369. *Physical Properties and Chemical Constitution. Part XXIII. Miscellaneous Compounds. Investigation of the So-called Co-ordinate or Dative Link in Esters of Oxy-acids and in Nitro-paraffins by Molecular Refractivity Determinations. Atomic, Structural, and Group Parachors and Refractivities.*

By ARTHUR I. VOGEL.

New determinations of the refractivities at 20° and of the parachors of esters of dichloroacetic and trichloroacetic acid have been made with the object of investigating the influence of two or three chlorine atoms respectively attached to the same carbon atom; the resulting constants were not exact multiples of those found for chlorine in monosubstituted compounds (Part XIV, this vol., p. 644). Similarly, the constants for $\geqslant$CH evaluated from measurements upon trialkyl orthoformates, $CH(OR)_3$, were not exactly equal to (C + H) deduced from aliphatic hydrocarbons (Part IX, *J.*, 1946, 133).

An analysis of the experimental results for dialkyl sulphites and sulphates and of trialkyl orthophosphates (Part VII, *J.*, 1943, 16) led to constants for the $>$SO, $>SO_2$, and $\geqslant$PO groups, but no evidence from parachors or refractivities of the presence of covalent double bonds was apparent. Similar results were obtained from $SO_2Cl_2 - SOCl_2$ and from $POCl_3 - PCl_3$. The physical constants of the $-N{=}O$ group in nitrosoamines, deduced from $R_2N{\cdot}NO + H - R_2NH$, were not comparable with those for $\geqslant$PO.

Determinations have also been made of the parachors and refractivities of dialkyl nitrosoamines, nitro-paraffins, alkyl nitrites, alkyl nitrates, dialkyl carbonates, alkyl thiocyanates and *iso*thiocyanates, and alkyl xanthates, and the constants of the following groups were evaluated: -N(NO), $-NO_2$, -ONO, $-NO_3$, -SCN, -NCS, and $>$CS. The constants for $>$CO in dialkyl carbonates were almost identical with those previously found for aliphatic ketones (Part XI, this vol., p. 610), and the constants for -CN in alkyl thiocyanates (-SCN − S, in sulphides) were in good agreement with those deduced from aliphatic nitriles (Part XVII, this vol., p. 674).

The parachor and refractivity constants for the covalent double bonds C=C, C=O, C=S, and N=O are not identical.

Revised values for the atomic, structural, and group parachors and refractivities so far determined are tabulated ; these supersede those of Sugden and of Eisenlohr.

The results, particularly for the molecular refractivities, do not support the view of Phillips, Hunter, and Sutton (*J.*, 1945, 146) that the esters and acid chlorides of the oxy-acids of sulphur and phosphorus contain covalent double bonds.

In the deduction of the parachor and refractivities of the halogens, the author (*loc. cit.*) has employed compounds in which only one halogen atom is attached to a carbon atom. Other workers have not confined their calculations to such simple compounds : for instance, Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 594) includes ethylidene chloride, " dichloroacetic ester ", ethyl dichloropropionate, chloroform, chloral, butyl chloral, carbon tetrachloride, perchloroethylene, and pentachloroethane, whilst Sugden (" The Parachor and Valency ", Routledge, 1930, p. **37**) includes carbon tetrachloride, chloroform, methylene chloride, acetylene tetrachloride, and ethylidene chloride. The possibility that the attachment of two or more halogen atoms or groups to the same carbon atom may be partly responsible for the variations found for the constants appears to have been overlooked by previous investigators ; preliminary experiments are now described which have been designed to study the effect of poly-groupings. Alkyl dichloroacetates may be readily prepared in a state of purity ; the contributions of Cl_2 to the physical properties may be computed from the relationship :

$$Cl_2 = CHCl_2{\cdot}CO_2R + H - 0{\cdot}5(CH_2{\cdot}CO_2R)_2$$

The constants for H are from Part IX (*loc. cit.*) and the experimental data for dialkyl succinates have been taken from Part XIII (this vol., p. 624). The results are given in Table I. It will be noted that the parachor is slightly lower and the refractivities appreciably higher than those deduced for monochloro-compounds, the values for which are included in the table for purposes of comparison. The results obtained for methylene chloride ($CH_2Cl_2 - CH_2$), ethylidene chloride ($CH_3{\cdot}CHCl_2 + H - C_2H_5$) and acetylene tetrachloride ($CHCl_2{\cdot}CHCl_2 + 2H - 2CH_2$) are also included ; the refractivities for these compounds are appreciably lower than those deduced for the dichloroacetates and, in the author's view, these figures are less trustworthy owing to the difficulty of preparing and *keeping* these polyhalogenated hydrocarbons in a state of purity.

Table I.

Values for Cl_2 *from compounds containing the* Cl_2 *grouping.*

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$
$CHCl_2{\cdot}CO_2Me$	106·9	11·99	12·05	12·20	12·31	99·96
$CHCl_2{\cdot}CO_2Et$	109·3	11·98	12·04	12·19	12·30	99·61
$CHCl_2{\cdot}CO_2Pr^n$	107·2	12·00	12·05	12·21	12·31	99·57
$CHCl_2{\cdot}CO_2Bu^n$	105·9	11·92	11·98	12·12	12·24	99·72
Mean (Cl_2)	107·3	11·973	12·030	12·180	12·290	99·72
CH_2Cl_2	107·5	11·68	11·73	11·88	11·98	100·21
$CH_3{\cdot}CHCl_2$	107·9	11·76	11·82	11·97	12·08	98·86
$CHCl_2{\cdot}CHCl_2$	104·6	11·64	11·68	11·82	11·92	102·29
Mean Cl (from monohalogen compounds)	55·2	5·821	5·844	5·918	5·973	50·41

The constants of the Cl_3 group were obtained from measurements upon alkyl trichloroacetates :

$$Cl_3 = CCl_3{\cdot}CO_2R + 2H - 0{\cdot}5(CH_2{\cdot}CO_2R)_2$$

The results, as well as those for the unstable chloroform ($CHCl_3 + H - CH_2$) and the somewhat more stable methylchloroform ($CH_3{\cdot}CCl_3 + 2H - C_2H_5$), are collected in Table II ; it will be

Table II.

Values for Cl_3 *from compounds containing the* Cl_3 *grouping.*

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$CCl_3{\cdot}CO_2Me$	156·7	17·94	18·03	18·28	18·42	149·68
$CCl_3{\cdot}CO_2Et$	159·4	18·10	18·19	18·43	18·58	148·84
$CCl_3{\cdot}CO_2Pr^n$	158·6	17·94	18·03	18·28	18·41	148·84
$CCl_3{\cdot}CO_2Bu^n$	158·0	17·96	18·06	18·31	18·46	148·93
Mean (Cl_3)	158·2	17·985	18·078	18·325	18·468	149·07
$CHCl_3$	158·9	17·67	17·75	17·97	18·12	149·51
$CH_3{\cdot}CCl_3$	160·7	17·85	17·96	18·19	18·33	148·06

observed that the parachor is lower and the refractivities are higher per chlorine atom than those for monochloro-compounds. Similar effects are exhibited by carbon tetrachloride (CCl_4 — C), which gives for Cl_4 : P 212·4; R_{C} 23·76; R_{D} 23·86; R_{F} 24·26; $R_{\mathrm{G'}}$ 24·42; $Mn_{\mathrm{D}}^{20°}$ 198·94.

Only a few polybromo-compounds have so far been examined, with the following results :

	P	R_{C}.	R_{D}.	R_{F}.	$R_{\mathrm{G'}}$.	$Mn_{\mathrm{D}}^{20°}$.
Br_2 from CH_2Br_2	135·1	17·14	17·25	17·55	17·79	247·36
Br_2 from $CHBr_2{\cdot}CHBr_2$	—	17·26	17·37	17·67	—	259·51
Br_3 from $CHBr_3$	203·5	26·06	26·24	26·72	27·09	380·68
Mean Br (from monohalogen compounds)	68·8	8·681	8·741	8·892	9·011	118·07

No trustworthy conclusions can be drawn from these results alone, particularly from bromoform which is known to be unstable in the pure state, but it would appear that the parachor and the refractivities are lower for compounds with the Br_2 grouping.

