Journal of Organometallic Chemistry, 373 (1989) 49–55
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20001

Investigation of heterocyclic compounds containing a P=C or As=C bond by ultraviolet photoelectron spectroscopy

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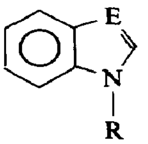
(Received March 17th, 1989)

Abstract

The He(I) ultraviolet photoelectron spectra of benzene-fused heterocycles containing As=C and P=C double bond have been recorded, and interpret MNDO and CNDO/S quantum-chemical calculation carried out to assist interpretation of the data. The analysis of the spectra indicates that there is a strong interaction between the E=C double bond and the π-system of the molecule. In contrast the conjugative effect of the phosphorous or arsenic lone pair gives rise to completely different spectra for 1,3-benzazaphospholes or -arsoles substituted in 1 or 3 positions.

The study of 1,3-benzazaphosphole and 1,3-benzazarsole derivatives substituted in position 3 (type II) indicated only a slight degree of conjugation between the lone electron pair of phosphorus and the π system of the molecules, and the degree of conjugation is even smaller in the case of arsenic derivatives [1]. Recording of the photoelectron spectra of 1-substituted-1,3-benzazaphospholes and 1,3-benzazarsoles (type I) has provided an opportunity to investigate the conjugative ability of P=C< and As=C< fragments, in these molecules. Previous investigations involving UV and NMR studies [2] have revealed significant differences between the properties of the two isomeric series. The aim of the present work was to interpret the differences in terms of the electronic structures.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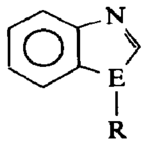
(II)

(E = P, As)

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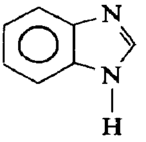
Only a few photoelectron spectroscopic (UPS) investigations have been reported of compounds containing the phosphorus(III)–carbon and arsenic(III)–carbon double bonds. The simplest compound, 2-phosphapropene ($CH_3P{=}CH_2$), was studied by Bock et al. [3]. They assigned the band at 9.69 eV to ionization from the π orbital and the band at 9.97 eV to the lone electron pair of phosphorus. Batich et al. [4] recorded the spectra of compounds analogous to pyridine, while Ashe et al. measured the angular distribution of the outgoing electrons [5]. The photoelectron spectrum of tri-t-butylphosphorine was reported and assigned by Oehling et al. [6]; Gudat et al. [7] studied the spectra of the compounds $RP{=}C(SiMe_3)_2$.

With the exception of the pyridine analogue arsabenzene [4], no compound containing As=C double bond has been studied by UPS. Quantum chemical calculations on $P{=}C\lessdot$ and $As{=}C\lessdot$ compounds [8,9] revealed the inverted polarity of these bonds compared to that of the $N{=}C\lessdot$ bond. While nitrogen is negatively charged, the heavy atoms of P and As bear a significant positive charge, so that protonation at the carbon side is favoured. The reactivities of the 1,3-benzazaphosphole heterocycles have been interpreted on the basis of CNDO/2 calculations [10].

We have investigated the following compounds: benzimidazole (**1**), 1-methyl-1,3-benzazaphosphol (**2**), 1-methyl-1,3-benzazarsol (**3**), 1.6-dimethyl-1,3-benzazarsol (**4**), 1,2,6-trimethyl-1,3-benzazarsol (**5**), 1-methyl-2-trimethylsilyl-1,3-benzazarsol (**6**), and compounds containing oxygen instead of nitrogen , namely 2-methylbenzoxazole (**7**), 2-methyl-1,3-benzoxaphosphol (**8**), 2-t-butyl-1,3-benzoxaphosphol (**9**), and 2-t-butyl-1,3-benzoxarsol (**10**), and some analogous compounds containing nitrogen instead of phosphorus or arsenic.



