XXXIII.—*The Parachor and Chemical Constitution. Part XIV. Tellurium Compounds.*

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IN earlier papers of this series (Sugden, Reed, and Wilkins, J., 1925, 127, 1525; Henley and Sugden, J., 1929, 1058), a number of compounds of sulphur and selenium have been examined in which these elements exert a valency which is greater than the normal, *viz.*, 2. In every case the shell of eight electrons around the sulphur or selenium atom is not exceeded, and the parachors show the presence of the correct number of semipolar double bonds or singlet linkages which are necessary to maintain the octet. As a result of the work described below, this conclusion can now be extended to tellurium compounds. We have so far not found any telluroxides or other compounds containing semipolar double bond which are sufficiently stable in the fused state for parachor measurements; the dialkyl- and diaryl-tellurium dihalides are, however, remarkably stable substances, and measurements can be made for a considerable temperature interval above their melting points. In all but one of the substances examined, the parachor anomaly

predicted for the singlet linkages in the molecule has been realised experimentally.

It was necessary in the first place to determine the atomic constant for tellurium by measurements of the parachors of compounds in which this element exerts its normal valency of two. Data for such compounds are given in Table I. The figure recorded for diphenyl telluride is that obtained by Lowry and Gilbert (J., 1929, 2087). The ditelluride (6) began to decompose at its melting point,
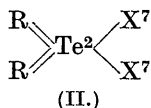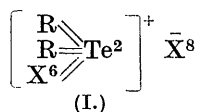
TABLE I.

Atomic Parachor of Tellurium.

Substance.	Formula.	[P] obs.	$\Sigma[P]$.	Te.
(1) Diphenyl telluride	Ph_2Te	457·4	380·0	77·4
(2) Dianisyl telluride	$(MeO·C_6H_4)_2Te$	575·2	498·0	77·2
(3) *Di-n-butyl telluride*	$(C_4H_9)_2Te$	426·8	346·2	80·6
(4) Phenoxtellurine*	$C_6H_4\!<^{Te}_{O}\!>C_6H_4$	452·9	371·9	81·0
(5) Di-2-chloro-*p*-phenetyl telluride†	$(EtO·C_6H_3Cl)_2Te$	731·2	650·4	80·8
(6) Di-*p*-phenetyl ditelluride	$(EtO·C_6H_4)_2Te_2$	723·0	576·6	(73·2)
			Mean, excluding (6)	79·4

* The heterocyclic 6-membered ring in this substance is assumed to have the normal value of 6·1 units.

† See p. 231.

so the value given for its parachor can only be regarded as approximate. The mean constant for tellurium, *viz.*, 79·4, is a little lower than the value 86 predicted from the parachors of adjacent elements (Henley and Sugden, *loc. cit.*), but lies satisfactorily between the constants for antimony (66·0) and iodine (91·0). The series, $O = 20$, $S = 48·2$, $Se = 62·5$, $Te = 79·4$, shows the same steady increase with atomic number which has been observed in other families of elements, *e.g.*, the halogens.

Table II gives the parachors of a number of tellurium compounds in which this element is quadrivalent, the data for compounds (3)—(5) being due to Lowry and Gilbert (*loc. cit.*). These substances are all of the type R_2TeX_2, where X is a halogen atom, and may be formulated electronically as salts (I) or as non-polar compounds (II); their properties, excepting those of (5), indicate a non-polar structure (compare Drew, J., 1929, 560; Lowry and Gilbert, *loc. cit.*),

$$\left[\begin{array}{c} R \\ R \\ X^6 \end{array}\!\!\!\!\Rightarrow Te^2\right]^{+}\ \bar{X}^8 \qquad\qquad \begin{array}{c} R \\ \\ R \end{array}\!\!\!>Te^2<\!\!\!\begin{array}{c} X^7 \\ \\ X^7 \end{array}$$

(I.)   (II.)

so the parachor should indicate the presence of two singlet linkages by an anomaly of −24·8 units. All the substances, save (3), give an anomaly which is close to this value.
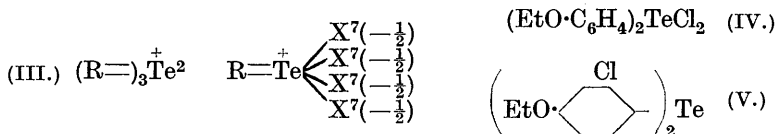
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TABLE II.

Quadrivalent Tellurium Compounds.