By combining the author's density determinations for methylene iodide with the refractive index measurements by Timmermans and Hennaut-Roland (*J. Chim. physique*, 1932, **29**, 529), the values for I_2 are found to be : R_{C} 27·58, R_{D} 27·89, and R_{F} 28·73. The constants determined from monoiodo-compounds (Part XIV, *loc. cit.*) were : R_{C} 13·825, R_{D} 13·954, and R_{F} 14·310.

In Part XII (this vol., p. 616) it was shown that the constants for oxygen in dialkyl ethers were greater than those in acetals, $CHR'(OR)_2$; this is probably another example of the influence of two groupings attached to the same carbon atom upon the physical properties. The acetals $CH_2(OR)_2$ are of particular interest in that they permit the calculation of the contributions of $(OR)_2$ to the physical constants by mere subtraction of the constants for CH_2 (Part IX, *loc. cit.*). To investigate the effect of three alkoxyl groups attached to the same carbon atom, the physical properties of three trialkyl orthoformates were measured and the values for $\gtrdot$CH computed from :

$$\gtrdot\mathrm{CH} = \mathrm{CH(OR)_3} - 3(\mathrm{OR})$$

The results are given in Table III; it will be noted that the mean values for $\gtrdot$CH thus obtained are lower than those for (C + H) derived from aliphatic hydrocarbons (Part IX, *loc. cit.*).

TABLE III.

Values for $\gtrdot$CH *from trialkyl orthoformates*, $CH(OR)_3$.

Compound.	P.	R_{C}.	R_{D}.	R_{F}.	$R_{\mathrm{G'}}$.	$Mn_{\mathrm{D}}^{20°}$.
$CH(OEt)_3$	22·1	3·46	3·48	3·51	3·53	22·41
$CH(OPr^n)_3$	20·4	3·52	3·55	3·58	3·61	22·52
$CH(OBu^n)_3$	19·3	3·51	3·55	3·56	3·58	22·48
Mean ($\gtrdot$CH)	20·6	3·497	3·527	3·550	3·573	22·47
C + H (Part IX)	24·3	3·598	3·619	3·644	3·695	23·15

The parachors and the refractivities of thionyl chloride, sulphuryl chloride, phosphorus trichloride, and phosphorus oxychloride were determined primarily with the object of obtaining new evidence on the nature of the oxy-bond from considerations of the molecular refractivities. The results are collected below, including the differences (SO_2Cl_2 — $SOCl_2$) and ($POCl_3$ — PCl_3).

	P.	R_{C}.	R_{D}.	R_{F}.	R_{G}.	$Mn_{\mathrm{D}}^{20°}$.
SO_2Cl_2	188·4	21·31	21·43	21·70	21·92	194·80
$SOCl_2$	174·7	21·95	22·12	22·56	22·98	180·06
O (SO_2Cl_2 — $SOCl_2$)	13·7	—0·64	—0·69	—0·86	—1·06	14·74
$POCl_3$	218·6	24·97	25·05	25·36	25·59	224·03
PCl_3	201·6	26·08	26·27	26·74	27·11	208·04
O($POCl_3$ — PCl_3)	17·0	—1·11	—1·22	—1·38	—1·52	15·99

The negative values for the refractivities are particularly noteworthy. Similar calculations have been made from the data for dialkyl sulphates and dialkyl sulphites R_2SO_4 — R_2SO_3 (Part VII, *loc. cit.*) and the results are presented in Table IV. These figures are more trustworthy owing to

TABLE IV.

Constants for oxygen from R_2SO_4 — R_2SO_3.

R.	P.	R_{C}.	R_{D}.	R_{F}.	$R_{\mathrm{G'}}$.	Mn_{D}^{20}
Me	18·2	—0·07	—0·08	—0·15	—0·19	19·79
Et	18·8	—0·11	—0·14	—0·20	—0·26	20·37
Pr^n	16·8	—0·30	—0·33	—0·40	—0·46	20·80
Bu^n	17·4	—0·21	—0·25	—0·32	—0·36	23·40

the difficulties attending measurements with acid chlorides. The only refractivity data available for trialkyl phosphites * are those of Jones, Davies, and Dyke (*J. Physical Chem.*, 1933, **37**, 583) for triethyl and tri-*n*-amyl phosphites; these lead to the following values for R_3PO_4 (VII, **44** and VII, **49**) — R_3PO_3 :

	R_C.	R_D.	R_F.
$Et_3PO_4 - Et_3PO_3$	−1·13	−1·23	−1·36
$Am^n{}_3PO_4 - Am^n{}_3PO_3$	−1·29	−1·33	−1·48

The constants for $>SO_2$ in dialkyl sulphates may be computed from the relationship $>SO_2 = SO_2(OR)_2 - \{CH_2(OR)_2 - CH_2\}$, and those for $>SO$ in dialkyl sulphites may be similarly calculated from $>SO = SO(OR)_2 - \{CH_2(OR)_2 - CH_2\}$. The data for the acetals are given in Part XII (*loc. cit.*). The results are collected in Tables V and VI. The differences $>SO_2 - >SO$ (representing the mean contributions of the additional oxygen atom in passing from dialkyl sulphites to dialkyl sulphates), $>SO - S$ (sulphides; Part XXI, this vol., p. 1820) and $>SO_2 - S$ (sulphides) are tabulated below; these are compared with the constants for the covalent double bonds in ketones, *i.e.*, with $>CO$ (ketones; Part XI, *loc. cit.*) — C (Part IX, *loc. cit.*).

TABLE V.

Values for $>SO_2$ *from dialkyl sulphates,* $SO_2(OR)_2$.

Compound.	*P*.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$SO_2(OMe)_2$	87·6	7·79	7·83	7·87	7·91	92·64
$SO_2(OEt)_2$	87·5	7·87	7·89	7·94	7·98	93·44
$SO_2(OPr^n)_2$	83·8	7·77	7·81	7·85	7·88	94·08
$SO_2(OBu^n)_2$	82·6	7·78	7·82	7·85	7·90	94·19
Mean ($>SO_2$)	85·4	7·803	7·838	7·878	7·918	93·59
SO_2Cl_2	78·0	9·67	9·75	9·86	9·97	93·98

TABLE VI.

Values for $>SO$ *from dialkyl sulphites,* $SO(OR)_2$.

Compound.	*P*.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$SO(OMe)_2$	69·4	7·86	7·91	8·02	8·10	72·85
$SO(OEt)_2$	68·7	7·98	8·03	8·14	8·24	73·07
$SO(OPr^n)_2$	67·0	8·07	8·14	8·25	8·34	73·28
$SO(OPr^i)_2$ *	68·3	8·13	8·21	8·32	8·42	72·79
$SO(OBu^n)_2$	65·2	7·99	8·07	8·17	8·26	73·33**
$SO(OBu^i)_2$	66·5	7·99	8·06	8·16	8·26	73·39
$SO(OAm^n)_2$	65·6	8·01	8·07	8·21	8·28	73·23
Mean ($>SO$ excluding *)	67·1	7·983	8·046	8·158	8·247	73·19
$SOCl_2$	64·3	10·31	10·44	10·72	10·82	79·24

** $Mn_D^{20°}$ for $Bu^n{}_2SO_3$ in VII, **34** should be 278·01 and not 275·07.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$>SO_2 - >SO$	18·3	−0·180	−0·208	−0·280	−0·329	20·40
$>SO - S$ (sulphides)	18·5	0·131	0·125	0·077	0·014	20·33
$>SO_2 - S$ (sulphides)	36·8	−0·049	−0·083	−0·203	−0·315	40·73
$>CO$ (ketones) — C	36·5	2·072	2·077	2·122	2·117	16·68

The constants for the $\geqslant PO$ grouping were calculated from the relationship $\geqslant PO = PO(OR)_3 - 1{\cdot}5\{CH_2(OR)_2 - CH_2\}$. The results, utilising the data of Part VII (*loc. cit.*) upon trialkyl orthophosphates, are in Table VII; the individual variations are somewhat larger than those found for alkyl sulphites and sulphates.

The experimental data required for the calculation of the parachor and the refractivities of phosphorus are scanty : approximate values for the parachor may be obtained from the author's measurements upon phosphorus trichloride and tribromide, and for the refractivities R_C, R_D, and

* Strecker and Spitaler (*Ber.*, 1926, **59**, 1773) have, however, investigated triethyl phosphite.

TABLE VII.

