*Inorg. Chem.* **1984**, *23*, 1113-1119 **1113**

which proceeds so rapidly that it cannot be followed even with pulse radiolysis.[25] If reaction 7 occurs prior to ejection of $HgCl_2^-$ from the micelle, the back-reaction between Ru(III) and HgCl· can compete effectively with the escape of the neutral radical. It is apparent that construction of micelle-based solar energy storage devices must consider processes other than the primary electron-transfer reaction.

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**Registry No.** $[Ru(Me_4phen)_3]^{2+}$, 64894-64-0; $[Ru(4,7\text{-}Me_2phen)_3]^{2+}$, 24414-00-4; $[Ru(Me_2bpy)_3]^{2+}$, 32881-03-1; $[Ru(5,6\text{-}Me_2phen)_3]^{2+}$, 14975-40-7; $[Ru(Me\text{-}phen)_3]^{2+}$, 14975-39-4; $[Ru(Ph_2phen)_3]^{2+}$, 63373-04-6; $[Ru(phen)_3]^{2+}$, 22873-66-1; $[Ru(bpy)_3]^{2+}$, 15158-62-0; $[Ru(Cl\text{-}phen)_3]^{2+}$, 47860-47-9; $[Ru(Br\text{-}phen)_3]^{2+}$, 66908-45-0; $HgCl_2$, 7487-94-7; $HgCl_4^{2-}$, 14024-34-1; $HgCl_3^-$, 14988-07-9; NaLS, 151-21-3.

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# He I and He II Photoelectron Spectra and Infrared Intensity Measurements of Alkynylmercury(II) Compounds: The Search for dπ–pπ Interactions

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The UV photoelectron spectra of various alkynylmercury(II) compounds of the type $Hg(C\equiv CR)_2$ (I), $R'HgC\equiv CR$ (II), and $R'HgC\equiv CHgR'$ (III) are reported and discussed with regard to structural implications. The spectra provide evidence for significant dπ–pπ interactions only for compounds in which a conjugation extended along the molecular axis between the π-acetylenic orbitals and other π systems is possible, as is evident from ligand field effects on the 5d mercury orbitals. This is substantiated by IR intensity measurements of the $\nu_{C\equiv C}$ stretching band of compounds I and II. From the comparison of this information with NMR results, it appears that dπ–pπ interactions are weak in any case. In general, the trends of $\pi_{C\equiv C}^{-1}$, $\sigma_{Hg-C}^{-1}$, and $d^{-1}$ ionizations are in agreement with changes in the magnitude of various NMR parameters ($\delta(^{13}C)$, $\delta(^{199}Hg)$, $J(Hg\text{—}C)$, $J(C\equiv C)$).

## Introduction

For many transition metals, dπ–pπ interactions between d metal orbitals and π systems of organyl ligands are in general readily established by various methods.[1] This appears to be more difficult, for obvious reasons, in the case of organomercury compounds.

In a recent NMR study of alkynylmercury(II) compounds,[2] it proved impossible to present unambiguous evidence for this by $^{13}C$ NMR spectroscopy although it appears that the nuclear shielding of mercury is related to changes in the energy of the mercury 5d orbitals.

As far as other spectroscopic methods are concerned, the measurement of infrared (IR) intensities and, in particular, UV photoelectron spectroscopy (UPS) may help to assess the existence and the extent of dπ–pπ interactions.

The infrared intensities of $\nu_{C\equiv C}$ in alkynes are determined by resonance interactions of the C≡C triple bond with the substituents,[3] and the IR intensities of $\nu_{C\equiv N}$ and $\nu_{C\equiv O}$ in transition-metal compounds reflect metal–ligand dπ–pπ interactions.[4]

UPS enables observation of the shape and energy of the ionization of valence orbitals, particularly of the 5d mercury ionization, and of the bands related to $\pi^{-1}$ organyl ionizations.[5]

The alkynylmercury(II) compounds that this paper deals with have been selected for several reasons: (i) extensive NMR data are available for comparison,[2] (ii) most of the compounds fulfill the criteria required for meaningful discussion of IR intensity data,[6] and (iii) previous work[5] on UPS of some bis(alkynyl)mercury(II) compounds shows that alkynyl ligands are suitable candidates to study dπ–pπ interactions.

In order to establish criteria that could be ultimately used to predict the extent of π interactions in organomercury compounds and similar classes of molecules, we extended our investigation to alkynylmercury(II) compounds of the types $Hg(C\equiv CR)_2$ (I: R = $CH_3$ (a), $n\text{-}C_4H_9$ (b), $t\text{-}C_4H_9$ (c), $C_6H_5$ (d), $p\text{-}CH_3OC_6H_4$ (e), Cl (f), Br (g)), $R'HgC\equiv CR$ (II: R = H, R′ = $CH_3$ (a), $C_2H_5$ (b), $CH{=}CH_2$ (c), $C_6H_5$ (d); R = R′ = $CH_3$ (e); R = $C_6H_5$, R′ = $CH_3$ (f); R = R′ = $C_6H_5$ (g)), and $R'HgC\equiv CHgR'$ (III: R′ = $CH_3$ (a), $C_2H_5$ (b), $C_6H_5$ (c)).

The NMR parameters ($^1H$, $^{13}C$, $^{199}Hg$) have been reported for compounds I–III[2] with the exception of Ig and IIe (see Experimental Section). IR intensities have been measured for compounds I, except for Ic (in Ic the C≡C stretching band occurs as two peaks, which is a common feature of disubstituted $t\text{-}C_4H_9$ alkynes and may be attributed to Fermi resonance with various bands[7]), and for compounds II, except for

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IId,g in which the C≡C stretching band does not occur well separated from other vibrations. Raman spectra in the solid state have been recorded for compounds III and If,g.

UP spectra of compounds Ia,c,f have been reported and discussed previously.[5] In this work we measured both He I (21.22 eV) and He II (40.81 eV) gas-phase UP spectra of compounds Id, IIa–d, and IIIa,b. We also measured the UP spectra of compounds Ig, IIg, and IIIc, but there was clear evidence of decomposition under our experimental conditions.

## Experimental Section

$^1$H, $^{13}$C (50.3 MHz), and $^{199}$Hg (35.8 MHz) NMR spectra were recorded on a Bruker WP 200 PFT NMR spectrometer. For data and experimental conditions see ref 2.

IR intensities $A_{C\equiv C}$ (cm mol$^{-1}$) were measured on a Perkin-Elmer PE 599 double-beam infrared spectrometer. The $\nu_{C\equiv C}$ band areas were integrated numerically by using a PE data station. Samples were measured as $CHCl_3$ solutions in variable path length cells with NaCl windows in the extinction mode (5–7 different concentrations per compound). The method of registration[8] and calculation[3] of $A = 1/cl\int \ln (I_0/I)\, d\nu$ was as described in literature ($c$ in mol cm$^{-3}$; $l$ in cm; $A$ in cm mol$^{-1}$). A Lambert–Beer's law plot for every compound measured served for quality control.

Raman spectra in the solid state were obtained with use of a Cary 82 Raman spectrometer, with an $Ar^+$ excitation line (514.5 nm) and 100-mW power.

