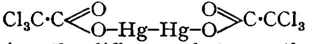
111. *The Electric Polarisation of Mercurous Trichloroacetate and of Quinol Bistrichloroacetate.*

By N. R. Davidson and L. E. Sutton.

Mercurous trichloroacetate is soluble in benzene. In order to discover whether this is due to any peculiarity in the structure of the solute molecule, its electric polarisation in this solvent has been determined at 25° and compared with that of *quinol bistrichloroacetate*, with which there might be a structural similarity if the O–Hg–Hg–O atoms are collinear in the former.

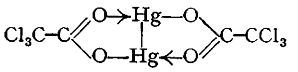
The apparent electric dipole moments are 2·65 ± 0·10 and 1·50 ± 0·20 D., respectively, the uncertainties being due to atom polarisation. The large value for the former excludes any rigid chelate structures and favours the simple covalent one  $\mathrm{Cl_3C{\cdot}C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown O}\mathrm{{-}Hg{-}Hg{-}}\genfrac{}{}{0pt}{}{O\diagdown\!\!\diagdown}{O\diagup}\mathrm{C{\cdot}CCl_3}$ in which the trichloroacetyl groups are free to rotate about the O–Hg–Hg–O axis : the difference between the moments of this and of the quinol ester may reasonably be attributed to the effects of resonance.

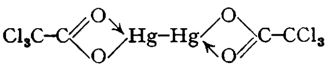
The number of chemical compounds which contain a metal and are appreciably soluble in organic solvents is relatively small. Apart from organo-metallic compounds proper, in which the metal atom is directly bound to a carbon atom, most of the members of the class are chelate compounds in which the covalent bonding is stabilised by resonance, and frequently the solubility in non-polar solvents is increased by the presence of large organic addenda. The solubility of silver perchlorate in benzene is apparently an isolated and unexplained case.

The observation by Bateman and Conrad (*J. Amer. Chem. Soc.*, 1915, **37**, 2559) that mercurous trichloroacetate is soluble in benzene is therefore of considerable interest, and in an effort to throw further light on the structure of this compound we have investigated its molecular weight and electric polarisation in benzene solution. Since our work was completed, Swarts (*Bull. Soc. chim. Belg.*, 1939, **48**, 176) has reported that mercurous trifluoroacetate is also soluble in benzene.

As was anticipated, cryoscopic measurements showed that the molecular formula of mercurous trichloroacetate is $Hg_2(C_2O_2Cl_3)_2$. Swarts's ebullioscopic measurements give a dimeric formula for the trifluoroacetate. In every known case of a mercurous compound, whether in ionic aqueous solution, in the gas phase, or as a solid, two mercury atoms are linked together (cf. Latimer and Hildebrand, " Reference Book of Inorganic Chemistry," The Macmillan Co., New York, 1933, p. 109), so it is reasonable to assume that the dimerisation of the trichloroacetate involves the formation of an Hg–Hg link.

The results of the electric polarisation measurements are : $P_2 = 245{\cdot}7 \pm 1$ c.c., ${}_{\mathrm{E}}P_2 = 79{\cdot}5 \pm 2$ c.c., whence $P_{\mathrm{A+O}} = 166 \pm 3$ c.c. It is clear that a compound with such a large value of $P_{\mathrm{A+O}}$ must have a permanent dipole moment and hence an unsymmetrical structure. Whatever the structure, there is a large number of polar groups in the molecule, so that we may expect (Coop and Sutton, J., 1938, 1269) a large atom polarisation; if P_{A} is 30 c.c., $\mu = 2{\cdot}56$ D.; if P_{A} is 6 c.c., μ is 2·78 D. We take $\mu = 2{\cdot}65 \pm 0{\cdot}10$ D.* A symmetrical chelate structure (I) for this compound, besides being incompatible with the observed moment, is stereochemically unlikely. If the mercury radius is the same as that in covalent mercuric compounds, the Hg–Hg distance is 2·92 A., whereas the distance between the two oxygen atoms in a carboxyl group is only

(I.) 