Values for $\geqslant$PO *from trialkyl orthophosphates,* $PO(OR)_3$.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$PO(OMe)_3$	60·7	5·87 *	5·91	5·94	—	72·05
$PO(OEt)_3$	56·5	5·93	5·95	5·98	6·03	71·63
$PO(OPr^n)_3$	53·3	5·89	5·93	5·96	6·01	72·41
$PO(OPr^i)_3$	50·6	6·03	6·08	6·10	6·16	71·62
$PO(OBu^n)_3$	48·2	6·03	6·07 †	6·09	6·11	72·52
$PO(OBu^i)_3$	49·0	5·72	5·76	5·78	5·82 ‡	72·27
$PO(OAm^n)_3$	—	5·61	5·64	5·68	5·75	72·43
Mean ($\geqslant$PO)	53·1	5·87	5·91	5·93	5·98	72·13
$POCl_3$	60·4	6·98	6·97	7·03	7·12	74·96

* Arithmetical error in VII, **43**; for R_C 27·67, read R_C 27·62.
† Arithmetical error in VII, **47**; for R_D 69·57, read R_D 69·73.
‡ Arithmetical error in VII, **48**; for $R_{G'}$ 70·68, read $R_{G'}$ 70·74.

R_F from the measurements upon three trialkyl phosphines by Jones, Davies, and Dyke (*loc. cit.*). These lead to the following results.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.
PCl_3	36·0	8·62	8·75	8·98	9·19
PBr_3	39·3	—	8·85	—	—
$P(C_3H_7{}^n)_3$	—	8·93	9·04	9·32	—
$P(C_4H_9{}^n)_3$	—	8·97	9·07	9·30	—
$P(C_5H_{11}{}^n)_3$	—	8·82	8·92	9·14	—
Mean (P)	37·7	8·91	9·01	9·25	—

If these constants for phosphorus be subtracted from the mean figures for $\geqslant$PO, the following values for $\geqslant$PO – P are obtained: *P* 15·4; R_C – 3·04; R_D – 3·10; R_F – 3·32. The large negative values for the refractivities are particularly noteworthy.

The constants of the $\geqslant PO_4$ grouping in trialkyl orthophosphates, the $>SO_3$ grouping in dialkyl sulphites, and of the $>SO_4$ grouping in dialkyl sulphates have been computed in the usual manner from the data given in Part VII (*loc. cit.*) by subtracting the values for the alkyl groups (Part XI, *loc. cit.*); the values of the differences $\geqslant PO_4$ – P, $>SO_3$ – S (sulphides) and $>SO_4$ – S (sulphides) are included in Tables VIII, IX, and X respectively for purposes of comparison.

TABLE VIII.

Values for $\geqslant PO_4$ *from trialkyl orthophosphates,* R_3PO_4.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Me_3PO_4	120·0*	10·71	10·78	10·83	—	141·20
Et_3PO_4	113·8	10·82	10·87	10·94	11·04	139·03
$Pr^n{}_3PO_4$	109·5	10·73	10·76	10·83	10·91	139·89
$Pr^i{}_3PO_4$	108·5	10·84	10·86	10·90	10·99	138·36
$Bu^n{}_3PO_4$	103·4	10·94	10·97	11·03	11·08	140.08
$Bu^i{}_3PO_4$	103·9	10·63	10·65	10·70	10·77	139·38
$Am^n{}_3PO_4$	—	10·46	10·49	10·54	10·64	140·21
Mean $\geqslant PO_4$ (excluding *)	107·8	10·733	10·769	10·821	10·905	139·74
$\geqslant PO_4$ – P	70·0	1·82	1·76	1·57	—	—

TABLE IX.

Values for $>SO_3$ *from dialkyl sulphites,* R_2SO_3.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Me_2SO_3 *	108·9	11·09	11·15	11·28	11·41	118·95
Et_2SO_3	106·9	11·24	11·31	11·44	11·58	118·06
$Pr^n{}_2SO_3$	104·5	11·30	11·36	11·50	11·61	118·27
$Pr^i{}_2SO_3$	106·9	11·34	11·40	11·52	11·64	117·28
$Bu^n{}_2SO_3$	107·0	11·26	11·34	11·46	11·57	118·40
$Bu^i{}_2SO_3$	103·1	11·26	11·32	11·44	11·56	118·13
$Am^n{}_2SO_3$	103·1	11·21	11·30	11·45	11·54	118·42
Mean $>SO_3$ (excluding *)	105·3	11·273	11·338	11·468	11·550	118·09
$>SO_3$ – S (sulphides)	56·7	3·421	3·417	3·387	3·317	65·23

TABLE X.

Values for $>SO_4$ *from dialkyl sulphates,* R_2SO_4.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Me_2SO_4	127·1	11·02	11·07	11·13	11·22	138·74
Et_2SO_4	125·7	11·13	11·17	11·24	11·32	138·37
$Pr^n{}_2SO_4$	121·3	11·00	11·03	11·10	11·15	139·07
$Bu^n{}_2SO_4$	119·4	11·05	11·09	11·14	11·21	139·26
Mean $>SO_4$	123·4	11·050	11·090	11·153	11·225	138·86
$>SO_4$ − S (sulphides)	74·8	3·198	3·169	3·072	2·992	86·00

A comparison of the physical constants of the $\geqslant$PO grouping with those of the $^-$NO grouping (which is generally accepted to contain a covalent double bond) in nitrosoamines has been made. The constants for this grouping are readily determined with the aid of the experimental data for secondary aliphatic amines (Part XXII, preceding paper) :

$$^-NO = R_2N{\cdot}NO + H - R_2NH$$

The results are given in Table XI, as are also the values of $^-$NO − N (tertiary aliphatic amines) (Part XXII, *loc. cit.*), of O (ethers) (Part XII, *loc. cit.*) + $\vDash$ (carbon to carbon) (Part XVI, this vol., p. 658), and of CO (ketones) (Part XI, *loc. cit.*) − C. It will be noted that the differences of the refractivities are positive and of the same order as (O + $\vDash$) and (CO − C). [Slightly different vales for (NO − O) are obtained if the constants for N derived from NH_2 (primary aliphatic amines) and NH (secondary aliphatic amines) are employed.] Exact agreement is, indeed, not to be expected as there is no real evidence that the constants for the covalent double bonds are independent of the containing atoms. Sugden, Reed, and Wilkins (*J.*, 1925, **127**, 1525) have stated that the same value is found for the parachor for double bonds between carbon and carbon, carbon and oxygen, carbon and sulphur, and nitrogen and oxygen; this general statement cannot be accepted (see also below) since it has been shown in earlier papers of this series that the parachors (and refractivities) of sulphur, nitrogen, and oxygen vary with the nature of the other atoms attached to these elements.

TABLE XI.

Values of the $^-N{=}O$ *grouping from dialkyl nitrosoamines,* $R_2N{\cdot}NO$.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$Et_2N{\cdot}NO$	55·2	5·10	5·16	5·35	5·53	42·91
$Pr^n{}_2N{\cdot}NO$	54·6	5·17	5·25	5·44	5·63	43·23
$Bu^n{}_2N{\cdot}NO$	50·4	5·12	5·19	5·40	5·57	43·27
Mean −N = O	53·4	5·130	5·200	5·397	5·577	43·14
$^-$NO − N (tertiary aliphatic amines)	46·2	2·432	2·456	2·577	2·663	18·77
O (ethers) + $\vDash$ (carbon to carbon)	39·7	3·298	3·339	3·458	3·525	16·67
CO (ketones) − C	35·8	2·007	2·010	2·053	2·047	16·70

The new determination of the refractivities at 20° and the parachors of the dialkyl nitrosoamines have been employed in the computation of the constants of the nitrosamine $^-N{\cdot}NO$ grouping; the results are presented in Table XII. The constants for phenyl-methyl- and -ethyl-nitrosoamines (XXII, **528** and XXII, **530**) were derived by subtraction of the figures for methyl- and ethyl-benzene respectively (Part X, this vol., p. 607).

TABLE XII.

