

STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY

XIV^a. ULTRAVIOLET ABSORPTION DUE TO BONDS
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INTRODUCTION

The ultraviolet absorption spectra of Group IV tetraphenyls, $M(C_6H_5)_4$, $M = C, Si, Ge, Sn,$ and Pb , are very similar. As in the absorption spectrum of benzene, a high maximum occurs in the region of 200–220 nm^c and a low maximum with vibrational fine structure¹ at approximately 255 nm. It is clear that absorption is connected primarily with the presence of aromatic rings. The situation is more complicated as soon as two tin or lead atoms are joined to each other.

MOLECULES WITH ONE METAL–METAL BOND

The spectrum^d of hexaphenyldilead (Fig. 1) shows strong absorption in the region around 210 nm, a shoulder in the neighbourhood of 250 nm and a band at 294 nm (Table 1). Hague and Prince² attribute this band to intense interaction between phenyl groups on different lead atoms across the metal–metal bond. However, an absorption maximum is also present in the spectrum of hexacyclohexyldilead (Fig. 2, Table 1) despite the absence of phenyl groups. The presence of a band in this molecule, though at somewhat shorter wavelength, suggests that it is primarily due to the lead–lead system. Thus, in the spectrum of hexaphenyldilead (Fig. 1), the strong absorption in the region of 210 nm and the shoulder at 250 nm are attributed to the benzene rings and the maximum at 294 nm to the lead–lead system.

In hexacyclohexyldilead the latter maximum is shifted from 294 to 254 nm. This substituent effect might be due to the difference in polarizability. The polarizability is larger for the unsaturated than for the saturated substituent.

Analogously, the absorption maximum of hexaphenylditin at 247 nm (Fig. 3) is

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^c 1 nm = 1 nanometer = 10^{-9} m = 1 m μ .

^d The spectra were determined with a Beckman spectrophotometer, type DU.

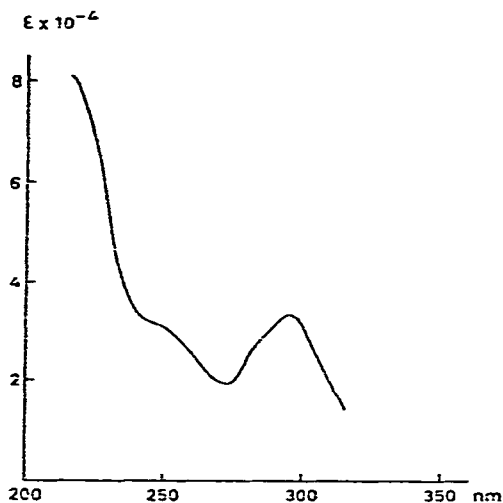


Fig. 1. Ultraviolet absorption spectrum of hexaphenyldilead.

TABLE I

WAVELENGTHS AND EXTINCTION COEFFICIENTS OF MAXIMUM ABSORPTION IN THE REGION OF 220-700 mμ FOR A NUMBER OF COMPOUNDS CONTAINING ONE OR TWO METAL ATOMS

Compound	Solvent	λ_{max} , (mμ)	ϵ_{max}	Reference*
$(C_6H_5)_4Sn$	iso-octane	approx. 260	approx. 500	1
$(C_6H_5)_6Sn_2$	cyclohexane	247.5	33,900	2
$(C_6H_5)_4Sn_2$	cyclohexane	247	33,000	
$(C_4H_9)_4Sn_2$	cyclohexane	no maximum		
$(C_6H_5)_4Pb$	iso-octane	approx. 260	approx. 1000	1
$(C_6H_5)_4Pb_2$	cyclohexane	293	35,000	2
$(C_6H_5)_6Pb_2$	cyclohexane	294	33,000	
$(cyclohexyl)_6Pb_2$	cyclohexane	254	32,000	

* Date for which no reference number is given were obtained in the authors' laboratory.

