Furyl- and Thienyl-mercury Derivatives studied by Means of Ultraviolet Photoelectron Spectroscopy. Evidence for the Participation in Bonding of the Vacant $6p_\pi$ Orbitals of Mercury in Bis-2-furyl- and Bis-2-thienyl-mercury

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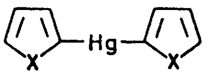
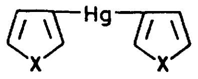
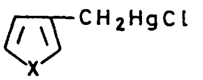
The ultraviolet photoelectron spectra (UPS) of several furyl- and thienyl-mercury derivatives have been recorded. The analysis of the furan-like π_2 and π_3 molecular orbitals (MOs) indicated that in bis-2-furylmercury there is a small charge-transfer interaction between the filled ring π orbitals and the empty $6p_\pi$ mercury atomic orbitals, that this interaction is larger than in the corresponding bis-3-furyl derivative, and, for both compounds, larger than the interaction with the $5d$ atomic orbitals of mercury. This conclusion is supported by X-ray photoelectron spectral (XPS) data and iterative extended Hückel MO (IEHMO) calculations, and applies equally well to the corresponding thiophen derivatives. The electron-releasing inductive effect of mercury, in these compounds, turned out to be similar to or slightly larger than that of a methyl group. The CH_2HgCl substituent exerts a hyperconjugative destabilization on the ring π_2 and π_3 MOs *via* the C–Hg σ bond. This effect is, however, smaller than that exerted on benzene and ethylene. The HgCl substituent was found to be slightly electron-withdrawing.

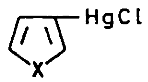
SEVERAL mercury(II) derivatives with a variety of ligands such as alkyl groups, halogens, or pseudohalogens have been analysed by means of ultraviolet photoelectron spectroscopy (UPS).[1-5] From these studies information on charge distribution and chemical bonding in mercury(II) derivatives has been obtained. In particular, from the spin–orbit splitting, similar to that of atomic mercury, it has been concluded that the mercury $5d$ orbitals are very much atom-like [1] even if, in the presence of ligands which are supposed to be good π-acceptors, they are involved in covalent bonding.[2] The existence of some p–π interaction between the mercury $6p$ orbitals and the halogens has been inferred [1] from the analysis of the spin–orbit splitting of the mainly halogen bands in the spectra of $HgBr_2$ and HgI_2. The participation of mercury $5d$ and $6p$ orbitals in bonding has also been indicated by some extended Hückel calculations on $Hg(CF_3)X$ ($X = I, N_3$, NCO, and NO_3).[3]

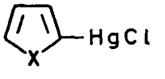
In the present paper the UPS of the isomers of bisfuryl- and bis-thienyl-mercury are analysed to obtain direct evidence for the participation in bonding of the $6p_\pi$ and/or $5d_\pi$ orbitals of mercury from the relative shifts of the π_3 and π_2 MOs of the aromatic rings.











X = O,S

The effects of the HgCl and CH_2HgCl substituents on the π_3 and π_2 orbitals of furan and thiophen have also been analysed and compared with those observed in allyl- and benzyl-mercury chlorides.[6,7] Theoretical calculations at the IEHMO level were performed on the furylmercury derivatives. In addition an XPS analysis was carried out on bis-2- and bis-3-furylmercury in order to have an independent observable to check the conclusions reached.

EXPERIMENTAL AND CALCULATIONS

The UPS were obtained with a Perkin-Elmer photoelectron spectrometer using the He(I) resonance line at 584 Å (21.22 eV) as ionizing radiation. The spectra were calibrated against Ar and Xe lines. The reproducibility of the ionization energies (IEs) was ±0.05 eV or better.

At variance with the spectra of the mercury derivatives, the bands in the spectra of the methyl derivatives of furan and thiophen often showed resolved vibrational fine structure. The IE values quoted in Table 2 refer to the maxima of the unresolved bands, which are considered to correspond to the vertical values, or to the most intense vibrational component of the resolved bands, which is the second component of the stronger vibrational progression for the methyl derivatives.

Partial decomposition of some of the mercury derivatives occurred during the analyses, as shown by the presence in the spectra of the sharp $5d$ lines of the free metal. In the case of bis-3-thienylmercury the relative intensity of the low-IE bands changes during the recording of the first spectrum, and then a reproducible spectrum is obtained. The possibility cannot be excluded that the reproducible spectrum contains signals from a decomposition product.