Values for $^-N{\cdot}NO$ *from dialkyl nitrosoamines,* $R_2N{\cdot}NO$.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$Me_2N{\cdot}NO$	73·1	7·85	7·96	8·20	8·46	70·12
$Et_2N{\cdot}NO$	69·0	7·73	7·83	8·08	8·35	69·43
$Pr^n{}_2N{\cdot}NO$	66·9	7·71	7·80	8·06	8·31	69·47
$Bu^n{}_2N{\cdot}NO$	62·9	7·70	7·81	8·06	8·31	69·44
Mean −N·NO	68·0	7·748	7·850	8·100	8·358	69·67
NPh(NO)Me	67·8	8·68	8·87	9·48	—	76·90
NPh(NO)Et	66·5	8·66	8·86	9·45	—	75·42

The parachors and refractivities of a number of nitro-paraffins and of alkyl nitrites have been determined, and the constants for the nitro-group and the nitrite group have been computed in the usual manner. The results are collected in Tables XIII and XIV, respectively. In

TABLE XIII.

Values for $-NO_2$ *from nitro-paraffins,* $R{\cdot}NO_2$.

Compound.	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20^\circ}$.
$MeNO_2$	77·2	6·65	6·71	6·82	6·94	65·42
$EtNO_2$	75·6	6·67	6·72	6·84	6·94	65·77
Pr^nNO_2	73·8	6·60	6·67	6·76	6·91	65·61
Pr^iNO_2 *	76·0	6·57	6·61	6·72	6·82	65·28
Bu^nNO_2	72·5	6·70	6·74	6·85	6·95	65·62
Am^nNO_2	71·9	6·67	6·71	6·82	6·92	65·60
$C_6H_{13}{}^nNO_2$	71·6	6·68	6·73	6·85	6·95	65·63
Mean $-NO_2$ (excluding *)	73·8	6·662	6·713	6·823	6·918	65·61
$Ph{\cdot}NO_2$	75·6	7·24	7·36	7·71	8·08	69·10

TABLE XIV.

Values for $-ONO$ *from alkyl nitrites,* $R{\cdot}O{\cdot}NO$.

Compound.	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20^\circ}$.
$Bu^n{\cdot}O{\cdot}NO$	75·6	7·23	7·28	7·42	7·55	62·17
$Am^n{\cdot}O{\cdot}NO$	74·9	7·14	7·19	7·32	7·46	62·30
$C_6H_{13}{}^n{\cdot}O{\cdot}NO$	75·4	7·19	7·24	7·39	7·51	62·34
Mean $-O{\cdot}NO$	75·3	7·187	7·237	7·377	7·507	62·27

comparing the mean constants for the nitro- and the nitrite group, it will be observed that the parachors differ only slightly but the refractivities of the former are appreciably less than those of the latter.

The constants for the nitrate group have been deduced from measurements upon three alkyl nitrates and are given in Table XV. The values for $-NO_3 - -O{\cdot}NO$ (nitrite) and for $-NO_3 - -NO_2$ (nitro) are included in the table; the former differences are of particular interest in that they give the influence of the additional oxygen, presumably attached by a co-ordinate link, in passing from alkyl nitrites to alkyl nitrates. It will be noted that these figures differ considerably from those obtained from alkyl sulphates — alkyl sulphites (Table IV) or $>SO_2 - >SO$.

TABLE XV.

Values for $-NO_3$ *from alkyl nitrates,* RNO_3.

Compound.	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20^\circ}$.
$EtNO_3$	93·8	8·92	8·98	9·12	9·25	87·44
Pr^nNO_3	92·0	9·01	9·06	9·20	9·32	87·65
Bu^nNO_3	92·8	8·99	9·05	9·19	9·31	87·73
Mean $-NO_3$	92·9	8·973	9·030	9·170	9·293	87·59
$-NO_3 - -O{\cdot}NO$ (nitrite)	17·6	1·786	1·793	1·793	1·786	25·32
$-NO_3 - -NO_2$ (nitro)	19·1	2·311	2·327	2·347	2·375	21·98

The parachors and the refractivities of a number of dialkyl carbonates have been determined and the constants of the $>CO_3$ group have been computed in the usual manner. The results are given in Table XVI. The new data may be employed to provide evidence for the usual formula of dialkyl carbonates $(RO)_2C{=}O$. The constants for the $>CO$ grouping may be calculated by subtraction of the values for $(OR)_2$, which are readily derived from acetals $CH_2(OR)_2 - CH_2$. The constants for $>CO$ thus obtained are in reasonable agreement with those for $>CO$ deduced from dialkyl ketones CORR′ (Part XI, *loc. cit.*).

TABLE XVI.

Values for $>CO_3$ *from dialkyl carbonates,* R_2CO_3.

Compound.	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20^\circ}$.
Me_2CO_3	85·0	7·62	7·66	7·72	7·80	87·02
Et_2CO_3	83·6	7·67	7·71	7·76	7·84	85·99
$Pr^n{}_2CO_3$	82·3	7·67	7·71	7·78	7·85	86·26
$Bu^n{}_2CO_3$	80·2	7·64	7·67	7·73	7·76	86·35
$Bu^i{}_2CO_3$	80·8	7·71	7·73	7·78	7·84	86·12
Mean $>CO_3$	82·4	7·662	7·696	7·754	7·818	86·35

TABLE XVII.

Values for >CO *from dialkyl carbonates,* $CO(OR)_2$.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$CO(OMe)_2$	45·4	4·39	4·42	4·46	4·49	40·92
$CO(OEt)_2$	45·4	4·41	4·43	4·46	4·50	41·16
$CO(OPr^n)_2$	44·8	4·46	4·49	4·53	4·58	41·27
$CO(OBu^n)_2$	43·4	4·37	4·40	4·44	4·45	41·28
$CO(OBu^i)_2$	44·2	4·44	4·47	4·50	4·54	41·38
Mean >CO	44·6	4·414	4·442	4·478	4·512	41·20
>C=O (ketones)	44·4	4·579	4·601	4·654	4·702	42·41

Determinations of the parachors and refractivities of a number of alkyl thiocyanates and *iso*thiocyanates have been made with the object of deducing the constants of these groups. The results are collected in Tables XVIII and XIX. It is now generally accepted that thiocyanates have the structure R–S–C≡N and *iso*thiocyanates R–N=C=S. Subtraction of the constants for S (in sulphides) (Part XXI, *loc. cit.*) from the mean values for the thiocyanate group –SCN gives the following values for the residual –CN; these are in reasonable agreement with the constants already deduced (Part XVII, *loc. cit.*) for –C≡N for alkyl cyanides.

TABLE XVIII.

Values for –SCN *from alkyl thiocyanates,* R•SCN.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
MeSCN	113·6	13·18	13·28	13·49	13·68	89·23
EtSCN	112·0	13·33	13·42	13·65	13·82	88·77
Pr^nSCN	111·7	13·34	13·42	13·65	13·84	88·77
Bu^nSCN	110·7	13·39	13·48	13·71	13·89	88·22
Mean –SCN	112·0	13·313	13·400	13·603	13·808	88·90

TABLE XIX.

Values for –NCS *from alkyl* iso*thiocyanates,* R•NCS.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
EtNCS	114·7	15·43	15·62	15·97	16·30	92·37
C_3H_5NCS	113·1	15·46	15·61	15·99	16·30	93·85
Mean –NCS	113·9	15·445	15·615	15·980	16·300	93·11

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
–CNS – S	63·4	5·461	5·479	5·522	5·575	36·04
–C≡N (Part XVII)	64·6	5·431	5·459	5·513	5·561	36·46

The refractivities and parachors of a number of alkyl xanthates have been determined with the object of deducing the constants for the >C=S grouping. It may be noted that the physical properties (parachor and refractivites) of *ethyl* S-n-*butylxanthate* CS(OEt)•SBu^n, n-*butyl* S-*ethylxanthate* CS(OBu^n)•SEt and of *di*-n-*propyl xanthate* are substantially identical. The constants for the >CS grouping were computed from the data for disulphides (Part VII, *loc. cit.*) and acetals (Part XII, *loc. cit.*) thus :

$$>CS = CS(OR)SR - [0{\cdot}5R_2S_2 + 0{\cdot}5\{CH_2(OR)_2 - CH_2\}]$$

The results are summarised in Table XX.

TABLE XX.

Values for >CS *from alkyl xanthates,* CS(OR)•SR.