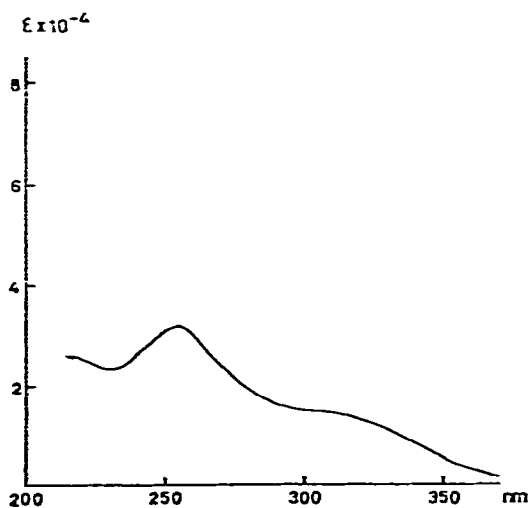


Fig. 2. Ultraviolet absorption spectrum of hexacyclohexyldilead.

ascribed to the tin-tin system. Again, the maximum of the spectrum of the hexaalkyl derivative, hexabutylditin (Fig. 4), is shifted to lower values and apparently lies below 215 nm.

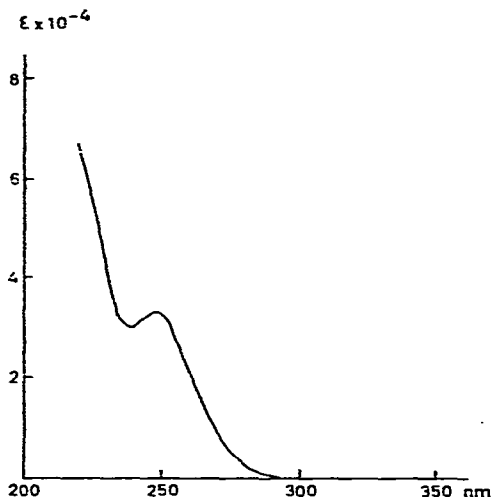


Fig. 3. Ultraviolet absorption spectrum of hexaphenylditin.

Generally, valence electrons forming a bond between two atoms do not give rise to absorption in the near-ultraviolet region. However, tin and lead atoms have radii much larger than those of atoms usually encountered in organic chemistry. The absorption maximum at 254 nm for hexacyclohexyldilead corresponds to a calculated

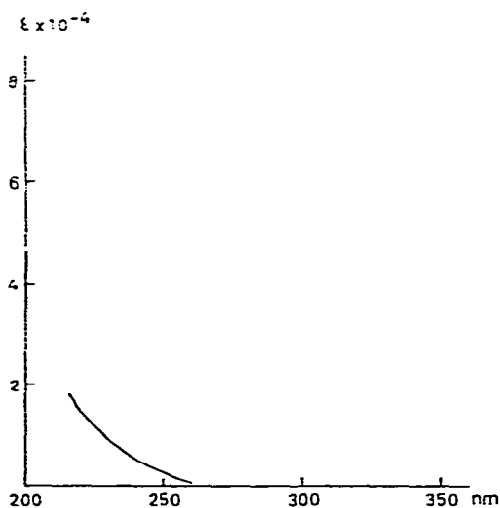


Fig. 4. Ultraviolet absorption spectrum of hexabutylditin.

box length of 4.79 Å, when the free electron method is applied and assuming a constant potential in a one-dimensional box. This is 3.3 times the covalent radius of a lead atom, which is an acceptable size in view of the rather rough approximations.

More elaborate calculations, e.g. by the molecular orbital method, were not performed because of insufficient knowledge of the necessary integrals.

MOLECULES WITH FOUR METAL-METAL BONDS

In the preceding section it was suggested that the absorption band at 294 nm in the ultraviolet spectrum of hexaphenyldilead should be assigned to the electrons of the lead-lead bond. Analogously, the absorption band at 247 nm in the spectrum of hexaphenylditin was assigned to the electrons forming the tin-tin bond.

A new class of organometallic compounds, containing five Group IV metals has been described by Willemsens and Van der Kerk³. The neopentane-like molecules have the general formula $[(C_6H_5)_3M]_4M'$, in which M and M' are either lead, tin or germanium. The near-ultraviolet spectra of a number of these molecules are shown in Figs. 5 and 6 and the maxima are listed in Table 2.

