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Investigation of 3-substituted benzazaphospholes and benzazarsoles by UV-photoelectron spectroscopy

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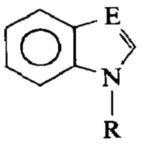
Abstract

The conjugative interaction in some phosphorus and arsenic analogues of benzimidazoles has been studied by UV photoelectron spectroscopy. The spectra have been interpreted with the aid of MNDO quantum-chemical calculations and comparison with other compounds containing trivalent P or As atoms. Comparison of the band positions for the P lone pair in various compounds indicated that the interaction with the π-system is small, and it is even lower for the arsenic lone pair.

The conjugative ability of the nitrogen atoms has been much studied. Participation of nitrogen in conjugated systems can be achieved in two different ways, either by the conjugation between the lone pair of nitrogen and a π-system (as in pyrrole) or between a C=N double bond and the π-system of the molecule (as in pyridine). Investigation of 1,3-benzazaphosphole and benzazarsole presents the opportunity to consider these two types of conjugation in the case of phosphorus and arsenic. The molecules can exist in two isomeric forms. If the substituent is linked to the nitrogen atom as in I, the heavy atom E can participate in conjugation of the pyridine type, whereas in the case of the isomer II, which has the substituent on the heavy atom there is an opportunity for conjugation of the pyrrole type.

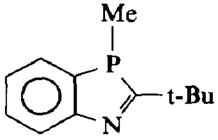


(I)

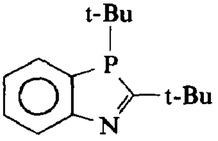
(II)

From UV and NMR studies it was found [1] that the properties of the two isomeric systems are markedly different. In this paper we report our ultraviolet photoelectron spectroscopic investigations of the electronic structures of 1,3-benzazaphosphole and 1,3-benzazarsole derivatives. The study involved 2-t-butyl-3-methylbenzazaphosphole (**1**), 2,3-di-t-butylbenzazaphosphole (**2**), and 2-t-butyl-3-

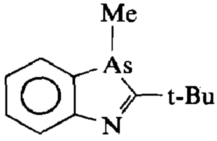
methylbenzazarsole (**3**), all belonging to type II systems.



(**1**)



(**2**)



(**3**)

The simplest compounds containing a phosphorus or arsenic atom with a lone electron pair are those analogous to ammonia. From the photoelectron spectra it was found [2] that the ionization energy assigned to the lone pair of fifth main group elements in the compounds from NH_3 to SbH_3 remained practically constant. Similar conclusions were drawn for the trimethyl substituted derivatives [3], but the replacement of hydrogen atoms by methyl groups lowers the ionization energy of the lone pair by more than 1 eV. For both series of compounds the constancy of the ionization energy can be interpreted in terms of the operation of two effects, the effect of the change in the bond angles around the central atom being countered by the decrease of the ionization energy in the case of the heavy atoms such as P or As. Another possible explanation can be given for the methyl derivatives involving a change in the interaction with the orbitals of appropriate symmetry.

The photoelectron spectrum of phenylphosphine [4–6] has been studied by several groups. According to Schmidt and Schweig [5] the interaction between the lone pair and the π-system of benzene is negligible, but Dewar et al. [6] judged this interaction to be significant. The corresponding interaction in vinylphosphine was also considered by Schmidt and Schweig [5] to be of little importance.

The photoelectron spectra of 1,2,3-trimethylphosphole (**4**) and 1-t-butyl-3,4-dimethylphosphole (**5**) were interpreted with the aid of CNDO quantum-chemical calculations and judged to indicate only a small degree of interaction between the lone pair and the ring [7]. The non-planar structure was accounted for in terms of a relatively significant π-σ(P–C) interaction.

Experimental

The synthesis of the investigated compounds was described previously [1]. Spectra were recorded at the HeI resonance line by use of a cylindrical mirror analyzer. The resolution at the $Ar\,^2P_{3/2}$ line was 0.045 eV (FWHM).

Quantum chemical calculations were carried out by MNDO method [8] with the assumption of Koopmans' theorem. The geometries of the compounds were optimized in terms of the total energy.

Results and discussion

The electronic structures of compounds **1–3** can be derived by combination of the lone electron pair of the heavy atom, the π-system, including the benzene π-orbitals, and the π-orbital of the C=N fragment. In addition a further band can be expected at lower ionization energies, arising from the lone pair of the nitrogen atom in the plane of the molecule; this lone pair cannot interact with the π-system.

The photoelectron spectra of compounds **1–3** and that of benzimidazole (**6**) are

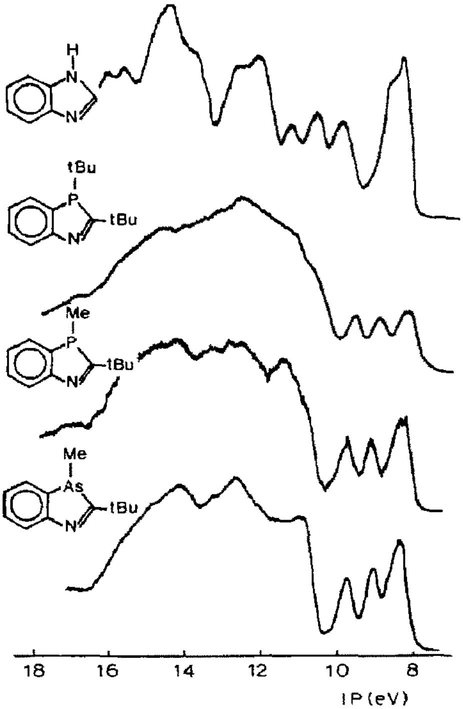
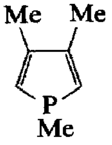
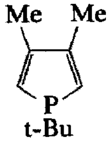


