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σ,π-CONJUGATION IN ORGANOMERCURIAL SYSTEMS

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Summary

Two series of compounds LHgL′ are described. In series I, L = L′ = organic radical with an oxo group in position 2 or L′ = Cl, in series II, L = L′ = allylic radical or L′ = Cl. Some compounds posses chemical properties of conjugated systems (IA, IIA), while others do not possess such properties (IB, IIB). The $J(^{13}C—^{199}Hg)$ coupling constants and chemical shifts in ^{13}C NMR spectra, the integral intensities of multiple bond vibrations in Raman spectra, the half-wave reduction potentials and the resonance energies in mass spectra of the negative ions are compared. The main contribution to the observed differences between compounds A and B is made by interaction of the C—Hg σ-bond with the π-system (σ, π-conjugation).

Introduction

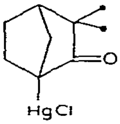
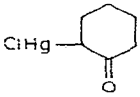
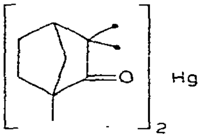
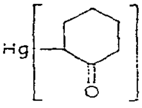
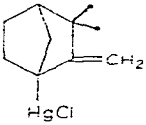
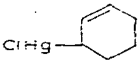
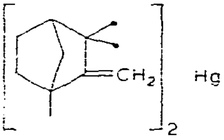
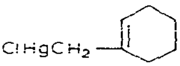
Nesmeyanov and Lutsenko [1] established that α-mercurated aldehydes and ketones are unusually highly reactive in reactions with Ph_3CCl, aqueous KI solution, sodium thiosulphate and in certain cases they react with transfer of the reaction center to oxygen (eq. 1), although no tautomeric form has been established for them. It was assumed [1—3] that a strong effect of the Nathan—Becker type is realized in these compounds. The absence of such chemical properties in sterically strained α-chloromercuricamphenylone [4] confirmed the assumption that it was a conjugation effect, and later it was shown [5] that compounds of other metals with similar structural elements display the same properties.

$$ClHgCH_2—CHO + RCl \rightarrow CH_2{=}CH—OR \qquad (1)$$

In the present work, some results of which have already been reported [6—9], we examine, using methods of ^{13}C NMR, vibrational (Raman) spectro-

TABLE 1

COMPOUNDS STUDIED [a]

	A		B
1	$\mathrm{ClHgCH_2CHO}$	1	
2	$\mathrm{ClHgCH_2COC_2H_5}$		
3			
4	$\mathrm{Hg(CH_2CHO)_2}$	2	
5	$\mathrm{Hg(CH_2COC_2H_5)_2}$		
6	$\mathrm{Hg(CH_2COC_6H_5)_2}$		
7		3	
8	$\mathrm{ClHgCH_2CH{=}CH_2}$		
9		4	
10			
11	$\mathrm{Hg(CH_2CH{=}CH_2)_2}$		

[a] Synthesis of these compounds has been described in refs. 1, 4, 6 and 29 and literature cited therein.

scopy, polarography and mass spectrometry of negative ions, two series of organomercurials, namely, mercurated aldehydes and ketones and mercury substituted allylic compounds (see Table 1). Both series include compounds with a conjugated system of bonds (column A, Table 1) and compounds which do not exhibit chemical properties of conjugated compounds (column B, Table 1). By comparing the corresponding parameters for compounds A and B

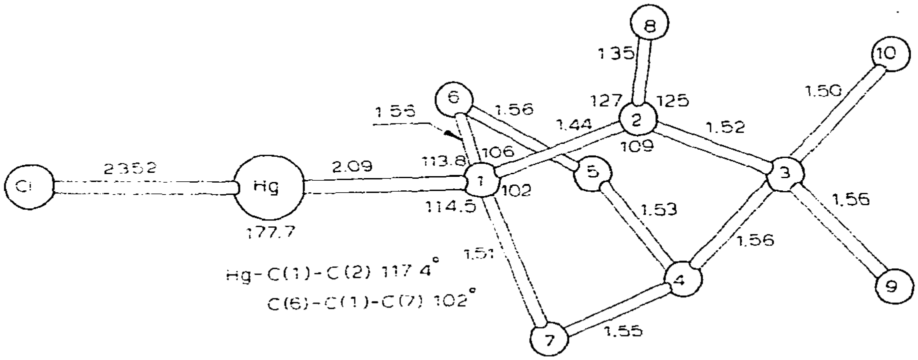


Fig. 1. Parameters of the molecular structure of α-chloromercuricamphene according to data of ref. 10.