The XPS spectra of bis-2- and bis-3-furylmercury were recorded by means of an AEI ES 200 B photoelectron spectrometer using Al-$K_{\alpha 1,2}$ as the ionizing radiation. The samples were sublimed *in vacuo* and condensed onto a cooled silver surface before and during the measurements. The $Ag_{3d5/2}$ line (binding energy taken as 367.9 eV) from this surface was obtained, together with the signals from the sample, and used for calibration purposes. When calibrating, very thin layers of sample were used so that the signal

TABLE 1

VOIP (eV) for isoelectronic mercury(I) series

Configuration	Electron	*A*	*B*	*C*
(Xe)$4f^{14}5d^{10}6s^2$	$6s$	0.84	9.08	10.45
(Xe)$4f^{14}5d^{10}6s6p$	$6p$	0.88	6.95	4.88
(Xe)$4f^{14}5d^{10}6s^2$	$5d$	−0.29	14.57	15.58

from the silver was in all cases much more intense than that of the sample to minimize charging effects. The reproducibility was of the order of ±0.1 eV for successive sublimations, but the accuracy of the IE values is probably much lower. To have an independent measurement of the shift of the Hg lines from one compound to the other, an internal calibration procedure was also used. A similar XPS analysis on other pairs of compounds was not possible because they showed partial decomposition when sublimed *in vacuo*.

The mercury derivatives were prepared according to standard literature methods (see *e.g.* refs. 8 and 9).

To assist in the analysis of the UPS results we have correlated the measured π-ionization energies with the orbital energies obtained from IEHMO calculations, assuming Koopmans' theorem to hold, the greatest attention to the results of calculations being devoted to the contribution from the Hg AOs to the π MOs.

In the IEHMO calculations [10] the diagonal Hamiltonian matrix elements were approximated as the valence orbital ionization potentials (VOIPs) given by equation (1).

$$H_{ii} = -Aq^2 - Bq - C \qquad (1)$$

The A, B, and C parameters were taken from ref. 11 for all the atoms except mercury, in which case they were obtained, by a least-squares procedure, fitting atomic spectral data [12] for the isoelectronic mercury(I) series up to Bi$^{(\mathrm{IV})}$ and are reported in Table 1. The net charge q on each atom was computed using a Löwdin charge analysis.[13]

The off-diagonal Hamiltonian matrix elements were estimated from the Wolsberg–Helmholz formula [14] [equation (2)].

The overlap matrix elements S_{ij} were evaluated using a Slater basis set with the orbital exponents given by Clementi

$$H_{ij} = K\, S_{ij}\, (H_{ii} + H_{jj})/2 \qquad (2)$$
$$\text{with } K = 1.75$$

and Raimondi,[15] except those for the mercury atom which were taken from ref. 16.

RESULTS AND DISCUSSION

Bis-furyl- and Bis-thienyl-mercury Compounds.—We begin our analysis with the furan derivatives for which more data are available. The conclusions will then be extended, by analogy, to the thiophen derivatives.

The UPS of bis-2- and bis-3-furylmercury are shown in Figure 1, and the IE values are collected in Table 2 together with those of the other compounds examined. It is evident that while bis-3-furylmercury, in the energy region of the furan π_3 and π_2 MOs, shows only two bands, the first of them is split into two components in the case of bis-2-furylmercury. Indeed the π_3 and π_2 orbitals of the aromatic rings should split giving in-phase ($\pi_3{}^+$ and $\pi_2{}^+$) and out-of-phase ($\pi_3{}^-$ and $\pi_2{}^-$) combinations in the presence of conjugative interaction through the $6p_\pi$ and/or $5d_\pi$ mercury orbitals.

In both cases, the in-phase and out-of-phase combinations of the π_3 and π_2 furan orbitals are destabilized with respect to the corresponding MOs of the unsubstituted ring; *i.e.* mercury has an overall electron-releasing effect when bound to furan.

A comparison with the effect on the π MOs of furan exerted by a methyl group could be useful to investigate the nature of the bonding between mercury(II) and aromatic ligands. The effect of an alkyl group on the IE values is well established:[17–19] owing to its inductive and hyperconjugative effects it destabilizes the π orbitals of the substrate to which it is attached more than a

TABLE 2

Experimental and theoretical (IEHMO) π_3 and π_2 IE values (eV) of furyl- and thienyl-mercury derivatives