 (II.)

about 2·4 A.; hence a considerable distortion of the mercury and oxygen valency angles, as shown roughly above, would be required in any ring structure. A structure (II), besides being stereochemically unlikely

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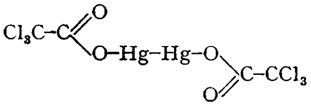
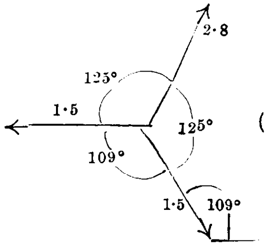
* From the principles laid down and the approximate values contained in the paper by Coop and Sutton (*loc. cit.*) we might expect that the two C=O bonds would give rise to about 10 c.c. of atom polarisation, the Hg–O bonds to about 7 c.c., and the remaining polar bonds to about 3 c.c., making *ca.* 20 c.c. in all and giving $\mu = 2{\cdot}65$ D.

because it has four-membered rings, is symmetrical, and hence incompatible with the observed dipole moment. An " open " structure (III) is thus left as the most likely one. The O–Hg–Hg–O system is supposed to be linear, in conformity with the linear configuration of mercuric compounds and of the crystalline mercurous halides.

On the assumptions (*a*) that, as in the esters (Marsden and Sutton, J., 1936, 1383), the O–Hg–Hg–O line is fixed *cis* with respect to the carboxyl groups, (*b*) that there is free rotation about the Hg–O bonds, (*c*) that the vector model (IV) is correct, it follows that the resultant moment of each rotating group is 1·34 D. directed

(III.)

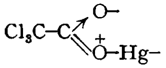




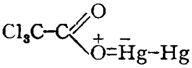
(IV.)

at about 12·5° above the C=O axis : the resolved components perpendicular to the O–Hg–Hg–O axis are each 1·20 D., whence the total moment should be 1·74 D. (*cf. Ann. Reports*, 1940, **37**, 59).

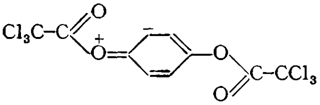
The effect of resonance with such structures as (V) would be markedly to increase this moment, and it is not inconceivable that the predicted value of the moment might rise to the observed value of 2·65 D. Since mercurous ion does not form complexes (*cf.* Latimer and Hildebrand, *op. cit.*) it seems unlikely that the structures (VI) need be considered.



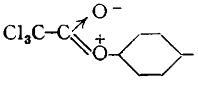
(V.)



(VI.)

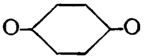


(VII.)



(VIII.)

If the open structure (III) is correct, it should be analogous to that of *quinol bistrichloroacetate*, in which again there are two trichloroacetyl radicals bound to oxygens on the end of a linear system. The analogy is imperfect because of the conjugating power of the benzene nucleus. This compound was, however, prepared and its electric polarisation observed to be : $P_2 = 143 \pm 1$, ${}_EP_2 = 79·0 \pm 0·5$, whence $P_{A+O} = 64$ c.c. If P_A is 4 c.c., $\mu = 1·70$ D. ; and if P_A is 24 c.c., $\mu = 1·32$ D. ; so the best value seems to be 1·50 ± 0·20 D.

It is difficult to estimate the influence of the benzene nucleus on the moment; it seems that the principal effect of resonance of the type (VII) would be to decrease the relative importance of structures of the type (VIII), and thus to prevent freedom of rotation about the  axis and to allow it about the  axis. On the basis of the same vector model as before, and of these new assumptions, the resultant of the C=O and the CCl_3 moments perpendicular to the C–O axis is 0·87, and the predicted value of the total moment is 1·23. This is less than the observed value of 1·5, as would be expected since the assumptions represent an extreme state of affairs though the difference is the opposite of that between the calculated and the observed value of the moment of quinol diacetate, *viz.*, 3·3 and 2·2 D. We may, at least, safely say that the low moment of quinol bistrichloroacetate is *not* evidence *against* the open structure for mercurous trichloroacetate.

It is difficult to understand why mercurous trichloro- and trifluoro-acetate should be soluble in benzene, whereas mercurous acetate is not. One would expect a greater tendency for covalent bond formation between the mercury atom and the oxygen atom of the *weaker* acid. It is not difficult to understand why, of all common non-polar solvents, *only* benzene is effective as a solvent for these compounds ; the greater solvating power and polarisability of benzene as a solvent are common experience, although little explicit recognition of this fact has been made in the literature (cf. Bloom and Sutton, J., 1941, 733).

Swarts (*Bull. Soc. chim. Belg.*, 1923, **32**, 111) observed that silver trifluoroacetate is soluble in benzene, and is polymerised at least to a dimer. We have observed that silver trichloroacetate is somewhat soluble in benzene, but the solution readily deposits silver chloride, so the matter was not studied further.

From the observed refractivity of mercurous trichloroacetate, and the calculated refractivity of the trichloroacetate group, the refractivity of mercurous mercury is calculated to be 13·2 c.c. The accepted value for mercuric mercury is 13·0 c.c., and this coincidence supports the belief that the electronic structures of the two are identical.