Compound.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CS(OEt)•SEt	75·8	12·57	12·77	13·35	13·88	77·09
CS(OPr^n)•SPr^n	74·6	12·96	13·19	13·80	14·37	77·41
CS(OBu^n)•SBu^n	72·3	12·99	13·24	13·86	14·42	77·11
Mean >C=S	74·2	12·84	13·07	13·67	14·22	77·20

The physical constants of the following groups containing covalent double bonds have so far been determined : C=O (Part XI, *loc. cit.*), C=S and N=O; it is of interest to compare the constants for the three different types of double bond with those for the carbon to carbon double bond (Part XVI, this vol., p. 658). As a first approximation, the following values for the atomic constants have been used : C (in CH_2), O (in ethers), S (in sulphides), N (in tertiary aliphatic amines) (*A*) and N (in secondary aliphatic amines) (*B*). Another series of values for the carbon–sulphur double bond may be computed from Timmermans and Martin's refractivity data (*J. Chim. physique*, 1928, **25**, 413) (R_C 21·12, R_D 21·39, R_F 22·05, $R_{G'}$ 22·64, and $Mn_D^{20°}$ 123·94) and Lek's parachor (Thesis, Brussels, 1930; Sidgwick, Sugden, and Adams, *B.A. Report*, 1932, p. 265) (143·6) for carbon disulphide. By subtracting the author's constants for C (in CH_2) and S (in sulphides), the following constants are obtained for the carbon–sulphur double bond in carbon disulphide: *P* 18·9, R_C 1·43, R_D 1·48, R_F 1·65, $R_{G'}$ 1·76, $Mn_D^{20°}$ – 3·75; these, it will be noted, differ considerably from the figures deduced from alkyl xanthates. The main feature of Table XXI is the variation of the constants for the different double bonds; these results do not

TABLE XXI.

Preliminary constants for covalent double bonds.

Nature of bond.	*P*.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
C=O	16·0	0·25	0·25	0·27	0·24	–6·04
C=S	17·0	2·42	2·56	2·99	3·33	–1·37
N=O (*A*)	26·4	0·68	0·69	0·79	0·76	–3·97
N=O (*B*)	20·9	0·83	0·85	0·99	1·08	–5·50
C=C	19·9	1·545	1·575	1·672	1·720	–6·07

support Sugden's assertion (*J.*, 1925, **127**, 1525; *op. cit.*, p. 38) that the parachor value is independent of the elements connecting the double bond, although it must be admitted that the variation of the parachor is less than that for the refractivities.

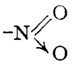
The physical constants of the carbon–nitrogen triple bond may be evaluated by subtraction of C (in CH_2) and N (in tertiary aliphatic amines) from those for nitriles $-C{\equiv}N$ (Part XVII, *loc. cit.*); these are compared with those already found for the terminal carbon to carbon triple bond (Part XVII, *loc. cit.*):

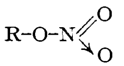
	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$\equiv$ (carbon–nitrogen)	48·8	0·161	0·124	0·092	–0·008	–13·62
$\equiv$ (carbon–carbon, terminal)	40·6	1·959	1·977	2·061	2·084	–12·56

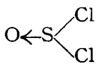
These results are not in agreement with Sugden's statement (*J.*, 1924, **125**, 1179) that the same triple-bond constant [for the parachor] can be used for nitriles and acetylenes (compare Sugden, Reed, and Wilkins, *loc. cit.*).

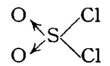
The parachor and refractivity values for the various elements, structural constants, and groups so far determined are collected in Table XXII; these supersede those of Sugden and of Eisenlohr.

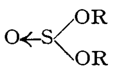
Discussion of the Structure of Esters of Oxy-acids and Related Compounds.—The structures for the nitro-group, alkyl nitrates, thionyl chloride, sulphuryl chloride, dialkyl sulphites, dialkyl sulphates, phosphorus oxychloride, and trialkyl orthophosphates were given as (I)—(VIII) by Sugden, Reed, and Wilkins (*loc. cit.*) from determinations of the parachor and the application of the octet rule:

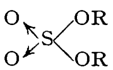

(I.)

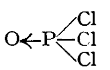

(II.)

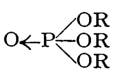

(III.)


(IV.)

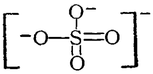

(V.)

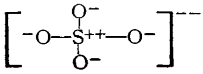

(VI.)

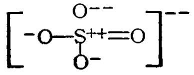

(VII.)

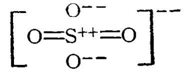

(VIII.)

The presence of co-ordinate or dative links in all these compounds, with the apparent exception of nitro-compounds and of esters of nitric acid, has been questioned on the basis of measurements of bond distances. Thus the S–O distance in the sulphate ion is 1·51 A., which is considerably less than the sum of the single-bond covalent radii (1·70 A.) and approximates to the sum of the double-bond covalent radii (1·49 A.), and has led Pauling (" The Nature of the Chemical Bond ", Cornell, 1940, pp. 240—243) to propose the structure (IX) together with such resonating


$$\left[{}^{-}O-\overset{O^{-}}{\underset{O}{S}}{=}O\right]^{--}$$
(IX.)


$$\left[{}^{-}O-\overset{O^{-}}{\underset{O^{-}}{S^{++}}}-O^{-}\right]^{--}$$
(X.)


$$\left[{}^{-}O-\overset{O^{--}}{\underset{O^{-}}{S^{++}}}{=}O\right]^{--}$$
(XI.)


$$\left[O{=}\overset{O^{--}}{\underset{O^{--}}{S^{++}}}{=}O\right]^{--}$$
(XII.)

structures as (X)—(XII) to account for the fact that the S–O distance is very close to that expected for pure double bonds. Wells (" Structural Inorganic Chemistry ", Oxford, 1945,

TABLE XXII.

Atomic, structural, and group parachors and refractivities.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CH_2	40·0	4·624	4·647	4·695	4·735	20·59
H (in CH_2)	15·7	1·026	1·028	1·043	1·040	−2·56
C (in CH_2)	8·6	2·572	2·591	2·601	2·655	25·71
O (in ethers)	19·8	1·753	1·764	1·786	1·805	22·74
O (in acetals)	18·0	1·603	1·607	1·618	1·627	22·41
CO (in ketones)	44·4	4·579	4·601	4·654	4·702	42·41
CO (in methyl ketones)	46·7	4·730	4·758	4·814	4·874	42·42
COO (in esters)	63·4	6·173	6·200	6·261	6·315	64·14
OH (in alcohols)	30·2	2·536	2·546	2·570	2·588	23·94
CO_2H	73·7	7·191	7·226	7·308	7·368	63·98
Cl	55·2	5·821	5·844	5·918	5·973	50·41
Br	68·8	8·681	8·741	8·892	9·011	118·07
I	90·3	13·825	13·954	14·310	14·620	196·27
F	26·1	0·81	0·81	0·79	0·78	21·84
NH_2 (in primary aliphatic amines)	44·0	4·414	4·438	4·507	4·570	22·64
NH (in secondary aliphatic amines)	28·4	3·572	3·610	3·667	3·732	23·34
NH (in secondary aromatic amines)	27·1	4·548	4·678	5·000	5·273	29·52
N (in tertiary aliphatic amines)	7·2	2·698	2·744	2·820	2·914	24·37
N (in tertiary aromatic amines)	?	4·085	4·243	4·675	5·155	30·23
NO (nitroso)	53·4	5·130	5·200	5·397	5·577	43·14
O·NO (nitrite)	75·3	7·187	7·237	7·377	7·507	62·27
NO_2 (nitro)	73·8	6·662	6·713	6·823	6·918	65·61
N·NO (nitrosoamine)	68·0	7·748	7·850	8·100	8·358	69·67
S (in sulphides)	48·6	7·852	7·921	8·081	8·233	52·86
S_2 (in disulphides)	97·2	15·914	16·054	16·410	16·702	106·52
SH (in thiols)	66·4	8·691	8·757	8·919	9·057	50·20
CS (in xanthates)	74·2	12·84	13·07	13·67	14·22	77·20
SCN (in thiocyanates)	112·0	13·313	13·400	13·603	13·808	88·90
NCS (in *iso*thiocyanates)	113·9	15·445	15·615	15·980	16·300	93·11
Carbon–carbon double bond, ⊨	19·9	1·545	1·575	1·672	1·720	−6·07
Carbon–carbon triple bond, terminal, ⫢	40·6	1·959	1·977	2·061	2·084	−12·56
CN (in nitriles)	64·6	5·431	5·459	5·513	5·561	36·46
Three-carbon ring	12·3	0·592	0·614	0·656	0·646	−4·72
Four-carbon ring	10·0	0·303	0·317	0·332	0·322	−4·67
Five-carbon ring	4·6	−0·19	−0·19	−0·19	−0·22	−4·56
Six-carbon ring	1·4	−0·15	−0·15	−0·16	−0·17	−3·53
CO_3 (carbonates)	82·4	7·662	7·696	7·754	7·818	86·35
SO_3 (sulphites)	105·3	11·273	11·338	11·468	11·550	118·09
NO_3 (nitrates)	92·9	8·973	9·030	9·170	9·293	87·59
SO_4 (sulphates)	123·4	11·050	11·090	11·153	11·225	138·86
PO_4 (orthophosphates)	107·8	10·733	10·769	10·821	10·905	139·74
CH_3	55·4	5·636	5·653	5·719	5·746	18·13
C_2H_5	95·4	10·260	10·300	10·414	10·481	38·72
$C_3H_7{}^n$	135·5	14·895	14·965	15·125	15·235	59·25
$C_3H_7{}^i$	133·8	14·905	14·975	15·145	15·255	58·95
$C_4H_9{}^n$	175·3	19·500	19·585	19·800	19·950	79·81
$C_4H_9{}^i$	173·8	19·530	19·620	19·840	19·990	79·54
$C_4H_9{}^s$	171·2	19·330	19·420	19·625	19·775	80·21
$C_5H_{11}{}^n$	215·0	24·140	24·250	24·515	24·700	100·46
$C_5H_{11}{}^i$ (from the synthetic alcohol)	212·6	24·095	24·195	24·460	24·650	100·30
$C_5H_{11}{}^i$ (from fermentation alcohol)	213·1	24·170	24·280	24·540	24·720	100·21
$C_6H_{13}{}^n$	255·0	28·725	28·855	29·160	29·385	121·10
$C_7H_{15}{}^n$	295·7	33·395	33·550	33·905	34·170	141·75
$C_8H_{17}{}^n$	335·7	37·960	38·135	38·535	38·830	162·43
C_3H_5 (allyl)	124·3	14·425	14·520	14·745	14·920	57·60
C_6H_5	188·3	25·136	25·359	25·906	26·356	122·03