we attempted to estimate the effect of conjugation of C—Hg and C=O, C=C and the degree in which it is reflected in the parameters of the methods listed above. For α-chloromercuricamphene, belonging to group B, we also carried out an X-ray diffraction study [10] which established that the dihedral angle between planes Hg—C(1)—C(2) and C(1)—C(2)—C(8) (Fig. 1) is 19°, i.e., the C—Hg bond lies almost precisely in the nodal plane of the π-system and this should therefore sharply reduce or exclude altogether σ—π interaction. It may be assumed that other compounds of group B with a bicyclo[1,2,2]heptane framework have the same geometry, which, on account of the rigidity of the bicyclic system, should be retained in solution. The Hg—C(2) and Hg—C(8) distances are 3.0 and 3.3 Å, respectively. Considering the van der Waals radii of mercury and carbon to be 1.5 [11] and 1.71 Å [12], respectively, we cannot completely exclude a weak direct intramolecular interaction between mercury and the π-system. However, it should be far weaker (or completely absent) than the competing interaction with the solvents in which the measurements were carried out (pyridine and tetrahydrofuran).

Results and discussion

Experimental results are listed in Table 2 and Figs. 2 and 3.

NMR spectra

In the discussion of NMR spectra [6,8] we assumed that "conjugation" implies an increase in the bond order of C(1)—C(2) bonds and a simultaneous decrease in C—Hg and C=O, C=C bond orders. It is known that magnetic shielding of ^{13}C nuclei is proportional to the total bond order of the corresponding carbon atom [13,14]. The ^1J(C—H) and ^1J(C—Hg) coupling constants also provide information about the valency state of the atoms participating in this interaction [15,16]. Data available at present make it possible to consider the absolute value of ^1J(C—Hg) to be roughly proportional to the C—Hg bond order.

As can be seen from Table 2, a considerable reduction in ^1J(C—Hg) is observed for models which can exhibit conjugation; by 884 Hz in the case of chloromercury derivatives and 371 Hz for symmetrical compounds of the ketone series I, and by 455 and 260 Hz (in average) for the corresponding derivatives in the allylic series II. At the same time shielding of C(1) and C(2) increases for C(1) by 15—20 ppm (I) and by approximately 36 ppm (II); for C(2) by 13—17 ppm (I) and 32—40 ppm (II). Shielding of C(3) in allylic compounds results in a decrease of the chemical shifts by 10—14 ppm. These findings confirm with our initial assumptions.

However, the established differences cannot be entirely attributed to the effect of σ,π-conjugation. Taking into account the polar effect of substituents and the decrease of ^1J(C—Hg) when passing from rigid, sterically strained bicyclic systems to non-rigid systems, the contribution of σ,π-conjugation for compounds with a carbonyl group may be considered 500 Hz (mercury chlorides) and 300 Hz (symmetrical compounds) and for allylic slightly more and slightly less than 200 Hz, respectively [8]. Therefore, on replacement of a carbonyl oxygen with a methylene group the contribution of σ,π-conjugation into the ^1J(C—Hg) constant is approximately halved.

