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PHOTOELECTRON SPECTRA AND THE STRUCTURE OF ORGANOMERCURY COMPOUNDS *

V.N. BAIDIN, M.M. TIMOSHENKO, YU. V. CHÍZHOV,

Research Institute of Physics of Zhdanov State University, 198904 Leningrad, Stary Petergof, Pervomaisky prospect, 100 (U.S.S.R.)

YU. A. USTYNYUK

Department of Chemistry, Lomonosov State University, 117234, Moscow (U.S.S.R.)

and I.I. KRITSKAYA

Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences, 117813 B-334, Moscow, ul Vavilova 28 (U.S.S.R.)

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Summary

The He(I) photoelectron spectra of 30 organomercury compounds of different structural types and of some model organic compounds were investigated. Also the values of vertical ionization potentials (*IP*) of highest occupied molecular orbitals (HOMO) were determined. Several relationships were studied in *IP* in this series of compounds. A method was developed to separate the contributions of electron effects to changes in the *IP* of HOMO. The induction effects of HgCl and CH₂HgCl groups as well as the effect of $\sigma(\text{C-Hg})$, π -conjugation in the alkene and benzyl derivatives of mercury were estimated. The influence of structural and other factors on the magnitude of this effect was studied.

Introduction

Organomercury compounds are one of the main subjects of research in the Russian organometallic school [1-4]. Characteristic chemical behaviour was discovered for organomercury compounds, which has enabled us to formulate the ideas concerning enhancement of electronic effects connected with substitution of metal for hydrogen, dual reactivity and transfer of the reaction center due to conjugation, and on comparing this phenomenon with that of tautomerism [5,6], also the substitution mechanisms of sp^2 and sp^3 carbons could be clarified [2].

* Dedicated to Professor Oleg Reutov on the occasion of his 65th birthday on September 5th, 1985.

The present research focusses on identification of the $\sigma(\text{C-Hg})$, π -conjugation from the sum of electron effects occurring in organomercury molecules of different structures.

It is well-known that the σ, π -conjugation problem has a complicated history with alternating periods of recognition, critical analysis [7] and renewal of interest [8]. This may be due to the fact that the experimental evidence which served as a basis for the idea of this hypothesis [9,10] and numerous data employed at later stages were developed using methods that were not quite adequate to attack the problem.

Application of photoelectron spectroscopy makes it possible to obtain information on the energies of HOMO and gain new insights into the nature of electron effects. Changes in the MO levels are caused by the sum of electron factors of which inductive interactions, conjugation and hyperconjugation effects appear to be the most important. To estimate each of them, it is necessary to develop a correct procedure to evaluate the contributions of each. To solve this problem for a series of organomercury compounds, we have compared data for a wide series of compounds and their corresponding organic analogs as well as concepts of simple MO perturbation theory whose useful application to *IP* interpretation is generally recognized.

Results and discussion

Tables 1 and 4 list the organomercury compounds we have studied. Synthesis was done according to described or specially developed techniques [1,11]. For spectral

TABLE 1
VERTICAL *IP* (eV) ^a OF ALKYL MERCURIC HALIDES

No.	Compound	<i>IP</i> ($\sigma(\text{C-Hg})$) ± 0.05	<i>IP</i> ($n(\text{Cl})$) ± 0.02	<i>IP</i> ($\sigma'(\text{C-Hg})$) ± 0.05	<i>IP</i> ($\sigma(\text{C-C}), \sigma(\text{C-H})$) ± 0.1 (ionization threshold)
1	CH ₃ HgCl	10.84	10.84	12.67	12.26
		10.88 ^b	10.88 ^b	12.70 ^b	
2	C ₂ H ₅ HgCl	10.22	10.70	12.55	11.85
3	n-C ₃ H ₇ HgCl	10.15	10.65		11.40
4	i-C ₃ H ₇ HgCl	9.80	10.58		11.58
5	n-C ₄ H ₉ HgCl	10.08	10.62		11.10
6	i-C ₄ H ₉ HgCl	10.04	10.61		11.22
7	s-C ₄ H ₉ HgCl	9.74	10.54		11.17
8	t-C ₄ H ₉ HgCl	9.52	10.49		11.22
9	n-C ₅ H ₁₁ HgCl	9.99	10.58		10.90
10	i-C ₅ H ₁₁ HgCl	9.95	10.59		
11	n-C ₆ H ₁₃ HgCl	9.96	10.58		
12	cyclo-C ₆ H ₁₁ HgCl	9.57	10.50		
13	cyclo-C ₆ H ₁₁ CH ₂ HgCl	9.82	10.53		
14	CH ₃ HgBr ^b	10.66	10.16 } 10.43 }	12.52	
15	cyclo-C ₆ H ₁₁ HgBr	9.40	9.74 } 10.05 }		

^a The *IP*($\sigma'(\text{C-Hg})$) for compounds 3–13 and 15 cannot be determined from their spectra due to overlapping by the bands of the $\sigma(\text{C-C}), \sigma(\text{C-H})$ orbitals. ^b From Eland [16].

TABLE 2

VERTICAL IP ($n(N)$) FOR ALKYLAMINES, IP 's (π) FOR ALKENES, AND IP ($\sigma(C-Hg)$) FOR SOME ALKYL MERCURY COMPOUNDS (eV)

Alkylamines [20]		Alkenes [22]		RHgCH ₃ [19]	
Compound	$IP(n(N))$	Compound	$IP(\pi)$	Compound	$IP(\sigma(C-Hg))$
NH ₃	10.92	CH ₂ =CH ₂	10.51	CH ₃ HgCH ₃	9.33
CH ₃ NH ₂	9.66	CH ₃ CH=CH ₂	9.74	CH ₃ CH ₂ HgCH ₃	8.84
C ₂ H ₅ NH ₂	9.50	C ₂ H ₅ CH=CH ₂	9.63		
n-C ₃ H ₇ NH ₂	9.44	n-C ₃ H ₇ CH=CH ₂	9.52		
n-C ₄ H ₉ NH ₂	9.40	n-C ₄ H ₉ CH=CH ₂	9.48		
		n-C ₅ H ₁₁ CH=CH ₂	9.44		
(CH ₃) ₂ NH	8.94	CH ₃ (CH ₃)CH=CH ₂	9.24	CH ₃ (CH ₃)CHHgCH ₃	8.48
		i-C ₄ H ₉ CH=CH ₂	9.53	i-C ₄ H ₉ CH ₂ HgCH ₃	8.75
		i-C ₅ H ₁₁ CH=CH ₂	9.45		
		C ₂ H ₅ (CH ₃)CH=CH ₂	9.15		
(CH ₃) ₃ N	8.50			(CH ₃) ₃ CHgCH ₃	8.31

analysis, analytically pure samples were used. Additionally a study was carried out of the photoelectron spectra (PES) of some related organic compounds listed in Table 5.

The photoelectron spectra were obtained using a spectrometer described in ref. 15. Resolution estimated by the band width of reference gases (Ar, Xe, CH₃I) and was 0.02–0.05 eV at half-height.

All the organomercury compounds studied are solids having low vapor pressure at room temperature. To ensure that the vapor pressure in the ionization region is adequate for reliably record the spectrum, the instrument used and the ampoule containing the sample were heated to 320–420 K. A helium discharge lamp with a quanta-emitting energy of 21.2 eV (He(I)) was used as ionization radiation source.

The photoelectron spectra of compounds having saturated and unsaturated radicals are shown in Fig. 1 and 9, respectively. The numbering of the spectra corresponds to that in Tables 1, 3, 4.

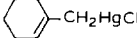

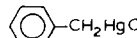
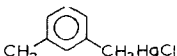
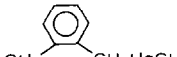
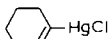
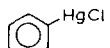
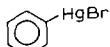
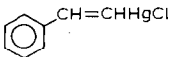

In the discussion of the photoelectron spectra, opposite-sign vertical IP were assumed to be equal to energies of corresponding MO (Koopmans' approximation). Previously we published parts of our results [12–15].

