

*Electronic Spectra of Some Aromatic Mercury Compounds.*

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The absorption spectra of phenyl-, thienyl-, and furyl-mercury derivatives have been measured, and the results correlated with the  $-M$  effect shown by mercury substituents. In the case of the thienyl and furyl derivatives, a greater degree of conjugation of the  $2p$  electrons of the oxygen than of the  $3p$  electrons of sulphur is assumed to be responsible for the more intense bathochromic effect on the primary band in the furyl derivatives.

THE aromatic substituent  $-Hg-X$  is linear. The sign of its inductive effect seems to be unknown, but this effect is likely to be weak in any case. However, the mercury atom has two vacant  $p$  orbitals in its valency shell and therefore should be able to exert a  $-M$  conjugative effect on the aromatic nucleus, although this effect will also be somewhat weak owing to the limitation to orbital overlap imposed by the difference in the principal quantum numbers of the carbon and mercury valency shells. Actually, there is evidence from dipole-moment measurements of such a  $-M$  effect (Hampson, *Trans. Faraday Soc.*, 1934, **30**, 877).

TABLE I. *Ultra-violet spectra (ethanol solutions).\**

X	$C_6H_5X$				$X \cdot C_6H_4 \cdot HgCl$				$X \cdot C_6H_4 \cdot Hg \cdot C_6H_4 \cdot X$			
	$\lambda_{max.}$ , m $\mu$	log $\epsilon$	$\lambda_{max.}$ , m $\mu$	log $\epsilon$	$\lambda_{max.}$ , m $\mu$	log $\epsilon$	$\lambda_{max.}$ , m $\mu$	log $\epsilon$	$\lambda_{max.}$ , m $\mu$	log $\epsilon$	$\lambda_{max.}$ , m $\mu$	log $\epsilon$
H .....	254.5	2.25	203.5	3.87 (1)	258	2.46 (a)	—	—	259	3.00	227	4.40 (e)
CH <sub>3</sub> .....	262	2.48	206.5	3.84 (1)	262.5	2.51	224.5	4.10 (a)	263	3.27	234	4.73 (f)
Cl .....	264	2.31	209.5	3.87 (1)	264.5	2.43	226	4.23 (b)	265	2.94	233	4.56 (g)
NO <sub>2</sub> .....	—	—	252	4.00 (2)	—	—	269	4.68 (c)	—	—	280	4.66 (h)
NH <sub>2</sub> .....	284.5	3.24	234	4.06 (1)	—	—	253	4.13 (d)	297	3.99	—	—
$C_6H_5 \cdot Hg \cdot C_6H_4 \cdot NO_2(p)$	—	—	—	—	—	—	—	—	—	—	273	4.44 (i)
ArX = Mesityl .....	265	2.34	216	3.89 (3)	—	—	—	—	—	—	257	4.01 (j)

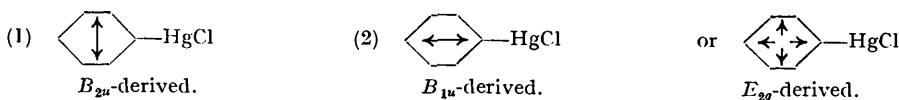
\* Numerals in parentheses refer to spectral data previously recorded; letters refer to preparations.

(1) Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714. (2) Rodd, "Chemistry of Organic Compounds," Elsevier Publ. Co., 1951, Vol. I-A, p. 88. (3) Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 2932.

(a) Nesmejanow, *Ber.*, 1929, **62**, 1013. (b) *Idem, ibid.*, p. 1016. (c) *Idem, ibid.*, 1934, **67**, 130, 134. (d) Otto, *ibid.*, 1902, **35**, 2041. (e) *Org. Synth.*, Coll. Vol. I, p. 228. (f) Nesmejanow, *Ber.*, 1929, **62**, 1019. (g) Under the same conditions as described by Nesmejanow, *ibid.* (h) *Idem, ibid.*, p. 1020. (i) Freidlina, Nesmejanow, and Kozeschkow, *Ber.*, 1935, **68**, 565. (j) Michaelis, *Ber.*, 1895, **28**, 591.

