Ultraviolet Absorption Spectra of Some Mercury Compounds.

By B. G. GOWENLOCK and J. TROTMAN.

[Reprint Order No. 6022.]

The absorption spectra of ethanol solutions of some inorganic mercury compounds and of some methyl- and phenyl-mercury derivatives have been measured. The results are discussed in terms of the absorption due to the metal and displacement of the high-intensity absorption band in phenyl and phenylmercury derivatives.

AS part of a fundamental study of organomercury compounds, it was decided to measure the ultraviolet absorption spectra of phenylmercury derivatives in dilute solution. The data available (Purvis and McClelland, *J.*, 1912, **101**, 1514) were suspect, the results implying that the well-known phenyl absorption bands were absent in diphenylmercury. Mann, Millar, and Smith (*J.*, 1953, 1130) have shown that Purvis and McClelland's data for triphenylarsine are unreliable. A preliminary notice of our work appeared (*Chem. and Ind.*, 1954, 309) before the publication by Leandri and Tundo (*J.*, 1954, 3377) of a discussion of the absorption spectra of some phenyl-, thienyl-, and furyl-mercury derivatives, the results having previously been published elsewhere (*Boll. Sci. Fac. Chim. Ind. Bologna*, 1952, **10**, 160). The work presented here overlaps, in some measure, that of Leandri and Tundo, their data being confirmed; however, we investigated absorption over a wider range than these authors and studied many other mercury compounds.

Absorption maxima in the region 206—214 mμ are common to all the mercury compounds studied, and it therefore seems probable that this absorption is due to the electrons of the covalently bonded mercury. For phenylmercury derivatives the increased intensity of the absorption in this region relative to that for inorganic and methyl compounds of mercury is probably caused by a combination of the absorption due to the mercury and the undisplaced high-intensity absorption of the phenyl group. Our results are presented in five groups, each containing comparable compounds.

The data for mercuric bromide and iodide (Table 1) are in fair agreement with the values of Butkow (*Z. Physik*, 1931, **71**, 678), who gives $\lambda_{max.}$ 233 mμ ($HgBr_2$), 217 and 272 mμ (HgI_2), and of Scheibe (*Z. Elektrochem.*, 1928, **34**, 497), who gives $\lambda_{max.}$ 210 and 270 mμ (HgI_2). Addition of excess of ammonia to the solutions of the mercuric halides did not alter the absorption, and hence it can be concluded that co-ordination by ammonia has no effect on the electronic transitions responsible for the absorption. A similar conclusion is probable for the diethyl sulphide complex which gives an extinction coefficient equal to twice the value for mercuric chloride plus that for diethyl sulphide with an almost unaltered $\lambda_{max.}$ (Et_2S, $\lambda_{max.}$ 210 mμ, log ε 3·25; Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**,

TABLE 1. *Inorganic mercury compounds* (see Fig. 1).*

Compound	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	Compound	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
$HgCl_2$	211	3·60	—	— (*a*)	HgI_2	215	4·36	273	3·74 (*b*)
$HgBr_2$	206	3·79	234	3·64 (*b*)	$2HgCl_2,Et_2S$	209	4·02	—	— (*c*)

* In every case data are for ethanol solutions; letters in parentheses refer to preparations.

(*a*) Mersey Chemicals Ltd. (*b*) B.D.H. (*c*) Faragher, Morell, and Comay, *J. Amer. Chem. Soc.*, 1929, **51**, 2774, and McAllan, Cullum, Dean, and Fidler, *ibid.*, 1951, **73**, 3627.

84). Confirmation of the ascription of the 206—214 mμ peak to mercury is provided by the fact that other inorganic compounds of mercury absorb in this range: mercurous sulphate, $\lambda_{max.}$ 214 mμ (Kato, *Bull. Inst. Phys. Chem. Res. Japan*, 1930, **12**, 230); mercurous perchlorate, $\lambda_{max.}$ 209 mμ (Higginson, *J.*, 1951, 1438); mercuric and mercurous acetate , $\lambda_{max.}$ 212 mμ; mercuric cyanide, $\lambda_{max.}$ 206 mμ (Gowenlock and Trotman, unpublished data).