Alkylmercuric halides

The spectra of some of the most simple representatives of this class of compounds are described in the literature [16–19]. We have studied a series of alkylmercuric halides to clarify the nature and magnitude of the effects depending on the structure of an alkyl radical on the HOMO energies ($\sigma(C-Hg)$, $\sigma'(C-Hg)$, $n(Cl)$, $\sigma(C-H)$, $\sigma(C-C)$, Fig. 2). It was also necessary to facilitate the interpretation of spectra of more complicated compounds. The IP data of compounds of this type are summarized in Table 1. As is seen from Fig. 1 and Table 1, the changes in length and structure of the alkyl radical noticeably affect the energy of the orbital $\sigma(C-Hg)$. Corresponding bands are normally located in the region of the lower IP values, as compared to $n(Cl)$ orbital bands. For example, in the spectra of *t*-C₄H₉HgCl and cyclo-C₆H₁₁HgCl, the splitting between these bands is ~ 1 eV. Relatively narrow

TABLE 3

 VERTICAL *IP* OF ORGANOMERCURY COMPOUNDS WITH UNSATURATED RADICALS (eV)
 (measurement error ± 0.05)










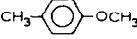
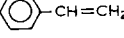






No.	Compound	<i>IP</i> (π)	<i>IP</i> (σ (C-Hg))	<i>IP</i> (n (Cl,Br,O))
16	<chem>CH2=CHCH2HgCl</chem>	11.61 9.35 ^a	9.44 11.55 ^a	10.75 10.78 ^a
17	<chem>CH2=CHCH2HgBr</chem>	11.46	9.33	10.04; 10.36
18		8.62	10.50	10.61
19		8.65(π_1) 11.80(π_2)	9.75	10.77
20		8.71(b_1) 9.42(a_2) 8.65(b_1) ^b 9.33(a_2) ^b	10.75 10.73 ^b	10.64 10.73 ^b
21	<chem>CH3O-C6H4-CH2HgCl</chem>	8.37(b_1) 9.31(a_2)	10.71	10.71(n (Cl)) 11.11(n (O))
22		8.57(π_1) 9.06(π_2)	10.60	10.60
23		8.63(π_1) 9.13(π_2)	10.63	10.63
24	<chem>F-C6H4-CH2HgCl</chem>	8.74(b_1) 9.68(a_2)	10.68	10.68
25	<chem>CH2=CHHgBr</chem>	10.85	10.50	10.05; 10.25
26		9.19	9.87	10.68
27		9.40($b_1 + a_2$) 9.46 ^c	10.45 10.36 ^c	10.84 10.82 ^c
28		9.33($b_1 + a_2$) 8.77(b_1)	10.15 10.40	10.15; 10.47 10.81
29		9.44(a_2) 10.6(π (C=C))		
30		9.10	9.72	10.58

^a From ref. 37. ^b From ref. 38. ^c From ref. 44.

intensive bands whose position varies from 10.4 to 10.9 eV correspond to n (Cl) orbitals of all compounds investigated. Ionization of the n (Br) orbitals in corresponding compounds gives rise to two bands due to marked spin-orbital interac-

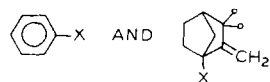
(Continued on p. 61)

TABLE 4
VERTICAL *IP* OF SOME ORGANIC COMPOUNDS (eV)

No.	Compound	<i>IP</i>	References
31	CH ₂ =CH ₂	10.51 (π)	22
32	CH ₂ =CHCH ₃	9.88 (π)	46
33		9.12 (π)	47
34		8.69 (π)	^a
35		8.56 (π_1); 10.72 (π_2)	48
36		9.24(e_{1g}); 11.49(e_{2g}); 12.30(a_{2u})	49
37		8.80(b_1); 9.15(a_2)	^b
38		8.37(b_1); 9.05(a_2)	50
39		8.50(a_2); 9.00(b_1)	50
40		8.45(b_1); 9.00(a_2)	50
41		8.39(b_1); 9.22(a_2); 11.06($n(O)$)	51
42		8.18(b_1); 9.11(a_2); 10.75($n(O)$)	52
43		8.50(b_1); 9.30(a_2); 10.55($\pi(C=C)$)	50
44		9.11(b_1); 9.82(a_2)	53
45		9.06(b_1); 9.69(a_2)	54
46		8.07(b_1); 9.17(a_2)	^c
47		9.93(a_2); 10.32(b_1)	51
48		9.50($b_1 + a_2$); 10.52($n(O)$)	^a
49		8.86(π)	^a
50	X = Cl	9.11(π); 10.23($n(Cl)$); 10.38($n(Cl)$)	
51	X = NH ₂	8.67($\pi-n(N)$); 9.05($\pi + n(N)$)	^a
52	X = COOH	9.05 (π)	^a
53	X = NO ₂	9.44 (π)	^a

^a This work. ^b Average *IP* values cited in ref. 41,51-53. ^c Average *IP* values cited in ref. 51-53.

TABLE 5

CONTRIBUTIONS OF THE INDUCTION EFFECT AND CONJUGATION TO $IP(\pi)$ (eV) OF COMPOUNDS

X

	$\Delta IP_{ind}(b_1, a_2)$	$\Delta IP_{conj}(b_1)$	$\Delta IP_X(\pi)$	$\Delta IP_{ind}(\pi)$	$\Delta IP_{conj}(\pi)$
Cl	-0.45	+0.63	-0.25	-0.40	+0.15
NH ₂	+0.07	+1.10	+0.19	0.00	+0.19
COOH	-0.26	0.00	-0.19	-0.19	0.00
NO ₂	-0.69	-0.39	-0.58	-0.48	-0.10
HgCl	-	-	-0.24	-0.24	0.00

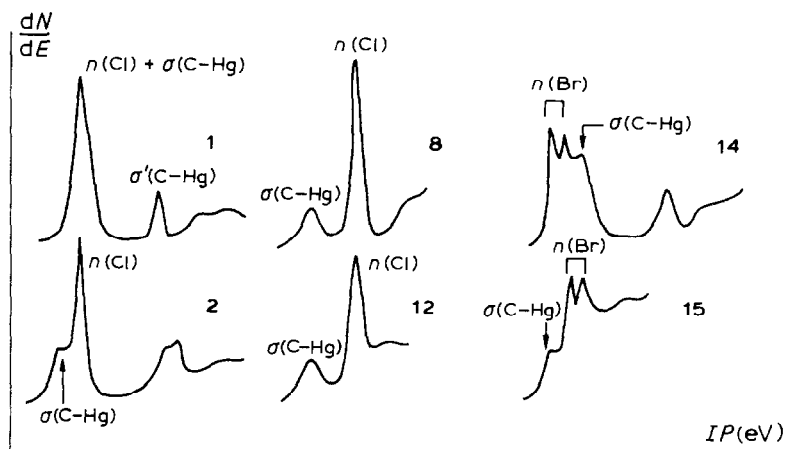
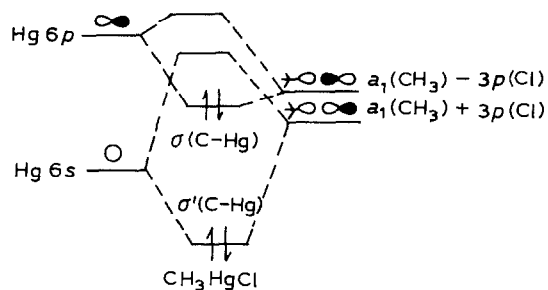


Fig. 1. PES of some alkylmercuric halides. Here and throughout the paper, the numbering of spectra corresponds to that of tabulated compounds.

Fig. 2. Formation of the CH_3HgCl molecular orbitals (schematic).

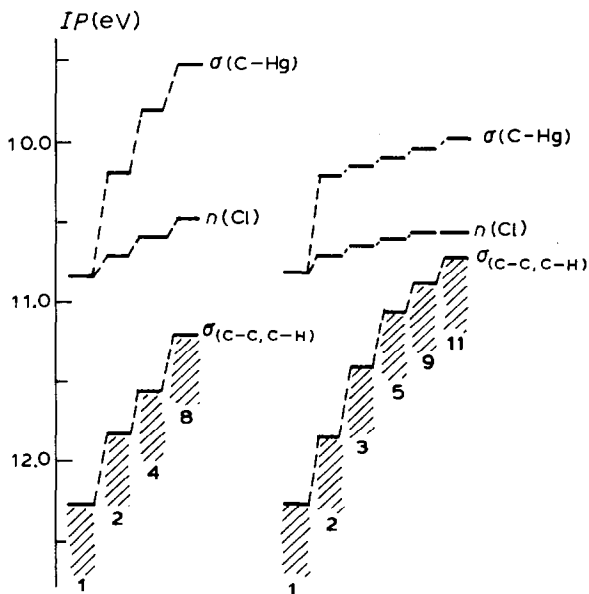


Fig. 3. *IP* correlation in a series of alkylmercuric chlorides, RHgCl : 1, 2, 3, 4, 5, 8, 9 and 11.

tions in the ions. The energy difference between them is 0.3 eV for all bromides investigated.

