PHOTOELECTRON SPECTROSCOPIC INVESTIGATIONS AT THE TECHNICAL UNIVERSITY OF BUDAPEST

POSSIBLE APPLICATIONS IN PHYSICAL CHEMISTRY

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Abstract

Four different physical-chemical applications of UV photoelectron spectroscopy have been presented in this work. In the first example the interpretation of electronic transitions of some five membered heterocycles have been studied. The second part gives an example for clarifying the mechanism of the tertiary butylation reaction of furan. The geometry of silyl pseudo-halides is considered in the third example, while the last topic is concerned by proving the aromaticity of cyclic molecules containing heteroatoms.

Keywords: photoelectron spectroscopy, molecular structure, quantum chemistry.

Introduction

The main attention of the research group dealing with molecular structural investigation at the Department of Inorganic Chemistry, TUB, has been focussed on photoelectron spectroscopic studies since 1983. At that time we began designing a UV photoelectron spectrometer which had been build and put into operation in 1985. Further development of the instrument, however, has been and is even nowadays being under progress. As we are in close contact with several foreign research groups, a significant part of our investigations is carried out as joint projects with other institutes.

Our main interest lies in the electronic structure of medium size molecules. Having installed the photoelectron spectrometer, our on-going study of organo-silicon compounds was gradually extended for derivatives of other elements, too. The subject of our investigation can be illustrated by the following segment of the periodic system:

C	N	
Si	P	S
	As	Se

The investigated compounds, however, cannot be unambiguously classi-
fied according to the heteroatom as some of them contain more than one
heteroatom. Generally it is possible to observe trends in the structure of
related compounds which allows us to study the similarities and the dif-
ferences in their properties. Although photoelectron spectroscopic investi-
gations for molecules of medium size are closely connected to MO theory
making use of Koopman's theorem and the one-electron model the scope
of our investigation is broader.

In this report we would like to single out some topics of our studies,
the detailed results of which have already been published in several papers
[1–34], but the following selection of our results would like to illustrate that
photoelectron spectroscopy can give help in the solution of quite different
physico-chemical problems.

The first example shows the interpretation of electron transitions by
UV photoelectron spectroscopy. The second part exhibits the applicability
of the method in question on the field of analytical and organic chemistry by
clarifying the mechanism of the tertiary butylation reaction of furan. The
geometry of silyl pseudo-halides is considered in the third example, while
the last topic is concerned by proving the aromaticity of cyclic molecules
containing heteroatom.

Results and Discussion

Photoelectron Spectra and Rydberg Transitions

The electronic transitions in the near UV spectrum of five membered hete-
rocycles were of interest for us for a long time, since this understanding is of
great importance in the interpretation of the photo-isomerization reaction
of this class of compounds [15, 20].

The problem is very difficult due to the large number of states present
in the investigated energy region. Rydberg transitions, however, can be
identified using the following criteria: (i) Rydberg transitions — observable
in the gas phase spectrum — disappear from the solution spectra, (ii)
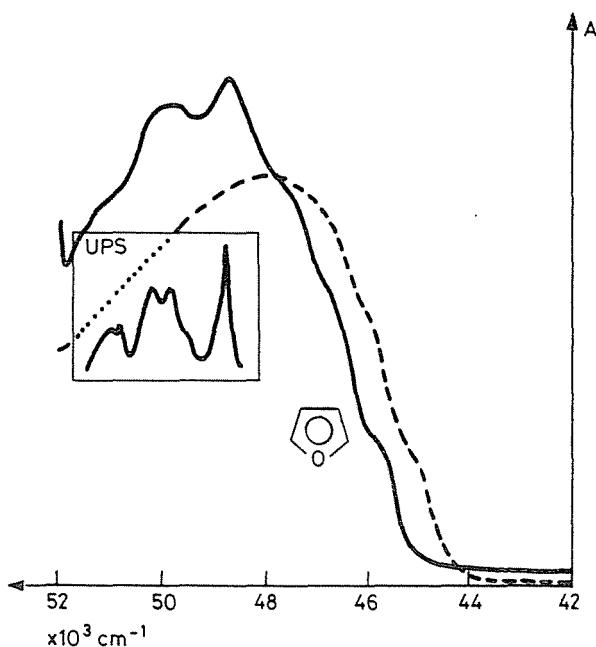Owing to the similarity of the Rydberg states to the ionic states the vibronic

Fig. 1. UV spectrum of furan in vapour (———) and in *n*-hexane solution (– – –). The photoelectron spectrum insert is plotted in the same frequency scale as the UV spectra. Absorbance in arbitrary units

structure and the Franck-Condon envelope of a Rydberg state are very similar to those of the corresponding ionic state [35].

