CYCLIC ORGANOLEAD COMPOUNDS PART IV[@]. SYNTHESIS AND MULTINUCLEAR NMR PROPERTIES OF SIX-MEMBERED HETEROCYCLIC ORGANOLEAD COMPOUNDS

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Abstract

Several six-membered heterocyclic organolead compounds were synthesized from the appropriate di-Grignard resp. organodilithio compounds and a (diorgano)lead dihalide. The compounds were investigated by multinuclear NMR spectroscopy. Variable temperature ¹H NMR measurements revealed a conformational equilibrium. In the ¹³C and ²⁰⁷Pb NMR spectra specific effects caused by the presence of a lead atom in the ring system could be observed.

Introduction

In several previous studies we had investigated some aspects of the chemistry of cyclic organolead compounds, including five-membered ring compounds, in particular [2,3]. Subsequently we studied several six-membered cyclic organolead compounds of the general type (1) and the results are presented here. We were particularly interested in the effects of variation of the element E on the multinuclear NMR properties. Results on 10,10-dimethylphenoxaplumbin, in which E denotes an oxygen atom and R is CH₃, have been previously published [1].

Materials and Methods

¹H and ¹³C NMR spectra were recorded on a JEOL-PFT-100 NMR spectrometer. ²⁰⁷Pb NMR spectra were recorded on a Bruker WH 90 multinuclear spectrometer. Experimental details on the recording and assignments of the various spectra have been published elsewhere [24,36].

All synthetic reactions were carried out under dry nitrogen. The solvents diethylether (ether) and tetrahydrofuran (THF) were distilled from lithiumaluminiumhydride before use. For more experimental details see ref.[39].

Synthesis of bis-(o-bromophenyl)methane [6]

A solution of 25.0 g of *o*-dibromobenzene (0.106 mol) and 19.9 g of 1,2-dibromoethane (0.106 mol) in 125 ml of ether was added dropwise to 5.15 g of magnesium (0.212 mol) in 15 ml of ether which was stirred magnetically. External cooling was applied by means of an ice bath and the reagents were added at such a rate that the temperature of the reaction mixture did not exceed 10°C. After the reaction was completed (ca. 3 h) the mixture was stirred for another 10 min. and at 0°C 19.7 g of *o*-bromobenzaldehyde (0.106 mol) was added dropwise. After refluxing for 2 h the mixture was cooled down to room temperature and hydrolysed with an aqueous ammonium chloride solution. The ether layer was isolated and the water layer was extracted with a 100 ml portion of ether. The combined ether fractions were dried over anhydrous magnesium sulfate. After filtration and evaporation, a yellow oil of 2,2'-dibromodiphenylmethanol was obtained.

[@]Part III, see ref.[1]

45 g of red phosphorus and 40 ml of hydrogen iodide (57% in H₂O) were added to the yellow oil of 2,2'-dibromophenylmethanol and the mixture was refluxed for 48 h. After cooling, the reaction mixture was poured into 200 ml of water and 200 ml of chloroform. The suspension obtained was filtered over hyflo and the organic layer was isolated. After washing twice with aqueous sodium bisulfite, drying over anhydrous magnesium sulfate and filtration the solvent was evaporated. Finally the residue was distilled under reduced pressure. At a boiling point of 129-131°C/0.03 mm (lit.[5] 120-121°C/0.01 mm) 8.6 g of 2,2'-dibromodiphenylmethane (27% based on *o*-dibromobenzene) was isolated. ¹H NMR (in CDCl₃): δH(CH₂) 4.12 ppm (s); δH(arom.) 6.85-7.62 ppm (m).

Synthesis of *N*-methyl-bis-(*o*-bromophenyl)amine resp. *N*-methyl-bis (2,4-dibromophenyl)amine
N-methyl-bis-(*o*-bromophenyl)amine was prepared as described in refs.[10,11]. The product was obtained in a yield of 16% (based on *o*-bromoaniline). The melting point (after recrystallisation from ethanol) was 104-106°C (lit.[11] 106-107 °C); ¹H NMR (in CDCl₃): δH(NCH₃) 3.19 ppm (s); δH(arom.) 6.71-7.65 ppm (m).

Bis (2,4-dibromophenyl)amine (m.p. 183-184°C) was synthesised in a yield of 75% by bromination of diphenylamine in ethanol. *N*-methylation was performed as described in ref.11 in a yield of 59%. After recrystallisation from ethanol the melting point was 140-142°C (lit.[12] 143-146°C); ¹H NMR (in CDCl₃): δH(NCH₃) 3.16 ppm (s); δH(3) 7.69 ppm (d); δH(5) 7.36 ppm (q); δH(6) 6.89 ppm (d).