The UP spectrometer was a Perkin-Elmer PS 18 modified with a dual He I/He II hollow-cathode lamp (Helectros Development). Calibration was performed by using as internal standards Ar, $CH_3I$, and self-ionized $He^+$. The spectra were run at temperatures allowing sufficient vapor concentration, varying for various compounds and generally in the range 30–160 °C.

The compounds were prepared following literature methods;[2,9–11] NMR spectra served for purity control ($^1$H, $^{13}$C, $^{199}$Hg). In the case of compound IIf, the best yield was obtained by reaction of $CH_3HgI$ with $HC\equiv CC_6H_5$ as described for IIe in ref 10. IIf was recrystallized from ethanol.

NMR parameters relative to internal $(CH_3)_4Si$ for $\delta(^{13}C)$, and $\delta(^1H)$ and external $Hg(CH_3)_2$ for $\delta(^{199}Hg)$ are given; the + sign denotes a shift to high frequency. Coupling constants are given in Hz. $Hg(C\equiv CBr)_2$ (Ig): $^{199}$Hg NMR in Me$_2$SO-$d_6$ $\delta$ – 1040.4, in acetone-$d_6$ $\delta$ –1073.9; $^{13}$C NMR in acetone-$d_6$ $\delta(HgC\equiv) = 114.25$ ($^1J_{Hg-C} = 2773$), $\delta(\equiv CBr) = 61.25$ ($^2J_{Hg-C} = 782.5$). $CH_3HgC\equiv CCH_3$ (IIe) ($CDCl_3$): $^{199}$Hg NMR $\delta$ –448.3; $^{13}$C NMR $\delta(CH_3Hg) = 6.85$ ($^1J_{Hg-C} = 1126$), $\delta(HgC\equiv) = 131.47$ ($^1J_{Hg-C} = 1390$), $\delta(HgC\equiv \mathit{C}) = 103.01$ ($^2J_{Hg-C} = 411$), $\delta(\equiv C\mathit{C}H_3) = 4.08$ ($^3J_{Hg-C} = 28.0$); $^1$H NMR $\delta$-$(CH_3Hg) = 0.52$ ($^2J_{Hg-H} = 144.8$, $^1J_{CH_3} = 132.3$), $\delta(\equiv CCH_3) = 1.78$ ($^4J_{Hg-H}$) = 18.6, $^1J_{CH_3} = 130.9$).

## Results and Discussion

**IR Intensity Measurements.** Although both frequencies and intensities depend, in principle, in a complex way on the electronic structure of a bond, the former is determined by the second derivative of energy with respect to the coordinate ($d^2E/dQ^2$) while the latter is a function of the dipole moment gradient ($d\mu/dQ$). So, it becomes evident that frequencies and intensities must not necessarily show the same trends.[4,6] Since it is known that variations in intensities are often relatively larger than variations in the corresponding frequencies,[6] the integral intensities $A$ of $\nu_{C\equiv C}$ of some of compounds I and II were determined. Due to the complex nature of $A$ and due to the expected complicated bonding situation in the compounds under consideration, it is also clear that trends are only to be discussed qualitatively.

Relevant IR and Raman data as well as the $\nu_{C\equiv C}$ integrated intensities $A$ for compounds I–III are given in Table I. The frequencies $\nu_{C\equiv C}$ or $\nu_{\equiv C-H}$ do not require further discussion.[12]

Table I. IR[a] and Raman Data and IR Intensities ($\nu_{C\equiv C}$) for Alkynylmercury(II) Compounds $Hg(C\equiv CR)_2$ (I), $R'HgC\equiv CR$ (II), and $R'HgC\equiv CHgR'$ (III)

| compd (R, R′) | $\nu_{\equiv C-H}$, cm$^{-1}$ | $\nu_{C\equiv C}$, cm$^{-1}$ | $\nu_{C\equiv C}{}^{1/2}$, cm$^{-1}$ | $10^5A$, cm mol$^{-1}$ |
|---|---|---|---|---|
| Ia ($R = CH_3$) | | 2169 | 18 | 38.2 |
| Ib ($R = n\text{-}C_4H_9$) | | 2158 | 18 | 45.5 |
| Ic ($R = t\text{-}C_4H_9$) | | 2172,<br>2137,<br>2175,<br>2140[b] | | |
| Id ($R = C_6H_5$) | | 2147 | 14 | 45.7 |
| Ie ($R = C_6H_4\text{-}p\text{-}OCH_3$) | | 2145 | 15 | 74.4 |
| If (R = Cl[c]) | | 2138,<br>2134[b] | 16 | 96.2 |
| Ig (R = Br[d]) | | 2118,<br>2115[b] | 18 | 68.0 |
| IIa ($R = H$, $R' = CH_3$) | 3277 | 2008 | 12 | 3.83 |
| IIb ($R = H$, $R' = C_2H_5$) | 3278 | 2001 | 13 | 3.81 |
| IIc ($R = H$, $R' = CH{=}CH_2$) | 3285 | 2017 | 12 | 4.16 |
| IId ($R = H$, $R' = C_6H_5$) | 3275 | 1997 | | |
| IIe ($R = R' = CH_3$) | | 2152 | 14 | 16.5 |
| IIf ($R = C_6H_5$, $R' = CH_3$) | | 2133 | 14 | 12.6 |
| IIg ($R = R' = C_6H_5$) | | 2140 | 14 | |
| IIIa ($R' = CH_3$) | | 2036[b] | | |
| IIIb ($R' = C_2H_5$) | | 2033[b] | | |
| IIIc ($R' = C_6H_5$) | | 2053[b] | | |

[a] IR spectra in $CHCl_3$ solution. [b] Raman spectra; in the solid state. [c] Further Raman bands: 342 (s), 253 (w), 171 cm$^{-1}$ (m). [d] Further Raman bands: 314 (s), 181 (w), 151 cm$^{-1}$ (m).

The monosubstituted ethynes (IIa–c) have to be discussed separately.[3] There are no appreciable differences in the $A$ values for the monoalkynyl derivatives IIa–c, just a slight increase in case of the vinyl derivative IIc with respect to the methyl and ethyl compounds IIa,b (due to the better $\sigma$-donor ability of alkyl groups, the reverse would be expected in case of significant d$\pi$–p$\pi$ interaction). The comparison of these $A$ values with those for other organometallic-substituted ethynes[3a] (e.g., $(C_2H_5)_3SnC\equiv CH$, $A = 4.3 \times 10^5$; $(C_2H_5)_3GeC\equiv CH$, $A = 4.65 \times 10^5$; $(n\text{-}C_4H_9)_3GeC\equiv CH$, $A = 3.91 \times 10^5$), for which the resonance interactions are expected to be very weak, classifies the $CH_3Hg$, $C_2H_5Hg$, and $CH_2{=}CHHg$ groups into the same category.