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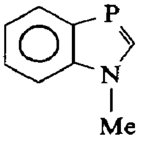

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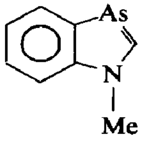

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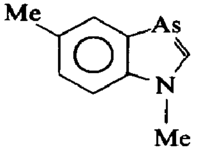

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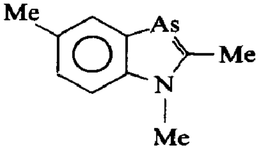

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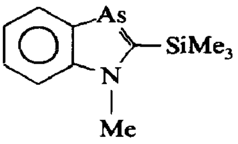

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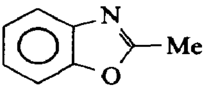

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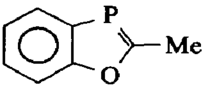

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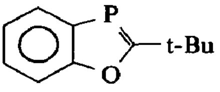

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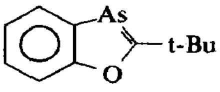

(10)

Experimental

The syntheses of the investigated compounds [2,11,12] and the photoelectron spectrometer used [13] were described previously. Spectra were recorded at the

He(I) resonance line, the resolution at the $Ar^2P_{3/2}$ line was 0.045 eV (FWHM). Calibration was carried out with Ar and MeI.

Quantum chemical calculations were carried out by the MNDO method [14] and a modified version of the CNDO/S method [15] with the assumption of the validity of Koopmans' theorem. Geometrical parameters for compounds containing arsenic were taken from the literature [16], while for other compounds the MNDO optimized geometry was used.

Results and discussion

The electronic structures of the investigated compounds can be established from the interactions between the π system of benzene and the system of the E=C–X fragment (E = N, P, As; X = NH, O). In the case of the fragment, two π orbitals and a lone pair orbital can be expected in the higher energy range. According to our

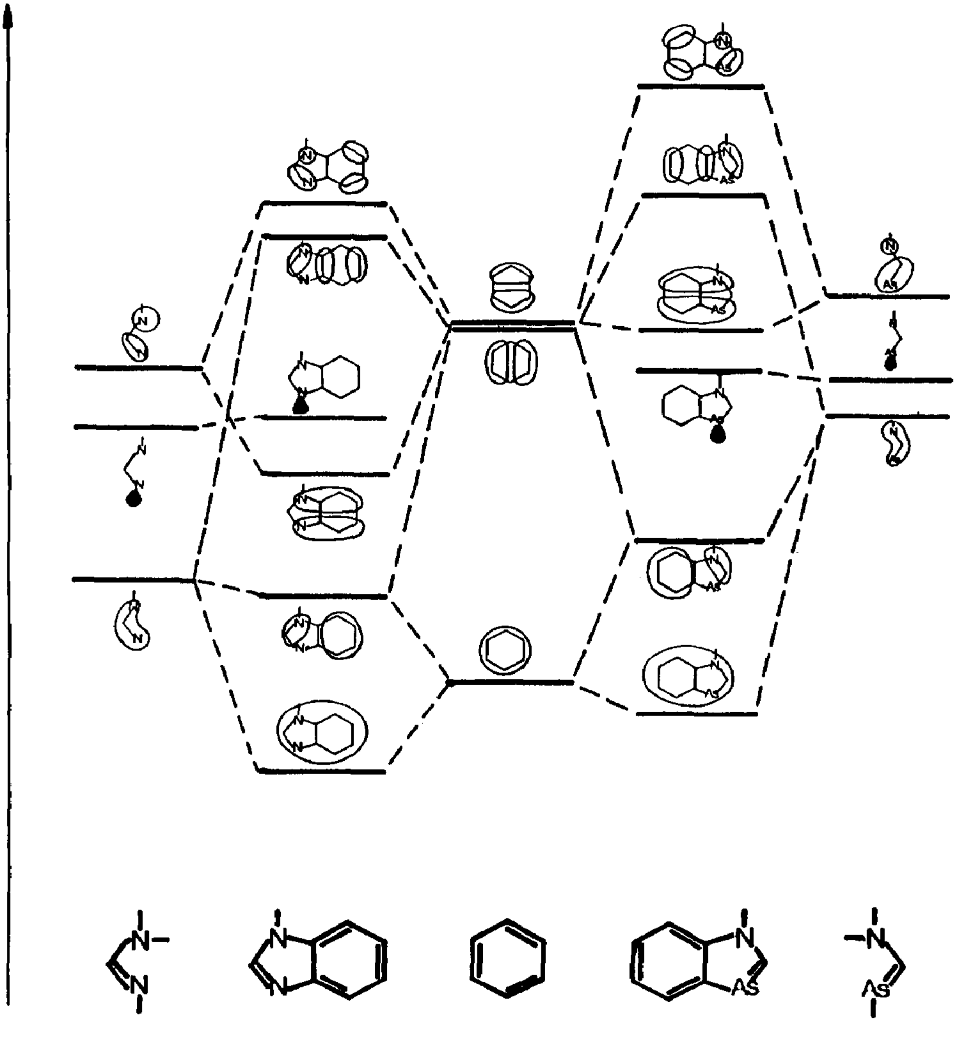

Fig. 1. Orbital correlation of benzene and E=C–N fragment.