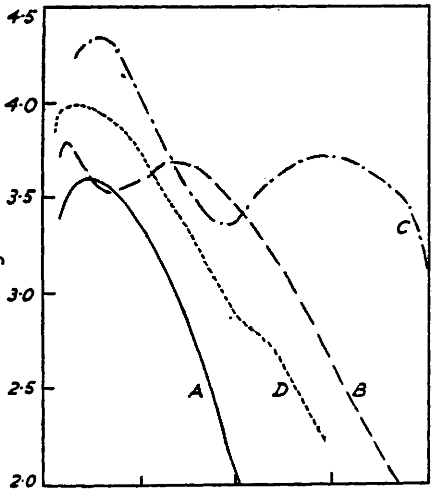
Addition of ammonia to the methyl compounds (Table 2) produces no alteration in the absorption. Methyl-, ethyl-, and *n*-propyl-mercury halides form co-ordination compounds with ammonia (Gowenlock, unpublished data) and it is again apparent that co-ordination has little effect upon the electronic transitions responsible for the absorption. An attempt to measure the absorption spectrum of bismethylmercury sulphate indicated a maximum at about 205—207 mμ, but accurate results are not possible owing to the very low solubility of this substance in ethanol.

TABLE 2. *Alkylmercury halides* (see Fig. 2).

Compound	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
MeHgCl	206	3·17	—	— (*a*)
MeHgBr	209—210	3·54	—	— (*a*)
MeHgI	206	3·89	230	3·60 (*b*)
trans-CHCl:CH·HgCl	212	3·80	—	— (*c*)

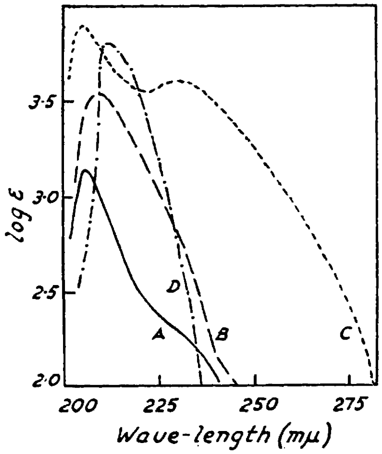
(*a*) Hartley, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 1019. (*b*) Frankland, *Annalen*, 1853, **85**, 363. (*c*) Friedlina and Nesmeyanov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **26**, 60.

FIG. 1.



A, $HgCl_2$. *B*, $HgBr_2$. *C*, HgI_2.
D, $2HgCl_2,(C_2H_5)_2S$.

FIG. 2.

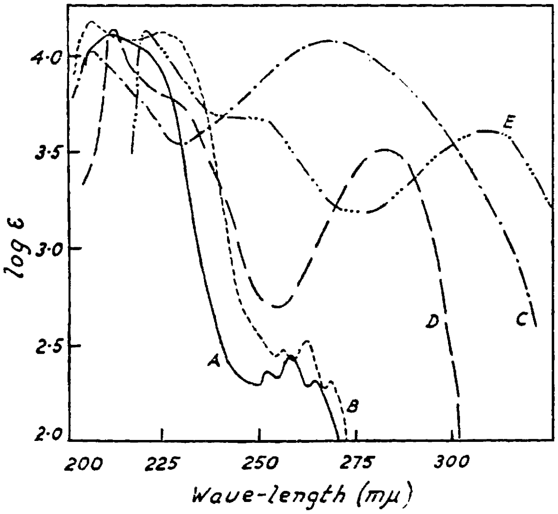


A, MeHgCl. *B*, MeHgBr. *C*, MeHgI.
D, *trans*-Cl·CH:CH·HgCl.