TABLE 2

PARAMETERS OF NMR ^{13}C SPECTRA, HALF-WAVE POTENTIALS OF REDUCTION, FREQUENCIES AND INTEGRAL INTENSITIES OF STRETCHING MODES OF MULTIPLE BONDS FOR CONJUGATED AND NONCONJUGATED ORGANOMERCURIALS OF THE TYPE Hg—C_1—C_2=O AND Hg—C_1—C_2=C_3

Compound	C(1)		C(2)		C(3) [a]		$-E_{1/2}$ [b] (V)	i (μA)	ν(C=C) [c] ν(C=O) Raman (cm^{-1})	I^{∞} [d] (C=C, C=O)
	δ (ppm)	J(C—Hg) (Hz)	δ (ppm)	J(C—Hg) (Hz)	δ (ppm)	J(C—Hg) (Hz)				
1A									1676	9,8
2A									1672	5,8
3A	58,26	1613	208,80				0,27 0,92	2,0 1,8	1665	3,3
IB	73,65	2507	222,51				0,63 2,26	2,0 1,4	1720	1
4A	50,33	768	199,18						1679	8,9
5A	48,39	742	210,42						1668	8,0
6A	45,20	753	200,17							
7A	61,96	697	209,32							
2B	81,52	1068	226,61							
8A	31,2	1682,5	138,4	200	111,9	232,4	0,44 1,76	2,70 2,80	1623	5,96
9A	36,6	1643	137,1		120,2	213	0,53 1,92	2,90 2,90	1653	9,23
10A	37,2	1645,5	119,9		116,8		0,34 2,03	2,10 2,10	1632	5,87
3B	72,5	2112	169,5		102,6	102,5	{0,62 [e] 1,07	2,30	1649	1
11A	46,4	649	140,9	91,2	110,4	106,6	2,42 2,13 [f]	2,60 3,50	1616	9,99 [g]
4B	81,8	909	173,1		100,1	80,9			1645	1,69 [g]
Acetaldehyde									1722	0,5
Methyl ethyl ketone									1715	0,7
Cyclohexanone									1708	1,8
Camphenylone									1739	1,4
α-Methylcamphenylone									1739	1,5
Cyclohexene									1652	2,88
Camphene									1656	1,32

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[a] Spectra in pyridine solution were obtained on a HX-Brucker instrument, chemical shifts are given in relation to tetramethylsilane. [b] For 0.1 N solutions of n-Bu_4NBF_4 in THF, in relation to saturated calomel electrode. [c] For solutions in pyridine, PHO Coderg instrument, He—Ne laser. [d] In relative units. I^{∞} was measured as the product of line half-width and peak height normalized for an equal number of molecules per unit volume. [e] The total height of these waves corresponds to addition of one electron. The cause of separation of the one-electron wave is unclear. [f] Ref. 24, dimethylformamide, 0.1 N Et_4NClO_4. [g] Calculated for one C=C group.