Increasing the length of the alkyl radical results in shifts of bands, associated with $\sigma(\text{C-C})$ and $\sigma(\text{C-H})$ orbital ionizations towards lower *IP* values, which, in the majority of cases, makes it difficult to determine the position of the $\sigma'(\text{C-Hg})$ orbital band. The *IP* threshold values of $\sigma(\text{C-C})$, $\sigma(\text{C-H})$ (Table 1) slightly differ from those of corresponding alkanes [20]. Figure 3 shows *IP* as a function of chain length and branching of the alkyl radical. Starting from C_2H_5 , increase in chain length affects poorly the *IP* of $\sigma(\text{C-Hg})$ and $n(\text{Cl})$, while introduction of a methyl group at the α -position of the alkyl radical leads to considerable decrease of the *IP*, especially the *IP* of $\sigma(\text{C-Hg})$.

It is reasonable to assume that $n(\text{Cl})$ orbitals are predominantly subject to the induction effect of alkyl groups, since they are not directly bonded to these groups, and their interaction with $\sigma(\text{C-C})$ and $\sigma(\text{C-H})$ via the $6p$ and $5d$ orbitals of mercury is insignificant due to high difference in their energies.

The energy of the $\sigma(\text{C-Hg})$ MO also is supposed to be affected by mixing with the $\sigma(\text{C-C})$ MO and $\sigma(\text{C-H})$ MO of neighbouring alkyl groups. Nevertheless, there is good linear correlation between the $n(\text{Cl})$ *IP* and $\sigma(\text{C-Hg})$ *IP* (Fig. 4). Additionally, it is noteworthy that satisfactory linear correlation of $n(\text{Cl})$ *IP* and $\sigma(\text{C-Hg})$ *IP* with Taft's constants exist (Fig. 5).

Excellent correlations have been observed between $\sigma(\text{C-Hg})$ *IP* in RHgCl and the *IP* of the same orbital in R_2Hg as well as between *IP*(π) in alkenes and *IP* of $n(\text{N})$ in alkylamines (Fig. 6). For the values of corresponding *IP*, required for the above correlations, see Table 2. It can be seen that the correlations mentioned above permit evaluation with good accuracy, the compounds *IP* for a given series on the basis of experimental evidence for other series. The changes in alkyl environments

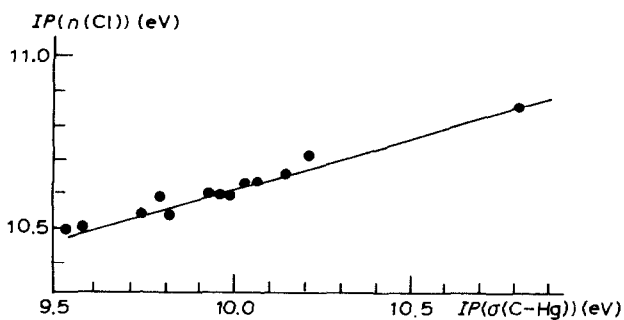


Fig. 4. Correlation between the first and second IP in a series of alkylmercuric chlorides.

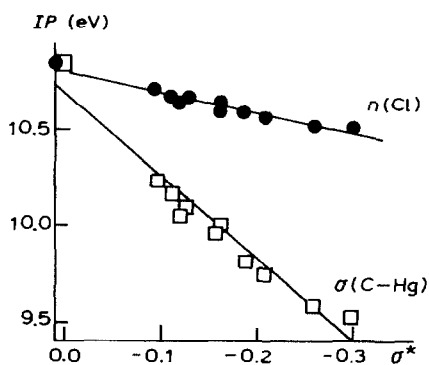


Fig. 5. Correlation between IP ($n(\text{Cl})$), IP ($\sigma(\text{C-Hg})$) and σ^* Taft's constants [21] in a series of alkylmercuric chlorides.

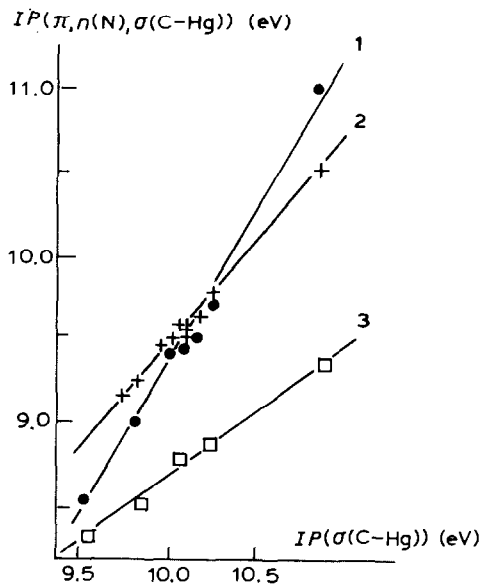


Fig. 6. Correlation between IP ($\sigma(\text{C-Hg})$) in RHgCl and IP ($n(\text{N})$) in alkylamines (1), IP (π) in alkenes (2), IP ($\sigma(\text{C-Hg})$) in RHgCH_3 (3); $r_1 = 0.995$; $r_2 = 0.998$; $r_3 = 0.997$.

differently affect the orbital energies of different types, which is reflected in the corresponding straight line slopes (Fig. 6) and is associated with the spatial orientation of the orbital, its energy, and the extent to which it has been localized on the atom involved. As can be seen from Fig. 6, the IP $\sigma(\text{C-Hg})$ in the RHgCl series vary somewhat more markedly with the radical than the IP of the same orbitals in the R_2Hg series. This can be partially or completely attributed to differences in energies of this orbital in the two types of compounds: IP $\sigma(\text{C-Hg})\text{CH}_3\text{HgCl}$ 10.84 eV, $(\text{CH}_3)_2\text{Hg}$ 9.33 eV. Thus, the delocalization extent of these MO in CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$ is approximately the same, for in the first compound the MO $\sigma(\text{C-Hg})$ contains almost equal contributions from the $a_1(\text{CH}_3)$ and $3p(\text{Cl})$ orbitals.

It is noteworthy that the energy of the MO $\sigma(\text{C-Hg})$ in alkylmercuric chlorides and that of the π -MO in alkenes are closely related. When changes occur in the alkyl environments, these orbitals also behave similarly.

Mercury compounds with unsaturated radicals

The mercury and other metal derivatives, containing the $\text{R}_n\text{M-C-C(X)}$ moiety, have various specific features in their chemical and spectral behavior. For instance, extreme kinetic lability of the carbon-to-metal bond [23]; ability for rapid intramolecular rearrangement [24]; ability to react with transfer of the reaction center to the unsaturated system [3,25,26]; significant decrease in frequencies of electron transitions in the charge-transfer complexes [27]; pronounced long-wave shift of the transfer band maximum in the electron absorption spectra [28]; considerable increase in the intensity of multiple-bond lines in the Raman spectra [29]; changes in the NMR parameters [29–31] and the mass spectra of negative ions, and polarography [29].

All the described anomalies are characterized by their pronounced dependence on mutual spatial orientations of the metal-to-carbon bonds and the π -electron systems [27,29]. Therefore, to explain the properties inherent to the behavior of such compounds, chemists have, for some time, been using the concept of σ, π -conjugation [5,8,26].

The behavioral features reflect the properties of the electronic structures of these molecules [23,32–34], which in turn, are related to the prevailing conformations (Fig. 7 and 8), facilitating the interaction of $\sigma(\text{C-M})$ and π orbitals, and to close energy values of the original orbitals, $\sigma(\text{C-M})$ and π .

In accordance with the MO perturbation theory [35], σ and π molecular orbitals, interact to form two novel orbitals, ψ'_π and ψ'_σ , which can be presented as a linear combination of the original molecular orbitals and whose energy differs from that of

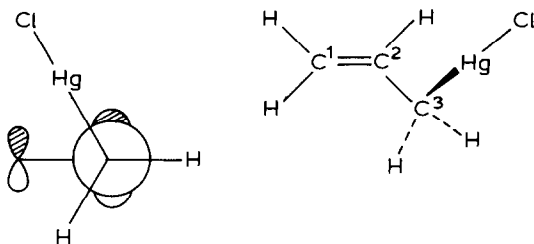


Fig. 7. Conformation of a molecule of allylmercuric chloride.