Fig. 1. UP spectra of 3-substituted 1,3-benzazarsole and benzazaphospholes.

illustrated in Fig. 1, and the observed and calculated ionization energies and the assignments of the bands are summarized in Table 1. The spectra of molecules containing heavy atom (P or As) show a new band at about 9 eV, whereas the positions of the other bands do not change significantly with respect to those for benzimidazole, and so the new band can be assigned to the lone pair of electrons of the heavy atom. The assignment is supported by the shift of the band by 0.2 eV when the methyl substituent on phosphorus is replaced by a t-butyl group (compounds **1** and **2** in Table 1). Practically the same shift is experienced in the case of 3,4-dimethylphospholes [1] (compounds **4** and **5** in Table 1).



(4)



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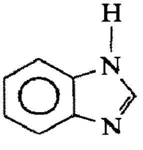

(6)

PMe_3 (7)

$AsMe_3$ (8)

The first broad band of high intensity arises from overlap of two ionizations, as in the spectrum of benzimidazole, and can be assigned to two π-orbitals. The replacement of the methyl group by a t-butyl group results in a shift of the band by 0.1 eV.

The third band in the spectra of compounds **1**–**3**, between 9.5 and 9.8 eV, can be recognised as an n_N band since it shows only a small shift compared with the band assigned to the lone pair of nitrogen in the spectrum of 1-*H*-benzimidazole.

Further diffuse overlapping bands include a π-band in the region of lower

Table 1

Observed and calculated ionization energies of compounds **1**–**8**

	π	π	n_E	n_N	π		
1 m	8.25	8.40	9.17	9.76	10.8	11.6	
c	9.19	9.44	10.47	11.20	11.77	12.25	
2 m	8.15	8.30	8.94	9.56	10.8		
3 m	8.25	8.45	8.96	9.66	10.84 [b]	11.5	
4 m			8.25		8.25		[6]
c			9.76		9.35		
5 m			8.05		8.05		[5]
c			9.51		9.28		
6 m	8.42	8.81	10.74	10.05	11.40		
c	8.86	8.95 [a]	11.32 [a]	11.36	11.95 [a]	14.99 [a] π	
7 m			8.60			11.34 $\sigma(p\text{-C})$	[3]
8 m			8.65		10.70 σ(AsC)		[3]

[a] The orbital has significant contribution of N lone pair. [b] $\pi + \sigma$(AsC), m = measured, c = calculated.

energies, and in the case of the arsenic derivative a σ band (σ(As–C)) shifted to the same region, as is suggested by comparison of the spectral data in Table 1 for trimethylphosphine (**7**) and trimethylarsine (**8**). The increase in the relative intensity at 10.8 eV for the benzazarsole derivative (**3**) also supports this interpretation.

The band at 10.74 eV in the spectrum of benzimidazole (**6**) can be assigned to a π-orbital in which the contribution from the out of plane p-orbitals of nitrogen atoms is significant, but the lone pair contribution to other π-orbitals cannot be neglected (see Table 1).

MNDO calculations support our assignments. Optimization of the geometry of **1** indicated a non planar structure, in accordance with conclusions drawn previously from NMR spectra [1].

The data in Table 1 present a comparison of the position of the band attributed to the lone pair of the heavy atom with those for other molecules containing trivalent atoms of phosphorus or arsenic (**4**–**8**). The shift with respect to the position of the band for trimethyl derivatives is slight (and even smaller for the benzazarsole derivatives than for the corresponding phosphorus compounds). The band in the case of phospholes (**4**,**5**) is displaced toward lower ionization energies compared relative to the band in the spectrum of trimethylphosphine, and a shift in the opposite direction occurs in the case of the benzazaphospholes.

Although this feature can be partly attributed to the change of the geometry in the neighborhood of the heavy atom, the observed shifts can be qualitatively

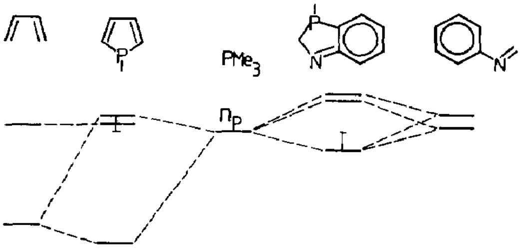

Fig. 2. Correlation diagram for the lone pair combination of phosphorus with π-systems.

accounted for in terms of the interaction diagram illustrated in Fig. 2. For symmetry reasons, in the case of the phosphole derivatives the n_p orbital can combine only with the lower energy π_1 orbital of the *cis*-diene fragment, whereas for the benzazaphospholes the lone electron pair can be combined with the first two π-levels of the substituted benzene. (According to EPIOTIS [9], interaction with π^* orbitals may also be of importance, but this effect is much the same for both systems.) The small shift indicates that there is only a small degree of conjugation is even less in the arsenic derivatives.

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