Applying these criteria to the spectra of furan-tellurophene series the lowest lying Rydberg transitions could be safely identified (see *Figs. 1-4*). These transitions should terminate at a Rydberg-orbital of '*s*' type based on their term values [35]. The originating orbital, however, might either be of a_2 or b_1 symmetry. According to earlier photoelectron spectroscopic investigations [36] the uppermost ionization is of a_2 symmetry in case of furan, thiophene and selenophene, while b_1 in case of tellurophene. In case of selenophene the energy difference of the two levels is $1300\,\mathrm{cm}^{-1}$. As in the one-photon spectrum the $R_s \Leftarrow a_2$ transition is forbidden and might appear only with low intensity due to the presence of a non- symmetric vibration, the $R_s \Leftarrow b_1$ transition should have a strong adiabatic band profile. The spectra are in agreement with this interpretation, e. g. for tellurophene (*Fig. 4*) an intense band has been observed in contrast to the other compounds (*Figs. 1-3*). In case of selenophene both transitions could be identified. The intensity of the $R_s \Leftarrow b_1$ transition is, however, dimin-
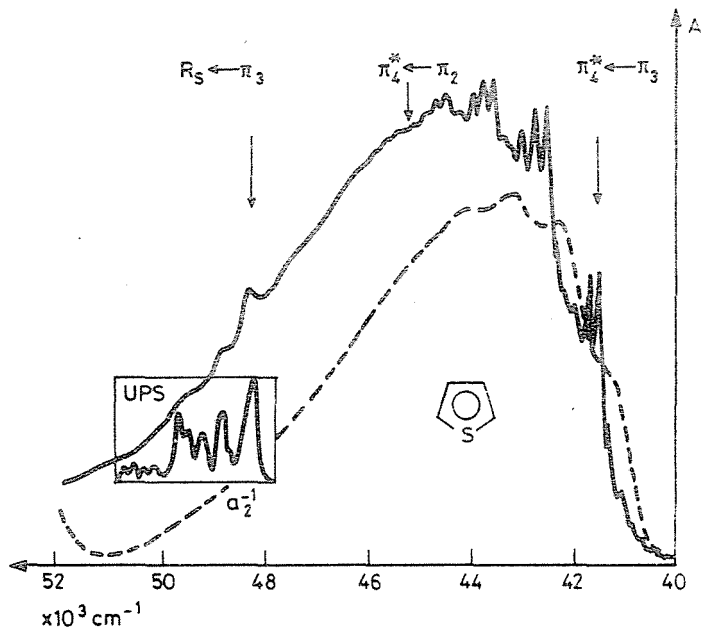
Fig. 2. UV spectrum of thiophene in vapour (———) and *n*-hexane solution (– – –). The photoelectron spectrum insert is plotted in the same frequency scale as the UV spectra. Absorbance in arbitrary units

ished and the $R_s \Leftarrow a_2$ transition is enhanced comparing to tellurophene suggesting some kind of perturbation between the two close lying states.

Tertiary Butylation of Five Membered Heterocycles

T-Butyl (TB) furan is a much studied compound by theoretical methods comparing its properties to the corresponding trimethylsilyl compounds and as a model compound for gathering information of steric effect of the TB group [5, 16], as well.