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Substance.	Formula.	[P] obs.	$\Sigma[P]$.	Anomaly.
(1) Diphenyl telluridichloride	$(C_6H_5)_2TeCl_2$	547·3	568·0	−20·7
(2) Di-*p*-anisyl telluridichloride	$(MeO \cdot C_6H_4)_2TeCl_2$	663·2	686·0	−22·8
(3) α-Dimethyl telluridichloride	Me_2TeCl_2	282·5	300·2	−17·7
(4) α-Diethyl telluridi-iodide	Et_2TeI_2	425·0	451·6	−26·6
(5) β-Diethyl telluridibromide	Et_2TeBr_2	377·3	405·6	−28·3

It has been shown by Drew (*loc. cit.*) that Vernon's β-compounds are probably dimerides with a polar structure, *i.e.*, $(R_3Te)^+ (RTeX_4)^-$. An electronic formula compatible with the octet rule may be written as in (III). Here both tellurium atoms have a complete octet and carry a positive charge; the anion contains four singlet-linked halogen atoms which give it a net charge of −1. On this view it will be seen that both the α- and the β-compounds contain two singlet linkages per tellurium atom so that the parachors will give no distinction between the two series. The parachor found by Lowry and Gilbert for the last substance (see Table II) shows, as would be expected, much the same anomaly as the other quadrivalent tellurium compounds.

The substance described by Morgan and Drew (J., 1925, **127**, 2307) as bis-*p*-phenetyl telluridichloride (IV) was also examined but proved to have very different properties from the corresponding anisyl compound (No. 2, Table II). The observed parachor, 731·2, is considerably lower than the value calculated for formula (IV), *viz.*, 739·2, but agrees well with the predicted value for formula (V), 729·8. The physical and chemical properties of this substance also

$$(EtO \cdot C_6H_4)_2TeCl_2 \quad (\text{IV.})$$

$$(\text{III.}) \quad (R{=\!=})_3\overset{+}{T}e^2 \qquad R{=\!=}\overset{+}{T}e\begin{cases} X^7(-\tfrac{1}{2}) \\ X^7(-\tfrac{1}{2}) \\ X^7(-\tfrac{1}{2}) \\ X^7(-\tfrac{1}{2}) \end{cases} \qquad \left(EtO \cdot \bigcirc\!\!-\!\!\overset{Cl}{} \right)_2 Te \quad (\text{V.})$$

indicate that it is not a quadrivalent tellurium derivative but a nuclear-substituted diphenetyl telluride (V). Its melting point, 108°, is much lower than those of the diphenyl and dianisyl telluridichlorides, *viz.*, 160° and 182° respectively. Unlike the latter substance, the phenetyl compound is readily soluble in ligroin and cannot be reduced by zinc dust to the corresponding telluride. Furthermore, the phenyl and anisyl compounds are readily converted into telluroxides by aqueous alkali, but the phenetyl compound only gives up its chlorine slowly to boiling potash (Morgan and Drew, *loc. cit.*). We understand that further work on this and similar substances is now proceeding in Prof. Morgan's laboratory; meanwhile, from the evidence set out above we consider that formula

(V) gives the most probable structure of Morgan and Drew's phenetyl derivative.

<div align="center">EXPERIMENTAL.</div>

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 158; 1924, **125**, 27) and densities by means of a U-shaped pyknometer (J., 1924, **125**, 1171). The tables below are set out in our usual manner; the parachors are calculated by the formula $P = M\gamma^{\frac{1}{4}}/D$, where γ is the surface tension in dynes/cm., and D the density of the liquid, the density of the vapour being negligible.

Diphenyl telluridichloride ($M = 352.5$). We are indebted to Prof. G. T. Morgan for a specimen of this substance. M. p. 160—161° (corr.). Densities determined : $D_4^{162.8°}$ 1·618, $D_4^{170°}$ 1·611, $D_4^{177.5°}$ 1·603, $D_4^{184.5°}$ 1·596, whence $D_4^{t} = 1.785 - 0.00103t$.

t	167·5°	179°	189°	
γ	39·47	38·23	37·17	
D	1·613	1·601	1·591	
$[P]$	547·6	547·4	547·0	Mean 547·3

Di-p-anisyl telluridichloride ($M = 412.5$), prepared as described by Morgan and Kellett (J., 1926, 1085) and purified by several crystallisations from chloroform, was colourless and melted sharply at 182° (corr.). Densities determined : $D_4^{186°}$ 1·544, $D_4^{195.5°}$ 1·533, $D_4^{206°}$ 1·523, $D_4^{216°}$ 1·512, whence $D_4^{t} = 1.734 - 0.00102t$. The substance showed little sign of decomposition even at these high temperatures.