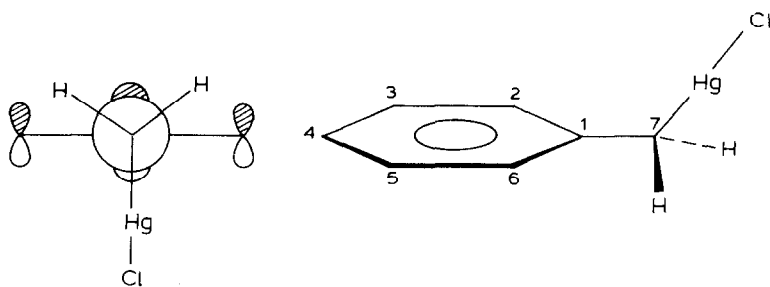


Fig. 8. Conformation of a molecule of benzylmercuric chloride.

the original orbitals. Changes in the energy of the original orbitals in CNDO approximation are as shown in eq. 1:

$$\delta E(\sigma) = -\delta E(\pi) = \pm \left\{ \left[4P^2(\pi, \sigma) + \Delta E^2(\pi, \sigma) \right]^{1/2} - \Delta E(\pi, \sigma) \right\} / 2 \quad (1)$$

where $\Delta E(\pi, \sigma) = E(\pi) - E(\sigma)$ is the difference in energies of the unperturbed orbitals, which can be estimated from the *IP* of appropriate model compounds on the basis of Koopmans' theorem, whereas a matrix element, $P(\pi, \sigma) = \int \psi(\pi) P \psi(\sigma) d\tau$, characterizing perturbation, can be expressed in terms of the coefficients of atomic orbitals (AO). If ΔE is large compared to P , then

$$\delta E = \pm a^2(\pi) a^2(\sigma) P^2 / \Delta E(\pi, \sigma) \quad (2)$$

The value a^2 corresponds to the electron density on the interacting atomic orbitals of neighboring atoms of the π and σ systems. Since the value of perturbation is inversely proportional to $\Delta E(\pi, \sigma)$, only interaction between HOMO and LUMO is usually taken into account.

Photoelectron evidence currently available corroborates the essential contribution of the $\sigma(\text{C-M})$, π -conjugation to variations in the energies of HOMO in the series of the allyl, benzyl and other derivatives of the Group IVA elements [36-42].

In addition, the induction effect, the interaction between the π -system and the $\sigma(\text{C-H})$ orbitals of the methylene group, and, in the case of mercury compounds, involvement in the binding of $6p$ and $5d$ orbitals should be taken into account.

In the course of our research several works concerning the study of mercury derivatives with unsaturated radicals appeared, involving allylmercuric chloride [37] and benzylmercuric chloride [38] by means of PES [37,38,43,44]. A significant interaction of the occupied π and $\sigma(\text{C-Hg})$ levels in the molecules of these compounds was found. Furlani et al. [44] also demonstrated that the $5d$ orbitals of mercury markedly interact with the adjacent π -system of an acetylene radical, while in the case of phenyl derivatives, this effect is insignificant.

Previously we discussed the PES of some allyl-type mercury compounds [12,45]. In this article, we make an attempt, using previous and newly obtained data and the concepts and conclusions of the MO perturbation theory, to define quantitatively the comparative role of various effects caused by the proximity of the HgCl group and the π -system, viz. the $\sigma(\text{C-Hg})$, π -conjugation effect, the induction effect of the HgCl group on the π -MO, the extent to which the π -MO interacts with the orbitals localized on mercury in the different types of compounds.

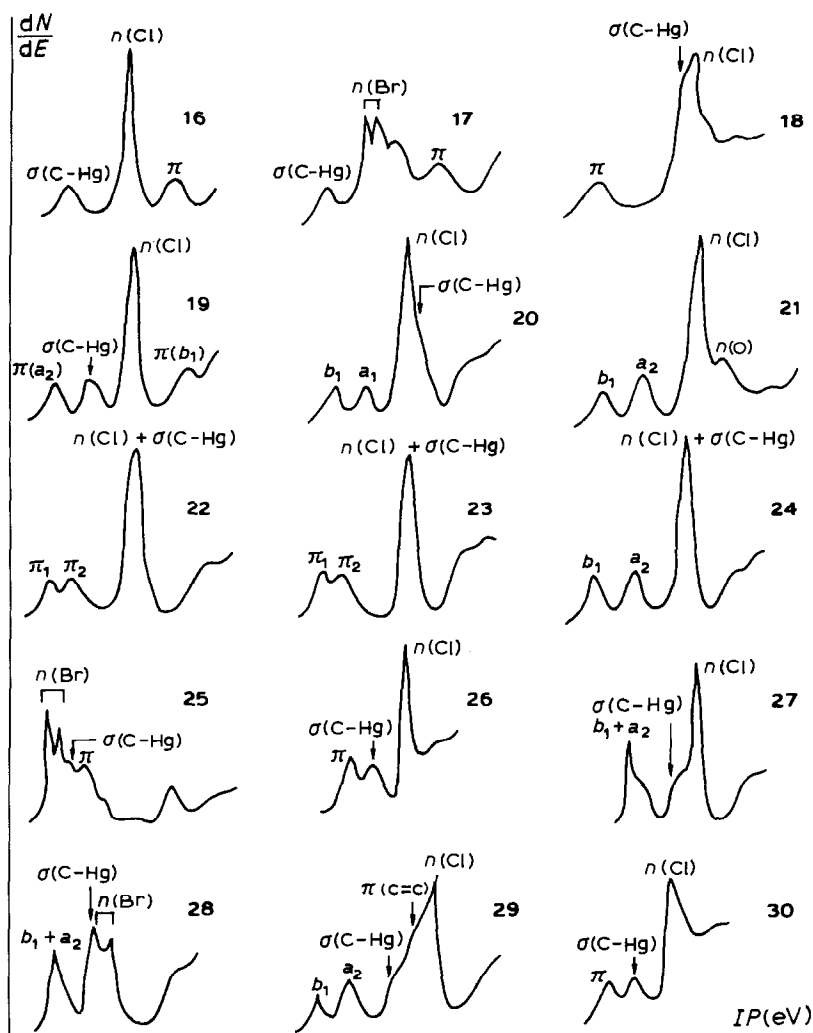


Fig. 9. PES of mercury compounds with unsaturated radicals.

The geometry of compounds 16–24 (Table 3) permits the $\sigma(\text{C-Hg}), \pi$ interaction; in compounds 25–29, the σ -carbon-to-mercury bond lies in the nodal plane of π -orbitals, and for this reason, no $\sigma(\text{C-Hg}), \pi$ interaction should occur. Yet, interaction with the orbitals localized on a substituent, HgCl , is not ruled out. Compound 30 should also be ascribed to the second group, for its geometry [55] precludes $\sigma(\text{C-Hg}), \pi$ -conjugation.

It is clear from the foregoing section that the $\sigma(\text{C-Hg}), n(\text{Cl}), n(\text{Br})$ orbitals, are the highest occupied MO but in unsaturated and aromatic hydrocarbons, the π -type orbitals are HOMO. Consequently, the bands in the low IP value region in the spectra of compounds 16–30 (Fig. 9) should be attributed to ionization of $\pi, \sigma(\text{C-Hg}),$ and $n(\text{Cl}, \text{Br})$ orbitals particularly. The narrow bands of $n(\text{Cl}, \text{Br})$ occur in the same spectral region as those of alkylmercuric halides.

The assigned values of $\sigma(\text{C-Hg})$ and π in Fig. 9 and Table 3 indicate the prevailing contribution of these orbitals to the resulting (mixed) MO. Similarly, in the case of benzyl compounds, the symbols b_1 and a_2 are preserved for the π -orbitals localized primarily on the ring, for the local symmetry of this moiety is retained.

Induction effects of the HgCl and CH₂HgCl groups

To estimate from PES data the induction effects produced by the groups we used the appropriate derivatives of benzene and camphene. Normally, introduction of a substituent into a benzene molecule splits its upper filled e_{1g} orbital, into two orbitals, b_1 and a_2 . The a_2 orbital, having a node at the substitution site, cannot interact with the orbitals localized on the substituent and is subjected only to its induction effect.

Both the induction effect of the substituent and interaction with its orbitals (vacant and filled) of suitable symmetry are responsible for the b_1 orbital energy.

Comparison of the *IP* of the a_2 orbitals of benzylmercuric chloride [20] (9.42 eV) and toluene (9.16 eV), on the one hand, with those of *p*-methoxybenzylmercuric chloride (**21**) (9.31 eV) and *p*-methylanisole (9.11 eV), on the other, indicates that substitution of HgCl in the methyl group for hydrogen leads to stabilization of the a_2 orbital at 0.26 and 0.2 eV, respectively, thus HgCl causes remarkable negative induction effect. Comparison of the *IP* of a_2 orbitals of compounds **20** and **21** with those for benzene and anisole (Table 4) shows that CH₂HgCl group in total is a poorly inductive electron acceptor (ΔIP_{a_2} 0.17 and 0.07 eV).