Table 1

Ionization potentials and calculated orbital energies of compounds **1**–**10** in eV

		π_5	π_4	π_3	n_E	σ(SiC)	π_2	σ(CEC)	π_1
$CH_3P{=}CH_2$	obs.	9.69			9.97			12.4	
	MNDO	10.40(π(P=C))			10.60			13.21	[3]
	CNDO	8.55			9.59			10.73	
1	obs.	8.42	8.81	10.74	10.05		11.40		
	MNDO	8.86	8.95	11.32	11.36		11.95		14.99
	CNDO/S	8.41	8.16	10.28	10.24		11.45		14.82
2	obs.	7.68	8.41	9.56	9.71		10.9	11.5	
	MNDO	8.54	9.10	10.26	10.98		11.95	12.62	13.82
	CNDO/S	7.64	8.52	9.46	9.76		11.41	11.37	13.27
3	obs.	7.49	8.49	9.37	9.66		11.1	10.6	
	CNDO/S	7.43	8.47	9.25	9.71		11.37	10.59	11.19
4	obs.	7.16	8.19	9.2	9.3	9.9			
	CNDO/S	7.16	8.19	9.07	9.40	9.64, 9.69	11.00	9.13	12.89
5	obs.	7.23	8.13	9.28	9.63		10.45	11.00	
	CNDO/S	7.31	8.14	9.21	9.67		10.50		13.04
6	obs.	7.29	8.15	9.33	9.54		10.66	10.66	
	CNDO/S	7.24	8.00	9.16	9.58		10.76	10.25	12.87
7	obs.	9.08	9.35	11.65	10.75				[18]
	MNDO	9.18	9.42	11.81	11.84		12.63		14.73
	CNDO/S								
8	obs.	8.15	8.81	9.88	10.15				
	MNDO	8.90	9.49	10.64	11.44		12.60	12.56	14.67
	CNDO/S	7.89	8.80	9.52	9.95				
9	obs.	7.90	8.68	9.70	9.80				
	MNDO	8.91	9.49	10.61	11.30		12.48	12.23	12.69
	CNDO/S	7.75	8.77	9.46	9.69				
10	obs.	7.85	8.75	9.62	9.90				
	CNDO/S	7.55	8.72	9.16	9.74				

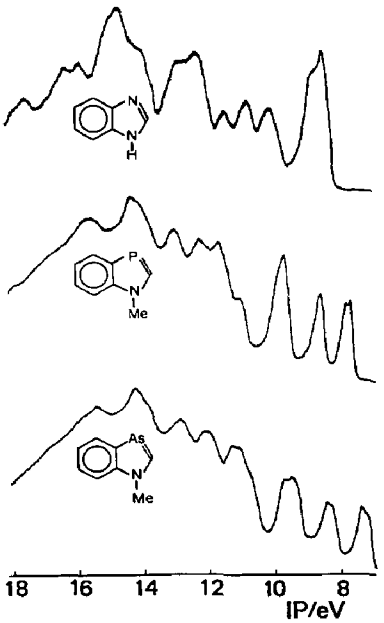

Fig. 2. UV photoelectron spectra of benzimidazole analogues.

CNDO/S quantum-chemical calculations the energy of the π orbitals increases and the energy of the lone pair orbital changes only slightly when nitrogen (E = N) is replaced by phosphorus (E = P), as can be seen from Table 1. The results for the position of the lone pair orbital are in accordance with the findings for the series of compounds from NH_3 to SbH_3 [17]. The E=C character of the HOMO level is significant. For the HOMO of the N=C–N system, however, the linear coefficients of both nitrogen atoms are quite large. The N=C–N fragment can be combined with the π system of benzene as illustrated in Fig. 1; from among the formed orbitals in the π_2 and π_4 orbital systems, the linear coefficient of atom E (N, P, As) is practically zero, and so these orbitals can be expected to undergo only a small shift when the heteroatom is changed. In contrast, the π_5 (HOMO), π_3 (and π_1) levels containing the heteroatom are markedly shifted. The data in Table 1 show that the calculations are consistent with observations.