The preparation of 2,5–di–t–butylfuran is the subject of several recent patents [37]. The reaction path that was first described by BROWN and WRIGHT created much interest for further investigations as the unexpected disubstituted compound was obtained instead of the monosubstituted product [38]:
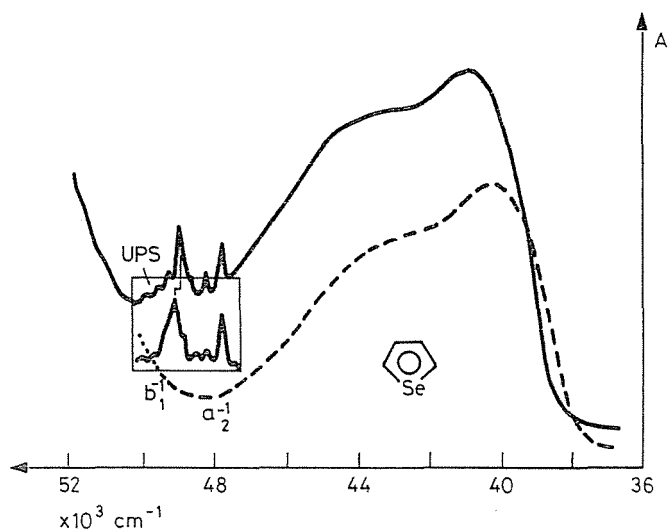
Fig. 3. UV spectrum of selenophene in vapour (———) and *n*-hexane solution (– – –). The photoelectron spectrum insert is plotted in the same frequency scale as the UV spectra. Absorbance in arbitrary units
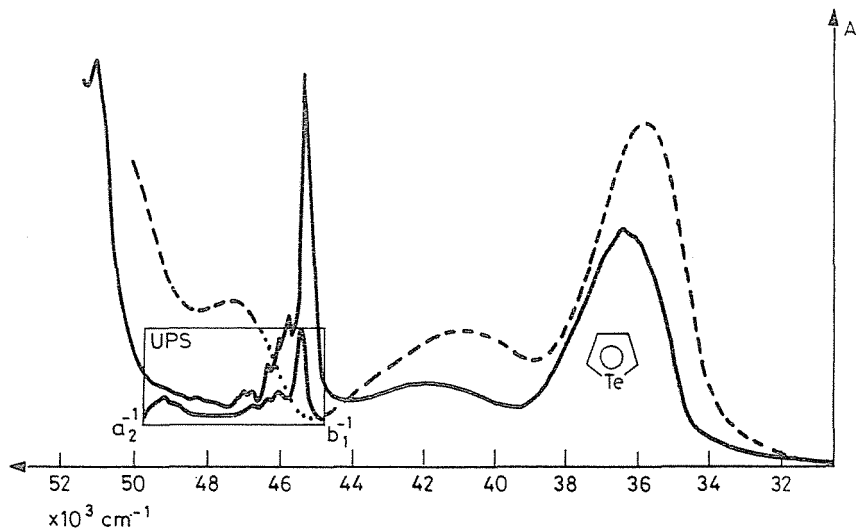

Fig. 4. UV spectrum of tellurophene in vapour (———) and *n*-hexane solution (– – –). The photoelectron spectrum insert is plotted in the same frequency scale as the UV spectra. Absorbance in arbitrary units
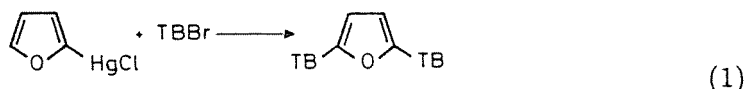
$$\text{[furan with HgCl]} + TBBr \longrightarrow TB \overset{}{\underset{O}{\diagup}} TB$$

$$(1)$$

2,5–Di–t–butylfuran was also obtained from 3–chloromercuryfuran and TBBr [38]. During the reaction two steps could be distinguished. In the first few seconds a rapid exothermic reaction took place followed by a much slower process that took about 14 days.
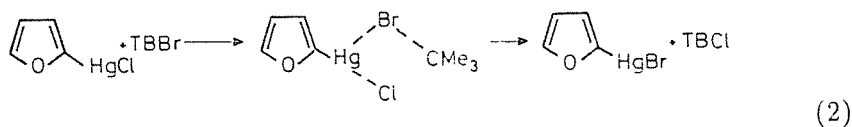
In our experiments the reaction was carried out in a small flask which was attached to the sample inlet system of the UPS instrument and all of the gases released were introduced into the spectrometer.

During the measurement the spectra were continuously scanned and the counts of electrons detected at each energy were accumulated digitally using a multi-channel analyser. The obtained spectra were continuously monitored. When new bands appeared suggesting a change in the vapour phase composition, the accumulated spectra were plotted and the spectrum accumulation was restarted. One scan took 50 seconds while each plot represents 4–8 accumulated scans. The whole measurement took about 25 minutes.

Identical methods were used to obtain photoelectron spectra of the corresponding thiophene derivatives. Similar reaction conditions were used and similar results were found but the reaction seemed to be less vigorous.

The spectra obtained in a typical experiment are given in *Fig. 5*. The appearance of TBCl in the reaction is a surprising observation. As it can be detected in the first seconds of the reaction it should be one of the products formed in the first step of the process. In order to investigate the role of TBCl in the reaction, TBCl instead of TBBr was added to 2–chloromercuryfuran. In this case no reaction was observed and after immediately analysing the mixture by UPS no other volatile product but TBCl was found. When the analysis was repeated four hours after starting the reaction isobutylene, furan and TB-furans were found among the products. The product peaks were enhanced relative to that of TBCl when larger reaction time (1 day) was applied. Based on this observation it is thought that the second slow period of the reaction is due to the reaction of TBCl and 2–chloromercuryfuran.