Since there can be seen from other spectroscopic data (UPS, NMR) that there is no reason to anticipate a different bonding situation for the remaining compounds II, a comparison of the $A$ value for IIe with that for Ia and, likewise, of the $A$ value for IIf with that of Id can give information about the bonding situation in compounds I. In the case of d$\pi$–p$\pi$ interactions, those are expected to be more important for $R = C_6H_5$ (Id) than for $R = CH_3$, (Ia). As can be seen from Table I, the relative increase in intensity is larger going from IIf to Id ($R = C_6H_5$) than going from IIe to Ia ($R = CH_3$), which is in accord with increased resonance interactions between mercury and the C≡C triple bond in Id as compared with the case for Ia. Furthermore, this also supports the view that, in fact, for bis(alkynyl)mercury(II) compounds I such d$\pi$–p$\pi$ interactions are of importance. Otherwise no such differences in increase in intensity between the pairs Ia/IIe and Id/IIf should be observed.

Another hint to interactions of this type is the fact that the $A$ value for If (R = Cl) is larger than for Ig (R = Br). The increase in the $A$ values for the compounds If,g as compared with those for Ia,B should also arise from increased d$\pi$–p$\pi$ interactions between mercury and the ethyne unit but may be partly attributed to resonance interactions between the halogen

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lone-pair electrons and the C≡C triple bond.

Compound Ie is an individual case due to the resonance effects of the para-methoxy group.

**Comparison of IR Data with NMR Results.**[2] It is remarkable that the average nuclear shielding of $^{13}C$ is not affected by these d$\pi$–p$\pi$ interactions: the $^{13}C$ resonance of the $\beta$-carbon atoms in the fragment –Hg—$C^{\alpha}$≡$C^{\beta}$– and that of the para-carbon atoms in the phenyl groups linked to the ethyne unit are practically the same in compounds of type II and I. It is particularly noteworthy that the $^{13}C$ resonances of the ipso- and of the para-carbon atoms in compounds Id and IIf are almost identical with those of phenylethyne itself, and the same applies to compound Ie and (*p*-methoxyphenyl)ethyne. In contrast, we observed appreciable effects upon the shielding of these carbon atoms in the square-planar compounds *trans*-$[(PR_3)_2M(C{\equiv}CC_6H_5)_2]$ (M = Ni, Pd, Pt), consistent with d$\pi$–p$\pi$ interactions.[13] Therefore, it appears that $^{13}C$ NMR spectroscopy, in the case of the alkynylmercury compounds, is not a sufficently sensitive probe.

Although the stretching band intensities present clear evidence for d$\pi$–p$\pi$ interaction between the 5d mercury orbitals and the ethyne unit, at least in case of compounds **I**, the failure of $^{13}C$ NMR to corroborate this leads to the conclusion that this interaction must be very weak. Since UPS has proved to be a sensitive tool in this context,[5] the comparison of UP spectra for compounds II and III with those for I should substantiate the results from the IR intensity measurements.

**UP Spectra.** The UP spectra for compounds IIa–d, IIIa,b, and Id,g are shown in Figures 1–7, respectively, and the ionization energies are listed in Table II. They are reported with two decimals and an accuracy of 0.05 eV whenever the corresponding bands are narrow and with one decimal when the bands are broad and without well-defined maxima.

A possible involvement of the 5d mercury orbitals in bonding should be revealed by the presence of up to five separate components in the UP spectrum due to a ligand field perturbation added to the spin–orbit coupling (always present as the main effect in 5d mercury orbitals) and especially by a considerable splitting between the Δ (nonbonding) and the Π components. In particular, one expects stabilization of the Π states with respect to the Δ and Σ ones as already observed in other cases.[5,14]

**RHgC≡CH (IIa–d).** As a starting point we discuss possibly the simplest cases of d$\pi$–p$\pi$ interaction, that is those of $CH_3HgC{\equiv}CH$ (IIa) and $C_2H_5HgC{\equiv}CH$ (IIb), whose electronic structures can be viewed as resulting from two partial $\pi$ systems (one belonging to Hg and the other one to the C≡C triple bond). Consistent with the sp hybridization of mercury, the CHgC≡CH skeleton is assumed to be linear in these molecules.

As is evident from Figures 1 and 2, in the He II spectra only three distinct d bands can be detected and just a slight stabilization of the $\pi^{-1}$ states occurs in these cases, not giving rise to five separate components. In agreement with the greater electron-withdrawing ability of the ethynyl group with respect to alkyl groups, the electron density on mercury seems to be lower than in $(CH_3)_2Hg$ and $(C_2H_5)_2Hg$, as judged from the IE value of the nonbonding Δ components of 5d ionization in IIa,b, $(CH_3)_2Hg$, and $(C_2H_5)_2Hg$.[15] The less intense bands falling in the same spectral region (ca. 17 eV) arise from $\sigma$-type ionizations of the organyl moieties (see Table II).

