Journal of Organometallic Chemistry, 102 (1975) 313—316
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PHOTOELECTRON SPECTROSCOPY STUDY OF THE TRIPHENYL DERIVATIVES OF THE GROUP V ELEMENTS

G. DISTEFANO*
Laboratorio dei Composti del Carbonio contenenti Eteroatomi e loro Applicazioni del C.N.R., Via Tolara di Sotto 89, Ozzano E., Bologna (Italy)
S. PIGNATARO
Istituto di Chimica Fisica dell'università, Cittadella Universitaria, Viale A. Doria, Catania (Italy)
L. SZEPES and J. BOROSSAY
Eötvös Lorand University, General and Inorganic Chemistry Department, Budapest, Múzeum Körút 6-8 (Hungary)

(Received June 24th, 1975)

Summary

The patterns of the *IE*'s below about 11 eV in the photoelectron spectra of ZPh_3 (Z = N,P,As and Sb) are discussed in terms of geometric energetic and overlap factors.

A deep mixing of the lone pair of the heteroatom with the π-system of the benzenic rings is found for the nitrogen derivatives. This mixing decreases on going towards the Sb derivative.

The participation of the heteroatom *d* orbitals in bonding is discussed.

Introduction

During the course of an investigation on the triphenyl derivatives of the elements of Groups IV [1] and V, we learned of the work by Debies and Rabalais [2] on phenyl derivatives of the elements of Group V. They interpreted the spectral differences between the N derivatives and the other congeners in terms of a shift of electron density from the phenyl groups toward the P, As and Sb atoms via their *d* orbitals. We think that the PES spectral features cannot be interpreted in terms of this factor alone, since energetic and geometric factors must also be taken into account.

Results and discussion

Table 1 lists the vertical *IE* values below about 11 eV for NPh_3, PPh_3, $AsPh_3$ and $SbPh_3$*. The Table includes data for shoulders not previously quoted. The figures for the main features of the spectra are in reasonable agreement with those reported by Debies and Rabalais [2]. The first *IE* of ZH_3 and $Z(CH_3)_3$ (Z = N, P, As and Sb) are also shown for comparison.

In agreement with previous proposals, the bands at about 9 eV (I_2 and I_3) are assigned to electrons mainly localized on the benzene rings. I_1 and I_4 are related to MO's deriving from the interaction of the lone pair of the heteroatom and the rings π-system (see below).

A comparison of the first *IE*'s of the ZH_3 and $Z(CH_3)_3$ series show that the substitution of three methyl groups for three hydrogen atoms reduces the *IE* of the lone pair MO of all the heteroatoms to about 8.6 eV. Since the inductive effect of the CH_3 and C_6H_5 groups do not differ greatly, if only the same kind of interactions operated in the phenyl and methyl [4] derivatives one would expect in the ZPh_3 series an almost equal reduction of the lone pair *IE*'s. This expectation approximately verified for Z = P, As and Sb. However, assuming [2] that the corresponding orbital in NPh_3 is that at 10.29 eV, it must be concluded that this compound behaves in an entirely different way. On the other hand, assuming that the orbital to be considered in this comparison is that at 7.00 eV, the behaviour of NPh_3 is rather similar to that of the other congeners. In both cases however, additional interactions play important roles, at least in the nitrogen compound.

A correct interpretation of the PES spectra of the ZPh_3 derivatives starts from the analysis of their structures and of all the symmetry-allowed** interactions which can take place among the various orbitals. The ZPh_3 molecules have propeller like conformations (C_3 symmetry) and all three aromatic rings in a given molecule have the same direction of twist [5-9]. Some interaction among the π_s-ring orbitals*** is to be expected and the resulting combinations might

TABLE 1

IONIZATION ENERGY VALUES (eV) BELOW ABOUT 11 eV FROM $Z(C_6H_5)_3$ AND FIRST *IE* VALUES FOR ZH_3 AND $Z(CH_3)_3$ (Z = N, P, As AND Sb)[a]

	I_1	I_2	I_3	I_4	I_5	ZH_3[b]	$Z(CH_3)_3$[c]
N	7.00	8.81	9.25	10.29		10.88	8.54
P	7.85	9.02[d]	9.18	9.68[d]	10.81	10.60	8.60
As	8.03		9.10	9.58[d]	10.47	10.51	8.65
Sb	8.08		9.06		10.04	10.02	8.48

[a] The data were obtained with a PS 18 Photoelectron Spectrometer. The spectra were calibrated against the Ar and Xe lines as internal standards. The reproducibility was ± 0.05 eV. [b] Ref. 3. [c] Ref. 4. [d] Shoulder.

---

* The corresponding spectra have been reported, see ref. 2.

** Due to the conformation of these molecules extensive interactions within the various MO's are present and the classification of the MO's as n, σ or π is no longer strictly correct. However, for sake of simplicity this classification will be retained.

*** S = symmetric, A = antisymmetric with respect to a plane perpendicular to the ring plane and passing through the carbon atom bonded to Z and that in the *para* position.

interact with some other orbitals like the lone pair or the *d* orbitals of the heteroatom and the MO's localized on the ZC_3 group.

It is evident from Table 1 that the π—π interactions among the rings decreases on going from the N to the Sb derivative: the π-ring manifold ($I_2 + I_3$) coalesces into a unique band on going toward $SbPh_3$. Also the n—π splitting, as measured by the I_1-I_4 (I_3 for the Sb derivative) energy difference, decreases in the same sense (2.3, 1.8, 1.5, and 1.0 eV for N, P, As, and Sb respectively).