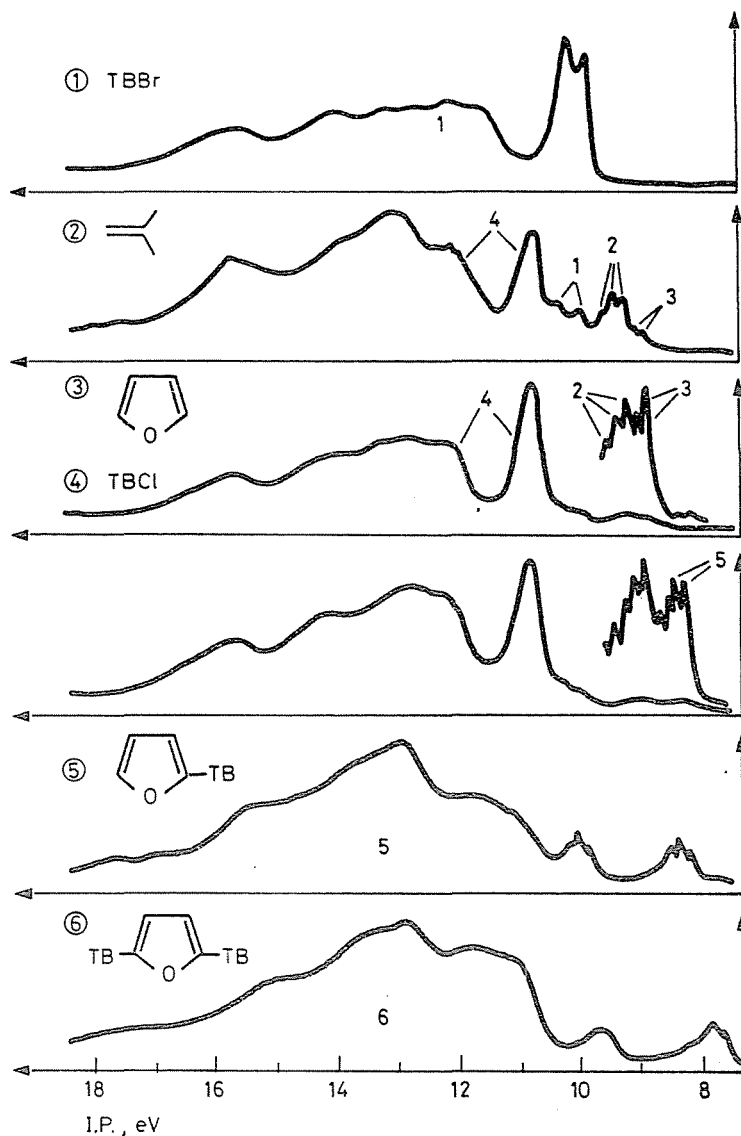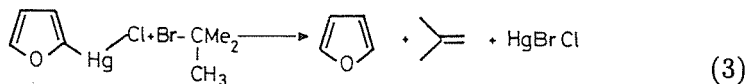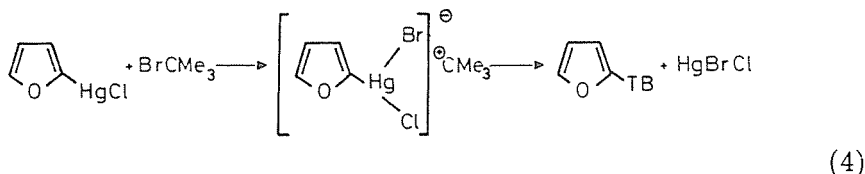A possible route for TBCl formation is given in *Eq. (2)*

$$\text{[furan-HgCl]} + TBBr \longrightarrow \text{[furan-Hg with Br, Cl, CMe}_3\text{]} \longrightarrow \text{[furan-HgBr]} + TBCl$$

$$(2)$$

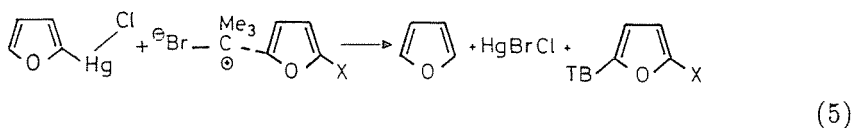*Fig. 5.* Photoelectron spectra recorded during the reaction of 2–chloromercuryfuran and t–butyl–bromide