	Experiment		Theory	
	π_3	π_2	π_3	π_2
Furan [a]	8.89	10.32	11.92	12.29
2-Methylfuran	8.54	10.12	11.58	12.19
2-HgCl-furan	8.96	10.40	$12.09\begin{pmatrix}p\text{: } 0.0100\\ d\text{: } 0.0057\end{pmatrix}$ [b]	$11.54\begin{pmatrix}p\text{: } 0.0015\\ d\text{: } 0.0000\end{pmatrix}$
Bis-2-furyl-Hg	8.39 8.69	10.05	11.37 (d: 0.0053) 11.58 (p: 0.1428)	11.99 (d: 0.0000) 11.99 (p: 0.0012)
3-Methylfuran	8.70	9.94	11.76	12.13
3-HgCl-furan	9.10	10.34	$11.61\begin{pmatrix}p\text{: } 0.0001\\ d\text{: } 0.0050\end{pmatrix}$	$12.05\begin{pmatrix}p\text{: } 0.0484\\ d\text{: } 0.0003\end{pmatrix}$
Bis-3-furyl-Hg	8.70	10.08	11.44 (d: 0.0036) 11.57 (p: 0.0858)	11.89 (d: 0.0009) 11.93 (p: 0.0455)
3-CH$_2$HgCl-furan	8.80	9.91		
Thiophen [a]	8.87	9.50		
2-Methylthiophen	8.59	9.23		
2-HgCl-thiophen	9.05	9.56		
Bis-2-thienyl-Hg	8.47 8.74	9.16		
3-Methylthiophen	8.70	9.15		
3-HgCl-thiophen	9.23	9.59		
Bis-3-thienyl-Hg	8.72	9.12		
3-CH$_2$HgCl-thiophen	8.79	9.25		

[a] From D. W. Turner, A. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, New York, 1970, p. 329. [b] The figures in parentheses are the orbital populations for mercury $5d_\pi$ and $6p_\pi$.

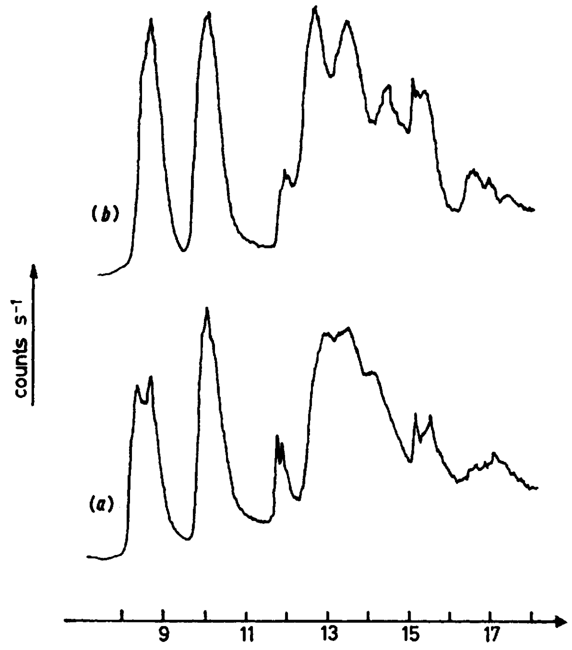
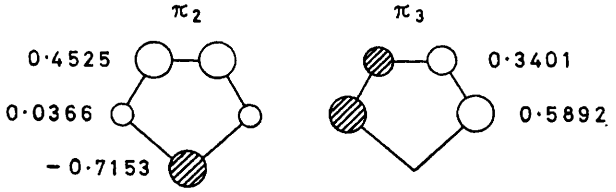


FIGURE 1 Photoelectron spectra of (*a*) bis-2-furylmercury and (*b*) bis-3-furylmercury

hydrogen atom does. The following argument is better understood by keeping in mind the localization properties of the two outermost occupied MOs of π symmetry of furan. Their shapes, as obtained in the IEHMO calculations, are sketched in the Scheme.



SCHEME

Since the wavefunction coefficient of π_2 at C-2 is very low, the substituent effect on this MO is essentially inductive. The IE value related to ionization from the π_2^- and π_2^+ MOs of 2-furylmercury is slightly lower (0.07 eV) than that observed for the corresponding MO in 2-methylfuran, confirming [1] that the inductive effect of mercury is similar to, or slightly larger than, that of a methyl group. On the other hand, π_3 has a large coefficient at C-2 and, therefore, all the conjugative interactions will be maximized. As observed above, the π_3^- and π_3^+ combinations are split, and appear at lower and higher energy than the π_3 MO in 2-methylfuran. By symmetry, π_3^- can be destabilized by interactions with the mercury $5d_\pi$ AOs, while π_3^+ can be stabilized by charge transfer towards the empty $6p_\pi$ orbital of mercury. In any case π_3^- will lie above π_3^+. Furthermore, recalling the $+I$ effect of mercury ($\geqslant +I_{Me}$) and the π_3 IE value of 2-methylfuran, it seems that both interactions are present, but it is likely that the stabilizing effect on π_3^+ is the major factor responsible for the small (0.3 eV) splitting observed.