In any attempt to rationalize such trends the participation of several factors must be taken into account. The first is a geometric factor: on going from N to Sb derivative the Z—C bond length increases [10], while the CZC angle decreases [6-9]. The first of these effects makes more difficult through space interactions within the rings, while the second favours them. Given that the π-orbital splitting decreases with a decreasing $\angle$ CZC angle, this factor has a smaller importance in determining the extent of through space interaction*.

Furthermore, the bonding combination of the π_S-ring orbitals has the appropriate symmetry to interact with the heteroatom lone pair MO**, and thus the situation in the N derivative is most favourable for a strong n—π interaction to occur. This kind of interaction is expected to increase the π—π splitting ("through lone pair" interaction).

Another factor which should operate to give the maximum n—π interaction in NPh_3 is the better ability of orbitals of the same quantum number to overlap with each other. In particular, neglecting all the other factors, the n—π overlap should decrease from N to Sb derivative because the quantum number of the lone pair increases down the series.

As to the possible interaction of the lone pair with the filled and virtual MO's localized on the ZC_3 group, it should be noted that these interactions are similar to those present in the $Z(CH_3)_3$ series, where a nearly constant effect along the series is found [4] and so this factor cannot explain the trends of the first *IE*'s and of the π—π and n—π splittings in ZPh_3.

A further factor affecting the n—π interaction is the energy gap between the lone pair and the benzene ring orbitals. The first *IE* of the ZH_3 molecules can be taken as a measure of the "n" orbital energy. It changes with the electronegativity of the Z atom, and the variation is relatively small (see Table 1). When the ZPh_3 molecule is formed from the ZH_3 and the three benzene rings, these group rings are influenced by the inductive effect of the heteroatom. For this effect the π-ring orbital energies are expected to vary in a parallel way with respect to the first *IE*'s of the ZH_3, and so the n—π energy gap does not differ greatly along the series, and this factor must play a minor role, at least for the P, As and Sb for which there are no effective π_S combinations.

It is thus apparent that geometrical and n—π overlap factors operate jointly to give the largest π—π and n—π interactions in NPh_3. In this compound the interaction is so strong that it is no longer possible to speak in terms of separate n and π orbitals. This mixing decreases on going down the fifth group. This is

---

* The angle of twist of the rings probably changes along the series, but data for the gaseous phase are available only for NPh_3 [6].

** The π_A orbitals have a node on the carbon atom bonded to Z, so that through space interaction among them should be of minor importance.

supported by: *(a)* the shape of the first PES band becomes sharper and sharper on going towards $SbPh_3$; *(b)* the first *IE* shows a downward shift with respect to the corresponding $Z(CH_3)_3$ and this shift decreases in the order $PPh_3 > AsPh_3 > SbPh_3$ (see Table 1).

The final factor which must be considered is that taken into account by Debies and Rabalais [2], namely a drift of charge from the rings towards the heteroatom *d* orbitals (or, generally speaking, towards virtual orbitals of suitable symmetry localized on Z). CNDO/2 calculations indicate about 3% *d* orbital participation in bonding for H_2PPh [2]. This value is exaggerated by the computational method used; it is unlikely to be additive in triphenyl derivatives [11] and probably decreases. In fact, while Si virtual orbitals are able to accept charge from the benzene ring in H_3SiPh [12], the photoelectron spectrum of $HSiPh_3$ does not show any significant evidence for involvement in bonding of vacant orbitals mainly localized on the silicon atom [1].

In conclusion, *d* orbital participation in bonding of the ZPh_3 derivatives cannot explain the gross features of the PE spectra, even if it cannot be entirely ruled out. In particular it may be responsible for the decrease of the first *IE* on going from the $Z(CH_3)_3$ to the ZPh_3 compounds (Z = P, As and Sb).

Acknowledgement

S.P. gratefully acknowledges financial support from C.N.R. L.S. thanks the Ministero per gli Affari Esteri Italiano for a grant. We thank Dr. P. Finocchiaro for useful discussions.

References

1 G. Distefano, S. Pignataro, L. Szepes and J. Borossay, submitted for publication.
2 T.P. Debies and J.W. Rabalais, Inorg. Chem., 13 (1974) 308.
3 A.W. Potts and W.C. Price, Proc. Roy. Soc. London, Ser. A 326 (1972) 181.
4 S. Elbel, H. Bergmann and W. Ensslin, J. Chem. Soc., Faraday II, (1974) 555.
5 D. Gust and K. Mislow, J. Amer. Chem. Soc., 95 (1973) 1535.
6 Y. Sasaki, K. Kimura, M. Kubo, J. Chem. Phys., 31 (1959) 477.
7 J.J. Paly, J. Chem. Soc., (1964) 3799.
8 J. Trotter, Can. J. Chem., 41 (1963) 14.
9 D.M. Hawley and G. Ferguson, J. Chem. Soc. A, (1968) 2059.
10 Interatomic Distances, in L.E. Sutton (Ed.), Chem. Soc. Special Publ., 11 (1958).
11 Organometallic Compounds of the Group IV Elements, in A.G. MacDiarmid (Ed.), Vol. 1, Part 1, Dekker, New York, N.Y., 1968 p. 28.
12 R.A.N. McLean, Can. J. Chem., 51 (1973) 2089.