Isobutylene can be formed from TBBr (and TBCl) by mercury catalyzed HBr (HCl) elimination. As neither HBr nor HCl appears in the spectra although these compounds have very sharp and intense bands, an other possible reaction is preferred:

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$$\text{(furan-Hg-Cl)} + \text{Br-CMe}_2\text{-CH}_3 \longrightarrow \text{(furan)} + \text{>=} + \text{HgBrCl} \tag{3}$$

With the help of this reaction the simultaneous formation of furan and isobutylene can easily be explained. 2–Chloromercuryfuran and TBBr can give 2–TB–furan via carbenium ion as it can be seen in *Eq.* (4).

$$\text{(furan-HgCl)} + \text{BrCMe}_3 \longrightarrow \left[\text{(furan-Hg}\overset{Br}{\underset{Cl}{\cdots}}\text{CMe}_3)\right]^{\ominus} \longrightarrow \text{(furan-TB)} + \text{HgBrCl} \tag{4}$$

However, as Brown and Wright reported the formation of 2,5–di–TB–furan from 3–chloromercuryfuran and TBBr, an alternative route can be suggested in which a neighbouring molecule is alkylated according to *Eq.* (5).

$$\text{(furan-Hg-Cl)} + {}^{\ominus}\text{Br}-\overset{Me_3}{\underset{\oplus}{C}}-\text{(furan-X)} \longrightarrow \text{(furan)} + \text{HgBrCl} + \text{(TB-furan-X)} \tag{5}$$

R may be H (2–TB–furan formation) or TB (2,5– di–TB–furan formation). Although R=HgCl or HgBr has not been observed in our experiment (because of the low volatility) its presence be excluded.

An alternative formation of 2–TB–furan may be considered in the addition of furan and isobutylene:

$$\text{(furan)} + \text{>=} \longrightarrow \text{(furan-TB)} \tag{6}$$
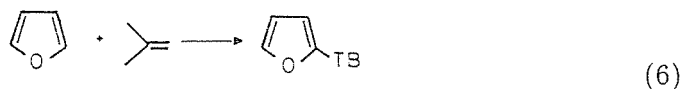
Since the relative intensity of TBCl, furan and isobutylene did not change noticeably after 4 hours, the latter reaction seems to be unimportant.

The same reaction mechanism was concluded in the tertiary butylation of thiophene.

The Electronic Structure and Quasi-linearity of Silyl-pseudo-halides

The molecular structure of silyl pseudo-halides has been studied by several different experimental methods in recent years. These investigations were mostly aimed at establishing the molecular geometry of these compounds. The most controversial question to be solved was the linearity of the SiNCX chain. This question is especially intriguing because, due to the vibrations and rotations, different experimental methods predict different equilibrium geometry.

The equilibrium structure of the smaller isocyanates and isothiocyanates is now relatively well understood. It is known that silyl isocyanate (H_3SiNCO) has a pseudo-linear frame in the gas phase. The molecules H_3SiNCS and $H_3SiNCSe$ show different behaviour: on the basis of their infrared and microwave spectra [39–41], these molecules clearly have a linear N–C–X frame in the gas phase. All the experimental methods indicate the same structure of carbon derivatives. In these molecules the CNCX chain is always bent, not only at the C–N–C angle but at the N–C–X angle, too.

The assignment of the photoelectron bands was made easier by the study of their intensity dependence on the number of NCX (X=O, S, Se) functional groups in the molecule. Increasing the number of pseudo-halide groups, some bands get stronger, indicating that these originate from NCX groups, while the relative intensities of others decrease giving rise to the conclusion that these bands are originating from ionization of the methyl groups. The assignment was well supported by ab initio quantum-chemical calculations using 6–31G basis set (augmented by polarization functions on Si, S, Se).