pp. 320, 321), in discussing Pauling's views on the structure of the sulphate ion, states : " It will probably be felt that this way of arriving at a picture of an ion apparently so simple as SO_4^{--} leaves much to be desired, but it seems the only method available at present. Similar difficulties are experienced with many molecular halides, oxy- and sulpho-halides and the more complex oxy-ions of Si, P, S, and the halogens."

Phillips, Hunter, and Sutton (*loc. cit.*) from considerations of dipole moments, thermal data, and bond distances maintain that the co-ordinate links in the above formulæ (nitrates and nitro-compounds, although formulated, are not discussed in any detail) are double bonds and that such structures as (X)—(XII) are of minor importance. Their arguments are based upon numerous approximations (which are inevitable in the present state of our knowledge) and include the use of Schomaker and Stevenson's empirical correction for the difference of the Pauling electronegativities between the bonded atoms (*J. Amer. Chem. Soc.*, 1941, **63**, 37) in order to establish their hypothesis that the co-ordinate link is nearly the same length as is to be expected for a normal single covalency between the same two atoms (compare, however, Wells, *op. cit.*, p. 322). It may be noted that the Schomaker and Stevenson correction does not always give the desired result: thus Rogers and Spurr (*J. Amer. Chem. Soc.*, 1947, **69**, 2102) found the Te–Br distance in tellurium dibromide by the electron-diffraction method to be 2·51 A.; the sum of the single bond radii is 2·51 A., and the value obtained after the electronegativity correction has been applied is 2·45 A. A powerful argument employed by Phillips, Hunter, and Sutton is based upon the dipole moments of Me_3NO, Ph_3PO, Ph_3PS, Me_3N,BCl_3, Me_3N,BF_3, Me_3P,BCl_3, Ph_3P,BCl_3, Et_2O,BF_3, and Et_2S,BCl_3. It may be pointed out that many of these compounds are hygroscopic and sparingly soluble in benzene so that the difficulties of measurement are not inconsiderable; furthermore many assumptions are made in deducing the dipole moments of the various links. On the whole it would appear that, although a reasonable case has been made by Phillips, Hunter, and Sutton, the approximations so frequently introduced leave one with the impression that conclusions of such importance require further confirmation with other compounds and by other methods less open to criticism.

Pauling ("General Chemistry", Freeman, 1947, pp. 161, 162) writes the structures of the oxy-acids (nitric, phosphoric, sulphuric, perchloric, sulphurous, and chlorous acids) on the basis of the octet rule, *i.e.*, with co-ordinate or dative bonds.

The experimental results on parachors and molecular refractivities described in the present communication provide data for the attack of the problem from another viewpoint. It may be said at once that there is no evidence from these two sources that the compounds, previously assumed to contain co-ordinate links, contain double bonds as asserted by Phillips, Hunter, and Sutton. Broadly speaking, the parachor is far less sensitive to changes of structure than the molecular refractivity, so that special consideration will be given to the latter. The evidence may be summarised under the following headings:

(1) The differences ($SO_2Cl_2 - SOCl_2$) and ($POCl_3 - PCl_3$) give values for the parachor approximating to that for the oxygen atom alone (in agreement with Sugden), whilst the molecular refractivites are *negative*. Similar results are obtained for the series (alkyl sulphates — alkyl sulphites), *i.e.*, ($R_2SO_4 - R_2SO_3$) (Table IV). Data for trialkyl orthophosphites are scanty, but for the triethyl and tri-*n*-amyl esters the R_D differences for $R_3PO_4 - R_3PO_3$ are negative (— 1·28).

(2) The constants for $>SO_2$ (dialkyl sulphates) and $>SO$ (dialkyl sulphites) have been evaluated (Tables V and VI, respectively). The differences in R_D * for $>SO_2 - S$ (sulphides) and for $>SO - S$ (sulphides) are either negative (P 36·8; R_D — 0·08) or quite small (P 18·5; R_D 0·13).

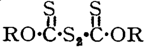
(3) Similarly the differences in P and R_D for $\geqslant PO$ (orthophosphates; Table VII) — P are 15·3 and — 3·10, respectively.

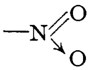
(4) The constants for the $-N{=}O$ grouping (P 53·4; R_D 5·20; Table XI) may be easily computed from the experimental data on aliphatic nitrosoamines; here the presence of a covalent double bond is generally accepted. The differences in P and R_D for $-N{=}O - N$ (tertiary aliphatic amines) are 46·2 (*i.e.*, O + *double bond*) and 2·56 (a *positive* value considerably greater than for O alone) respectively.

(5) The constants for $S{=}$, computed from $>C{=}S$ deduced from alkyl xanthates (Table XX), are P 65·6 and R_D 10·48 † (*i.e.*, $>C{=}S - C$); the corresponding values deduced from carbon disulphide are 67·5 and 9·40 respectively. The constants for S (sulphides) are P 48·6 and R_D 7·92. It is generally agreed that both alkyl xanthates and carbon disulphide contain covalent double bonds. The corresponding values for (S + "bond attached to oxygen") calculated from $>SO$ (alkyl sulphites) — O (ethers) are P 47·3 and R_D 4·52, whilst for $>SO_2$ (alkyl sulphates) — 2 × O (ethers) the figures are P 47·8 and R_D 0·78 respectively. The "bond attached to oxygen" in alkyl sulphites and sulphates would therefore not appear to be a double bond.

---

* Although R_D is specifically mentioned, the remarks apply equally to R_C, R_F, and $R_{G'}$ throughout the disscussion.

† A higher value (11·29) for the refractivity for $S{=}$ (D line) is obtained from the ethyl and *n*-propyl dithiothioncarbonate  $RO\cdot\overset{\overset{S}{\|}}{C}\cdot S_2\cdot\overset{\overset{S}{\|}}{C}\cdot OR$ (Price and Twiss, *J.*, 1912, **51**, 1263; Nasini and Skala, *Gazzetta*, 1887, **17**, 67); this value must be regarded as approximate as it is based upon early measurements of the refractivities.

