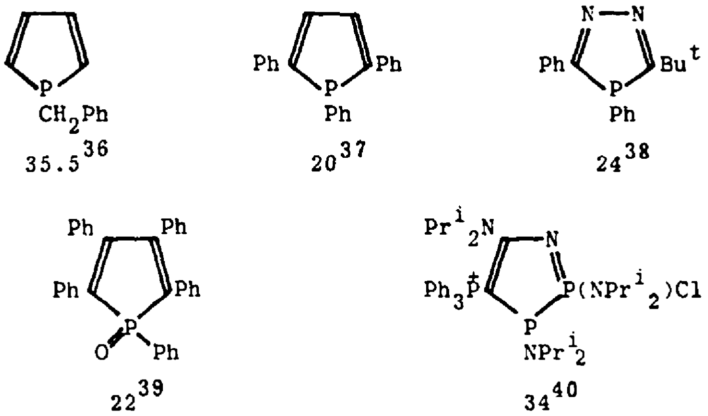
The I_6 values calculated for six-membered phosphorus containig heterocycles are shown in Figure 1. The values of ca. 70 to 74 obtained for the phosphorin ring may be compared to the I_6 value of 86 for pyridine[7]. A particularly interesting feature is the moderating effect of P-substituents on ring aromaticity in the λ^5-phosphorins. 2-Phenylbenzo[b]phosphorin[24] yields an $I_{6,6}$ value of 79 compared to 70 for quinoline. The unexpectedly low value of 44 for the 3,4-diaza-λ^5-phosphorin, relative to 86 for 1,2,4-triazine, is attributable to the former's adoption of a non-planar conformation described as a distorted boat[17]. Thus replacement of a pyridine nitrogen in a six-membered ring by phosphorus does not result in much change in aromaticity. Similar conclusions may be deduced for the results of comparable modifications of five-membered ring heterocycles as shown in Figure 2.



$I_6 = 67$[10] $I_6 = 50$[35] $I_5 = 77$[34]

FIGURE 3 Aromaticity indices for arsacycles. (The references are to the source of bond lengths used for their calculation.)

Aromaticity indices for those arsenic containing heterocycles for which molecular dimensions are available are shown in Figure 3. It is clear that introduction of an arsenin-type arsenic into a ring results in retention of a substantial level of aromaticity though less than bestowed by nitrogen or phosphorus.



35.5[36] 20[37] 24[38]

22[39] 34[40]

FIGURE 4 Aromaticity indices for 1H-phospholes (I_5).(The references are to the source of bond lengths used for their calculation.)

A contrasting situation is encountered with the 1H-phospholes, cf. Figure 4, where the phosphorus ring atom is significantly displaced from the plane containing C(2) - C(5). Unlike the situation in pyrrole where the nitrogen substituent lies in the plane of the ring as a result of sp^2 hybridisation of the nitrogen with the remaining $2p^2$ orbital orthogonal and able to overlap fully with the carbon 2p orbitals, the phosphorus in 1H-phospholes retains pyramidal geometry. It has been shown[41] that comparable behaviour in the case of nitrogen would result in a resonance interaction of only about 80% of that realised with sp^2 hybridised nitrogen, and a decrease of similar magnitude would be anticipated with phosphorus. The data in Figure 4 attest to the low aromaticity of these phospholes which have I_5 values lower than furan, $I_5 = 43$[6]. The low aromaticities displayed by the other heterocycles in this group are also attributable to these effects. It may be noted that the only phosphindole for which partial dimensions are available[42], is also nonplanar with a pyramidal phosphorus thus predicating the possession of similar minimal aromaticity.

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