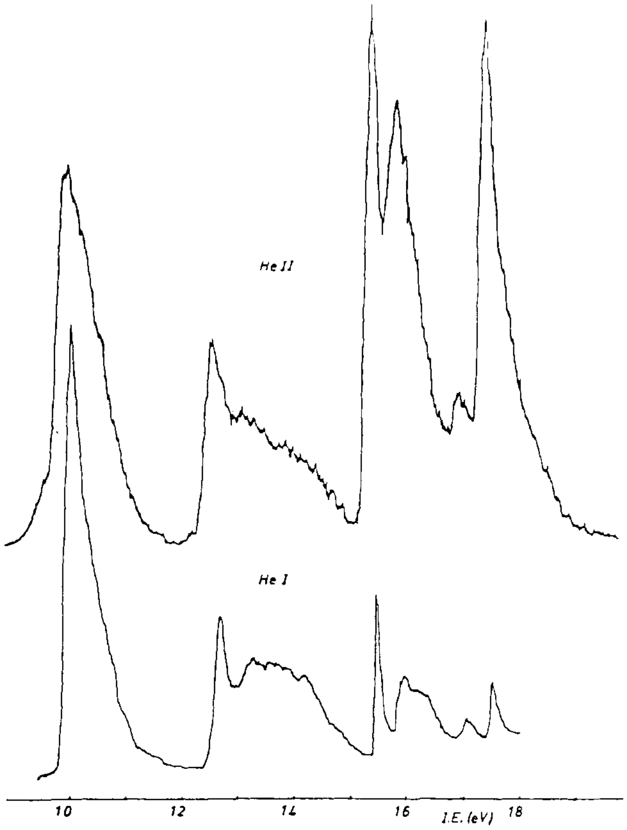

**Figure 1.** Gas-phase UP spectra of $CH_3HgC{\equiv}CH$ (IIa).

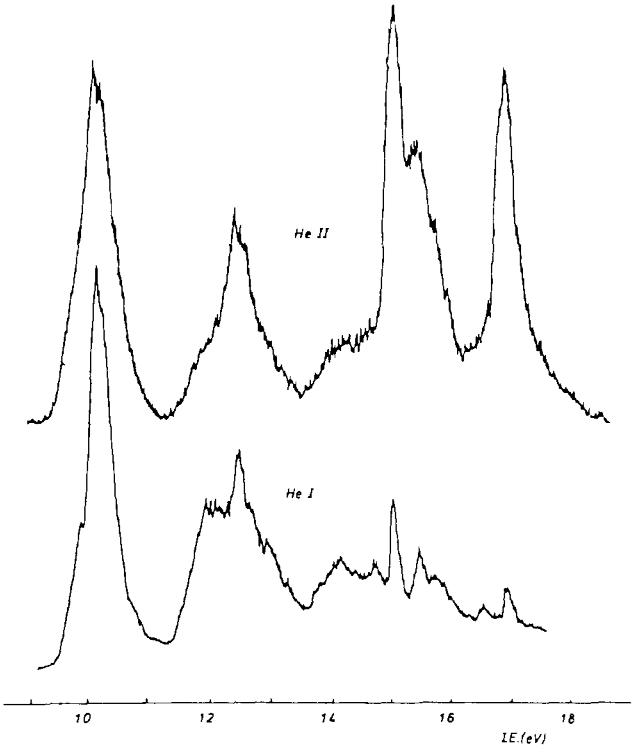

**Figure 2.** Gas-phase UP spectra of $C_2H_5HgC{\equiv}CH$ (IIb).

The $\pi$ orbitals of the acetylenic triple bond are degenerate in IIa, transforming as an irreducible representation in the $C_{3v}$ point group, to which the molecule belongs; their ionizations are therefore expected to give rise to only one double band. In fact, the low-energy region of the spectrum shows a band peaked at 10.05 eV, which clearly accounts for such an ionization ($\pi^{-1}$ band in propyne falls at 10.37 eV[16]), the shift to

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**Table II.** Ionization Energies Measured by UPS for Some Alkynylmercury(II) Compounds

| compd | sym | IE, eV | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\pi_{C\equiv C}$ + $\sigma_{Hg-C}$ | | | $\sigma_{Hg-C}$ | $\sigma_{C-H}$, $\sigma_{C-C}$ | $^2\Delta_{5/2}$ | $^2\Sigma_{1/2}$ + $^2\Pi_{3/2}$ | | $\sigma_{C\equiv CH}$ | | $^2\Delta_{3/2}$ + $^2\Pi_{1/2}$ | | |
| $CH_3HgC\equiv CH$ (IIa) | $C_{3v}$ | 10.05 (e + $a_1$) | | | 12.63 ($a_1$) | 13.8 | 15.44 | 15.86 | | 16.98 | | 17.42 | | |
| $C_2H_5HgC\equiv CH$ (IIb) | $C_{3v}$ | (9.79) 10.06 | | | 12.55 | 12.3, 14.3 | 15.26 | 15.73 | | 16.84 | | 17.23 | | |
| | | $\pi_{C\equiv C}$ + $\pi_{C=C}$ + $\sigma_{Hg-C}$ | | | $\sigma_{Hg-C}$ | $\sigma_{C-H}$, $\sigma_{C-C}$ | $^2\Delta_{5/2}$ | $^2\Sigma_{1/2}$ + $^2\Pi_{3/2}$ | | $\sigma_{C\equiv CH}$ | | $^2\Delta_{3/2}$ + $^2\Pi_{1/2}$ | | |
| $CH_2=CHHgC\equiv CH$ (IIc) | $C_s$ | 10.42 (a' + a'' + a' + a'') | | | 12.72 (a') | 13.6, 14.8 | 15.44 | (15.72) (16.18) | | 16.91 | | 17.37 | | |
| | | $\pi_{Ph}$ | $\pi_{C=C}$ | $\sigma_{C-H}$, $\sigma_{C-C}$ | $\sigma_{Hg-C}$ | | $^2\Delta_{5/2}(Hg)$[a] | $^2\Delta_{5/2}$ | $^2\Sigma_{1/2}$ | $^2\Pi_{3/2}$ | $^2\Delta_{3/2}(Hg)$[a] | $\sigma_{C\equiv CH}$ | $^2\Delta_{3/2}$ | $^2\Pi_{1/2}$ |
| $C_6H_5HgC\equiv CH$ (IId) | $C_{2v}$ | 9.13, 9.24 ($b_2$ + $a_2$) | 10.30, 10.34 ($b_1$ + $b_2$) | 11.9 | 12.58 ($a_1$) | | 14.84 | 15.30 | 15.53 | 15.99 | 16.71 | 17.04 | 17.18 | 17.88 |
| | | $\pi_{C\equiv C}$ | $\sigma_{Hg-C}$ | $\sigma_{Hg-C}$ | $\sigma_{Hg-C}$ | $\sigma_{Hg-C}$, $\sigma_{C-H}$, $\sigma_{C-C}$[b] | $^2\Delta_{5/2}$ | $^2\Sigma_{1/2}$ + $^2\Pi_{3/2}$ | | | | $^2\Delta_{3/2}$ + $^2\Pi_{1/2}$ | | |
| $CH_3HgC\equiv CHgCH_3$ (IIIa) | $D_{\infty h}$ | 9.32 ($\pi_u$) | 9.82 ($\sigma_u^+$) | 10.52 ($\sigma_g^+$) | 12.04 ($\sigma_u^-$) | 13.5, 13.8, 14.4 | 15.07 | 15.59 (16.08) | | | | 17.04 | | |
| | | $\pi_{C\equiv C}$ | | $\sigma_{Hg-C}$ | | $\sigma_{Hg-C}$, $\sigma_{C-H}$, $\sigma_{C-C}$ | $^2\Delta_{5/2}$ | $^2\Sigma_{1/2}$ + $^2\Pi_{3/2}$ | | | | $^2\Delta_{3/2}$ + $^2\Pi_{1/2}$ | | |
| $C_2H_5HgC\equiv CHgC_2H_5$ (IIIb) | $D_{\infty h}$ | 9.23 ($\pi_u$) | | 9.87 ($\sigma_u^+$) | | 11.7, 12.6, 14.1 | 14.88 | 15.30 | | | | 16.91 | | |
| | | $\pi_{Ph}$ | $\pi_{Ph}$ + $\pi_{hC\equiv C}$ | $\pi_{vC\equiv C}$ | $\pi_{hC\equiv C}$ + $\pi_{vC\equiv C}$ | $\sigma_{Hg-C}$, $\sigma_{C-H}$, $\sigma_{C-C}$ | $^2\Delta_{5/2}(Hg)$[a] | $^2\Delta_{5/2}$ | $^2\Sigma_{1/2}$ | $^2\Delta_{3/2}(Hg)$[a] | $^2\Pi_{3/2}$ | $^2\Delta_{3/2}$ | | $^3\Pi_{1/2}$[b] |
| $C_6H_5C\equiv CHgC\equiv CC_6H_5$ (Id) | $D_{2h}$ | 8.40 ($b_{2g}$), 9.67 ($b_{1u}$) | 9.51 ($b_{3g}$ + $a_u$ + $b_{1g}$) | 10.01 ($b_{2g}$) | 10.66 ($b_{2u}$ + $b_{1u}$) | 12.1, 14.4 | 14.84 | 15.30 | 15.53 | 16.71 | 17.04 | 17.23 | | 19.21 |

[a] Atomic mercury impurity due to partial decomposition. [b] For an alternative assignment, see text.

