BONDING STUDIES OF COMPOUNDS OF BORON AND THE GROUP IV ELEMENTS

X*. PHOTOELECTRON SPECTRA OF COMPOUNDS Me₄M (M=C, Si, Ge, Sn, or Pb) AND THE LACK OF PARTICIPATION OF M d-ORBITALS

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SUMMARY

The question of d-orbital participation by the central metal M in molecules containing second and higher row elements is critically examined in relation to the photoelectron spectra of the Group IV compounds Me₄M. It is shown that the splitting between the two strictly symmetry-determined CH levels $1t_1$ and $1e$ drops monotonically from 1.3_5 eV in neopentane to approximately zero in tetramethyl-plumbane, as is consistent with the decreasing through-space interactions in the $(CH_3)_4$ tetrahedron. Within the limits of the spectroscopic resolution, d-orbital participation is therefore discounted, as this would tend to increase the separation between these two levels on going down the series.

INTRODUCTION

This study of the He(I)-photoelectron (PE) spectra of the Group IV tetra-methyls and bonding implications is a continuation of our earlier interest in similar features in the series Me_nSiCl_{4-n}[2] and in saturated hydrocarbons, including neo-pentane[3,4]. During the course of this investigation we were made aware of the work of others on the same series Me₄M (M=C, Si, Ge, Sn, or Pb)[5] : we shall therefore not reproduce our spectra, nor provide details of assignments, since these agree in all essential respects with those reported in ref. 5, but confine the discussion to the question of d-orbital participation by the central atom M in the bonding scheme (further data will be included in ref. 6).

There has been much interest in the problem of Si d-orbital participation in quadrivalent compounds such as Me_3Si-X (X = halogen, OR, NR₂, etc.) or Me_3Si-R (where R is an unsaturated group such as an aryl or vinyl group, cf. ref. 8), and to a lesser extent also for the heavier Group IV elements. These are relatively complex molecules, because a π-type molecular orbital (MO) *may* involve either or both (*i*) Si_dX or Si_dR conjugation and (*ii*) Me_3Si_d hyperconjugation (σ–π-conjugation)[9].

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* For Part IX see ref. 1.

The most recent speculations are based on PE spectra of the vinyl- and allylsilanes Me_nSiR_{4-n} ($R = CH_2=CH-$ or $CH_2=CHCH_2-$)[10]. It is relevant, therefore, now to consider the problem in the simple molecules Me_4M. These molecules offer a unique opportunity to assess the possible availability of central atom d-orbitals, for the following reasons: (*i*) Their level ordering, which is largely dictated by symmetry, is immediately obvious from intensity and band shape considerations, and has furthermore been rigorously ascertained for the first member, neopentane, by an *ab initio* calculation[3]. (*ii*) Inductive effects or strong mixing between the two highest occupied t_2 levels (features which obscure the spectra of the "isoelectronic" Group IV tetrahalides[11]) are largely absent. (*iii*) The valence shell t_1 and e orbitals are unique in their symmetry species and exclusively confined to the CH bonds. Their splitting is thus entirely a consequence of their through-space interaction. On changing from C to Pb, this interaction should approach zero, unless the e level mixes with the $d_{x^2-y^2}/d_{z^2}$ AO's of the central atom.

Central metal d-orbital participation should therefore be detectable by PE spectroscopy, as it would manifest itself in a splitting between the degenerate ($M = Pb$) or nearly degenerate ($M = Sn$, Ge) e and t_1 levels. We consider this measure for d-orbital participation to be physically more relevant than the criteria applied by others who sought evidence for d-orbital effects by comparing the ionisation potentials (IP's) of the molecule in question with those of an appropriate model, evidence which we think is inconclusive, since inductive and hyperconjugative effects may be different in the model.

Further motivation for the work reported here derives from our interest in the PE spectra of saturated hydrocarbons[3,4]. The analysis of the spectra is considerably facilitated if certain carbon atoms are replaced by, *e.g.*, silicon, in such a way that the molecular symmetry is retained.

EXPERIMENTAL

PE spectra were recorded on a Perkin–Elmer PS-16 spectrometer, with rare gases as calibrants. The purity of neopentane (Fluka, *puriss.*) was checked by means of GLC. The other compounds were synthesised and purified by methods described in the literature[7], and were distilled *in vacuo* before use.

DISCUSSION

The MO scheme of these molecules, neglecting inner shells, is of the general form:

$$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4(1t_1)^6(3t_2)^6 \quad (cf., \text{ refs 3 and 4})$$

The MO's can be roughly classifed as follows: $2a_1$ and $3t_2$ are the principally MC-bonding orbitals and on ionisation give rise to the third and first PE bands, respectively; $1a_1$ and $1t_2$ are primarily involved in CH-bonding and can be thought to originate from the a_1-type orbitals of the isolated methyl groups; they are at energies below 21 eV and consequently not accessible by the He(I) experiment. The remaining three levels, $2t_2$, $1e$, and $1t_1$, are symmetry orbitals built from the e-type CH orbitals of the methyl groups, and upon ionisation give rise to the 14 eV band.