Synthesis of 9,10-dihydro-9-plumbaantracenes

A solution of 6.52 g of bis-(*o*-bromophenyl)methane (20 mmol) and 3.76 g of 1,2-dibromoethane (20 mmol) in 20 ml of THF was added dropwise to 1.67 g of magnesium (67 mmol) in 50 ml of THF. When the addition was complete the mixture was refluxed for 1 h, upon which a red solution was obtained. This solution was transferred to a dropping funnel and added dropwise to a suspension of 20 mmol of a diorganolead dibromide [3] or 20 mmol of lead dichloride in 150 ml of THF. After stirring for 0.5 h at room temperature and 1 h at reflux temperature, the mixture was cooled and hydrolysed with an ammonium chloride solution. The ether layer was isolated and the water layer was extracted with 100 ml of chloroform. The combined organic layers were dried over anhydrous magnesium sulphate, filtrated and evaporated. The resulting yellow oil was dissolved in 20 ml of chloroform and filtrated, after which 50 ml of ethanol was added. The product crystallised in the refrigerator. Recrystallisation was performed with a chloroform/ethanol mixture.

Synthesis of 5-methyl-5,10-dihydrophenazaplumbines

To a solution of 20 mmol of *N*-methyl-bis-(*o*-bromophenyl)amine resp. *N*-methyl-bis-(2,4-dibromophenyl)amine in 100 ml of ether, which was stirred magnetically at 0°C, was added dropwise 16.54 g of a 15% (w/v) solution of *n*-butyllithium in *n*-hexane. After stirring at 0°C for 1 h the solution was transferred to a dropping funnel and added dropwise to 20 mmol of a diorganolead dibromide [3] in 150 ml of ether at 0°C. The mixture was refluxed for 2.5 h and worked up as the plumbaantracenes, using chloroform and petroleum ether (40-60°) as solvents.

Synthesis of 10,10-diphenylphenoxaplumbin

A solution of 6.56 g of bis-(*o*-bromophenyl)ether (20 mmol) and 3.67 g of 1,2-dibromoethane (20 mmol) in 30 ml of THF was added dropwise to 1.46 g of magnesium (60 mmol) in 20 ml of THF and subsequently refluxed for 2.5 h. A 125 ml portion of THF was added and the mixture was cooled to 0°C, upon which the di-Grignard compound crystallised. 10.42 g of diphenyllead dibromide (20 mmol) [3] was added and the mixture was stirred for 0.5 h at room temperature and for 1 h at reflux, which resulted in a clear solution. Work up was as described for the plumbaantracenes. Ether and petroleum ether (40-60°) were used as solvents.

Synthesis of 5,5-diphenyl-10,11-dihydro-5-*H*-dibenzo[b,f]plumbepin

The compound was synthesised from the corresponding di-Grignard compound of 1,2-bis-(*o*-bromophenyl)ethane. The latter was synthesised according to a published procedure [37]. In spite of several attempts the seven membered ring compound could not be obtained pure. It appeared to be contaminated with 1,2-diphenylethane, which resulted from the hydrolysis of the di-Grignard compound. It was possible, however, to determine the ¹³C NMR characteristics as shown in Table 5. ¹H NMR (in CDCl₃): δH(CH₂) 3.13 ppm (⁴J(²⁰⁷Pb-¹H) 11 Hz). The dilithio compound, which according to the literature [38] would give the desired seven membered ring compound, failed to give proper results.

For more experimental details see ref.[39].

Results and Discussion

a. Synthesis

Cyclic organolead compounds can be synthesised conveniently by reacting a di-Grignard or an organolithio compound with a diorganolead dibromide. In the synthesis of 9,10-dihydro-9-plumbaanthracene derivatives, in which E of (1) is a CH₂ group, bis-(o-bromophenyl)methane was used as a starting material rather than the corresponding dichloro compound [4,5]. The dibromo compound was prepared according to eq.(2) in an overall yield of c. 30% [6]. This method is more attractive than those previously reported in the literature [5,7].

Bis-(o-bromophenyl)methane is converted into the di-Grignard compound by reaction with magnesium in THF in the presence of 1,2-dibromoethane. Reaction of the di-Grignard compound with a diorganolead dibromide leads to the monocyclic product, reaction with lead(II) chloride gives the spirobicyclic compound (eq.(3)).