The electronic transitions of benzene, with which we shall compare the transitions now reported for its mercury-substitution products, are the first two singlet (forbidden) transitions. The first, designated in Table 1 by the frequency of its strongest (second)

vibrational maximum, 255  $m\mu$ , is well known to belong to a  $B_{2u}$  upper state. The nature of the second transition is still under discussion, inasmuch as its upper state could be of either species  $B_{1u}$  or  $E_{2g}$ . The oscillating electric vectors associated with transitions to



these states lie in the ring-plane, but otherwise have no prescribed direction. However, when the ring is monosubstituted, or  $p$ -disubstituted with a group such as  $HgX$ , whose bonding direction is an axis of symmetry, the total symmetry drops from  $D_{6h}$  to  $V_h$ , or  $C_{2v}$ , and now the transition derived from the benzene  $B_{2u}$  transition becomes polarised perpendicularly to the line of the substituents, while that derived from the  $B_{1u}$  or  $E_{2g}$

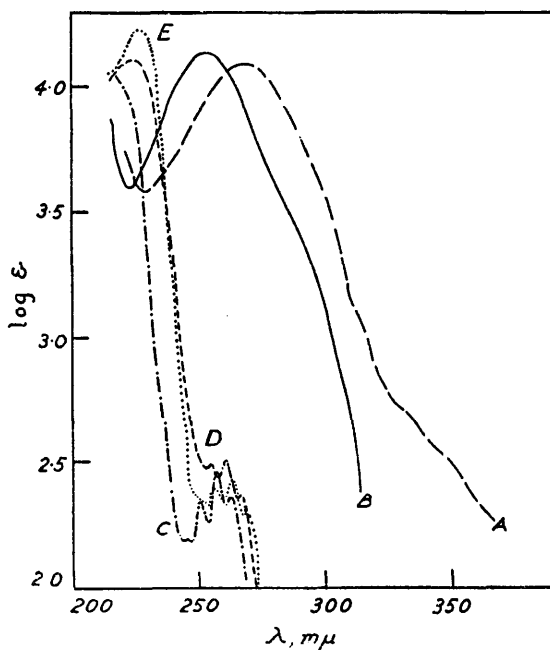


FIG. 1.

A,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ .  
 B,  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ .  
 C,  $\text{C}_6\text{H}_5\cdot\text{HgCl}$ .  
 D,  $p\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ .  
 E,  $p\text{-Cl}\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ .

benzene transition becomes polarised, or contains a component polarised, along that line. Labelling the two transitions (1) and (2) as shown, we can plausibly make the following deductions.

(a) Transition (1) should be relatively little affected, while transition (2) might be considerably affected by the chloromercuri-substituent: any observable effect is likely to involve a bathochromic shift with intensification in view of the capacity for conjugation of the substituent, and its comparatively low electronegativity.

(b) The introduction into the  $p$ -position of a second substituent, such as methyl or chloro, which itself interacts only weakly with the benzene chromophore, should scarcely affect transition (1), but might substantially influence transition (2), again in the sense of a bathochromic shift with intensification.