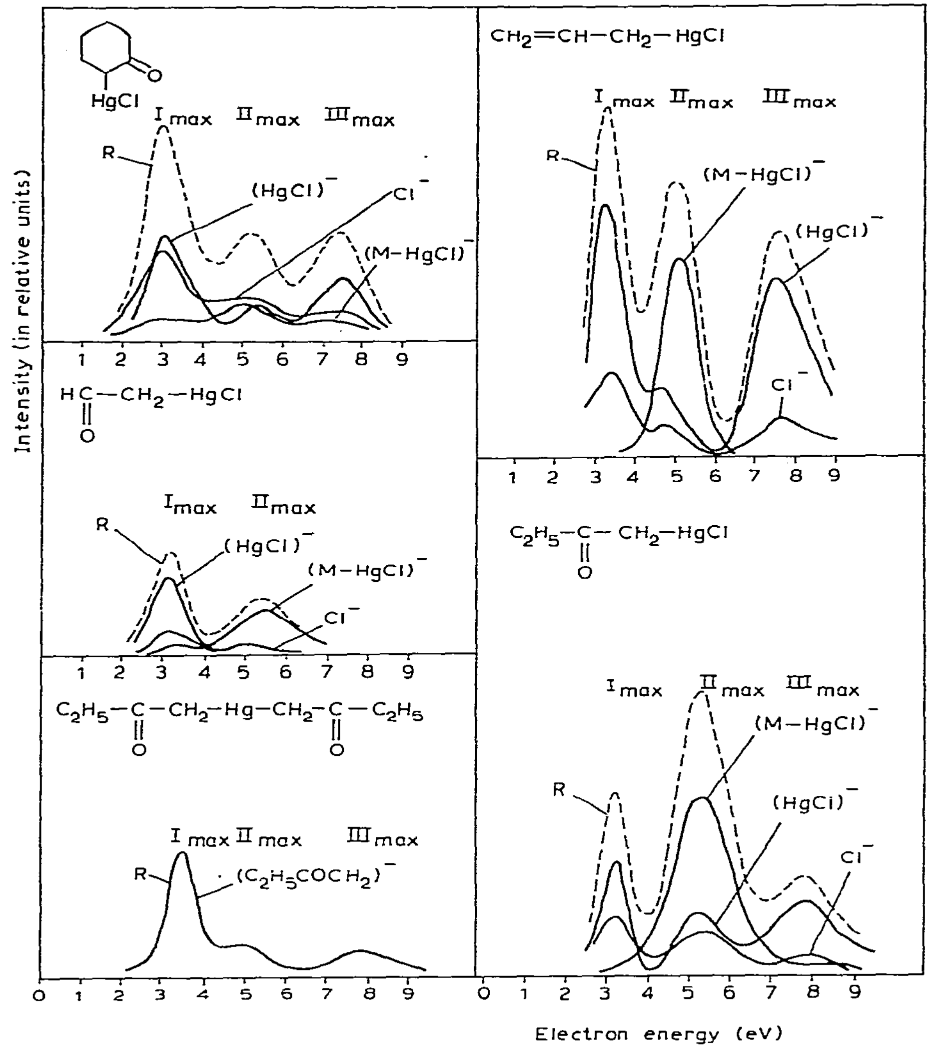

Fig. 2. Effective yield curves for negative ion fragments of group A compounds (solid lines) and resonance curves (R, dotted line). Spectra were obtained on a MX-1303 instrument [9].

Unlike the case of ^1J(C—Hg), the σ,π-conjugation concept does not accommodate the behaviour of ^3J(C—Hg) constants in allylic systems. A considerable increase in ^3J is observed in systems with σ,π-conjugation. These differences may be due to the angular dependence of ^3J(C—H) and to the difference in C(1)—C(2) bond lengths in different types of compounds [10,17,18].

Raman line intensities

The Raman line intensities of multiple bonds is a sensitive indicator of the presence of conjugation (both of π, π- and σ,π). This effect, revealed in a sharp increase in the intensity of multiple bond lines, shows a dependence upon the spatial arrangement of interacting fragments; on distortion of the coplanarity of the π-system it decreases [19], the same occurs in the case of σ,π-conjugated