As mercuric bromide and iodide possess two absorption maxima, aromatic derivatives of ·HgCl alone have been investigated so as to obviate the possibility of other absorptions interfering with the characteristic benzenoid absorption (see Table 3).

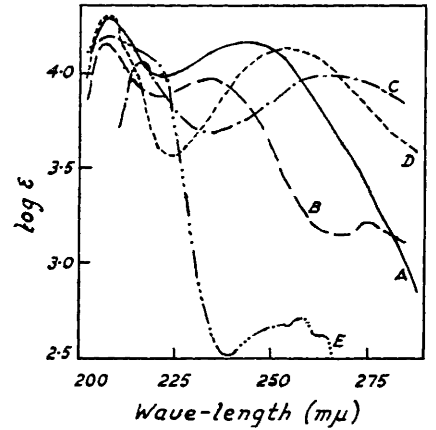
Data for $X = H$, Me, NO_2, and NH_2 have been given by Leandri and Tundo (*loc. cit.*) and are in good agreement with ours in the range 220—300 mμ. (For $X = NO_2$ their value for log ε should read 4·08 instead of 4·68.) It is well known that substitution in the benzene ring produces bathochromic shifts both in the low-intensity bands, designated *B* bands (Bowden and Braude, *J.*, 1952, 1068) and B_{2u} bands (Craig, *Discuss. Faraday Soc.*, 1950, **9**, 5; Leandri and Tundo, *loc. cit.*), and in the high-intensity bands, designated *E* bands (Bowden and Braude, *loc. cit.*), E_{1u} bands (Craig, *loc. cit.*), and B_{1u} or E_{2g} bands (Leandri and Tundo, *loc. cit.*). Both our observations and those of Leandri and Tundo indicate that in some *para*-substituted ·HgCl derivatives, the *B* bands (in Bowden and Braude's terminology) are merged in the displaced *E* bands; discussion is therefore restricted to the high-intensity *E* bands, our data being compared with those for other *para*-disubstituted benzene derivatives (Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; Fehnel and Carmack, *ibid.*, 1949, **71**, 2932). Doub and Vandenbelt have shown that in *para*-disubstituted compounds the effect of substituents on the displacement of the *E* band can be correlated with the directive effect of the substituent groups (*i.e.*, *ortho-para-* or *meta*-directing). On this basis, HgCl is essentially similar to Cl, Me, and SMe and different from CO_2H and NO_2. This implies that HgCl is an *ortho-para*-directing group, the effect being weak. A search of the literature suggests that direct experimental evidence is lacking, since most reagents used in substitution in the benzene ring remove the HgCl group from the ring.

FIG. 3.



A, PhHgCl. *B*, *p*-CH_3·C_6H_4·HgCl. *C*, *p*-NO_2·C_6H_4·HgCl. *D*, *o*-HO·C_6H_4·HgCl. *E*, *o*-O^-·C_6H_4·HgCl.

FIG. 4.



A, PhCH$_2$·HgCl. *B*, *p*-HO·C_6H_4·HgCl. *C*, *p*-O^-·C_6H_4·HgCl. *D*, *p*-NH_2·C_6H_4·HgCl. *E*, *p*-NH_3^+·C_6H_4·HgCl.

TABLE 3. *p*-X·C_6H_4·HgCl (see Figs. 3 and 4).

X	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	Ref.
H	211—212	4·10	—	—	252 258 264	2·37 2·46 2·36	(*a*)
Me	206	4·19	224	4·14	256 262 268	2·47 2·53 2·38	(*a*)
NO_2	205	4·02	269	4·09	—	—	(*b*)
NH_2	207	4·29	254	4·14	—	—	(*c*)
NH_3^+	208	4·15	—	—	252 258 264	2·67 2·69 2·60	(*d*)
OH	207	4·15	234	3·97	274—275	3·21	(*e*)
O–	216 †	4·05	265	4·00	—	—	(*f*)
OH *	212	4·14	225 ‡	3·80	282	3·52	(*e*)
O^- *	220 †	4·15	246 ‡	3·68	309	3·61	(*f*)