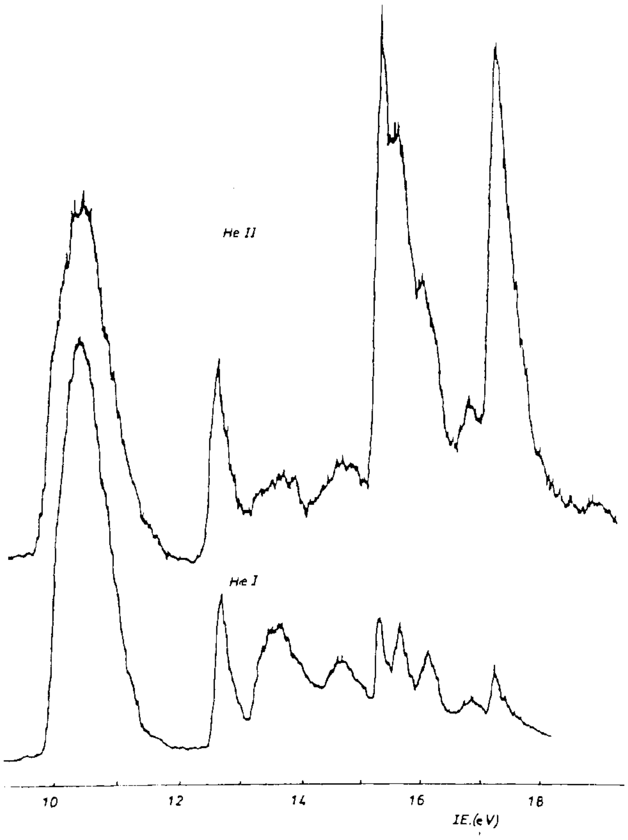

**Figure 3.** Gas-phase UP spectra of $CH_2=CHHgC\equiv CH$ (IIc).

lower IE in our compound being due to the higher electron-releasing power of the $CH_3Hg$ group, with respect to $CH_3$, besides the $\pi$ destabilization by interaction with the d metal orbitals. This band is actually too broad to be related just to the ionizations from the degenerate $\pi_{C\equiv C}$ orbitals; furthermore, in the same region one also expects the first $\sigma_{Hg-C}^{-1}$ ionization by analogy with other cases (e.g., 9.3 eV in $Hg(CH_3)_2$).[15]

It is likely that this ionization corresponds to the high-energy side of the first band, while the second $\sigma^{-1}_{Hg-C}$ ionization is related to the following band at 12.63 eV, as confirmed by its increase in intensity switching from He I to He II ionizing radiation, with the higher photoionization cross section of mercury orbitals in He II relative to the other orbitals.[15]

The energy difference between the two $\sigma^{-1}_{Hg-C}$ ionizations in this compound is comparable to that one in other compounds in which the mercury–carbon bonds are mainly covalent in character (e.g., $Hg(CH_3)_2$).[15]

The assignment is analogous for the spectra of IIb. In the low-energy side of the first band a shoulder is observed, which is attributed to the first $\sigma_{Hg-C}^{-1}$ ionization, shifted to lower IE with respect to the corresponding band in IIa due to the presence of the more electron-releasing ethyl in place of the methyl group.

A more extended interaction between the $\pi$ systems could be expected in $CH_2=CHHgC\equiv CH$ (IIc) in which mercury is bonded to two unsaturated carbon atoms. Actually, the d region of the He II spectrum of this molecule (see Figure 3 and Table II) is not much different from the previously discussed cases: only two intense bands are shown, the first one with two shoulders in the high-energy side, again indicating a weak stabilization of the IId$^{-1}$ states by conjugation with the $\pi$ systems of the organyl groups.

Our finding of a weak d$\pi$–p$\pi$ interaction in the series $RHgC\equiv CH$ (with R = $CH_3$, $C_2H_5$, $CH_2=CH$) is in agreement with the observation that the IR intensities for $\nu_{C\equiv C}$ are practically the same, which should not be the case if there would be appreciable $\pi$ back-bonding.

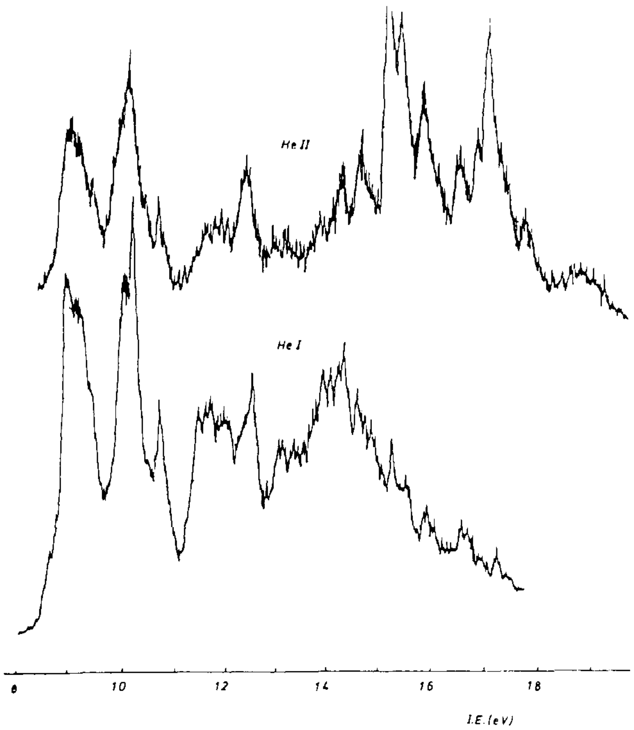

**Figure 4.** Gas-phase UP spectra of $C_6H_5HgC{\equiv}CH$ (IId).

In the spectral region around 10 eV the three $\pi^{-1}$ ionizations, two arising from the triple bond, in principle not degenerate in the $C_s$ point group, and one from the double bond (the corresponding band in ethylene UP spectrum falls at 10.51 eV[17]) are coalesced into one broad band centered at 10.42 eV. It accounts also for the lowest $\sigma_{Hg-C}{}^{-1}$ ionization, the highest one giving rise to the band at 12.72 eV, which clearly increases in relative intensity on passing from He I to He II.

A different behavior is displayed by $C_6H_5HgC{\equiv}CH$ (IId) (molecular symmetry $C_{2v}$). In fact, the region between 14 and 18 eV in the He II spectrum of IId (see Figure 4 and Table II) is richer in bands than in the preceding cases and strictly resembles the spectral features of compounds in which a significant mixing of d mercury orbitals with $\pi$ systems of the ligands occurs, such as Ia,c,f,[5] mercury dicyanide,[14] etc. The two weak bands at 14.84 and 16.71 eV are atomic mercury impurity structures (due to partial decomposition); the band, also weak, at 17.04 eV, detected in all the compounds of the series, is related to a $\sigma^{-1}$ ionization of the ethynyl groups. The five sharp bands at 15.30, 15.53, 15.99, 17.18, and 17.88 eV are the resolved components of the $d^{-1}$ ionizations split by combined spin–orbit and ligand field effects; by analogy with the previously mentioned cases the sequence of state energies should be

$$^2\Delta_{5/2} > {}^2\Sigma_{1/2} > {}^2\Pi_{3/2} > {}^2\Delta_{3/2} > {}^2\Pi_{1/2}$$

The assignment of the peaks at 15.99 and 17.88 eV to the ionization of the $\pi$ components of the d set is supported by the observation that similar bands are absent in the corresponding region of the spectrum of diphenylmercury;[5] this rules out the possibility that these ionizations are associated with phenyl group orbitals.