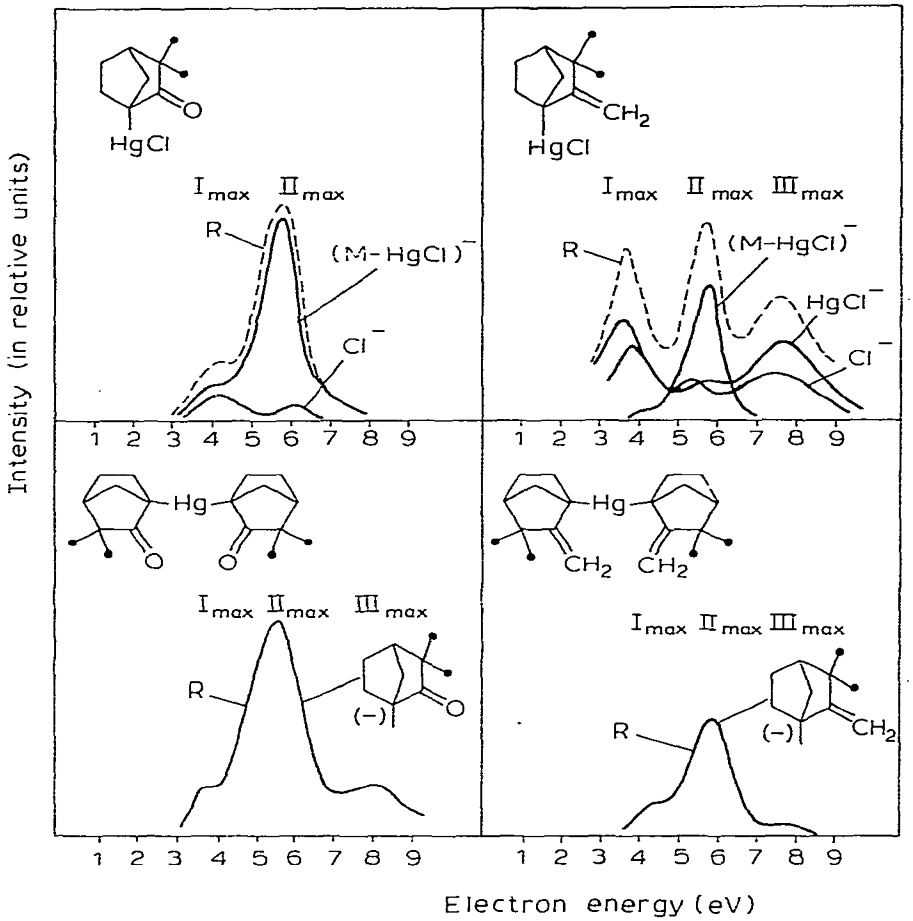

Fig. 3. Effective yield curves for negative ion fragments of group B compounds (solid lines) and resonance curves (R, dotted lines).

systems [20—22]. An increase in the trace and anisotropy of Raman tensor of the multiple bond line [23] indicates that in conjugated systems the C=C—C=C and C=C—C—X fragments are the characteristic structural elements, not the isolated multiple and single bonds, i.e., the effect is electronic in nature. Bearing this in mind, we investigated [7,8] the organomercurials listed in Table 1 and, for comparison, several hydrogen analogues. First, the effect of hydrogen replacement by mercury on the integral intensities of multiple bond lines in compounds of groups A and B should be mentioned. The effect is most pronounced in acyclic molecules (8—20 fold increase), whereas in monocyclic compounds it is slightly less and in bicyclic compounds the intesnities are even slightly reduced when compared with the hydrogen analogues.

Comparison of Γ^{∞} values for organomercurials A and B shows that the weakest are the ν(C=C) and ν(C=O) lines of group B compounds and that the greatest difference is observed between bicyclic and acyclic molecules. The Γ^{∞} values for monocyclic molecules lie between these two extreme cases and a certain dependence on the position of the HgCl group can be detected; mercury in the side chain of substituted cyclohexene has a weaker effect than mercury directly bonded to the ring. Presumably this qualitative pattern reflects the gradual decrease in the degree of σ,π-conjugation with an increase in steric restrictions when passing from open chains to cyclic structures.

Polarographic reduction

Polarographic reduction of organomercury halides proceeds in two single-electron steps [24].

$$LHg{-}Cl + e^- \rightarrow LHg^{\cdot} + Cl^- \qquad (2)$$

$$L{-}Hg^{\cdot} + e^- \rightarrow L^- + Hg^0 \qquad (3)$$

Attack of the first electron leads to rupture of the Hg—Cl bond and formation of radical LHg$^{\cdot}$ (eq. 2). Carbanion L$^-$ is formed as a result of reductive scission of the C—Hg bond in LHg$^{\cdot}$ (eq. 3). In the literature [25] it has been shown that in radical L—Hg$^{\cdot}$, adsorbed on the surface of a mercury drop, the C—Hg bond is weakened but not sufficiently for radical L$^{\cdot}$ to exist as a kinetically independent species. Analysis of published data shows that $E_{1/2}$ for the first step mainly depends on the nature of the halogen and is practically independent of L. The effect of the organic radical is revealed at the second step; a linear dependence is observed between $E_{1/2}$ of LHg$^{\cdot}$ and the electron affinity of radical L$^{\cdot}$ or basicity of carbanion L$^-$, expressed in terms of the p*K*a of LH [24].