The calculations reproduce the degeneracy of the π_2^+ and π_2^- MOs as well as the splitting between π_3^+ and π_3^-, and their relative ordering (see Table 2). They indicate also that the splitting essentially derives from a charge transfer from π_3^+ towards the $6p_\pi$ AO of mercury, and that the $5d$ AOs of mercury participate very little in the π_3 and π_2 MOs of both bis-2- and bis-3-furyl derivatives. The wavefunction coefficients of the π_2 and π_3 MOs at C-3 are smaller than that of π_3 at C-2, and therefore the interactions with the mercury AOs will be reduced, preventing the experimental observation of band splitting in the UPS and bis-3-furylmercury. The observed IE values are very similar to those characteristic of 3-methylfuran.

Finally it is to be noted that the area of the second band is, for both compounds, larger than that of the first band. This is at variance with the ratio of 1 : 0.85 found [20] for furan. The intensity of the second band could be augmented by ionization from the σ_{C-Hg-C} MO which occurs at *ca.* 9.5 eV in $HgMe_2$ [1] and which is, according to calculations, the outermost σ MO in the present systems.

In the energy region of the bis-3-thienylmercury spectrum corresponding to the thiophen π_3 and π_2 MOs, two bands are present, the second of which has a shoulder (at 9.6 eV) on the high-IE side, whereas the bis-2-thienylmercury spectrum shows a split first band with two components (Δ 0.27 eV) and the appearance of a new, low-intensity band at 10.0 eV.

On the basis of the preceding arguments regarding the furan derivatives, and the IE values of the π_3 and π_2 MOs of thiophen and methylthiophens (see Table 2), it is possible to assign the first two bands of the bis-2- and bis-3-thienyl derivatives to the combinations of the ring π_3 and π_2 orbitals.

Considering the close similarity of both π_3 and π_2 band shifts and splitting in the spectra of furan and thiophen derivatives, the conclusions on the involvement of the Hg AOs in bonding reached for the former would seem to apply equally well to the latter.

During discussion of the UPS of the furan derivatives, we hypothesized the existence of a band, associated with a σ_{C-Hg-C} orbital, under the second band. In the thiophen derivatives, the band corresponding to the ionization of the π_2^+ and π_2^- MOs is present at lower energy, allowing direct observation of the hidden band.

It is therefore possible to assign the new band and the shoulder in Figure 2 to this σ MO. The destabilization (0.4 eV) on going from the bis-2- to the bis-3-compound compares well with the shift calculated (0.34 eV) for the corresponding furan derivatives.

To confirm experimentally the larger charge-transfer from the ring to Hg in bis-2-furylmercury compared to bis-3-furylmercury, we have determined the IE value of the $4f$ orbitals of mercury by means of X-ray photoelectron spectroscopy. In chemically similar compounds, the core IE shifts are related to the charge

TABLE 3

Core ionization energy values (eV) of bis-3-furyl- and bis-2-furyl-mercury and their differences

	$Hg_{4f_{7/2}}$	C_{1s}	O_{1s}
Bis-3-furyl-mercury	101.5	285.2	534.3
Bis-2-furyl-mercury	101.2	285.1	534.2
	$\Delta(O_{1s} - C_{1s})$	$\Delta(C_{1s} - Hg_{4f_{7/2}})$	$\Delta(O_{1s} - Hg_{4f_{7/2}})$
Bis-3-furyl-mercury	249.1	183.7	432.8
Bis-2-furyl-mercury	249.1	183.9	433.0

present on the atom in the ground state.[21,22] The O_{1s}, C_{1s}, and $Hg_{4f_{7/2}}$ IE values for these compounds are collected in Table 3. The mercury orbital is stabilized by 0.3 eV on going from bis-2-furylmercury to bis-3-furylmercury when the IE values are measured by subliming a very thin layer of sample onto a cooled silver surface, and calibrating against the $Ag_{3d_{5/2}}$ line. This shift is only slightly larger than the reproducibility of the measurements (± 0.1 eV) but is confirmed by internal calibations using the Hg–C_{1s} and Hg–O_{1s} energy separations, which turned out to be consistently larger by 0.2 eV in bis-2-furylmercury. Given that in furan the negative charge density at C-2 is smaller than at C-3,[23] in the absence of additional interactions the mercury line of bis-2-furylmercury should have been stabilized by the larger inductive effect of the C-2 atom. These results, therefore, confirm the above conclusion regarding a small involvement of the mercury $6p_\pi$ orbitals in bonding in bis-2-furylmercury.