The X-ray data for 1-chloromercuric camphene (**30**) [55] suggest that in this compound $\sigma(\text{C-Hg})$ and π orbitals are almost orthogonal. Therefore, the effect of σ, π -conjugation on the energies of these orbitals should be negligible. Then the difference in the *IP* (π -MO) of compound **30** and camphene (**49**) (0.24 eV) can serve as a measure of the induction effect of the HgCl group. This is close to the stabilization values of the a_2 orbital of benzylmercuric chloride with respect to toluene. The second band in spectrum **30** (*IP* 9.72 eV) is related to ionization of the $\sigma(\text{C-Hg})$ orbital.

We have somewhat extended the range of benzene and camphene derivatives to compare the induction effect produced by the HgCl group with a similar effect exerted by other substituents and to assess the potentials of each model system in separating the electron effect contributions as well as the validity of choosing camphene as a system that rules out the σ, π -conjugation effect. The benzene derivatives are not always convenient models for determination of the substituent effects: in the case of weak perturbation of $b_1(\pi)$, b_1 and a_2 bands essentially overlap (see e.g. the toluene spectrum [41,51–53]).

In Table 4 and Fig. 10 are listed the results from 1-substituted camphene studies (**49–53**). The effect of substituent X on the energy of the π -MO in these compounds can be represented by the equations:

$$\Delta IP_X(\pi) = \Delta IP_{\text{ind}}(\pi) + \sqrt{\Delta} IP_{\text{conj}}(\pi)$$

$$\Delta IP_X(\pi) = IP_{\text{H}}(\pi) - IP_X(\pi)$$

where X = Cl, NH₂, NO₂, COOH.

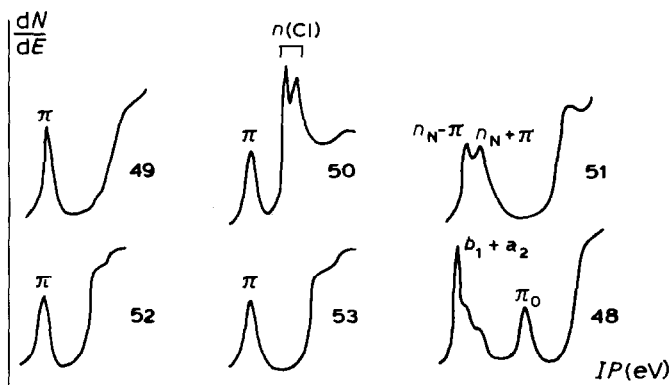


Fig. 10. PES of camphene, its derivatives, and benzoic acid.

The $\Delta IP_X(\pi)$, $\Delta IP_{ind}(\pi)$ and $\Delta IP_{conj}(\pi)$ values have been found from the photoelectron spectra of these compounds and of corresponding phenyl derivatives 45–48 (for a detailed discussion of these data see ref. 45) and are summarized in Table 5. It is easily seen that the inductive effects in these two series of compounds differ only slightly, while the camphene derivatives exhibit significantly weaker interaction between the π -MO's and X orbitals.

The $\Delta IP_{ind}(\pi)$ values for compounds 30 and 51–53 exhibit good linear correlation with the inductive constants derived by Taft's method (Fig. 11). The value of $\sigma(I) = 0.31$ has been used for the HgCl group [56]. In summary, according to the extent of inductive effects on the π -MO, the group HgCl is placed between the electron acceptors Cl and COOH. The evidence obtained using the camphene system is consistent with the conclusions made by Kravtsov et al. [56] about a large inductive effect of the HgCl group, while conjugation of mercury with an aromatic ring is weak, and is not consistent with the assumption of a zero induction effect of this group [37,38].

Interaction of 6p and 5d-atomic orbitals of mercury with the π -orbitals of an organic system

To gain some insight into these interaction types, we have studied a series of

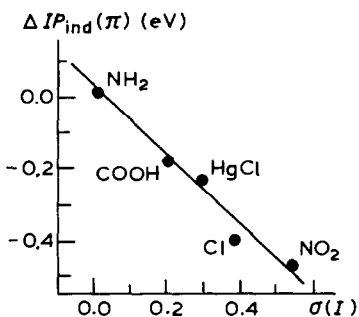


Fig. 11. Correlation of $\Delta IP_{ind}(\pi)$ with the induction constants, $\sigma(I)$ in a series of camphene derivatives.

compounds (**25–29**, Table 3), where mercury is directly bonded to an sp^2 -carbon system. The $\sigma(\text{C-Hg}),\pi$ -conjugation effect is obviously missing and, for this reason, the π -MO energy should be dependent primarily influenced by the following two factors: the induction effect of the HgX group and interaction with orbitals localized on this group (vacant $6p$, occupied $5d$, and $n(\text{Cl})$). The foregoing has shown that the character of the induction effect of HgX should result in a pronounced (0.2–0.3 eV) stabilization of an adjacent π -system. A similar effect can be expected from the interaction of the MO with a $6p_\pi$ -atomic orbital of mercury, whereas interaction with occupied orbitals, $5d$ and $n(\text{Cl})$, must destabilize the π -MO.

The spectrum of $\text{C}_6\text{H}_9\text{HgCl}$ (**26**) was the easiest to analyse. To assign the bands observed in the low IP region, we compared the spectrum of **26** with that of cyclohexane, and with that cyclo- $\text{C}_6\text{H}_{11}\text{HgCl}$, taking into account the greater electronegativity of the radical C_6H_9 than that of C_6H_{11} . In this way, the first band (IP 9.19 eV) was attributed to ionization of the $\sigma(\text{C-Hg})$ MO. Consequently, the stabilizing effect produced by the HgCl group on the π -MO in molecule **26** amounts merely to 0.07 eV. Such a low effect can be due to the effect of the opposite sign, that is, interaction with occupied orbitals. It can be seen, however, that the latter is not pronounced either, which appears to be due to the π and $5d$ orbital energies varying widely (~ 6 eV). Interaction with the $n(\text{Cl})$ and $6p_\pi$ orbitals neither seems to be pronounced, although these contributions could not be separated. Therefore, the effects involved can be ignored.

It is clear from Tables 3 and 4 that $IP(b_1 + a_2)$ of phenylmercuric chloride and bromide are close to $IP e_{1g}$ of benzene, which indicates that the π -orbitals of the ring interact weakly with the vacant and occupied orbitals of the HgX group.

The results for vinylmercuric bromide (**25**) also corroborate the conclusion on the nature of interactions between the π -system and the HgX group. A decrease of 0.34 eV in the $IP(\pi)$ with regard to ethylene is due to the stabilizing induction effect produced by HgBr and some interaction with higher $n(\text{Br})$ orbitals.

For a detailed discussion of this evidence, see ref. 13.

$\sigma(\text{C-Hg}),\pi$ -conjugation effect

To reveal the σ,π -conjugation effect, we have investigated compounds **16–24** (Table 3). While characterizing their electronic structure we refer to the data described above for simpler compounds and the principal equations in MO perturbation theory [33,35].

When the CH_2HgCl group and the π -system of allylmercuric chloride (**16**) are oriented as in Fig. 7, an interaction between the molecular orbitals π and $\sigma(\text{C-Hg})$ can occur, whose extent will be characterized by the $\delta E(\pi,\sigma(\text{C-Hg}))$ value. To determine this value, knowledge of the unperturbed orbital energies, π and $\sigma(\text{C-Hg})$, is required. The energy of the “unperturbed” π -molecular orbital in **16** (10.69 eV) was found from the $IP(\pi)$ of ethylene (10.51 eV) and from the induction effect produced by the CH_2HgCl group: $IP(a_2)$ (benzylmercuric chloride) – $IP(e_{1g})$ (benzene) = 0.18 eV. The IP value of the “unperturbed” $\sigma(\text{C-Hg})$ orbital was estimated from the relationship, found earlier, between $IP(n(\text{Cl}))$ and $IP(\sigma(\text{C-Hg}))$ in the alkylmercuric chloride series, assuming that this relationship also holds for more complicated compounds with no σ,π -conjugation. The $IP(\sigma(\text{C-Hg}))$ value for **16**, found in this manner, is 10.65 eV. Corresponding values for compounds **17–20** are given in Table 6. Thus, the energies of the original orbitals, π and $\sigma(\text{C-Hg})$, are

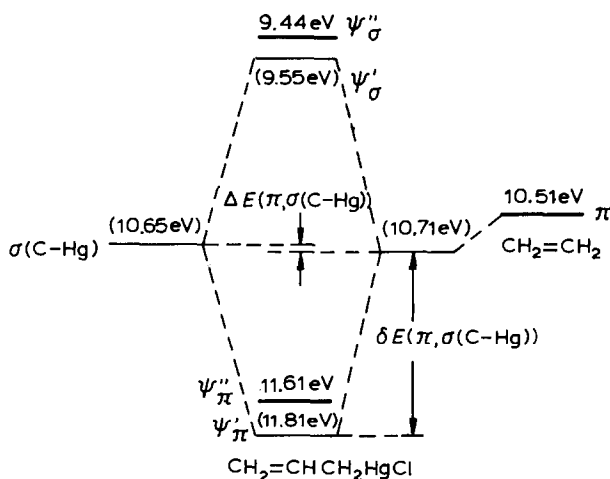


Fig. 12. Interaction of π , $\sigma(\text{C-Hg})$, and $\sigma(\text{C-H})$ orbitals in a molecule of allylmercuric chloride (schematic).

very closely related and hence their contributions to wave functions, ψ'_{π} and ψ'_{σ} , are roughly identical.