(*a*) HgR_2 (B.D.H.) + $HgCl_2$. (*b*) Nesmeyanov, Gluschnev, Epifansky, and Flegontov, *Ber.*, 1934, **67**, 130. (*c*) Dimroth, *Ber.*, 1902, **35**, 2032. (*d*) Addition of HCl to –NH_2. (*e*) Whitmore and Middleton, *J. Amer. Chem. Soc.*, 1921, **43**, 619. (*f*) Addition of NaOH to –OH. * *ortho*-Compound. † Absorption due to NaOH masks absorption below 210 mμ. ‡ Inflection.

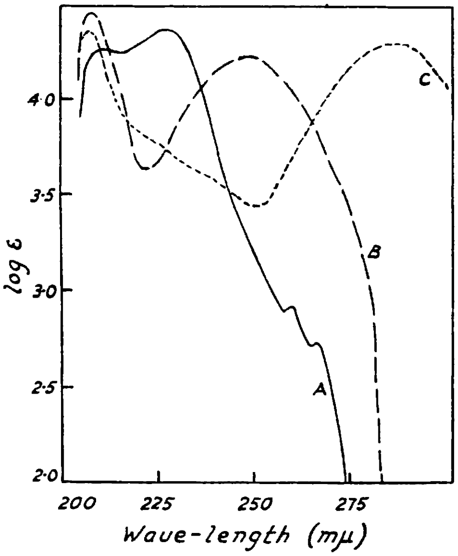
A further comparison can be made in the effect of the ionization OH ⟶ O^- on the *E* band for both *para*- and *ortho*-substituted phenols. For the *para*-substituents SMe, Cl, COMe, CHO, and NO_2 the ionization leads to a displacement of $\lambda_{max.}$ to longer wavelengths by 7, 19, 49·5, 46·5, and 85 mμ, respectively, log ε increasing by amounts varying between 0·12 and 0·29. HgCl similarly displaces $\lambda_{max.}$ to longer wavelengths in this ionization (30 mμ) but in contrast to all the other cases log ε is virtually unaltered. For the *ortho*-substituents SMe, COMe, CHO, NO_2, $CO{\cdot}NH_2$, CN, and CO_2^-, $\lambda_{max.}$ is displaced to longer wavelengths on ionization by the relatively smaller amounts 1, 3·5, 8·5, 3·5, 5·5, 9, and 11·5 mμ, respectively, the log ε alterations being +0·06, −0·28, −0·23, −0·19, −0·04, −0·07, and −0·02. The only substituent giving a comparable displacement to HgCl (21 mμ) is OH (21·5 mμ), log ε alterations being −0·12 and +0·03, respectively. It is apparent that for the groups COMe, CHO, and NO_2 which form strong hydrogen bonds when *ortho* to OH (Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1940, p. 318) there is a large decrease in the intensity of absorption for the ionization $OH \longrightarrow O^-$, only when these substituents are in the *ortho*-position, this being accompanied by a markedly smaller shift in the absorption maximum than for the *para*-case. It is suggested that destruction of hydrogen bonding on ionization may be responsible for this effect. If such a conclusion is correct, then it can be concluded that only weak hydrogen bonding can occur within *o*-hydroxyphenylmercuric chloride.

TABLE 4. *Diphenyl compounds* (high-intensity bands only) (see Fig. 5).

Compound	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	Compound	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
Ph_2Hg	209	4·28	226	4·38 (*a*)	Ph_2NH	207—208	4·33	286	4·29 (*a*)
Ph_2CH_2	—	—	220	4·00 (1)	Ph·Ph	207	4·43	248	4·21 (*a*)
$Ph{\cdot}CH_2{\cdot}CH_2Ph$	—	—	219	4·08 (1)	Ph_2S	—	—	250	4·08 (2)

(*a*) Product of B.D.H. Ltd. (1) Braude, *J.*, 1949, 1902. (2) Jaffé, *J. Chem. Phys.*, 1954, **22**, 1430.