An important question which is to be discussed here is the possibility of finding some trend for the bond angles of the SiNCX chain in the mono-functional compounds on the basis of the photoelectron spectra. The two π_2 orbitals are degenerate if this chain is linear and they would be split if the molecule is bent. No splitting could be observed experimentally in the photoelectron spectrum of the trimethylsilyl derivatives (*Fig. 6*). The situation is less unambiguous in case of the tertiary-butyl derivatives: the corresponding band is clearly split in the NCO derivative, while only a shoulder can be observed for the NCS and one completely symmetric band for the NCSe derivative (*Fig. 7*). As microwave spectroscopy predicts a bent structure with a C–N–C angle of 135.6° for CH_3NCO [45] and 147.7° for CH_3NCS [46] it seems likely that the tertiary-butyl derivatives should also have a bent structure. However, in order to be able to conclude from the photoelectron spectra that the molecule has a linear structure, it has to be estimated what kind of splitting would be at all observable in the spectrum.
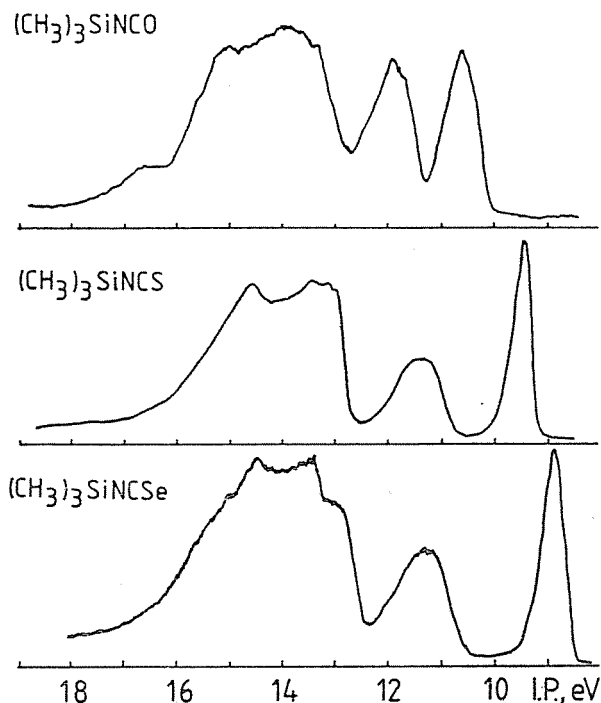
Fig. 6. Photoelectron spectra of trimethyl-silyl pseudo-halides

In order to answer this question, the geometries of the molecules $(CH_3)_3YNCX$ (where Y=C, Si and X=O, S) were optimized at the Hartree-Fock level of theory and the Y–N–C angle was varied keeping the rest of the geometry constant to study the splitting of the π_2 orbitals. The results are shown in *Fig. 8.* The experimental geometries of the corresponding methyl-derivatives are marked in this figure with asterisks. The figure shows that the splitting of the π_2 orbitals decreases in the O–S–Se series because of two reasons. First, the splitting of these orbitals is the largest in $(CH_3)_3CNCO$ and secondly the C–N–C angle is the smallest in this molecule. According to the calculations the splitting of π_2 orbitals is about three times larger in $(CH_3)_3CNCO$ than in $(CH_3)_3CNCS$. These calculations also show that as the experimental resolution of the photoelectron spectrometer is 40 meV, a relatively small deviation from linearity ($>15°$) could be observed from the splitting of the π_2 bands in the photoelectron spectrum of $(CH_3)_3CNCO$, whereas in case of the silicon analogues, this deviation must be much larger
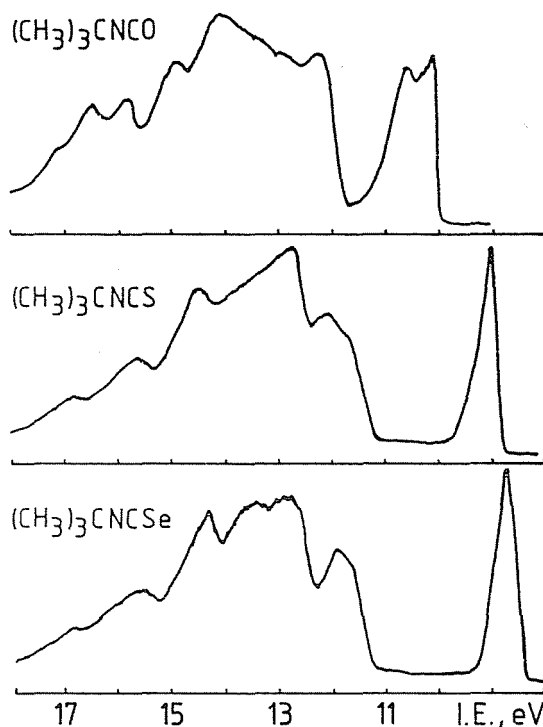
Fig. 7. Photoelectron spectra of t-butyl pseudo-halides

to be observed (>25°) as it can be seen from *Fig. 8.* This also means that conclusions on the linear or pseudo-linear behaviour of the silicon analogues cannot be drawn from the photoelectron spectra alone.