The interaction of the π -system with the $\sigma(\text{C-H})$ -orbitals of the methylene group should also be considered. Ethylene and propylene represent model compounds for this purpose. The induction effect of the CH_3 group, 0.1 eV ($IP(a_2)$ (toluene) – $IP(\epsilon_{1g})$ (benzene)). Therefore, a rise in the $IP(\pi)$ of propylene regarding ethylene equaling 0.63 eV is primarily due to interaction of the π -MO with two $\sigma(\text{C-H})$ orbitals (one of the three C-H bonds in the methyl group is located at the nodal plane of the π -system). Then $\delta E(\pi, \sigma(\text{C-H})) = (0.63 - 0.1)/2 = 0.27$ eV. With this in mind we estimated $P(\pi, \sigma(\text{C-H}))$, a matrix element characterizing the $\sigma(\text{C-H})$, π interaction effect, and used it in subsequent calculations. Negative $IP(\pi)$ in ethylene and negative $IP(\sigma(\text{C-H}))$ in methane equaling 14.1 eV [33] were taken as the energies of unperturbed levels, π and $\sigma(\text{C-H})$. Since in molecule **16** both ψ'_{π} and ψ'_{σ} contain considerable contributions from the π -MO, each of them is perturbed by the $\sigma(\text{C-H})$ orbitals of the methylene group. It may be assumed that this is proportional to the squares of coefficients, $a_{\pi\pi}$ and $a_{\pi\sigma}$, with which the π -MO enters these orbitals.

Figure 12 illustrates interaction involving π , $\sigma(\text{C-Hg})$, and $\sigma(\text{C-H})$ levels. The ψ'_{π} and ψ'_{σ} orbitals perturbed by interaction with $\sigma(\text{C-H})$ are designated ψ''_{π} and ψ''_{σ} , with a first and a third band corresponding to them in the spectrum of **16** (Fig. 9).

Thus, eq. 1 enables us to evaluate the extent to which $\sigma(\text{C-H})$ affects the energies ψ'_{π} and ψ'_{σ} , using the calculated value of $P(\pi, \sigma(\text{C-H}))$, the energy of $\sigma(\text{C-H}) = -14.1$ eV, and taking as first approximation, the experimental negative values of the $IP(\psi''_{\pi})$ and $IP(\psi''_{\sigma})$ as the energy of ψ'_{π} and ψ'_{σ} , it was assumed that only one of two $\sigma(\text{C-H})$ MO interacts with ψ'_{π} and ψ'_{σ} (the second C-H bond is in the π -MO nodal plane).

The value of the parameter $P(\pi, \sigma(\text{C-H}))$ has been found from eq. 1 using the $E(\pi)$ and $E(\sigma)$ determined above and considering $\delta E(\pi, \sigma(\text{C-Hg}))$ to equal the

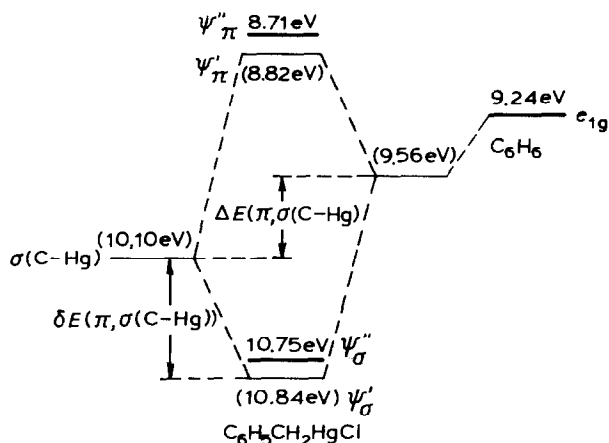


Fig. 13. Interaction of π , $\sigma(\text{C-Hg})$, and $\sigma(\text{C-H})$ orbitals in a molecule of benzylmercuric chloride (schematic).

average value between $IP(\psi''_{\pi}) - IP(\pi)$ and $IP(\sigma(\text{C-H})) - IP(\psi'_{\sigma})$. The coefficients $a_{\pi\pi}$ and $a_{\pi\sigma}$ were calculated by means of known equations of perturbation theory [33]. Thus, determination of $\delta E(\psi'_{\pi}, \sigma(\text{C-H}))$ and $\delta E(\psi'_{\sigma}, \sigma(\text{C-H}))$ allowed us to evaluate the position of the ψ'_{π} (IP 11.81 eV) and ψ'_{σ} (IP 9.55 eV) levels. Bracketed figures in Fig. 12 and 13 correspond to the IP calculated by one of the methods described above. The difference, $IP(\sigma(\text{C-Hg})) - IP(\psi'_{\sigma})$ yields an absolute value $\delta E(\pi, \sigma(\text{C-Hg}))$. Subtracting the latter from $IP(\psi'_{\sigma})$ gives the IP of the unperturbed π -MO (10.71 eV), which is very close to 10.69 eV found from $IP(\pi)$ of ethylene and the induction effect of the CH_2HgCl group. This corroborates to the fact that the theoretical approach employed agrees well with the experiment.

The IP values obtained (Fig. 12) have made it possible to calculate, as a second approximation, the value of the parameter $P(\pi, \sigma(\text{C-Hg}))$ and the values of the $a_{\pi\pi}$ and $a_{\pi\sigma}$ coefficients (see Table 6).

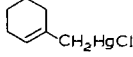
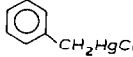
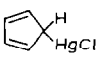
Analysis of the parameters shows that in a allylmercuric chloride molecule, interaction involving $\sigma(\text{C-Hg})$ and π is fairly pronounced. It results in mixing the original orbitals and formation of new MO whose energies differ more than 1 eV from those of the unperturbed π and $\sigma(\text{C-Hg})$ orbitals. The effects of the $\sigma(\text{C-H})$ orbitals on the HOMO are much less essential due to greater energy difference in $\sigma(\text{C-H})$, π and $\sigma(\text{C-Hg})$ molecular orbitals.

The photoelectron spectra and electronic structure of compounds **17**, **18** and **20** (Table 3) have been treated in a similar way. Table 6 lists the parameters characterizing the interaction of the π , $\sigma(\text{C-Hg})$, and $\sigma(\text{C-H})$ levels. Figure 13 illustrates how these levels interact in benzylmercuric chloride.

The IP value of the unperturbed orbital, $\sigma(\text{C-Hg})$, for allylmercuric bromide (10.45 eV) was derived from the IP value unperturbed ($\sigma(\text{C-Hg})$) for compound **16** by subtracting 0.2 eV. Eland [16] reported that the IP of this orbital increased by the above value proceeding from CH_3HgCl to CH_3HgBr . As mentioned above, changes in the structure and volume of the alkyl radical equally affect $IP(\sigma(\text{C-Hg}))$ in a series of alkylmercuric chlorides and bromides.