t	186·5°	198·5°	211·5°	
γ	37·82	36·49	35·57	
D	1·543	1·530	1·517	
$[P]$	663·0	662·5	664·0	Mean 663·2

Di-p-anisyl telluride ($M = 341.6$) was obtained by Morgan and Kellett from the foregoing dichloride by reduction with zinc dust in benzene. A better yield (90%) was obtained by heating the dichloride in the water-bath with excess of zinc dust and glacial acetic acid; the filtered solution was poured into water and the precipitated telluride crystallised repeatedly from methyl alcohol; m. p. 53—54° (corr.). Densities determined : $D_4^{62.5°}$ 1·515, $D_4^{72°}$ 1·502, $D_4^{82.5°}$ 1·492, $D_4^{92.5°}$ 1·481, whence $D_4^{t} = 1.582 - 0.00109t$.

t	76·5°	88·5°	100·5°	111°	121°	
γ	40·60	38·84	38·75	36·68	35·63	
D	1·499	1·486	1·473	1·461	1·450	
$[P]$	575·1	574·0	576·1	575·4	575·5	Mean 575·2

Dichlorodiphenetyl telluride ($M = 438.5$) was prepared as described by Morgan and Drew (*loc. cit.*) and crystallised from alcohol; m. p.

108° (corr.). Densities determined : $D_{4°}^{113·5°}$ 1·493, $D_{4°}^{124·5°}$ 1·482, $D_{4°}^{135°}$ 1·472, $D_{4°}^{145°}$ 1·462, whence $D_{4°}^{t°} = 1·604 - 0·000979t$.

t	124·5°	136°	147·5°	157·5°	
γ	37·52	35·93	35·12	34·12	
D	1·482	1·471	1·459	1·450	
$[P]$	732·1	729·9	731·7	731·0	Mean 731·2

Phenoxtellurine ($M = 295·5$), prepared as described by Drew (J., 1926, 230), melted at 79° (corr.). Densities determined : $D_{4°}^{93°}$ 1·662, $D_{4°}^{107°}$ 1·645, $D_{4°}^{133·5°}$ 1·615, $D_{4°}^{147·5°}$ 1·602, whence $D_{4°}^{t°} = 1·770 - 0·00117t$.

t	120·5°	132°	147°	
γ	38·32	37·62	36·71	
D	1·630	1·616	1·599	
$[P]$	451·0	452·9	454·8	Mean 452·9

Di-p-phenetyl ditelluride ($M = 497·1$), prepared by reduction of *p*-phenetyl telluritrichloride with aqueous bisulphite (Morgan and Drew, *loc. cit.*), crystallised from ligroin in orange-brown needles, m. p. 108° (corr.). As appreciable decomposition occurred when the substance was heated above its melting point, only one observation of the parachor was made. At $t = 118°$, $\gamma = 34·44$, $D = 1·666$, whence $[P] = 723·0$.

Di-n-butyl telluride ($M = 241·6$). This new substance was prepared as follows. The Grignard compound (2 mols.) from *n*-butyl bromide was added slowly to tellurium tetrachloride (1 mol.) suspended in dry ether. The mixture was heated for 2 hours on the water-bath, the ether distilled off, and the residue extracted with chloroform. The extract was shaken with water to decompose the excess of reagents and dried over calcium chloride, and the solvent removed. The residual red gum was dissolved in glacial acetic acid, and zinc dust added in slight excess. After a few minutes' heating on the water-bath, the solution was filtered and poured into water. The *telluride* then separated as a dark oil, which was dried over calcium chloride and distilled under diminished pressure in a stream of carbon dioxide. The product was a yellow oil, b. p. 132—135°/ 99 mm. (Found : Te, 52·5. $C_8H_{18}Te$ requires Te, 52·8%); it possessed an unpleasant odour and oxidised on exposure to air. Exposure to light caused the yellow colour to deepen to a reddish tint.

Densities determined: $D_{4°}^{30°}$ 1·302, $D_{4°}^{36°}$ 1·294, $D_{4°}^{41°}$ 1·289, $D_{4°}^{46°}$ 1·284, whence $D_{4°}^{t°} = 1·334 - 0·00109t$.

t	18°	28°	38°	
γ	29·07	28·24	27·03	
D	1·314	1·303	1·293	
$[P]$	426·9	427·5	426·0	Mean 426·8

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