FIG. 5.



A, Ph_2Hg. *B*, Ph·Ph. *C*, Ph_2NH.

Jaffé (*loc. cit.*) has concluded from a study of the ultraviolet absorption spectra of polyphenyl and monophenyl compounds that groups not possessing unshared electron pairs produce only a relatively minor perturbation of the π-electron system in benzene. This would imply that for diphenylmercury and diphenylmethane the transitions in the phenyl groups involve only the electrons of those groups acting independently of one another, whereas in diphenylamine, diphenyl sulphide, and diphenyl these electrons are delocalized over the whole molecule. Inspection of Table 4 confirms Jaffé's conclusions, suggesting that only very weak interaction (presumably through one of the 6*p*π or 6*d*π orbitals) is possible between the two phenyl groups in diphenylmercury. The marked difference in absorption between diphenylmercury and phenylmercury compounds in the 226 mμ region of the spectrum makes possible a determination of diphenylmercury in the presence of phenylmercury compounds without the use of dithizone (Miller and Polley, *Analyt. Chem.*, 1954, **26**, 1333).

There is a marked difference between the spectrum of benzylmercuric chloride and those of other benzyl compounds (see Table 5). The possibility of dissociative absorption of the

TABLE 5. *Benzyl compounds* (high-intensity bands only).

Compound	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	Compound	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
$Ph{\cdot}CH_2{\cdot}HgCl$	208	4·29	245	4·16 (*a*)	$Ph{\cdot}CH_3$	209	3·91	—	— (1)
$Ph{\cdot}CH_2Cl$	217	3·85	—	— (*b*)	$Ph{\cdot}C_2H_5$	208	3·89	—	— (2)
$Ph{\cdot}CH_2{\cdot}CH_2Cl$	209	3·87	—	— (*c*)					

(*a*) Hilpert and Gruttner, *Ber.*, 1915, **48**, 913. (*b*) B.D.H. (*c*) Eastman Kodak. (1) Platt and Klevens, *Chem. Reviews*, 1947, **41**, 301. (2) Braude, *loc. cit.*

weak benzyl–mercury bond cannot be ignored, but it was found that absorption did not vary with time. A search of the literature indicates that all other benzyl–X compounds investigated exhibit *B* bands in the region of 250—270 mμ and that any *E* bands are all at lower wavelengths than 230 mμ (X = CO_2H, $CO{\cdot}NH_2$, Guilmart, *Bull. Soc. chim.*, 1938, **5**, 1209; X = OH, CN, Mohler and Polya, *Helv. Chim. Acta*, 1936, **19**, 1222). Comparable data for other benzyl-metal compounds are desirable.

EXPERIMENTAL

All substances, whether obtained commercially or prepared by us (see footnotes to tables), were, where possible, recrystallized from spectroscopic ethanol (Bladon, Henbest, and Wood, *J.*, 1952, 2737) and dried under oil-pump vacuum. Spectra were measured in this solvent, the concentrations being chosen so as to obtain optical densities between 0·3 and 0·6 at the absorption maxima, and a Unicam Spectrophotometer SP 500 with corrected scale and 1-cm. quartz cells being used throughout. Absorption could be studied to about 202 mμ under these conditions. All results could be reproduced accurately, the limits being $\lambda_{max.} \pm 0{\cdot}5$ mμ, $\varepsilon \pm 1\%$.

We thank the Department of Scientific and Industrial Research for a Maintenance Grant (to J. T.), and Imperial Chemical Industries Limited for the loan of the Unicam Spectrophotometer.

UNIVERSITY OF WALES, UNIVERSITY COLLEGE, SWANSEA. [*Received, January* 10*th*, 1955.]