Figure 2 shows the photoelectron spectra of the investigated compounds. The spectra and the data in Table 1 illustrate that on going from the nitrogen derivative to the arsenic derivative the bands are generally shifted toward lower ionization energies; in each spectrum bands are found near 8.4 and 10 eV. On the basis of the expected changes in the position of the bands, the band at about 8.4 eV can be related to π_4 level, in agreement with the calculations, and the band near 10 eV corresponds to the level of the nonbonding electron pair. The latter assignment is supported by the fact that in the spectra of pyridine and its analogues the lone electron pair bands also appear at around 10 eV for all the compounds containing nitrogen, phosphorus, or arsenic. Upon change of the heteroatom there is a significant displacement of the π_5 and π_3 levels. According to the calculations the π_5 level (HOMO) has considerable E=C character in the case of phosphorus and arsenic derivatives.

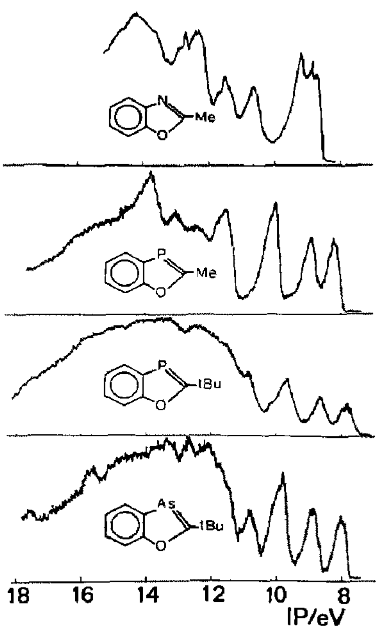

Fig. 3. UV photoelectron spectra of benzoxazole analogues.

The assignment of the spectra above 10 eV is difficult owing to the presence of a number of overlapping bands, but some help is given, as we previously mentioned, by the slight shift in the position of the π_2 level. For benzimidazole and benzazaphosphol the fifth band of the spectra is probably the π_2 band, the increase in the relative intensity of the corresponding band in the case of 1,3-benzazarsole suggests the presence of another peak in this region, due to σ(CAsC) ionization. (In the spectrum of trimethylarsine this band can be observed at 10.6 eV [19].) The position of the π_1 level of lowest energy cannot be unambigously decided.

Figure 3 shows the spectra of benzoxazole analogues. The electronic structures of these molecules are similar to that of benzimidazole, and so it can be expected that the replacement of nitrogen by phosphorus or arsenic will result only in a slight shift in the positions of the π_2, π_4 levels and the energy of the lone pair. The spectra and the calculated data for these compounds in Table 1 are consistent with the expected changes. The bands are found at energies lower by about 0.4 eV than those for compounds analogous to benzimidazole, but similar assignments can be made for the oxygen-containing molecules as for the corresponding benzimidazole species. The contribution of $E{=}C<$ fragment to the HOMO is significant when E = P or As, the band assigned to the lone electron pair is close to 10 eV, and the π_4 and π_2 levels are insensitive to the change in the heteroatom.

The quantum chemical calculations for all the investigated compounds containing a heavy atom (P or As) indicate that the HOMO possesses predominant $E{=}C<$ character. This does not, however, mean that the $E{=}C<$ fragment is not in conjugative interaction with the π system of the rest of the molecule. As is illustrated by the data in Table 1 for compounds containing phosphorus, in the photoelectron spectra of the heterocyclic compounds the band assigned to the P=C double bond exhibits a significant shift compared with the P=C band for 2-phosphapropene. The band corresponding to the lone electron pair in the plane of the molecule is practically unshifted upon changing the heteroatom, as was observed for pyridine analogues and for compounds of the series EH_3 and EMe_3.

We conclude that the significant differences between the photoelectron spectra of the two isomeric compounds containing arsenic can be attributed to the fact that whereas the As=C double bond is involved in strong conjugative interaction with the π system of the rest of the molecule, the arsenic lone pair has only a small conjugative ability.

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