The $\Delta$–$\Pi$ splitting (0.7 eV) is smaller than in dipropynylmercury (Ia) (1.1 eV[5]); the participation of the metal d orbitals of $\pi$ symmetry to the bonding with the organic moieties is therefore less important in IId, while being more important than in the other members of the series $RHgC{\equiv}CH$.

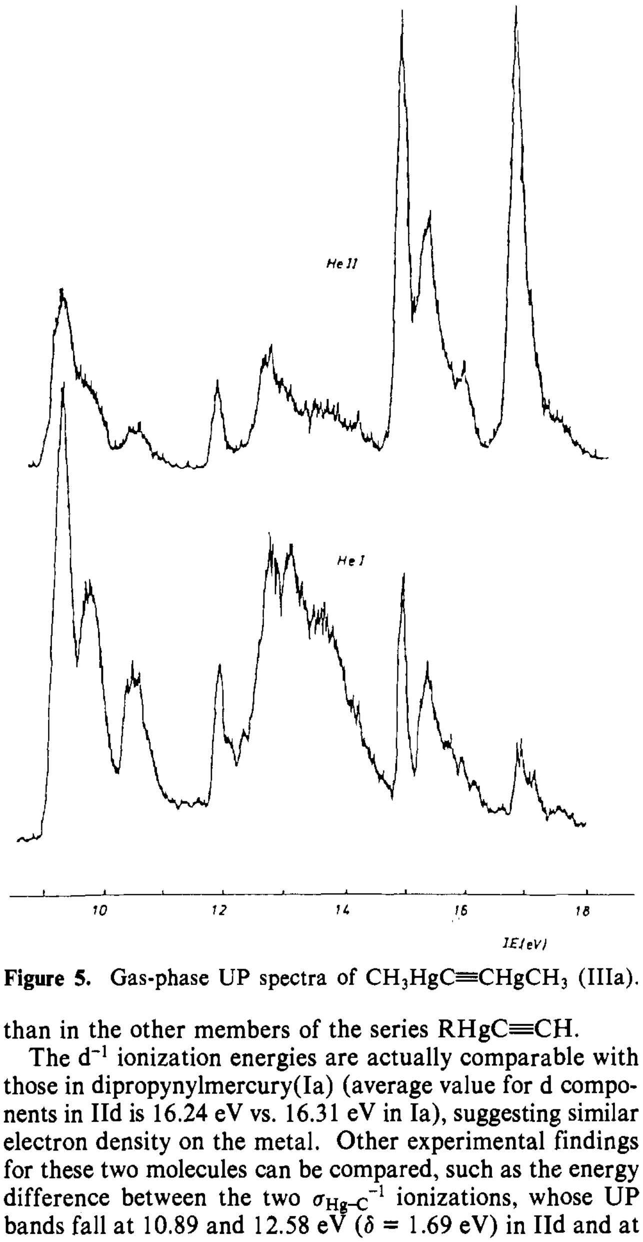

**Figure 5.** Gas-phase UP spectra of $CH_3HgC{\equiv}CHgCH_3$ (IIIa).

The $d^{-1}$ ionization energies are actually comparable with those in dipropynylmercury(Ia) (average value for d components in IId is 16.24 eV vs. 16.31 eV in Ia), suggesting similar electron density on the metal. Other experimental findings for these two molecules can be compared, such as the energy difference between the two $\sigma_{Hg-C}{}^{-1}$ ionizations, whose UP bands fall at 10.89 and 12.58 eV ($\delta$ = 1.69 eV) in IId and at 11.88 and 12.76 eV ($\delta$ = 0.88 eV) in $(CH_3C{\equiv}C)_2Hg$(Ia), indicating a lower degree of interaction between the $\sigma_{Hg-C}$ orbitals in the latter compound.

The region between 9 and 10.5 eV yields significant information regarding the ionizations of the $\pi$ orbitals of the organyl groups and their interactions. In $C_{2v}$ symmetry the three filled $\pi$ levels of the phenyl ring ($e_{1g}$ and $a_{2u}$ in benzene) transform as $A_2 + B_2$ ($e_{1g}$) and $B_2$ ($a_{2u}$), while the ethynyl $\pi$ orbitals transform as $B_1 + B_2$. No Degenerate $\pi$ states are therefore expected in the ground state. The spectra are consistent with these considerations showing two doublets, the first one with peaks at 9.13 and 9.24 eV, the second one with peaks at 10.20 and 10.34 eV; the former is clearly related to ionizations of the phenyl orbitals, while the latter accounts for the two $\pi^{-1}$ ionizations of the ethynyl group.

The sharp bands at 10.89 and 12.58 eV are related to the two $\sigma_{Hg-C}$ bonding orbitals; their ionization energies and splitting are in line with those observed in the other members of the series.

**$RHgC{\equiv}CHgR$ (IIIa,b).** For the molecule $CH_3HgC{\equiv}C$-$HgCH_3$ (IIIa) in our experimental conditions we assume an average $D_{\infty h}$ symmetry, i.e. a quasi-free rotation along the central linear skeleton.

The contribution of the d orbitals of the two mercury atoms to the bonding in this molecule should be not very different

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(17) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1970.