Therefore, one should expect that the effect of σ,π-conjugation in organomercurials, other conditions being equal, will be revealed in a decrease of the negative value of $E_{1/2}$ for the second step of reduction. This was confirmed experimentally. Thus, for allylmercury chloride $E_{1/2}(2) = -1.62$ V, while for CH_3HgCl -1.96 V [24].

$E_{1/2}$ potentials for both steps of reduction are listed in Table 2. For compounds of group A, for which σ,π-conjugation is possible (3A, 8A) the $E_{1/2}$ values for the second step are less negative than for group B compounds (1B, 3B). Diallylmercury is reduced at -2.13 V, while for dicamphenylmercury the reduction wave is not observed up to the discharge potential of the supporting electrolyte (-2.8 V). The observed differences in $E_{1/2}$ potentials of the second step are greater for oxo compounds than for the allylic compounds. Thus, $E_{1/2}$ for 3A and 1B is 1.34 V, whereas for compounds 8A and 3B it is 0.66 V. Therefore, the effect in the allylic series is about half as strong as in the series of carbonyl compounds. This is in good agreement with NMR data.

Mass spectra of negative ions

Mass spectrometry of negative ions was employed in the study of σ,π-conjugation because it provides information about molecular features which directly depend on bond conjugation, namely, information about the relative arrangement of the appropriate molecular orbitals. As can be seen from Figs. 2 and 3, ion fragments formed by rupture of only Hg—C and Hg—Cl bonds (Cl$^-$, HgCl$^-$ and L$^-$ for asymmetrical compounds and L$^-$ for symmetrical compounds) are present in the spectra. Resonance curves (R, Figs. 2—4), obtained by summation of effective yield curves of ion fragments, display three maxima. In accordance with the energy region in which they are observed [26,27] they may be assigned