EXPERIMENTAL.

Preparation and Purification of Materials.—Benzene was purified as described by Hampson, Farmer, and Sutton (*Proc. Roy. Soc.*, 1933, *A*, **143**, 147).

Mercurous trichloroacetate was prepared by addition of a freshly prepared solution of mercurous nitrate to an aqueous solution of trichloroacetic acid (Bateman and Conrad, *loc. cit.*). The precipitate of very small white crystals, after drying, was never completely soluble in benzene, so it was purified by dissolution in benzene, filtering the solution, and precipitating it with ligroin (b. p. 40—60°) from which olefinic impurities had been removed with sulphuric acid (when untreated ligroin was used, the precipitate gave low analytical results for mercury and chlorine and liberated a distinct odour of ligroin when dissolved in water) (Found : C, 6·6; H, 0·064; Cl, 28·9. Calc. for $Hg_2C_4O_4Cl_6$: C, 6·6; Cl, 29·3%).

Two methods were used to prepare ***quinol bistrichloroacetate***. (1) Quinol was fused with a slight excess of trichloroacetic acid, about 2 c.c. of phosphorus oxychloride being added per g. of quinol. The mixture was kept at 110° for several hours, with stirring, until hydrogen chloride ceased to be evolved. The excess of phosphorus oxychloride was then carefully decomposed with water (cooling in ice-water). The resulting white powder was collected, washed with water, dried, and recrystallised from ligroin (b. p. 60—80°). This is a modification of Dzierzgowski's procedure for the monochloroacetate (*Ber.*, 1893, **26**, Ref. bd., p. 590). (2) Quinol and trichloroacetyl chloride were allowed to react in pyridine solution; the brown solid formed was collected and recrystallised from ligroin. The yield in either reaction was only about 15%; m. p. 136—136·5° (Found : C, 29·6; H, 1·05; Cl, 53·2. $C_{10}H_4O_4Cl_6$ requires C, 29·9; H, 1·0; Cl, 53·1%).

Stannic chloride does not cause reaction between trichloroacetyl chloride and quinol, although it causes an extremely vigorous reaction between acetyl chloride and quinol. Dimethylaniline also was not effective as a condensing agent for the former reaction.

Cryoscopic Measurements.—The molecular weight of mercurous trichloroacetate was determined in a Beckmann apparatus [$Hg_2(O_2C_2Cl_3)_2$ requires M, 726] :

Solute, g.	0·205	0·439	0·640	0·625	0·465
Solvent, g.	11·17	11·17	11·17	13·16	14·75
ΔT	0·125°	0·286°	0·408°	0·352°	0·234°
M	773	723	726	715	714

Electric Polarisation Measurements.—These were made with the apparatus described by Hampson, Farmer, and Sutton (*loc. cit.*) :

Mercurous trichloroacetate.

f_2.	ϵ.	d.	$d\epsilon/df_2$.	dd/df_2.	P_2.	n^2.	$_EP_2$.
0	2·2727	0·8733	—	—	—	2·2571	—
0·003124	2·3133	0·8930	13·00	6·328	245·7	2·2631	81·7
0·005545	2·3448	0·9084	13·00	6·316	245·0	2·2667	78·3
0·006109	2·3528	0·9118	13·11	6·297	248·3	2·2678	79·4
* 0·004106	2·3277	0·8989	—	—	244·3	2·2676	83·0

$$_\infty P_2 = 245{\cdot}7 \pm 1 \text{ c.c.}; \quad _EP_2 = 79{\cdot}5 \pm 2 \text{ c.c.}; \quad P_{A+O} = 166 \pm 3 \text{ c.c.}$$

Quinol bistrichloroacetate.

0	2·2727	0·8734	—	—	—	2·2571	—
0·007627	2·3084	0·8887	4·681	2·0152	144·0	2·2397	78·9
0·01509	2·3404	0·9032	4·487	1·9775	142·3	2·2622	79·2

$$_\infty P_2 = 143 \pm 1 \text{ c.c.}; \quad _EP_2 = 79{\cdot}0 \text{ c.c.}; \quad P_{A+O} = 64 \pm 1 \text{ c.c.}$$

* These data are for the sample used for analysis and for the first molecular-weight determination; this dissolved in benzene to leave a slight milky precipitate, presumably mercurous chloride. The agreement with the other data is satisfactory.

The authors thank Prof. N. V. Sidgwick, F.R.S., for his interest and advice, and Imperial Chemical Industries, Ltd., for a grant towards the cost of this research.

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[*Received, June 27th,* 1942].