TABLE 6

PARAMETERS CHARACTERIZING INTERACTION OF ORBITALS π , $\sigma(\text{C-Hg})$, AND $\sigma(\text{C-H})$ IN MOLECULES OF COMPOUNDS 16-20 (eV, except for a^2)

Parameter	$\text{H}_2\text{C}=\text{CHCH}_2\text{HgCl}$	$\text{H}_2\text{C}=\text{CHCH}_2\text{HgBr}$			
$IP(\sigma(\text{C-Hg}))$	10.65	10.45	10.01	10.10	10.60
$IP(\pi)$	10.71	10.64	9.29	9.56	10.95
$\Delta E(\pi, \sigma(\text{C-Hg}))$	0.06	0.19	0.72	0.54	0.35
$\delta E(\pi, \sigma(\text{C-Hg}))$	1.10	1.02	0.56	0.74	0.85
$P(\pi, \sigma(\text{C-Hg}))$	1.13	1.11	0.85	0.97	1.01
$a^2\pi\pi$	0.51	0.54	0.70	0.63	0.59
$a^2\pi\sigma$	0.49	0.46	0.30	0.37	0.41
$P(\pi, \sigma(\text{C-H}))$	1.02	1.02	0.94	0.95	-
$\delta E(\psi'_\pi, \sigma(\text{C-H}))$	0.20	0.20	0.11	0.11	-
$\Delta E(\psi'_\pi, \sigma(\text{C-H}))$	2.30	2.49	5.37	5.28	-
$\delta E(\psi'_\sigma, \sigma(\text{C-H}))$	0.11	0.10	0.07	0.09	-
$\Delta E(\psi'_\sigma, \sigma(\text{C-H}))$	4.55	4.64	3.53	3.26	-

The $IP(\psi'_\sigma)$ values for compounds **18** and **20** have been established roughly because of pronounced overlapping with $n(\text{Cl})$ orbital bands. For these two compounds the difference $\Delta E(\pi, \sigma(\text{C-Hg}))$ is markedly greater than the corresponding values for **16** and **17** (Table 6). As a result, the absolute value $\delta E(\pi, \sigma(\text{C-Hg}))$ drops, i.e. the effect of the $\sigma(\text{C-Hg})$, π -interaction weakens, and the contributions of $\sigma(\text{C-Hg})$ to ψ'_π and of π to ψ'_σ decrease. The parameters $P(\pi, \sigma(\text{C-Hg}))$, $\delta E(\psi'_\pi, \sigma(\text{C-H}))$, and $\delta E(\psi'_\sigma, \sigma(\text{C-H}))$ for these compounds were determined analogously using $IP(\pi)$ of cyclohexane, methylcyclohexane, benzene, and toluene. It should be noted that the approach described does not allow for the interaction effects with vacant orbitals π^* and $\sigma^*(\text{C-Hg})$. Yet, good agreement observed between the theoretical model and the experiment indicates that the effects in question are negligible, which seems to be due to greater energy differences between occupied and vacant orbitals.

As can be seen from Table 6, the parameter value $P(\pi, \sigma(\text{C-Hg}))$ varies in the series of compounds studied. Different orientations of the C-Hg bond and the π system may be one, but not the only, reason [50,57]:

$$P = P_0 \cos \alpha \quad (3)$$

where α is the deviation of the C-Hg bond from the optimum position (90° to the plane of the π -system) and P_0 corresponds to the maximum σ, π interaction. Structural data for the compounds investigated are, unfortunately, lacking. A closely-related analog of benzylmercuric chloride, $\text{PhCH}_2\text{HgSCPh}_3$, has a dihedral angle of 90° between the planes of the phenyl ring and $\text{C}(1)\text{C}(7)\text{Hg}$ [58]. It may be assumed that the benzylmercuric chloride molecule has a similar structure. Since the $P(\pi, \sigma(\text{C-Hg}))$ value is proportional to the coefficient of the term for the $2p$ -AO of the carbon bonded to the CH_2HgX group contributing to the π -orbital ($1/\sqrt{2}$ in ethylene and $1/\sqrt{3}$ in benzene), the $P(\pi, \sigma(\text{C-Hg}))$ value for benzylmercuric chloride is multiplied by the ratio $1/\sqrt{2} : 1/\sqrt{3}$ and the value obtained 1.19 eV is assumed to be P_0 . Thus, eq. 3 enables the evaluation of angles α for other

compounds analyzed. These angles are 18.21 and 24° for compounds **16**, **17** and **18** respectively.

Since the HgCl group tends to intramolecular rearrangement, the study of the electronic structure of cyclopentadienylmercuric chloride (**19**) is of special interest. In the cyclopentadienyl derivatives of Si, Ge, Sn, Hg a mercury compound is characterized by high migration rate and small changes in the reaction free energy [24,59]. We attribute the first band in the spectrum of **19** to ionization of the a_2 orbital, for its IP differs only slightly from $IP(a_2)$ for an unsubstituted cyclopentadiene (**35**). The IP value of the unperturbed $\sigma(\text{C-Hg})$ molecular orbital of **19**, estimated from correlation between $IP(n(\text{Cl}))$ and $IP(\sigma(\text{C-Hg}))$, equals 10.60 eV. Therefore, the second and fourth bands in the spectrum are related to ionization of the orbitals ψ'_σ and ψ'_π . The original orbitals b_1 and $\sigma(\text{C-Hg})$ exhibit pronounced interaction, parameters have been obtained in the same way as for compounds **16–18** and **20** and are given in Table 6. The effects of $\sigma(\text{C-Hg})$ π -conjugation in **19** and **16** are similar.

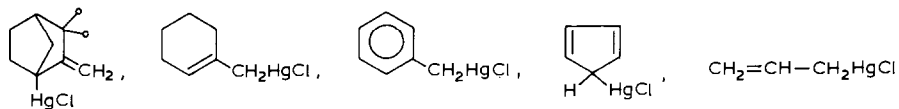
A qualitative correlation of $\sigma(\text{C-M})$, π -interaction and the migration rate of the element-containing group follows from a comparison between $\delta E(\pi, \sigma)$ for **19** and $\text{R}_3\text{SiC}_5\text{H}_5$, $\text{R}_3\text{GeC}_5\text{H}_5$ [60].

We have investigated some benzylmercuric chlorides containing ring substituents (**21–24**). A $b_1(\pi)$ molecular orbital in compounds **21** and **24** is further destabilized as a result of interaction with $n(\text{O})$ and $n(\text{F})$. For the above compounds, the difference $IP(a_2) - IP(b_1)$ is greater than for benzylmercuric chloride. On the other hand, $IP(n(\text{O}))$ for compound **21** is markedly higher than for *p*-methylanisole, which appears to be due to interaction between the molecular orbitals, $n(\text{O})$ and $\sigma(\text{C-Hg})$, as well as to the negative induction effect produced by the HgCl group. Introduction of the CH_2HgCl group into the *p*-position of a molecule of fluorobenzene decreases $IP(a_2)$, which is evidently associated with the extremely high electronegativity of fluorine.

Steric perturbations occurring in a molecule of substituted benzylmercuric chloride have been studied for compounds **22** and **23**. In the absence of such an effect, the energy difference between $b_1(\pi)$ and $a_2(\pi)$ molecular orbitals for the *o*- and *m*-substituted compounds should be roughly equal [52]. This is deduced from an analysis of the spectra of compounds **22** and **23**: $IP(b_1) - IP(a_2)$ and $IP(\sigma(\text{C-Hg}))$ almost fully coincide for these two isomers. Thus, introduction of a methyl group into the *o*-position of benzylmercuric chloride does not affect the spatial arrangement of the b_1 and $\sigma(\text{C-Hg})$ orbitals. This conclusion is in agreement with the NMR data for a series of methyl derivatives of benzylmercuric chloride [61].

In summary, it is important to note the relationship between the $\sigma(\text{C-Hg})$, π -conjugation effects in compounds **16–20** and their chemical behavior. Stabilization of an intermediate during electrophilic substitution in an aromatic ring is affected by mixing the vacant π -molecular orbital and $\sigma(\text{C-H})$ as well as by transferring electron density onto the π -orbital. It may be assumed that the process under discussion is governed by the same factors that are responsible for the $\sigma(\text{C-M})$, π -interaction occurring in the ground state of a molecule. Indeed, Traylor and co-workers demonstrated [27] that the ability of organometallic groups to stabilize a cation center and facilitate electrophilic substitution in an aromatic ring is linearly dependent on perturbation of the highest occupied π -molecular orbital as a result of its interaction with the $\sigma(\text{C-M})$ orbital.