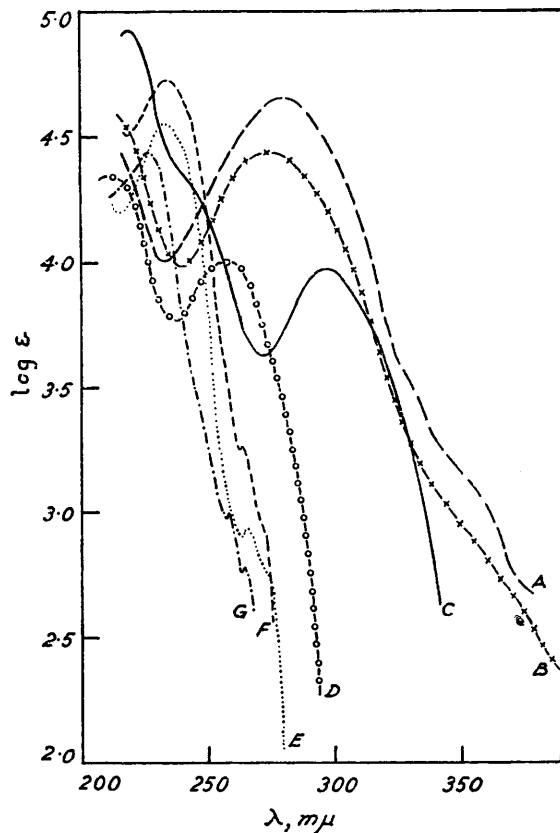
(c) A  $p$ -substituent, such as nitro, which interacts strongly with, and becomes merged in, the benzene chromophore, thereby mixing the characters of the first few benzenoid transitions, should lead to transitions of the combined chromophore, even the first of which should be depressed in frequency and intensified by the chloromercuri-substituent.

(d) A  $p$ -substituent such as amino, which not only merges in the aromatic chromophore, but probably also conjugates through the benzene ring with the mercury atom, should

lead to transitions subject to similar, and possibly more marked, effects of the chloromercuri-substituent.

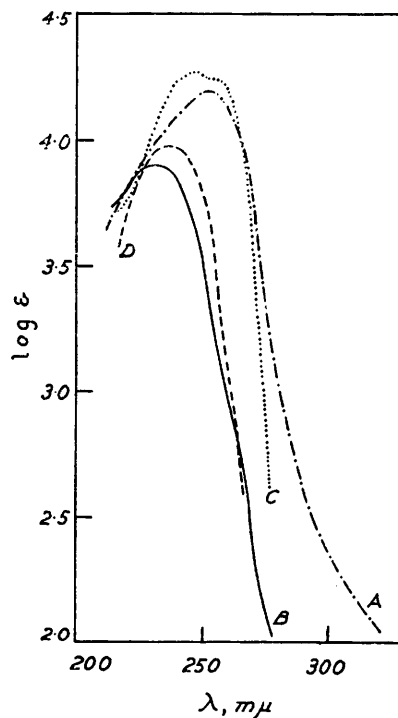
All these points are illustrated in the left-hand and middle divisions of Table 1. For the first transition, the detailed diagrams show, more clearly than does the Table, that, as long as the only substituents are chloromercuri, methyl, and chloro, excitations of the almost pure benzene chromophore are under observation. The vibrational structure of

FIG. 2.



- |   |   |
|---|---|
| A, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}p)_2$ .                         | E, $\text{Hg}(\text{C}_6\text{H}_4\text{Cl-}p)_2$ .               |
| B, $\text{B}_6\text{H}_5\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}p$ | F, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{CH}_3\text{-}p)_2$ . |
| C, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NH}_2\text{-}p)_2$ .                         | G, $\text{HgPh}_2$ .  |
| D, $\text{Hg}(\text{mesityl})_2$ .  |   |

FIG. 3.



- |                             |
|-----------------------------|
| A, Di-2-furylmercury.       |
| B, 2-Chloromercurithiophen. |
| C, Di-2-thienylmercury.     |
| D, 2-Chloromercurifuran.    |

the benzene  $B_{2u}$  system is closely reproduced in the spectra of these derivatives, with similar band separations and intensity variations, thus showing that the ring undergoes almost the same enlargement (about  $2\frac{1}{2}\%$ ) in the upper state, and possesses almost the same internal forces, in the presence of these substituents.