5,10-Dihydrophenazaplumbine derivatives, in which E denotes a nitrogen atom with an alkyl substituent R, can be obtained according to eq.(4). From the literature, a synthesis is known in which R = C₂H₅, X = H and R' = C₆H₅ [8,9]. We have synthesised the corresponding N-methyl-5,10-dihydrophenazaplumbines, in which R = CH₃, from N-methyl-bis (2,4-dibromophenyl)amine [10,11]. When X = Br the starting material appears to be selectively lithiated at the ortho positions of the aromatic rings [12,13], as a result of the presence of the free electron pair at the nitrogen atom [14].

Although 10,10-dimethylphenoxaplumbin in which E denotes an oxygen atom, could be synthesised from bis-(o-lithiophenyl)ether and the appropriate diorganolead dibromide [1], it was not possible to synthesise the corresponding diphenyl compound in this way. In the field of phenoxastannin derivatives the same phenomenon was observed. It was suggested that a trans lithiation reaction between the bis-(o-lithiophenyl)ether and diphenyltin dichloride was responsible for the formation of tetraphenyltin [15]. An alternative route to the desired diphenyllead compound proceeds *via* the di-Grignard derivative, which can be prepared from bis-(o-bromophenyl)ether [16,17]. The 10,10-diphenylphenoxaplumbin is obtained according to eq.(5).

Table I: Synthesis of six-membered cyclic organolead compounds of the type

E	X	R	Yield (%)	Melting point (°C)
CH ₂	H	CH ₃	31	68-70
CH ₂	H	C ₆ H ₅	40	113-116
CH ₂	H	spiro	46	216-219
NCH ₂	H	CH ₃	51	133-136
NCH ₃	H	C ₆ H ₅	19	125-127
NCH ₃	Br	CH ₃	13	94-97
NCH ₂	Br	C ₆ H ₅	28	184-186
O	H	CH ₃	26	a
O	H	C ₆ H ₅	12	121-125

^a Liquid product ($n_D^{20} = 1.6069$) [1].

Table II: Characteristic ¹H NMR data^a of six-membered cyclic organolead compounds of the type

E	X	t (°C)	Methyl groups	Other substituents
CH ₂	H	25 -100	$\delta(\text{CH}_2) = 1.22$ $^2J(^{207}\text{Pb}-^1\text{H}) = 73$	$\delta(\text{CH}_2) = 3.95$ $^4J(^{207}\text{Pb}-^1\text{H}) = 10$
NCH ₃	H	25 -100	$\delta(\text{CH}_2) = 1.17$ $^2J(^{207}\text{Pb}-^1\text{H}) = 75$ $\delta(\text{CH}_2(\text{i})) = 1.11$ $^2J(^{207}\text{Pb}-^1\text{H}) = 81$ $\delta(\text{CH}_2(\text{ii})) = 1.26$ $^2J(^{207}\text{Pb}-^1\text{H}) = 74$	$\delta(\text{NCH}_3) = 3.35$ $\delta(\text{NCH}_3) = 3.35$
NCH ₃	Br	25 -100	$\delta(\text{CH}_2) = 1.25$ $^2J(^{207}\text{Pb}-^1\text{H}) = 78$ $\delta(\text{CH}_2(\text{i})) = 1.19$ $^2J(^{207}\text{Pb}-^1\text{H}) = 85$ $\delta(\text{CH}_2(\text{ii})) = 1.37$ $^2J(^{207}\text{Pb}-^1\text{H}) = 77$	$\delta(\text{NCH}_3) = 3.32$ $\delta(\text{NCH}_3) = 3.32$
O	H	25 -100	$\delta(\text{CH}_2) = 1.26$ $^2J(^{207}\text{Pb}-^1\text{H}) = 67$	

^a $\delta(^1\text{H})$ in ppm (reference TMS); $J(^{207}\text{Pb}-^1\text{H})$ in Hz; solvent CD₂Cl₂.

The results of the various syntheses are summarized in Table I.

b. ¹H NMR spectroscopy

It is likely that the six-membered heterocyclic organolead compounds exist in solution as an equilibrium mixture of two boat conformers. As is demonstrated for the dimethyllead derivatives in eq.(6), one of the substituents on the lead atom is in the flagpole position, while the other substituent is in the bowsprit position of the boat conformer. This should lead to magnetically inequivalent methyl groups, resulting in different chemical shift values for the methyl protons.