PES data suggest, therefore, the stability of the C–Hg bond with respect to acids should decrease in the series:



References

- 1 L.G. Makarova and A.N. Nesmeyanov, *Metody elementoorganicheskoi khimii. Rtut.* (The methods of organoelemental chemistry. Mercury), Nauka, Moscow, 1965 (in Russian).
- 2 O.A. Reutov, I.P. Beletskaya and V.I. Sokolov, *Mekhanizmy reaktsii metalloorganicheskikh soedinenii* (The reaction mechanisms of organometallic compounds), Khimiya, Moscow, 1972 (in Russian).
- 3 I.F. Lutsenko, *Pure and Appl. Chem.*, 30 (1972) 409.
- 4 Yu.A. Ol'dekop and N.A. Mayer, *Sintez metalloorganicheskikh soedinenii dekarboksilirovaniem atsilatov metallov* (Synthesis of organometallic compounds by decarboxylation of metal acylates), Nauka i tekhnika, Minsk, 1976 (in Russian).
- 5 A.N. Nesmeyanov, *Uchyonye zapiski MGU*, No. 132 (1950) 5.
- 6 A.N. Nesmeyanov, *J. Organomet. Chem.*, 100 (1975) 161.
- 7 M.Y.S. Dewar, *Hyperconjugation*, Ronald Press, New York, 1962.
- 8 T.G. Traylor, H.J. Berwin, J. Jerkunica and M.L. Hall, *Pure and Appl. Chem.*, 30 (1972) 599.
- 9 J.W. Baker and W.S. Natan, *J. Chem. Soc.*, (1935) 1844.
- 10 J.W. Baker, W.S. Natan and C.W. Shoppe, *J. Chem. Soc.*, (1935) 1847.
- 11 A.N. Nesmeyanov, V.A. Blinova, I.V. Shirina-Eingorn and I.I. Kritskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1977) 2345.
- 12 A.N. Nesmeyanov, V.N. Baidin, M.M. Timoshenko, Yu.V. Chizhov, Yu.S. Nekrasov and I.I. Kritskaya, *Dokl. Akad. Nauk SSSR*, 251 (1980) 1172.
- 13 V.N. Baidin, Yu.V. Chizhov, M.M. Timoshenko, Yu.A. Ustynyuk and I.I. Kritskaya, *Izv. Akad. Nauk SSSR*, (1981) 2831.
- 14 V.N. Baidin, M.M. Timoshenko, Yu.V. Chizhov, Yu.K. Grishin, O.K. Sokolova and Yu.A. Ustynyuk, *Zh. strukt. khim.*, 22 (1981) 164.
- 15 V.N. Baidin, I.I. Kritskaya, M.M. Timoshenko, Yu.A. Ustynyuk and Yu.V. Chizhov, *Uspekhi Fotoniki*, No. 8 (1983) 8.
- 16 J.H.D. Eland, *Int. J. Mass Spectrom. Ion. Phys.*, 4 (1970) 37.
- 17 T.P. Fehlner, J. Ulman, W.A. Nugent and J.K. Kochi, *Inorg. Chem.*, 15 (1976) 2544.
- 18 L.L. Coatsworth, G.M. Bancroft, D.C. Creber, R.J.D. Lazier and P.W.M. Jacobs, *J. Electron. Spectrosc.*, 13 (1978) 395.
- 19 D.C. Creber and G.M. Bancroft, *Inorg. Chem.*, 19 (1980) 643.
- 20 V.I. Vovna and F.I. Vilesov, *Uspekhi Fotoniki*, No. 5 (1975) 3.
- 21 Yu.A. Zhdanov and V.I. Minkin, *Korrelyatsionnii Analiz v Organicheskoi Khimii* (Correlation analysis in organic chemistry), Publ. Rostov University, 1966, p. 470 (in Russian).
- 22 P. Masclet, D. Grosjean, G. Mouvier and J. Dubois, *J. Electron Spectrosc.*, 2 (1973) 225.
- 23 R.D. Bach and P.A. Scherr, *J. Am. Chem. Soc.*, 94 (1972) 220.
- 24 P. West, M.C. Woodville and M.D. Rausch, *J. Am. Chem. Soc.*, 91 (1969) 5649.
- 25 Yu.G. Bundel', N.D. Antonova and O.A. Reutov, *Dokl. Akad. Nauk SSSR*, 166 (1965) 1103.
- 26 A.N. Nesmeyanov and I.F. Lutsenko, *Dokl. Akad. Nauk SSSR*, 59 (1948) 707.
- 27 W. Hanstein, H.J. Berwin and T.G. Traylor, *J. Am. Chem. Soc.*, 92 (1970) 829.
- 28 V.A. Petukhov, V.F. Mironov and P.P. Shorygin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1964) 2203.
- 29 A.N. Nesmeyanov, V.T. Aleksanyan, L.I. Denisovich, Yu.S. Nekrasov, E.I. Fedin, V.I. Khvostenko and I.I. Kritskaya, *J. Organomet. Chem.*, 172 (1979) 133.
- 30 W. Kitching and G.M. Drew, *J. Org. Chem.*, 46 (1981) 2695.
- 31 Yu.K. Grishin, Yu.A. Strelenko, Ya.A. Ustynyuk, A.A. Erdman, I.V. Shchirina-Eingorn and I.I. Kritskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1038.
- 32 P.A. Scherr, M.D. Glick, J.H. Siefert and R.D. Bach, *J. Am. Chem. Soc.*, 97 (1975) 1782.
- 33 C.G. Pitt, *J. Organomet. Chem.*, 61 (1973) 49.

- 34 U. Weidner and A. Schweig, *J. Organomet. Chem.*, 39 (1972) 261.
- 35 M.J.S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969, Chapt. 6.
- 36 A. Schweig, U. Weidner and G. Manuel, *J. Organomet. Chem.*, 67 (1974) C4.
- 37 H. Schmidt, A. Schweig and G. Manuel, *J. Organomet. Chem.*, 55 (1973) C1.
- 38 H. Schmidt, A. Schweig and G. Manuel, *J. Chem. Soc. Chem. Commun.*, (1975) 667.
- 39 H. Bock, G. Becker and G. Fritz, *J. Organomet. Chem.*, 46 (1972) 89.
- 40 C.G. Pitt and H. Bock, *J. Chem. Soc. Chem. Commun.*, (1972) 28.
- 41 P.K. Bischof, M.J.S. Dewar, D.W. Goodman and T.B. Yones, *J. Organomet. Chem.*, 82 (1974) 89.
- 42 R.S. Brown, D.F. Eaton, A. Hosomi, T.G. Traylor and J.M. Wright, *J. Organomet. Chem.*, 66 (1974) 249.
- 43 F.P. Colonna, G. Distefano, M. Guerra and A. Modelli, *J. Chem. Soc. Dalton Trans.*, (1979) 2037.
- 44 C. Furlani, M.N. Piancastelli, C. Cauletti, F. Faticanti and G. Ortaggi, *J. Electron. Spectrosc.*, 22 (1981) 309.
- 45 A.N. Nesmeyanov, V.N. Baidin, Yu.V. Chizhov, M.M. Timoshenko, Yu.S. Nekrasov and I.I. Kritskaya, *Dokl. Akad. Nauk SSSR*, 256 (1981) 121.
- 46 A. Katrib and J.W. Rabalais, *J. Phys. Chem.*, 77 (1973) 2358.
- 47 P. Bischof, J.A. Hashmall, E. Heilbronner and V. Hornung, *Helv. Chim. Acta*, 52 (1969) 1745.
- 48 D.J. Derrick, L. Asbrink, O. Edqist, B.O. Jonsson and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, 6 (1971) 203.
- 49 C.R. Brundle, M.B. Robin and N.A. Cuebler, *J. Am. Chem. Soc.*, 94 (1972) 1466.
- 50 J.P. Maier and D.W. Turner, *J. Chem. Soc. Faraday Trans. II*, 69 (1973) 196.
- 51 T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Japan*, 47 (1974) 2563.
- 52 J.P. Maier and D.W. Turner, *J. Chem. Soc. Faraday Trans. II*, 69 (1973) 521.
- 53 T.P. Debics and J.W. Rabalais, *J. Electron Spectrosc.*, 1 (1973) 355.
- 54 D.W. Turner, A.D. Baker, C. Baker and C.R. Brundle, *High Resolution Molecular Photoelectron Spectroscopy*, Wiley, London, 1970, p. 386.
- 55 V.G. Andrianov, Yu.T. Struchkov, V.A. Blinova and I.I. Kritskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 2021.
- 56 D.N. Kravtsov, B.A. Kvasov, L.S. Golovchenko and E.I. Fedin, *J. Organomet. Chem.*, 36 (1972) 227.
- 57 C. Batich, P. Bischof and E. Heilbronner, *J. Electron. Spectrosc.*, 1 (1973) 333.
- 58 R.D. Bach, A.T. Weibel, W. Schmonscs and M.D. Glick, *J. Chem. Soc. Chem. Commun.*, (1974) 961.
- 59 Yu.N. Luzikov, N.M. Sergeyev and Yu.A. Ustynyuk, *J. Organomet. Chem.*, 65 (1974) 303.
- 60 S. Craddock, E.A. Ebsworth, H. Moretto and D.W.H. Rankin, *J. Chem. Soc. Dalton Trans.*, (1975) 390.
- 61 Yu.A. Strelenko, Yu.G. Bundel', F.H. Kasumov, V.I. Rosenberg, O.A. Reutov and Yu.A. Ustynyuk, *J. Organomet. Chem.*, 159 (1978) 131.