TABLE 2

WAVELENGTHS AND EXTINCTION COEFFICIENTS OF MAXIMUM ABSORPTION IN THE REGION OF 250-700 nm FOR A NUMBER OF COMPOUNDS CONTAINING FIVE METAL ATOMS

Compound	Solvent	λ_{max} , (nm)	ϵ_{max}
$[(C_6H_5)_3Sn]_4Pb$	chloroform	298	59,500
$[(C_6H_5)_3Sn]_4Sn$	chloroform	277	79,000
$[(C_6H_5)_3Sn]_4Ge$	chloroform	276	73,000
$[(C_6H_5)_3Pb]_4Pb$	benzene	358	56,000
$[(C_6H_5)_3Pb]_4Sn$	benzene	444	29,000
$[(C_6H_5)_3Pb]_4Ge$	chloroform	319	67,000
$[(C_6H_5)_3Pb]_4Ge$	chloroform	328	63,000

The molecules contain four equivalent metal-metal σ -bonds and therefore they can be expected to show an absorption maximum connected with the electrons of these bonds just as do hexaphenyldilead and hexaphenylditin. The maxima are indeed present. In Fig. 5 they are located at 298, 277 and 276 nm for the Sn-Pb,

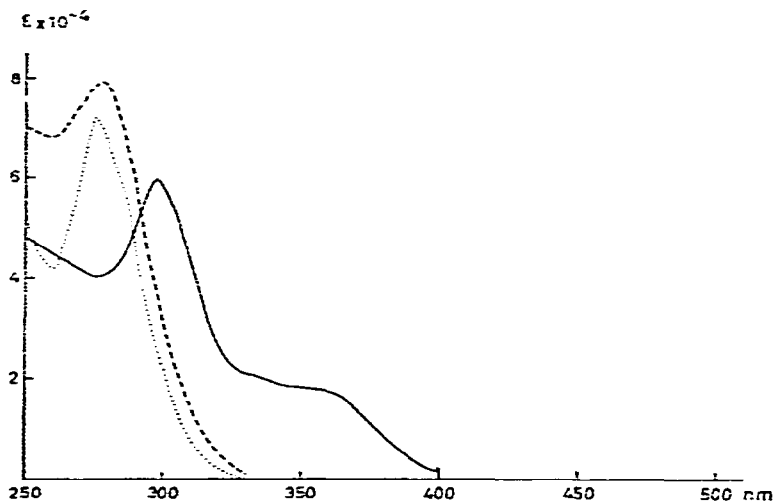


Fig. 5. Ultraviolet absorption spectra of molecules $[(C_6H_5)_3M]_4M'$: —, M = Pb; ---, M = Sn; ·····, M = Ge.

Sn-Sn and Sn-Ge bonds, respectively. The maximum in the spectrum of the pentatin molecule, $[(C_6H_5)_3Sn]_4Sn$, occurs at higher wavelength than the maximum in the spectrum of hexaphenylditin and the maximum of the tetratin-monogermanium compound is higher than could be expected from the somewhat smaller germanium radius. This is not surprising as it is known from a comparison of hexaphenyl- and hexacyclohexyldilead that these absorption bands are sensitive to substitution.

Fig. 6 shows the spectra of compounds which have four lead atoms around a lead, a tin and a germanium atom. Here, the absorption bands of the electrons of the metal-metal bonds occur at 358, 319 and 328 nm, respectively. In addition, the pentalead compound shows an absorption band at 444 nm. Closer inspection of Fig. 5

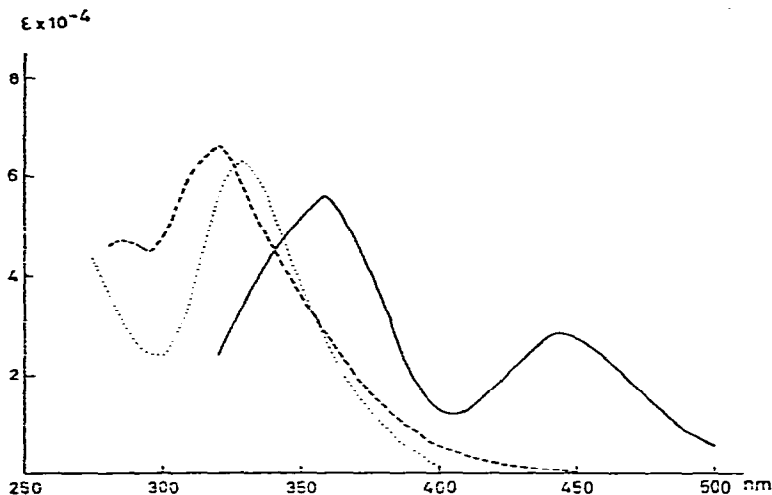


Fig. 6. Ultraviolet absorption spectra of molecules $[(C_6H_5)_3M]_4M$:
—, M = Pb; ---, M = Sn; ·····, M = Ge.

shows that such an additional absorption band is also present in the spectrum of the compound in which a lead atom is surrounded by four tin atoms. Here it occurs at approximately 355 nm. Preliminary investigation of the analogous compound with four germanium atoms around a central lead atom also shows such an additional absorption. Thus, a second band at higher wavelength and of lower intensity than the main band seems to be connected with the presence of a central lead atom surrounded by four metal atoms.