Table III: ^{13}C NMR data of cyclic organolead compounds of the type

E	X	R	C(2,6)	C(3,5)	C(4)	C(2')	Σ^1J
CH ₂	H	CH ₃	149.0 (328)		146.3 (34)	49.6 (79)	-1/7 (310)
CH ₂	(1276)	H					
		C ₆ H ₅	150.5 (400)		146.5 (38)	49.3 (86)	147.4 (531)
CH ₂	(1862)	H					
		spiro	148.8 (449)		146.3 (42)	49.7 (95)	
NCH ₃	(1796)	H					
		CH ₃	140.6 (287)		153.4 (14)		-1.8 (342)
NCH ₃	(1258)	H					
		C ₆ H ₅	142.7 (362)		153.5 (16)		146.9 (579)
NCH ₃	(1882)	Br					
		CH ₃	142.9 (236)		151.8 (12)		-0.4 (357)
NCH ₃	(1186)	Br					
		C ₆ H ₅	144.8 (314)		151.9 (14)		146.2 (614)
O	(1856)	H					
		CH ₃	139.7 (257)		160.7 (16)		-1.6 (296)
O	(1106)	H					
		C ₆ H ₅	137.9 (336)		161.9 (6)		146.3 (621)
	(1914)						

^aδ(¹³C) in ppm (reference TMS); J(²⁰⁷Pb-¹³C) values in Hz (in parentheses); solvent CDCl₃.

The ^1H NMR spectra of the cyclic dimethyllead compounds were recorded in CDCl_3 at various temperatures. Some characteristic data are presented in Table II. From the fact that at room temperature only one methyl proton signal was observed in these compounds, it must be concluded that the equilibrium process is rapid on the NMR time scale. When the temperature was lowered to about -100°C , the single methyl proton signal persisted in both the carbon- and oxygen-containing six-membered ring compounds. This was also observed in the corresponding organosilicon and organotin six-membered ring compounds [18,19]. With the two phenazaplumbine compounds, however, two methyl proton signals with different lead-proton coupling constants were observed, indicating that the rate of the equilibrium process in eq.(6) was slow enough on the NMR time scale to mark the two methyl groups. In both compounds a coalesce of the methyl proton resonance occurred at -85°C from which a free energy of activation of the conformational transition of 40 kJmol^{-1} could be calculated [20] for 5,10,10-trimethyl-5,10-dihydrophenazaplumbine as well as for 2,8-dibromo-5,10,10-trimethyl-5,10-dihydrophenazaplumbine.

Table IV: ^{13}C NMR data^a of cyclic organolead compounds of the type

	R		C(2)	C(3)	C(2')	Σ^1J
N=0 (acyclic) ^b	CH ₃	149.0	136.6 (395)	-1.0 (65)	(295)	(1380)
	C ₆ H ₅		150.1 (481)	137.7 (68)	150.1 (481)	(1924)
n=0 (cyclic)	CH ₃		149.3 (344)	148.6 (107)	1.6 (300)	(1288)
	C ₆ H ₅		149.8 (418)	148.4 (124)	149.8 (532)	(1900)
	Spiro		147.8 (471)	147.0 (141)		(1884)
n=1	CH ₃		149.0 (328)	146.3 (34)	-1.7 (310)	(1276)
	C ₆ H ₅		150.5 (400)	146.5 (38)	147.4 (531)	(1862)
	Spiro		148.8 (449)	146.3 (42)		(1796)
	C ₆ H ₅		150.9 (454)	151.8 (66)	150.5 (462)	(1832)

^a $\delta(^{13}\text{C})$ in ppm (reference TMS); $J(^{207}\text{Pb}-^{13}\text{C})$ in Hz (in parentheses); solvent CDCl_3 ; ^bData from ref. [27].

From the equal values for these compounds it can be concluded that the presence of the bromine atoms in the latter compound had no influence on the rate of the equilibrium process. The difference between the two nitrogen ring compounds on the one hand and the carbon and oxygen ring compounds on the other, might be attributed to the presence of a methyl substituent on the hetero atom E in the nitrogen ring compounds.

c. ^{13}C NMR spectroscopy

Table III presents $\delta(^{13}\text{C})$ and $J(^{207}\text{Pb}-^{13}\text{C})$ values of the six-membered heterocyclic organolead compounds. Although all the signals in the ^{13}C NMR spectrum can be assigned, only the values of the carbon atoms in the lead-containing six-membered ring and those of the carbon atom of the substituent R directly attached to the lead atom are given here for simplicity. In Table III Σ^1J values, the sum of the one-bond lead-carbon coupling constants, are also presented.