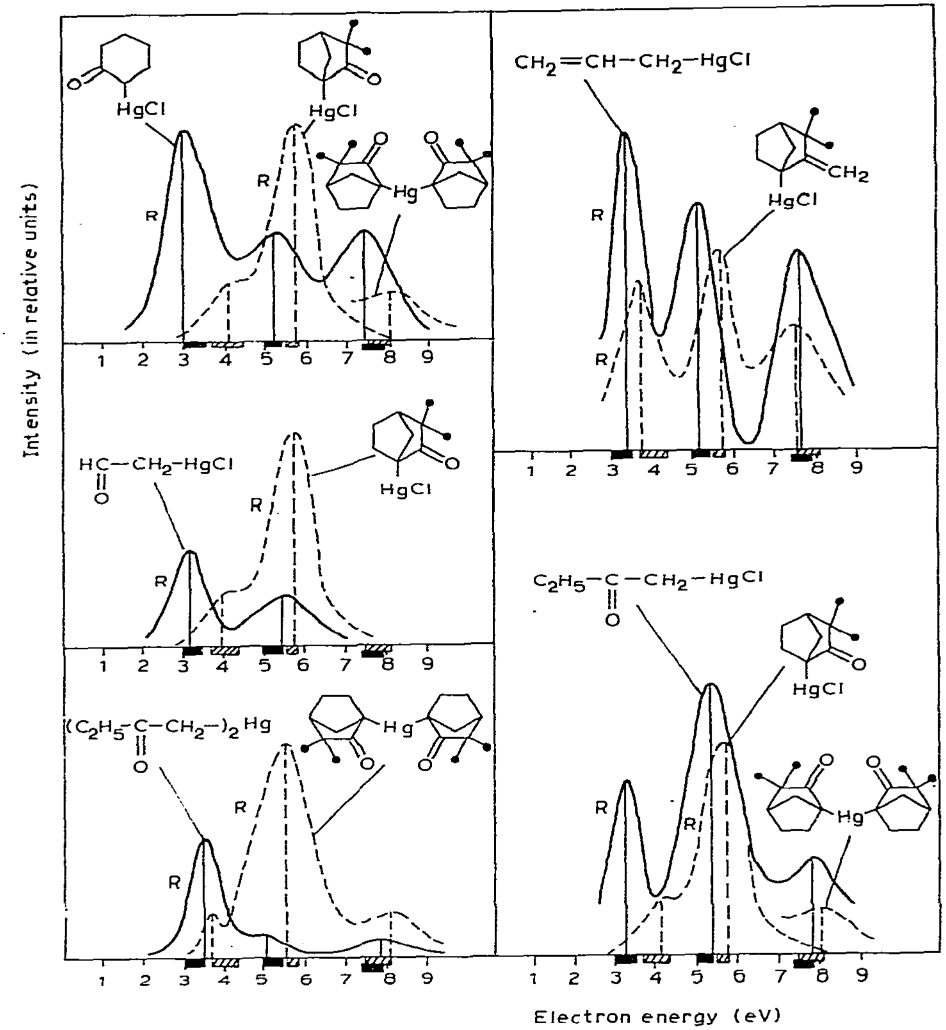

Fig. 4. Resonance curves of group A (solid lines) and group B (dotted lines) compounds. Black rectangles show regions of electron energy corresponding to resonance curve maxima of all group A compounds, crosshatched rectangles designate the same for group B compounds.

to a certain type of resonance: I_{max} to electron-excited Feshbach resonance in the region of the first excited states of the molecule; II_{max} to electron excited shape resonance; III_{max} to electron-excited Feschbach resonance in the region of Rydberg states of the molecule. Since on electron capture one of the electrons of the molecule is transferred to an excited level (low-lying for I and II_{max} and high-lying for III_{max}), the energy of the electrons on which resonance maxima are observed is equal to the energy distance between the two molecular orbitals associated with this resonance (with a small correction for the electron affinity of the excited molecule). Since any conjugation (including σ,π) leads to a change in the energy distance between molecular orbitals, the effect of σ,π-conjugation on the electron shell of the molecule may be followed by the shift of each resonance maximum when passing from group B to group A compounds.

Recurrence of the same qualitative pattern of resonances in all compounds studied makes it possible to consider all processes occurring in these molecules during interaction with electrons as having the same nature, and retention by each resonance of its energy region and character of fragmentation allows us to assume that in different molecules each resonance is associated with similar pairs of molecular orbitals. Therefore, the displacement of resonance maxima in the electron energy scale may be correlated precisely with the effect of σ,π-conjugation. It should be noted that the resonance curve obtained by summation of the effective yield curves for fragmented ions does not fully describe the character of resonance, since it does not take into account the competition of electron autoabstraction. Since the studied compounds have similar structure this inaccuracy may be neglected, as autoabstraction shifts the maxima in the same direction and by approximately the same value. The correction for the electron affinity of the excited molecule (the value of which is quite small in any case [28]) may also be omitted for the same reason.

In Fig. 4 the black rectangles represent the three regions of electron energy corresponding to resonance maxima for group A compounds, the crosshatched rectangles the resonance maxima for group B compounds. The maxima of resonance curves for all conjugated compounds fall within the region of smaller energies than the same maxima for unconjugated compounds. This means that the distance between molecular orbitals associated with each resonance are shorter in the first group of compounds. This difference is greatest in the first resonance peak, less in the second and negligible in the third.

Therefore, in the series of compounds studied the effect of conjugation of C—Hg σ-bond with the double bond is sufficient for the observed shifts of resonance maxima caused by this effect to be greater than the dispersion of maxima positions due to differences in the structure of the molecules.

Conclusions

Data obtained in the present work confirm completely the presence of a considerable conjugation effect between C—Hg and C=O, C=C bonds in organomercurials of type A, postulated in [1—3] on the basis of chemical studies. According to our estimations in allylic compounds this effect is reduced by half as compared with oxo compounds. The contributions of σ,π-conjugation into the obtained shifts apparently exceeds the contribution of such factors as the degree of substitution of the key carbon atom and the solvation effect. The degree of conjugation between σ-C—Hg and π-bonds is primarily determined by geometrical factors, this follows from comparison of data for acyclic, monocyclic and bicyclic compounds.

Good qualitative agreement was observed for mass-, NMR- and Raman-spectroscopic and polarographic data, which all may be accommodated within the concept of σ,π-conjugation

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