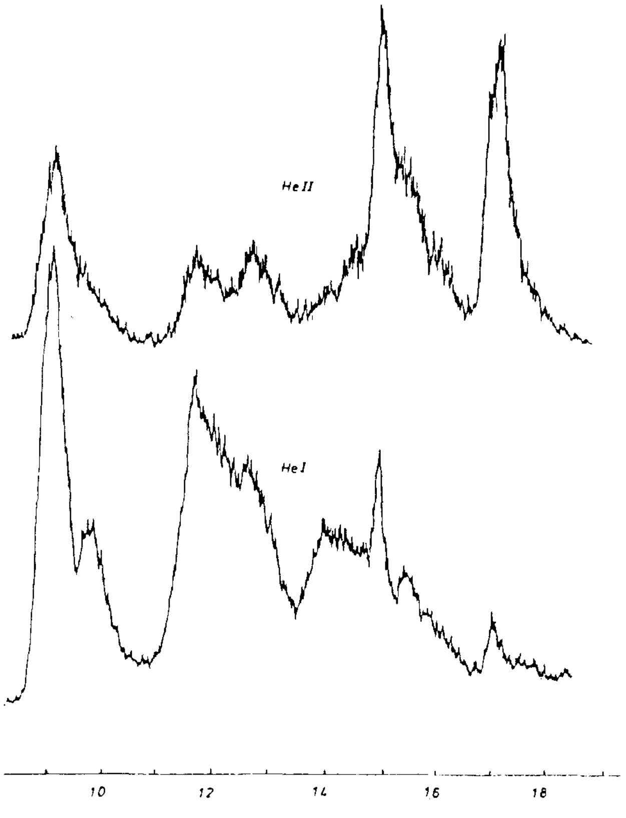

**Figure 6.** Gas-phase UP spectra of $C_2H_5HgC{\equiv}CHgC_2H_5$ (IIIb).

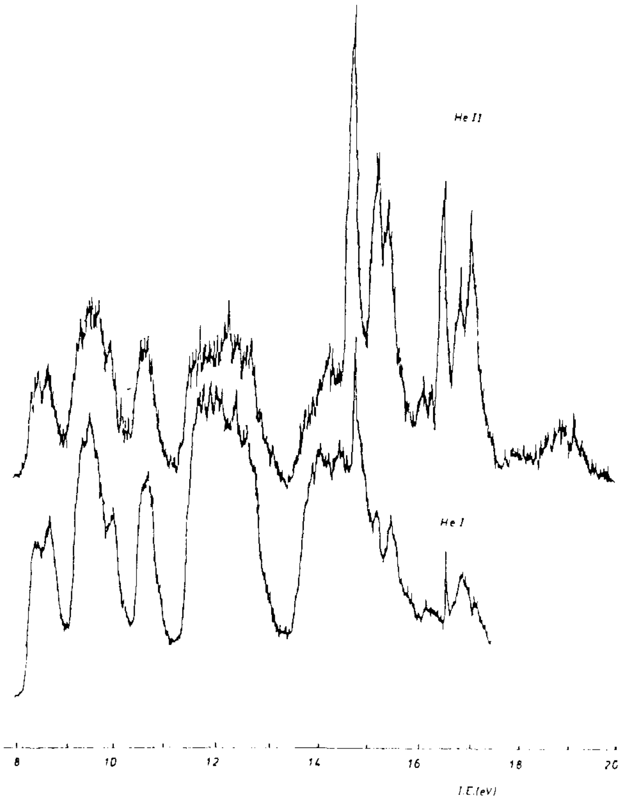

**Figure 7.** Gas-phase UP spectra of $Hg(C{\equiv}CC_6H_5)_2$ (Id).

from that one in $CH_3HgC{\equiv}CH$ (IIa); in fact, the spectral regions of the $d^{-1}$ ionizations are similar for the two compounds (for IIIa see Figure 5 and Table II) suggesting analogous assignments.

As for the ionization of the two $\pi$-bonding orbitals of the triple bond, no splitting of the corresponding photoelectron band in the spectrum of IIIa is expected since they are degenerate in the $D_{\infty h}$ average symmetry (actually they are degenerate in all the possible trigonal symmetries as $D_{3h}$ or $D_{3d}$). A shift of this band to lower IE is observed with respect to IIa (9.32 vs. 10.05 eV) due to the combined effect of two strongly electron-releasing $CH_3Hg$ groups.

A marked difference between the spectra of IIa and IIIa is evident in the region of the $\sigma_{Hg-C}{}^{-1}$ ionizations: three bands associated with such ionizations are present in the spectrum of the bimetalated ethyne in accord with the nondegeneracy of the four mercury–carbon $\sigma$-bonding orbitals in the $D_{\infty h}$ point group (the fourth ionization contributes to the broad band envelope between 12.5 and 14.5 eV). In terms of localized orbitals, the bands at 9.82 and 10.52 eV may arise from the ionization of two levels with predominant $\sigma_{Hg-CH_3}$ character (see 9.3 and 11.6 eV for the analogous bands in $(CH_3)_2Hg$;[15] the smaller splitting in IIIa is consistent with the larger distance of the two $CH_3Hg$ groups). The band at 12.04 eV is then associated with the highest $\sigma_{Hg-C}$ orbital. However, the intensity ratio between the two bands at 9.82 and 10.52 eV is not well-defined, due to the overlapping of the band at 9.82 eV with the first band at 9.32 eV. Therefore, an alternative assignment can be considered, relating the band at 9.82 eV with the ionizations of two $\sigma_{Hg-CH_3}$ levels, quasi-degenerate because of the large distance between the two $HgCH_3$ moieties. The bands at 10.52 and 12.04 eV can be assigned as the ionizations of the two $\sigma_{Hg-C}$ with a larger mercury–acetylenic carbon bond character. According to this, the interaction between the four $\sigma_{Hg-C}$ would be slightly weaker.

Anyway, this description is in both cases a simple model since a mixing of all the orbitals contributing to the bonds should be, in principle, taken into account, although it is likely to occur to a small extent.

The assignment of the spectrum of $C_2H_5HgC{\equiv}CHgC_2H_5$ (IIIb) is analogous (Figure 6).

**$(C_6H_5C{\equiv}C)_2Hg$ (Id).** In the following discussion we will assume for this molecule a planar structure, implying $D_{2h}$ symmetry. In our previous work on mercury derivatives[5] dealing with the compounds Ia,c,f (R = $CH_3$, $t$-$C_4H_9$, Cl) we observed a strong stabilization of the d$\pi$ mercury levels, yielding evidence for interaction with the p$\pi$ orbitals of the ethynyl groups. We expected therefore a similar behavior of the molecule with R = $C_6H_5$ (Id). Actually, the assignment of the UP spectrum of this compound is unfortunately not straightforward, because a severe though partial decomposition causes the appearance of two spurious bands in the d region (at 14.84 and 16.71 eV) due to atomic mercury ionizations (see Figure 7 and Table II). Of the other three bands present in the same region, three, at 15.30, 15.53, and 17.23 eV, are related to 5d orbitals of mercury in the molecule, those at 16.26 and 19.21 eV arise from ionization of $\sigma$-type electrons, while the origin of the band at 17.03 eV is less clear. It could be attributed to a $\sigma^{-1}$ ionization of phenyl-based orbitals analogously to the band at 17.04 eV in $C_6H_5HgC{\equiv}CH$ (IId). Alternatively one could assign this band to the ${}^2\Pi_{3/2}$ ionization, assuming that the broad band at 19.21 eV accounts also for the ${}^2\Pi_{1/2}$ ionization. The former hypothesis implies no significant d$\pi$–p$\pi$ interaction in this compound, at variance with all the other investigated diethyne derivatives, while the latter one suggests an important contribution of the mercury orbitals to the covalent bonding with a separation between the $\Delta$ and $\Pi$ components of 1.7 eV, larger than in all the other members of the series (1.1 eV for Ia (R = $CH_3$), 1.0 eV for Ie (R = $t$-$C_4H_9$), 1.4 eV for If (R = Cl)[5]). This result is actually in agreement with IR intensity data as already discussed.

As for the first spectral region (8–11 eV), the assignment can be aided by a comparison with the spectrum of the related molecule diphenylbutadiyne,[18,19] which shows in the same IE region five bands at 8.23, 8.55, 8.87, 9.48, and 10.48 eV. The second band is related[18] to an ionization from the antisymmetric combination of the two in-plane levels of the triple bonds ($\pi_h^-$) (the symmetric one is higher in IE and falls beyond 11 eV). The first, third, and fourth bands arise from ionizations of orbitals with a large contribution from the levels of the phenyl groups. The bands at 8.23 and 8.87 eV are precisely related to the ionizations of the $\pi$-phenyl orbitals ($b_{2g}$ and $b_{1u}$ in $D_{2h}$ point group) that interact with the $\pi$-out-of-plane orbitals of the acetylenic groups, being therefore destabilized. The broad band at 9.48 eV (with a shoulder at 9.72 eV) accounts for the ionizations of the $a_u$ and $b_{3g}$ levels that do not have the symmetry to mix with $\pi$-out-of-plane acetylenic orbitals. The fifth band at 10.48 eV arises from the ionization of a $b_{2g}$ orbital with mainly vertical $\pi_{C\equiv C}^-$ character, stabilized by interaction with the phenyl ring (the second vertical $\pi_{C\equiv C}^+$ level, of $b_{1u}$ symmetry, is lower in orbital energy, and the related band falls beyond 11 eV).