From Table III it is clear that the ^{13}C NMR data depend both on the substituent R and on the nature of E. For a certain substituent R the $\delta(^{13}\text{C})$ values of C(2,6) are shifted towards low frequency going from E = CH_2 to E = O, while simultaneously for the carbon atoms C(3,5) a low field shift is observed. These findings are in agreement with the substituent chemical shift parameters found in the ^{13}C NMR spectroscopy of compounds of the type Ar_2Pb [21,22]. The chemical shift values of the six-membered ring compounds in which E = CH_2 are in reasonable agreement with those of $(o\text{-CH}_3\text{C}_6\text{H}_5)_4\text{Pb}$, while the $\delta(^{13}\text{C})$ values of the phenoxaplumbin compounds (E = O) can be compared with those of $(o\text{-CH}_3\text{OC}_6\text{H}_4)_4\text{Pb}$ [22].

As might be expected, with a particular hetero atom E the $J(^{207}\text{Pb}-^{13}\text{C})$ values appear to depend on the nature of the substituent R on the lead atom. The values of $^1J(^{207}\text{Pb}-^{13}\text{C})$ increase when the methyl substituents are replaced by phenyl groups; this is particularly shown by the value of Σ^1J . In view of the Fermi contact term which dominates the coupling constants in which heavy metals such as lead are involved [23], variations in the values of $^1J(^{207}\text{Pb}-^{13}\text{C})$ can be explained on the basis of variations of the nuclear charge and/or the hybridisation of the atoms participating in the coupling mechanism [24]. The variations in the $^1J(^{207}\text{Pb}-^{13}\text{C})$ values with the substituent R might be described by a "polar group effect", affecting hybridisation and nuclear s-electron density [25,26].

Furthermore, it is clear there is a dependence of the coupling constant values on the nature of E. For example, within the series in which X = H and R = C_6H_5 , going from E = CH_2 to E = O the

$^1J(^{207}\text{Pb}-^{13}\text{C}(\text{ring}))$ values decrease (from 400 to 366 Hz) and the $^1J(^{207}\text{Pb}-^{13}\text{C}(\text{R}))$ values increase (from 531 to 621 Hz). In this series the values of Σ^1J also show an increase (from 1862 to 1914 Hz). The variation in these coupling constant data can be attributed to different "ring effects".

On the basis of the ^{13}C NMR data a possible interaction between the hetero atom E and the lead atom cannot be excluded. This interaction could occur within the oxygen and nitrogen containing ring compounds, because of the lone pairs on the hetero atoms.

Finally, ^{13}C NMR data of the six-membered cyclic organolead compounds in which $\text{E} = \text{CH}_2$ were compared with those of the corresponding acyclic compounds, the five-membered plumbole and the seven membered plumbepin derivatives. Illustrative data are summarized in Table IV. It is clear that the $J(^{207}\text{Pb}-^{13}\text{C})$ value depends on the magnitude of n . A typical trend is observed in the value of Σ^1J : for a certain substituent R on the lead atom this value decreases going from $n = 0$ (acyclic) to $n = 2$ (e.g. when $\text{R} = \text{C}_6\text{H}_5$ from 1924 for $n = 0$ to 1832 Hz for $n = 2$).

Table V: $\delta(^{207}\text{Pb})$ values of cyclic and corresponding acyclic organolead compounds^{a,b}

Five-membered ring compound ($\Delta\delta(^{207}\text{Pb})$)	$\delta(^{207}\text{Pb})$ ($\Delta\delta(^{207}\text{Pb})$)	Acyclic compound	$\delta(^{207}\text{Pb})$	Six-membered ring compound	$\delta(^{207}\text{Pb})$
+205.3 (+152.3)	Et_2PbMe_2	+53 ^c
+149.3 (+187.3)	Me_2PbPh_2	-38 ^d
+416.3 ^e (+341.5)	Et_4Pb	+74.8 ^f		-199 ^e (-273.8)
+0.3 (+38.3)	Me_2PbPh_2	-38 ^d		-201.4 (-163.4)
-95.4 (+82.6)	Ph_4Pb	-178.0		284.1 (-106.1)
+10.7 (+188.7)	Ph_4Pb	-178.0		-396.2 (-218.2)

^a $\delta(^{207}\text{Pb})$ in ppm (reference external TML); solvent CDCl_3 (unless otherwise indicated);

^b $\Delta\delta(^{207}\text{Pb}) = \delta(^{207}\text{Pb})$ (cyclic compound) - $\delta(^{207}\text{Pb})$ (acyclic compound); ^cfrom ref. [29] (in toluene); ^dfrom ref. [30]; ^efrom ref. [31] (neat liquid); ^ffrom ref. [31] (in CH_2Cl_2).