We shall consider merely the levels $1e$ and $1t_1$. Of these, only the former can interact with the occupied or unoccupied d-orbitals of the central atom which transform as $e + t_2$ in a tetrahedral molecule. It is clear that the extent of this interaction, and the consequent $1e/1t_1$ splitting, are intimately related to the energy difference between the interacting d- and CH-orbitals. While there is to date little information about the energies of the empty d-levels[12] of Si through Pb, for they lie close to the ionisation continuum, the position of the filled inner d-subshell is readily deduced from ESCA spectroscopy to be -34, -30, and -27 eV for the neutral elements Ge, Sn, and Pb, respectively[13]. (In neutral molecules slightly different energies have been observed; see $e.g.$, ref. 14.)

There are three comments to be made about this measure of the extent of p_π–d_π mixing.

First, the degeneracy of the three CH levels can also be lifted as a result of through-space interactions within the $(CH_3)_4$ tetrahedron. These interactions, antibonding in the t_1 and bonding in the t_2 component, but largely absent in the e component, depend strongly on the distance between the individual methyl groups. In neopentane, where the shortest distance between the hydrogen atoms of neighbouring methyl groups is estimated[15] at 2.51 Å, the observed splitting is symmetrical, as expected, and amounts to roughly 2.7 eV. Intensity considerations and $ab\ initio$ calculations confirm that the orbital sequence is $1t_1 > 1e > 2t_2$ in order of decreasing energy. On passing to $Si(CH_3)_4$, the overall separation between the CH orbitals reduces to ca. 0.9 eV as a result of the increased H$\cdots$H distance of 3.05 Å. The exact level ordering is not known, as the individual band components overlap considerably. In any event, the observed shift by about 0.4 eV of the band centre (ca. 13.7 eV) to lower IP, relative to the centre of the $1t_1$, $1e$, and $2t_2$ bands in neopentane, is as expected on the basis of the inductive effect of the silicon atom and thus argues against any p_π–d_π bonding in $Si(CH_3)_4$, as this would operate in the opposite direction. In $Ge(CH_3)_4$ and $Sn(CH_3)_4$, this band becomes progressively sharper and symmetrical and moves further to lower IP (in both cases, band centre at about 13.4 eV). Both observations are consistent with the decreasing electronegativity of the central atom and the diminished through-space interaction (H$\cdots$H distances 3.18 and 3.50 Å, respectively). However, in $Pb(CH_3)_4$, where this distance is 3.76 Å, some diffuse structure is discernible; we will comment on this below.

Secondly, electronically degenerate states of the molecular ions are, in principle, susceptible to a Jahn–Teller (JT) distortion. In the present case, such an effect is most likely to arise if the photoelectron vacates the $3t_2$ (MC) level. The distorting forces and the resulting JT-splitting in the first PE band are expected to diminish steadily (in the same way as the through-space interactions between the CH levels) with increasing size of the central atom, that is, with increasing distance between the ligand carbon atoms. This simple interpretation is supported by the shape of the first PE band: in neopentane it consists of two intense JT components, at 10.9 and 11.3 eV, and a third, less pronounced component at ca. 11.7 eV; for the heavier elements M, the three components progressively collapse, so that the second becomes the most prominent. $Pb(CH_3)_4$, however, does not fit well into this picture.

Thirdly, there is the possibility that the $^2T_2$ ionic states of the higher members of the series suffer a multiplet splitting under the influence of the spin-orbit (SO) coupling associated with the p-AO's of the central atom[16]. This effect acts specifically

on the $^2T_2(MC)$ ground state of the ion, splitting it into a non-degenerate $E_{\frac{1}{2}}$ component, at lower energies, and a spatially degenerate, less stable $G_{\frac{3}{2}}$ component. Their separation is expected to be of the same order of magnitude as the SO coupling constant ζ of the free central atom ($\zeta = 0.004$, 0.024, 0.146, 0.351, and 1.163 eV for C^+, Si^+, Ge^+, Sn^+, and Pb^+, respectively[12]). As the $G_{\frac{3}{2}}$ state is still orbitally degenerate, it can be further split by JT forces into two components, whereas the $E_{\frac{1}{2}}$ state cannot. If we accept this interpretation, then the observed SO splitting in the first band of $Pb(CH_3)_4$ would amount to 0.9 eV, and the doublet structure of the $G_{\frac{3}{2}}$ component would be the result of JT forces acting in the ion. No SO interaction with the *p*-AO's of the central atom can arise in the $^2T_1(CH)$ and $^2E(CH)$ states, for the $1t_1$ and $1e$ orbitals are exclusively confined to the CH bonds, the SO coupling constants for C and H being extremely small. The degeneracy of the $^2T_2(CH)$ state could in principle be lifted, because the $2t_2$ level has a small, but finite coefficient on the Pb atom; the incipient splitting in the second band would then be explicable in terms of such an electron delocalisation.

CONCLUSIONS

In the Group IV tetramethyl compounds, the observed energy level trends across the series are as expected on the basis of the increasing size and decreasing electronegativity of the central atom, provided that allowance is made for through-space interactions within the $(CH_3)_4$ tetrahedron, for JT effects, and SO interactions. The inclusion of *d*-orbitals into the bonding scheme is unnecessary. This finding shows that considerable scepticism has to be placed on the arguments put forward elsewhere in favour of *d*-orbital participation, because in molecules of lower symmetry there is no easy way to differentiate between π- and σ-interactions.

We emphasise, however, the need to examine the He(II) spectra of the present molecules. Qualitative overlap arguments suggest, and semi-empirical MO calculations confirm, that the $1t_2$ level is the most likely candidate to undergo a σ-type mixing with *d*-orbitals of M.

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