In the spectrum of Id there are two bands at 8.40 and 8.67 eV that can be related to the bands at 8.23 and 8.87 eV in the spectrum of diphenylbutadiyne, can account for the ionizations of the first two orbitals localized on the phenyl groups, and can be lowered in IE by mixing with the $\pi$-out-of-plane levels of the triple bonds; the third broad band in the spectrum of Id, at 9.51 eV, is likely to be associated with at least three orbitals and then is related to the two $\pi$ levels of the phenyl groups that cannot interact with the acetylenic subunits plus the antisymmetric combination of the $\pi$-in-plane levels of the triple bonds. The fourth and fifth band, at 10.01 and 10.66 eV, account for levels mainly localized on the acetylenic systems; namely, the single band at 10.01 eV is associated with the antisymmetric combination of the $\pi$-out-of-plane levels, and the double band at 10.66 eV is related to the two symmetric combinations of in-plane and out-of-plane $\pi$ orbitals. Both out-of-plane combinations have the right symmetry to mix with $\pi$-phenyl levels. The splitting in the spectrum of Id between the symmetric and antisymmetric combination of $\pi$-in-plane acetylenic levels (0.5 eV) is much lower than in diphenylbutadiyne, and the same consideration can be done with respect to the analogous combinations of the $\pi_{C\equiv C}$ out-of-plane (again $\delta \cong 0.5$ eV). This fact can be explained by the presence of the mercury atom between the two acetylenic moieties, splitting them far apart and therefore weakening any interaction between them. In fact the splitting is comparable to that one observed in other compounds of type I. As for the $\sigma_{Hg-C}^{-1}$ ionizations, they are expected to be located under the broad band envelope between 11 and 12.5 eV, together with $\sigma_{C-C}^{-1}$ and $\sigma_{C-H}^{-1}$ ionizations.

**Comparison of UPS Data with NMR Results.**[2] The isotropic nuclear shielding of carbon atoms ($\delta(^{13}C)$) linked to mercury and of mercury itself ($\delta(^{199}Hg)$) is significantly affected by the polarization of the Hg–C bond. This is also true as far as indirect nuclear spin coupling constants ($^1J(^{199}Hg^{13}C)$ or $^1J(^{13}C{\equiv}^{13}C)$) in the fragment HgC≡C– are concerned.[2]

The UPS data obtained in this work are in good agreement with many NMR results: the $\pi^{-1}$ organyl IE are lower with respect to simple alkynes as a result of the combined effect of the rather high electron-releasing power of mercury and of the $\pi$ destabilization due to d$\pi$–p$\pi$ interactions. This is in accord with the decrease in shielding of the alkynyl carbon atoms and with the reduced magnitude of the coupling constants $J(^{13}C{\equiv}^{13}C)$. The trend in the $\pi^{-1}$ organyl ionizations is paralleled by the various $\sigma_{Hg-C}^{-1}$ ionizations. Thus, we observe a rather large coupling constant $^1J(^{199}Hg^{13}CH_3)$ (1145 Hz) in IIa ($\sigma_{Hg-CH_3}^{-1}$ 10.05 eV) and a smaller one in $(CH_3)_2Hg$ (692 Hz) ($\sigma_{Hg-CH_3}^{-1}$ 9.3 eV).[15] Similarly, a larger (by ca. 500 Hz) coupling constant $^1J(^{199}Hg^{13}C)$ is found in IIa ($\sigma_{Hg-C}^{-1}$ 12.63 eV) than in compounds of type III ($\sigma_{Hg-C}^{-1}$(IIIa) 10.52, 12.04 eV).

Analogous behavior is displayed by the $\delta(^{13}C)$ values of carbon atoms linked to mercury. A deshielding of these carbon atoms is connected with lower ionization energies of $\sigma_{Hg-C}^{-1}$.

Because of a number of counteracting influences upon the nuclear shielding of mercury, a direct relationship with the IE values is much more difficult to establish. However, within a series of bis(alkynyl)mercury(II) compounds (I), effects upon $\delta(^{199}Hg)$ other than changes in the electron density at mercury brought upon by various substituents at the C≡C triple bonds may be neglected in a first approximation. The IE values of $\sigma_{Hg-C}^{-1}$ ionizations are available for Ia,f, showing the expected increase in the order Ia < If that would account for a decrease in the shielding of mercury in the same order. In contrast, an increase in the shielding of mercury is observed in the series

| | | Ic | < | Id | < | Ia | < | Ig | < | If |
|---|---|---|---|---|---|---|---|---|---|---|
| $\delta(^{199}Hg)$ | $CDCl_3$ | −837 | | −864 | | −873 | | insol | | −975 |
| | $Me_2SO$-$d_6$ | | | −930 | | | | −1040 | | −1041 |

Interestingly, there is a roughly linear relationship between the $\delta(^{199}Hg)$ values and the IE values of most of the 5d$^{-1}$ ionizations, in particular of those of the nonbonding $^2\Delta_{5/2}$, $^2\Delta_{3/2}$, and of the $^2\Sigma_{1/2}$ components. Therefore, it appears that the mercury shielding is mainly affected by the probability of magnetic field induced mixing of electronic ground and excited states. This probability is reduced in the presence of electronegative ligands attached to mercury, increasing the IE values not only of $\sigma_{Hg-X}^{-1}$ ionization but also of d$^{-1}$ ionizations.

## Conclusions

Both IR intensity measurements and UP spectra provide evidence for significant d$\pi$–p$\pi$ interaction between mercury 5d orbitals and the C≡C triple bond in all the diethyne derivatives of the series I (the case of $(C_6H_5C{\equiv}C)_2Hg$ (Id) is unclear mainly due to decomposition effects) and in $C_6H_5HgC{\equiv}CH$ (IId). The same does not occur in the other compounds of the series II, R′HgC≡CR (R′ = alkyl, alkenyl; R = H). This is at variance with the case of the cyanide-mercury derivatives. In fact, such differences were not observed between $CH_3HgC{\equiv}N$ and $(C{\equiv}N)_2Hg$ studied by Borrough et al.[14] The main indication given by the data discussed above is therefore that one of a specific role played by the two partial $\pi$ systems of the ethyne units bonded to mercury in promoting the d$\pi$–p$\pi$ interaction.

It is appropriate to point out that such extent is probably very small since the $^{13}C$ NMR spectroscopy, otherwise very sensitive to the presence of this type of interaction, failed to detect it. This shows that the application of a single method to these problems may tempt to overestimate the effects.

Future work will include XPS studies of mercury compounds of the types I–III, and from this it is hoped that a more quantitative picture will emerge.[20]

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**Registry No.** Ia, 64705-15-3; Ib, 69261-09-2; Ic, 73838-84-3; Id, 6077-10-7; Ie, 82490-23-1; If, 64771-59-1; Ig, 88496-74-6; IIa, 1189-66-8; IIb, 82490-17-3; IIc, 82490-27-5; IId, 64705-13-1; IIe, 72250-66-9; IIf, 4342-28-3; IIg, 1017-74-9; IIIa, 82490-19-5; IIIb, 82490-20-8; IIIc, 82490-22-0.

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