The results of the geometry optimization are shown in *Table 1.* The calculated bond distances show good agreement with the experimental values. Some smaller deviations, e. g. the systematically shorter calculated bond lengths can be explained by the small basis set used. The only controversial question is the Y–N–C angle which is calculated to be linear in all molecules. On the basis of experimental measurements on H_3SiNCO described above, a pseudo-linear structure is anticipated for $(CH_3)_3SiNCO$ and linear for $(CH_3)_3SiNCS$ and $(CH_3)_3SiNCSe$ molecules, which is also supported by the calculations. The only available experimental data for these molecules are given by electron diffraction measurements [47, 48] which, however, predict a bent structure. The failure of electron diffraction to predict the equilibrium bond angle for molecules with small frequency, large amplitude motions is well known and therefore a pseudo-linear or linear structure of these species seems quite likely. For the $(CH_3)_3CNCX$ derivatives, however, a bent equilibrium structure would be expected from microwave experiments and also from the photoelectron spectra. The C–
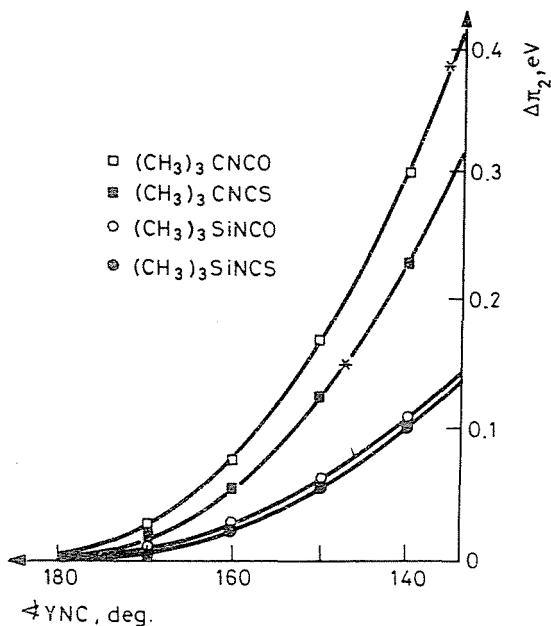
Fig. 8. Calculated π_2 orbital splitting versus Y–N–C angle

N–CX angles, nevertheless, were calculated to be linear in all of the t-butyl derivatives. As it was assumed at this stage that this deviation may be due to the neglect of correlation, the geometry of $(CH_3)_3CNCO$ was optimized at the MP2 level of theory. The results of this optimization are also given in *Table 1*. It can be seen that by taking the correlation energy into consideration, the correct behaviour of the C–N–C and N–C–O angles is predicted in very good agreement with experiment.

The Electronic Structure and Aromaticity of 1,3–Azaphosphole and 1,3–Azarsole

According to the empirical 'double bond rule' [50] cited often in inorganic chemistry textbooks second and higher row elements do not form stable compounds in which they are involved in double bonding of $p\pi$-$p\pi$ type. Recent developments [51, 52], however, were leading to revise this concept, and in the case of trivalent phosphorus a great number of compounds containing P=C double bond were synthesized. The aim of one of our recent works was to investigate the electronic structure of several possibly aromatic five membered unsaturated ring systems containing phosphorus or

Table 1

Calculated equilibrium geometries[a] for the molecules $(CH_3)_3YNCX$ (where Y=C, Si and X=O, S) and some related experimental values[a]

$(CH_3)_3YNCX$	Y–N	N–C	C–X	Y–C	NCX	YNC	Method
$(CH_3)_3CNCO$	1.4431	1.1642	1.1940	1.5565	180.0	180.0	HF[c]
	1.4892	1.2287	1.2232	1.5690	170.3	142.5	MP2
CH_3NCO	1.451	1.214	1.166		170.3	135.6	MW [45]
$(CH_3)_3CNCS$	1.4420	1.1588	1.6120	1.5572	180.0	180.0	HF[c]
CH_3NCS	1.429	1.207	1.567		169.3	147.7	MW [46]
$(CH_3)_3SiNCO$	1.7352	1.1810	1.1810	1.8856	180.0	180.0	HF[c]
	1.7526	1.2219	1.2191	1.8910	177.4	164.2	MP2
	1.740	1.202	1.176	1.864	165.8[b]	156.9[b]	ED [43]
H_3SiNCO	1.703	1.1975	1.174		180.0	159.56	MW [42]
$(CH_3)_3SiNCS$	1.7518	1.1158	1.5983	1.8839	180.0	180.0	HF[c]
	1.743	1.191	1.587	1.866	176.0[b]	158.2[b]	ED [44]
H_3SiNCS	1.6725	1.2208	1.5745		180.0	180.0	MW [49]

a) Bond lengths in Å and bond angles in degree
b) Angle originating from the presence of large amplitude motions
c) Calculated with a 6–31 G basis set

arsenic in order to study the delocalization and aromatic stabilization of the ring.