(6) The constants for the nitro group  $-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ are P 73·8 and R_D 6·71 (Table XIII) and for the nitrite group $-O{\cdot}N{=}O$ are P 75·3 and R_D 7·24 (Table XIV); the co-ordinate link in nitro-compounds has only a minor effect upon the parachor but produces an appreciable diminution of the molecular refractivity. The contribution of the additional oxygen atom in passing from alkyl nitrites to alkyl nitrates may be calculated from $-NO_3 - -O{\cdot}N{=}O$ and is P 17·6 and R_D 1·793 [compare $>SO - S$ and $>SO_2 - S$ and also $\geqslant PO - P$ in (2) and (3) above].

The following conclusions may be drawn:

(*a*) Parachor and particularly molecular refractivity determinations do not appear to provide any evidence for the presence of double covalent bonds in the compounds (I)—(VIII), which include the simple derivative of the oxy-acids of sulphur and phosphorus.

(*b*) The co-ordinate link in nitro-paraffins and in alkyl nitrates has little effect upon the parachor but there is a distinct decrease in the molecular refractivity.

Calculations are in progress of the bond refractivities and refractivities of electron groups utilising the experimental data described in this and the previous papers of this series; it is hoped that these will help to throw further light on *inter alia* the nature of oxy-bonds.

Structure of the Azide Group.—Sugden (*op. cit.*, p. 123) claims to have shown that the cyclic structure for the azide group is supported by the parachors of a number of covalent azides (Lindemann and Thiele, *Ber.*, 1928, **61**, 1529) and gives a mean value for the azide group of 77·2. In deducing the theoretical value for the cyclic structure he has assumed, without experimental evidence, that the parachor increments for the three-membered nitrogen ring and the nitrogen–nitrogen double bond are identical with those for the corresponding carbon structures; furthermore, the constant for the three-carbon ring is 12·3 (Part XVIII, this vol., p. 1804) and not 16·7 (the figure employed by Sugden). The theoretical parachors for the various alternative structures cannot at present be computed owing to the absence of suitable data for nitrogen compounds. An approximation may, however, be arrived at by comparing the *iso*thiocyanate group $-N{=}C{=}S$ (i) with the azide structure $-N{\leftarrow}N{=}N$ (ii). By subtracting the values for C (15·7) and S (48·6) and substituting values for 2 × N (12·0; mean constant deduced from $NH_2 - 2H$ and $NH - H$) in the constant for the *iso*thiocyanate group (113·9), the figure of 73·6 is obtained for the structure (ii). This is sufficiently close to the observed value 77 to support the linear configuration. A similar calculation cannot be made for the molecular refractivity, which is far more sensitive to changes of structure than the parachor. The experimental molecular refractivity data for covalent azides provided by Philip (*J.*, 1908, **93**, 918; 1912, **101**, 1866) cannot at present be employed to decide between the cyclic and the open-chain structures.

Comments on the Work of Strecker and Spitaler (*Ber.*, 1926, **59**, 1755).—This paper was overlooked when the author's experimental work was first planned during 1940 and the literature searched. It is essentially an attempt to deduce the structures of certain inorganic compounds, largely oxy-derivatives of sulphur, by spectrochemical methods; the compounds investigated included the dimethyl, diethyl, and di-*n*-propyl sulphides, sulphones, sulphoxides, symmetrical and unsymmetrical sulphites, and sulphates, and also triethyl phosphite, phosphate, and thiophosphate. Their general discussion is based upon formulæ for sulphoxides, sulphones, *s*-sulphites, *as*-sulphites, and sulphates incorporating covalent double bonds. The refractivity results are similar to those of the present author, and have been interpreted *inter alia* by assigning values for S according to the so-called valency, *e.g.*, for R_{He} they give $C - S^{II} - C$ 7·80, $C - S^{IV} - C$ 6·98, and $C - S^{VI} - C$ 5·34.

Their measurements may be employed to give preliminary values for certain constants by combining them with the experimental data given in this series.

(1) Subtraction of the constants for alkyl groups (Part XI, *loc. cit.*) from the refractivities found for sulphoxides gives $R_2SO - R_2$, *i.e.*, c — SO — c.

	R_C.	R_D.	R_F.	$R_{G'}$.
$Me_2SO - Me_2$	8·64	8·72	8·86	9·05
$Et_2SO - Et_2$	8·53	8·64	8·79	8·98
$Pr^n{}_2SO - Pr^n{}_2$	8·52	8·59	8·76	8·92

These constants differ from those found for dialkyl sulphite o — SO — o (Table VI).

(2) The contributions of the oxygen atom in sulphoxide can be deduced directly from $R_2SO - R_2S$ (Part VII, *loc. cit.*) and are:

	R_C.	R_D.	R_F.	$R_{G'}$.
Me_2SO — Me_2S	0·89	0·90	0·89	0·93
Et_2SO — Et_2S	0·70	0·71	0·67	0·69
$Pr^n{}_2S$ — $Pr^n{}_2S$	0·72	0·73	0·73	0·75

(3) The measurements on the solid dialkyl sulphones were carried out at temperatures of the order of 100° and these values have been employed in the evaluation of the constants for O_2 in sulphones (they are clearly very approximate), *i.e.*, R_2SO_2 — R_2S (Part VII, *loc. cit.*) :

	R_C.	R_D.	R_F.	$R_{G'}$.
Me_2SO_2 — Me_2S	8·62	8·66	8·73	8·85
Et_2SO_2 — Et_2S	8·58	8·67	8·74	8·86
$Pr^n{}_2SO_2$ — $Pr^n{}_2S$	8·66	8·68	8·77	8·89

(4) The differences (*as*-dialkyl sulphites — *s*-dialkyl sulphites) are negative. In the results given below the data for dialkyl sulphites are those from Part VII (*loc. cit.*); *as*.-diethyl sulphite has already been investigated in Part VII and the figures are given in the line Et (V).

as-Sulphite — *s*-sulphite : R =	R_C.	R_D.	R_F.	$R_{G'}$.
Me	−1·25	−1·27	−1·33	−1·34
Et	−1·42	−1·45	−1·49	−1·49
Et (V)	−1·61	−1·70	−1·70	−1·77
Pr^n	−1·47	−1·50	−1·55	−1·53

Further comments on the above are deferred pending the completion of the calculations of bond refractivities and refractivities of electron groups.

EXPERIMENTAL.

Dichloroacetic Acid.—This acid was prepared from pure chloral hydrate (*Org. Synth.*, 1939, **19**, 38) and had b. p. 105—106°/26—27 mm.

Silver salt. 160 G. of the pure acid were treated with 386 ml. of 3·22N-ammonia solution in a 2-l. beaker, and then a solution of 232 g. of silver nitrate in 500 ml. of water was added with mechanical stirring during 30 minutes. After standing overnight in the dark, the crystalline solid was collected (the filtrate was kept), washed, and dried first between filter paper and finally in a vacuum desiccator over silica gel and anhydrous calcium chloride in the dark to constant weight: the yield of silver dichloroacetate was 148 g. (theory: about 290 g.). The filtrate from the silver salt was treated with excess of dilute hydrochloric acid, filtered, the filtrate extracted three times with ether, dried, and distilled: about 75 g. of dichloroacetic acid were recovered.

Methyl dichloroacetate. 39 G. of silver dichloroacetate were suspended in 75 ml. of sodium-dried A.R. benzene in a flask fitted with a reflux condenser, and 26 g. of pure methyl iodide were added dropwise. The mixture was warmed gently until reaction commenced: when the violent reaction was over, the mixture was refluxed for 2 hours, filtered at the pump, and the solid washed with benzene. The combined filtrate and extracts were washed twice with saturated sodium hydrogen carbonate solution and water, dried ($CaSO_4$), and distilled. The yield of ester, b. p. 143°/763 mm., was 9 g.