A definite explanation for the presence of this band cannot be given, but two suggestions will be made.

The first suggestion involves the symmetry properties of the molecule. The molecules, or at least their metallic parts, probably have T_d symmetry*. Therefore, the bonds between the central atom and its neighbours can be described by delocalized orbitals belonging to the irreducible representations of the T_d symmetry group. Assuming for simplicity that the atomic orbitals of the central atom, used for bonding, are of s - and p -type then the following symmetry orbitals can be constructed, where the ligand orbitals are called $l_1, l_2, l_3,$ and l_4 .

* An X-ray investigation is in progress in the Laboratory for Crystal Chemistry of the University under the direction of Prof. A. F. PEERDEMAN.

bonding m.o.'s		symmetry	antibonding m.o.'s	
$\sin \alpha (s)$	$\div \frac{1}{2} \cos \alpha (l_1 \div l_2 \div l_3 \div l_4)$	a_1	$\cos \alpha (s)$	$-\frac{1}{2} \sin \alpha (l_1 \div l_2 \div l_3 \div l_4)$
$\sin \beta (p_x)$	$\div \frac{1}{2} \cos \beta (l_1 - l_2 - l_3 \div l_4)$	t_2	$\cos \beta (p_x)$	$-\frac{1}{2} \sin \beta (l_1 - l_2 - l_3 \div l_4)$
$\sin \beta (p_y)$	$\div \frac{1}{2} \cos \beta (l_1 - l_2 \div l_3 - l_4)$	t_2	$\cos \beta (p_y)$	$-\frac{1}{2} \sin \beta (l_1 - l_2 \div l_3 - l_4)$
$\sin \beta (p_z)$	$\div \frac{1}{2} \cos \beta (l_1 \div l_2 - l_3 - l_4)$	t_2	$\cos \beta (p_z)$	$-\frac{1}{2} \sin \beta (l_1 \div l_2 - l_3 - l_4)$

When the bonding molecular orbitals are abbreviated as a_1 and t_2 and their anti-bonding counterparts as a^* and t^* , the singlet-singlet absorptions can be described as follows:

transition	symmetry
$a_1 \rightarrow a_1^*$	A_1
$a_1 \rightarrow t_2^*$	T_2
$t_2 \rightarrow a_1^*$	T_2
$t_2 \rightarrow t_2^*$	A_1, E, T_1, T_2

In molecules with T_d symmetry the electronically permitted transitions occur between the ground state (A_1 symmetry) and excited states with T_2 symmetry. Thus, symmetry considerations show that the valence electrons of the metal-metal bonds can give rise to more than one absorption.

In a second suggestion the additional absorption band is ascribed to an interaction between the filled $5d$ -orbital of the central lead atom and empty orbitals of the surrounding metal atoms. The central lead atom is surrounded by four electro-positive atoms. In this situation expansion of its orbitals and increased overlap of its $5d$ -orbital with empty orbitals of the outer metal atoms might occur. In this way a set of molecular orbitals could be formed. The additional long wavelength band could be connected with a transition between these molecular orbitals. This suggestion in which only d -orbitals are considered is somewhat an oversimplification. In fact, a mixture of s -, p - and d -orbitals of the right symmetry will be involved.

In principle, an analogous transition could be present in molecules in which tin instead of lead is the central atom. Apparently, in this case the absorption band is shifted to lower wavelengths and is not detectable.

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SUMMARY

Ultraviolet absorption spectra are discussed for a number of molecules containing metal-metal bonds, viz. $(C_6H_5)_6Sn_2$, $(C_6H_5)_6Pb_2$, $(cyclohexyl)_6Pb_2$, $[(C_6H_5)_3Sn]_4M$, and $[(C_6H_5)_3Pb]_4M$ with $M = Pb, Sn$, and Ge . Long wavelength absorptions are attributed to the metallic part of the molecules.

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