When replacing nitrogen by a heavier group V/a element a diminished interaction is expected due to the small overlap between carbon $2p$ and phosphorus $3p$ (or arsenic $4p$) orbitals. However, in a recent ab initio study [53], phosphabenzene was found as 88–89% aromatic in comparison to pyridine, while phosphole is a non-planar compound in contrast to pyrrole indicating that the aromatic stabilization of the planar state is insufficient to overcome the high inversion barrier for trivalent phosphorus. These facts indicate that the two different phosphorus atoms are not equally good building blocks of aromatic systems as happens in the case of nitrogen.

The simplest phosphorus compound that can form an aromatic system containing either P=C subunit or a P–H bond is 1,3–azaphosphole, that can exist in two tautomeric forms (I and II).


I   II

Table 2

Delocalization stabilization from bond separation reactions

Compound	ΔE	%	Compound	ΔE	%
(pyrrole, N)	46.67	100	(1,2-diphospholе, P–P)	18.74	40
(N–N diazole)	52.74	114	(P–N)	18.15	39
(N–P)	49.43	106	(As)	16.63	36
(N–As)	53.82	116	(As)	14.67	31

*ΔE in kcal/mol

Table 3

Observed and calculated ionization energies (eV)

| (N–N)		(P–N)		(As–N)		(P)	(As)
obs.*	calc.	obs.	calc.	obs.**	calc.	calc.	calc.
8.81	8.95 π	8.44	7.97 π	7.76	7.72 π	9.52 π	9.79 π
10.38	10.74 π	9.19	9.17 π	8.8	9.54 π	10.18 n_p	10.18 n_{As}
	11.40 n_N	9.93	10.23 n_p	9.79	10.19 n_{As}	11.27	11.21
14.03	15.66 σ	12.06	13.14 σ	11.19	10.52 σ	11.33	12.84
14.77	16.38 π	12.8	15.40 π	12.3	15.70 π	14.48	14.50
15.38	16.51 σ	13.9	15.78	14.1	16.11	15.40	15.15
	16.68	14.06	16.03		16.59	16.11	16.44
	20.90		19.78		19.55	18.50	18.59
						20.32	20.35

* Reproduced from [55]

** Data of 2-methyl-1,3-azarsole

The comparison of the electronic structure of these two tautomers gives some informations concerning the conjugative ability of the lone pair of the phosphorus or arsenic atom in relation to that of the P=C (As=C) subunit.

For the investigation minimum energy geometries were computed at the SCF level using 4–31G basis set augmented by polarization functions on phosphorus.

Three different aspects of aromaticity have been investigated for 1,3–azaphospholes and 1,3–azarsoles: the molecular geometry, the bond separation reactions and the electronic structure derived from the UV photoelectron spectra. The predicted geometry of these molecules is in good agreement with the available experimental structures. Comparing the two possible tautomeric forms, the 1–H–derivatives have planar structures while the 3–H–derivatives show puckered structures where the phosphorus or arsenic move out of the molecular plane. The C–X bond length in the first type of molecules is shorter than in type II molecules, indicating clearly a large scale of double bond character. The degree of double bond is between 45–47% in type I and 18–20% in type II molecules. The same value for the C–C bond in benzene (comparing to the C–C bond distance in ethane and the C=C distance in ethylene) is 68%.

Studying the bond separation reactions the molecules can be classified into two groups (*Table 2*). In the first group, which contains the structure I molecules, the compounds are highly aromatic and no substantial difference could be found in aromaticity. The second group consists of the structure II molecules. phosphole and arsole. The aromaticity is diminished to 33–44% (as compared to pyrrole) and does not change significantly. Nevertheless, the existence of this residual aromatic stabilization can be concluded from the structure of some transition-metal π–complexes of phosphole derivatives [54].

The aromatic character of structure I molecules can be observed from the photoelectron spectra, too (*Table 3*). The structure of the spectra is similar to that of pyrrole, showing that the replacement of a C=C bond by a P=C bond has little effect on the electronic structure.

From the comparison of the molecular structure of compounds with different degree of aromaticity, it seems that despite of the double bond rule the heavy elements of the V-th group of the periodic table are good building blocks of an aromatic system, if an optimum arrangement of the atoms can be found.

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