The right-hand division of Table 1 refers to diarylmercury compounds, and requires further comment. To a first approximation these spectra should be similar to those of monoarylmercury compounds, but with a degeneracy derived from the two equivalent chromophores. In second approximation, weak interaction between the chromophores should split the degeneracies, though the split bands might not always be resolved. The splitting should be much greater in transition (2) than in transition (1), for reasons quite similar to those given above for the difference in the sensitivity of the two transitions to the influence by the mercury atom: here we are dealing with their influence on each other,

through the common mercury atom. This major splitting of transition (2) is expected to have three main observable effects on the spectrum. (a) One may be able to observe the splitting directly. (b) The broadening of transition (2) by splitting, whether resolved or not, will cause it to overlap more with transition (1), and because transition (2) is much the stronger, this will confer on the bands of transition (1) a false appearance of intensification. (c) The broadened transition (2) will, on its other side, overlap more with, and will really "steal" more intensity from, what we may call transition (3) in the shorter-wave ultra-violet, a transition which will also be split, and will be still more intense, being derived from the strong (allowed) transition  $E_{1v}$  of benzene at 185 m $\mu$ . These splittings or broadenings, and the apparent and real intensifications, will be found in Table 1, and can be seen still more clearly on the detailed diagrams.

The effect of mercury substitution on the first electronic band of thiophen and furan has been investigated, with the results summarised in Table 2. In these molecules the

TABLE 2. *Ultra-violet spectra (ethanol solutions).\**

	$\lambda_{\max.}$ m $\mu$	log $\epsilon$		$\lambda_{\max.}$ m $\mu$	log $\epsilon$		$\lambda_{\max.}$ m $\mu$	log $\epsilon$
Thiophen .....	231	3.85 (1)	2-Chloromercuri- thiophen ...	236.5	3.99 (a)	Di-2-thienyl- mercury	246	4.26 (a)
Furan .....	<220	(2)	2-Chloromercuri- furan .....	232	3.91 (b)	Di-2-furyl- mercury .....	252	4.20 (b)

\* See footnote to Table 1.

(1) Hartough, "Thiophene and Derivatives, The Chemistry of Heterocyclic Compounds," 1952, Interscience Publ., Inc., New York. (2) Raffauf, *J. Amer. Chem. Soc.*, 1950, **72**, 753. (a) Steinkoff, *Helv. Chim. Acta* 1952, **35**, 162. (b) Gilman and Wright, *J. Amer. Chem. Soc.*, 1933, **55**, 3302.

aromatic system is, of course, fundamentally different from that of benzene; and, indeed, the first excited states of thiophen and furan have not yet been physically characterised. There can, however, be little doubt that they are states of the  $\pi$ -electron shell.

The first electronic band of thiophen is on the red side of that of furan. One might have expected this by analogy with the general convergence of atomic energy states with increasing principal quantum number, inasmuch as the atomic principal quantum numbers of the molecular electrons of the  $\pi$  shell of thiophen are in part 3 and in part 2, whereas those of the  $\pi$  electrons of furan are wholly 2. On the other hand, the red shift produced by mercury substituents is greater in the furan than in the thiophen derivatives. This might also have been expected, because the 3p sulphur electrons of thiophen will conjugate less well with 2p carbon electrons than will the 2p oxygen electrons of furan, with the result that electrons will be less available at the carbon atoms of thiophen than at those of furan, consistently with the well-known chemical differences of these aromatic nuclei. It follows from this that conjugation with a vacant orbital of a mercury substituent must be more effective in the derivatives of furan than in those of thiophen.

#### EXPERIMENTAL

Carefully purified materials, prepared as indicated in the footnotes to the Tables, were examined with the Beckman D.U. Quartz Spectrometer, a hydrogen lamp being employed as light source. Spectra were taken in solution, of concentration 1 in 10<sup>5</sup>, in 95% ethanol, readings being normally 1—2 m $\mu$  apart. In the Tables, spectral positions and intensities of characteristic points are expressed in m $\mu$  and log  $\epsilon$ /mole, respectively.

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