The $^2J(^{207}\text{Pb}-^{13}\text{C})$ values of the plumbole derivatives ($n = 0$) are remarkably different from those of the other compounds considering the number of bonds concerned in the coupling between the lead and the carbon atom. The coupling with the lead atom for a certain C(3) atom in the plumbole derivatives can be considered to proceed through two bonds along one side, but through three bonds along the other side of the plumbole ring. From the ^{13}C NMR data of organolead compounds

it is known that for the absolute magnitudes of the lead-carbon coupling constants the relationship $|^1J| > |^3J| > |^2J|$ holds [24,25]. Obviously, with the plumbale derivatives there is a considerable $^3J(^{207}\text{Pb}-^{13}\text{C})$ contribution to the value of $^2J(^{207}\text{Pb}-^{13}\text{C}(3))$, which is of course not possible with the other compounds in Table IV (see also ref.[28]).

d. ^{207}Pb NMR spectroscopy

^{207}Pb data of several five and six-membered cyclic organolead compounds are presented in Table V, together with those of the corresponding acyclic compounds. As can be seen from the $\Delta\delta(^{207}\text{Pb})$ values, the ^{207}Pb NMR chemical shifts of the five-membered ring compounds have been shifted towards higher frequency compared to those of the acyclic compounds. The same phenomenon was observed in ^{119}Sn NMR spectroscopy of cyclic organotin compounds. This effect was explained in terms of a decrease of the interbond angle at the tin atom in the ring system compared to that in the acyclic derivative [32]. A similar explanation might also account for the $\Delta\delta(^{207}\text{Pb})$ values in Table V, although it is likely that there is also a certain "ring contribution" to the value of $\delta(^{207}\text{Pb})$, as can be concluded from the difference between the $\Delta\delta(^{207}\text{Pb})$ values in the saturated and unsaturated cyclic organolead compounds.

With the six-membered ring compounds the lead resonance is shifted towards lower frequency compared with those of the corresponding acyclic compounds. These results are in agreement with the results obtained in ^{119}Sn NMR spectroscopy of several cyclic organotin compounds [28,32-35]. Furthermore it is remarkable that the $\Delta\delta(^{207}\text{Pb})$ values of the spirobicyclic compounds are about twice as large as those of the corresponding monocyclic compounds.

Table VI: $\delta(^{207}\text{Pb})$ values of cyclic organolead compounds of the type

E	X	R	$\delta(^{207}\text{Pb})^a$
CH_2	H	CH_3	-201.4
CH_2	H	C_6H_5	-284.1
CH_2	H	Spiro	-396.2
NCH_2	H	CH_3	-238.0
NCH_3	H	C_6H_5	-334.7
NCH_3	Br	CH_3	-219.9
NCH_3	Br	C_6H_5	-333.4
O	H	CH_3	-41.5
O	H	C_6H_5	-363.4

^a $\delta(^{207}\text{Pb})$ in ppm (reference external TML); solvent CDCl_3 .

This can be understood from the number of lead-containing ring fragments in the cyclic organolead compounds. It is speculated that a certain "ring contribution" to the value of $\delta(^{207}\text{Pb})$ caused by the presence of the lead atom in a spirobicyclic compound is larger than that in a monocyclic derivative.

The $\delta(^{207}\text{Pb})$ values of the six-membered heterocyclic organolead compounds are presented in Table VI. All compounds appear to absorb at low frequency from tetramethyllead. The absorption of 10,10-dimethylphenoxaplumbin is at markedly lower field than the values of the other compounds. The reason for this phenomenon is not clear.

With the exception of the compound mentioned above, the absorptions of the nitrogen- and oxygen-containing six-membered ring compounds have shifted towards lower frequency compared to the corresponding plumbaanthracene derivatives. This might be due to an interaction of the lead atom with the lone pairs of the heteroatom E, as was also observed with *o*-methoxysubstituted tetraaryllead compounds [36].

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