3-CH_2HgCl *Derivatives*.—In these compounds the interaction between the 5*d* and 6*p* AOs of mercury and the π orbitals of the aromatic ring is expected to be very small, because of the large distance over which the orbitals would have to interact. On the other hand, a new kind of interaction could be present. In fact a destabilizing hyperconjugative interaction with the filled σ_{C-Hg} orbital has been shown to reduce sizeably the π ionization values in allyl- and benzyl-mercury chlorides with respect to the π MOs of the corresponding unsubstituted compounds by 1.16 and 0.59 eV, respectively.[6,7]

A destabilization due to this interaction is observed also for the present compounds (see Table 2) and is of the order of 0.1—0.4 eV. The smaller effect in the present cases is related to the larger energy gaps between the interacting orbitals (the σ_{C-Hg} orbital has an energy of *ca.* −10.9 eV in HgMeCl [1]) or to the smaller wave function coefficients at C-3 of the π_2 MOs.

Furyl- and Thienyl-mercury Chlorides.—The substitution of an HgCl group for an H atom has a small stabilizing effect ($\leqslant$0.1 eV) on the IE value related to the π_2 MO of all four compounds. No sizeable variations are observed on going from the 2- to the 3-derivative, despite the large variation in the wavefunction coefficients, or from furan to thiophen despite the difference in energy gap between the orbitals which should interact (ring π_2 and mercury 5*d* and 6*p* orbitals). The electronic effect of the HgCl group is therefore essentially inductive (−*I*) and small. Even the π_3 orbitals are moderately stabilized (0.07—0.36 eV) by this substitution.

The calculations (on the furan–HgCl derivatives) confirm that the participation of atomic ($6p_\pi$ and $5d_\pi$) mercury orbitals to π_3 and π_2 in these compounds is very small (see orbital populations in Table 2). This finding could be attributed to a preferred interaction of the Hg $6p_\pi$ orbital with chlorine as evidenced by its finite participation (orbital populations 0.1201 and 0.1630 in the 3- and 2-derivatives, respectively) in the π MO of prevalent chlorine lone pair character.

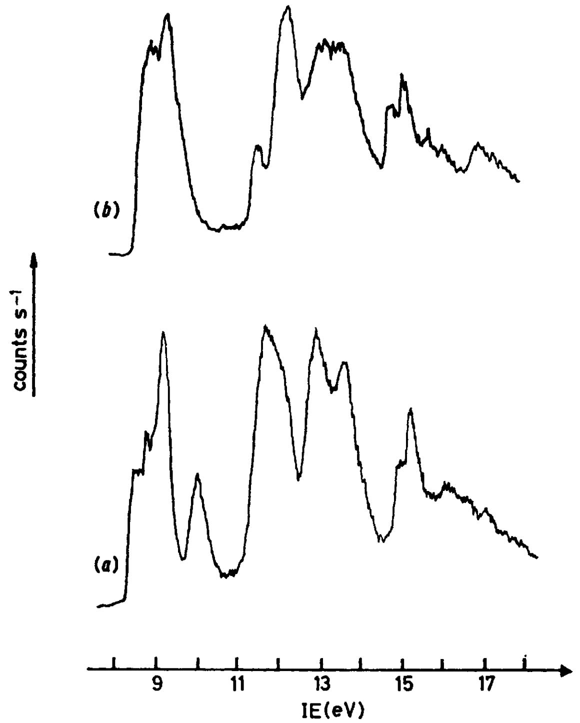


FIGURE 2 He(I) photoelectron spectra of (*a*) bis-2-thienylmercury and (*b*) bis-3-thienylmercury

Mercury 5d *Electrons*.—As for other mercury(II) compounds previously examined,[1-5] a group of three bands, at IE above *ca.* 15 eV, is present in the spectra of the arylmercury derivatives. The first band is always sharp, while the second at 0.1—0.3 eV higher IE, and the third at *ca.* 1.9 eV higher IE, are rather broad. These features are attributed to ionization from the full $5d^{10}$ orbital of the mercury atom.[1]

Because of the small cross-section of the mercury 5*d* orbitals in the He(I) spectra [5] the corresponding bands have low intensities, especially those due to the $^2D_{3/2}$ state, and sometimes it is impossible to determine with accuracy their IE values; also there is overlap with other bands deriving from ionization of the σ framework. Owing to this uncertainty, the variation of the involvement of mercury 5*d* orbitals in bonding, on going from one sample to another, cannot be quantified from the analysis of the 5*d* lines. On the other hand, the large, nearly constant spin–orbit splitting (*ca.* 1.9 eV) shown by the d^{-1} states indicates that the involvement of the mercury 5*d* orbitals in bonding must be rather small in all cases, in agreement with calculations.

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