Ethyl dichloroacetate. This was prepared from 39 g. of dry silver dichloroacetate, 75 ml. of dry benzene, and 29 g. of pure ethyl iodide. The mixture was refluxed for 5 hours and yielded, as detailed for the methyl ester, 10 g. of ethyl dichloroacetate, b. p. 155·5°/764 mm.

n-*Propyl dichloroacetate.* A mixture of 31 g. of silver dichloroacetate, 75 ml. of dry benzene, and 25 g. of *n*-propyl iodide was refluxed for 1·5 hours, and afforded 11·5 g. of ester, b. p. 174·5—175°/769 mm.

n-*Butyl dichloroacetate.* A mixture of 39 g. of silver dichloroacetate, 75 ml. of dry benzene, and 32 g. of *n*-butyl iodide yielded, as for the methyl ester, after refluxing for 4 hours, 12 g. of *ester*, b. p. 192°/749 mm. (Found: Cl, 38·5. $C_6H_{10}O_2Cl_2$ requires Cl, 38·3%).

Methyl Trichloroacetate.—A mixture of 32 g. of B.D.H. A.R. trichloroacetic acid, 64 g. of Burrough's synthetic absolute methyl alcohol, and 3·2 g. of concentrated sulphuric acid was refluxed for 20 hours, about half of the excess of alcohol was distilled off on a water-bath, the residue poured into excess of water, and the lower layer of ester (24 g.) separated. This was washed with saturated sodium hydrogen carbonate solution and water, dried, and distilled; the ester boiled constantly at 152°/758 mm.

Ethyl Trichloroacetate.—A mixture of 32 g. of the A.R. acid, 92 g. of absolute ethyl alcohol, and 4·6 g. of concentrated sulphuric acid was refluxed for 60 hours and yielded, as for the methyl ester with the modification that the ester was isolated by ether extraction, 20 g. of pure ethyl trichloroacetate, b. p. 166°/755 mm.

n-*Propyl Trichloroacetate.*—A mixture of 32 g. of the A.R. acid, 24 g. of pure *n*-propyl alcohol, 50 ml. of sodium-dried A.R. benzene, and 10 g. of concentrated sulphuric acid was refluxed for 40 hours, poured into excess of water, and ether added to assist the separation of the benzene layer. The ether–benzene extract of the ester was washed with saturated sodium hydrogen carbonate solution and water, dried, and distilled. The yield of ester, b. p. 68°/8·5 mm., was 30 g.

n-*Butyl Trichloroacetate.*—A mixture of 32 g. of the A.R. acid, 30 g. of pure *n*-butyl alcohol, 50 ml. of dry benzene, and 10 g. of concentrated sulphuric acid was refluxed for 60 hours and yielded, as for the *n*-propyl ester, 40 g. of n-*butyl trichloroacetate*, b. p. 204°/762 mm., 81·5°/7·5 mm. (Found: Cl, 48·3. $C_6H_9O_2Cl_3$ requires Cl, 48·5%).

Methylene Chloride.—The commercial product was fractionated and the fraction of b. p. 40—41° was collected. This was washed with 5% sodium carbonate solution and water, dried, and distilled through a Widmer column; b. p. 40°/763 mm.

Methylene Bromide.—This was prepared from commercial 96% bromoform by treatment with alkaline sodium arsenite solution, prepared from A.R. arsenious oxide (*Org. Synth.*, 1929, **9**, 56), and boiled constantly at 97°/760 mm.

Methylene Iodide.—This was prepared by reduction of pure iodoform with alkaline sodium arsenite solution (from A.R. arsenious oxide) (*Org. Synth.*, 1921, **1**, 57). After two distillations, the methylene iodide had b. p. 80°/25 mm. and was straw-coloured. Shaking with a little pure silver powder before distillation reduced the intensity of the colour of the crude product.

Ethylidene Chloride.—A 100-g. sample (Eastman Kodak) was washed with saturated sodium hydrogen carbonate solution until effervescence ceased, then with water, dried, and fractionated; b. p. 57·5°/761 mm.

s-*Tetrachloroethane.*—135 Ml. of the technical product were stirred mechanically for 10 minutes with 17 ml. of concentrated sulphuric acid at 80—90°; the brownish-yellow acid layer was removed, replaced by a further 17 ml. of concentrated sulphuric acid, and the process repeated twice, whereupon the acid appeared unaffected. The acid was separated, and the tetrachloroethane well washed with water and distilled in steam. The organic layer was washed with water, dried (K_2CO_3), and distilled in an all-glass apparatus through a Widmer column; b. p. 147°/770 mm.

Chloroform.—About 100 ml. of A.R. chloroform were shaken with 5 ml. of concentrated sulphuric acid, washed with water until the washings were neutral to litmus, dried ($CaSO_4$), and distilled in an all-glass apparatus through a Widmer column; b. p. 61·5°/765 mm.

Methylchloroform.—The Eastman Kodak product was dried ($CaSO_4$) and distilled in an all-glass apparatus through a Widmer column. All boiled constantly at 73·5°/758 mm.

Carbon Tetrachloride.—The A.R. product was dried ($CaCl_2$) and distilled through a Widmer column; b. p. 76·5°/766 mm.

Ethylidene Bromide.—An Eastman Kodak preparation was washed with sodium hydrogen carbonate solution until effervescence ceased, then with water, dried ($CaCl_2$), and distilled from a Claisen flask with fractionating side arm; b. p. 108°/771 mm. The purified product was colourless, but upon keeping for a few days acquired a pale yellow colour and traces of hydrogen bromide were evolved.

s-*Tetrabromoethane.*—The yellow commercial product (B.D.H.) was shaken three times with 12% of its volume of concentrated sulphuric acid, then washed thrice with water, dried (K_2CO_3, followed by $CaSO_4$), and distilled; b. p. 124°/19 mm., a colourless liquid.

Bromoform.—The B.D.H. product, containing 4% of alcohol, was washed with a saturated solution of calcium chloride to remove the alcohol, dried ($CaCl_2$), and fractionated. Pure bromoform was collected at 148·5°/761 mm. as an almost colourless liquid; this is comparatively unstable and after a day or two a yellow cloudiness is present at the surface.

1 : 2 : 3-*Tribromopropane.*—A large sample, prepared by the interaction of allyl bromide and bromine (*Org. Synth.*, 1925, **5**, 99), was carefully fractionated; b. p. 100°/16 mm.

Triethyl Orthoformate.—A B.D.H. sample was dried ($CaCl_2$) and fractionated through a Widmer column; b. p. 143°/765 mm.

*Tri-*n*-propyl Orthoformate.*—The Eastman Kodak product was dried and fractionated; b. p. 91°/17 mm.

*Tri-*n*-butyl Orthoformate.*—The Eastman Kodak product was dried and fractionated; b. p. 127°/16 mm.

Thionyl Chloride.—B.D.H. " redistilled " thionyl chloride was mixed with 10% of its weight of pure quinoline and distilled in an all-glass apparatus through a Widmer column, moisture being carefully excluded; b. p. 76·5°/768 mm.

Sulphuryl Chloride.—B.D.H. " redistilled " sulphuryl chloride was distilled in an all-glass apparatus through a Widmer column, entrance of moisture being prevented; b. p. 69·5°/775 mm.

Phosphorus Trichloride.—A pure commercial product was fractionally distilled as for sulphuryl chloride; b. p. 75°/772 mm.

Phosphorus Oxychloride.—The B.D.H. pure product was fractionally distilled as for sulphuryl chloride; b. p. 106·5°/775 mm.

Phosphorus Tribromide.—In a 500-ml. three-necked flask, equipped with a dropping funnel, reflux condenser, and carbon tetrachloride-sealed mechanical stirrer, were placed 28 g. of dry purified red phosphorus and 200 ml. of dry A.R. carbon tetrachloride: ground glass joints are to be preferred, but " neoprene " or used rubber stoppers may also be used. The mixture was vigorously stirred and 198 g. of A.R. bromine were added during 1·5—2 hours. The reaction mixture was gently refluxed on a water-bath for 15 minutes, allowed to settle, and the clear solution filtered through a fluted filter paper into the 500-ml. flask of an all-glass distillation apparatus, which included a well-lagged, all-glass 15 cm. Dufton column. The solvent was distilled off on a water-bath; upon rise of the temperature, the phosphorus tribromide (190 g.) passed over at 168—169°/765 mm. Upon redistillation from an all-glass apparatus, without a column, the product boiled constantly at 171·5°/763 mm.

Dimethylnitrosoamine.—This was prepared from pure dimethylamine hydrochloride and nitrous acid (compare Cohen, " Practical Organic Chemistry ", 1924, p. 96) and boiled constantly at 151°/767 mm.

Diethylnitrosoamine.—36·5 G. of pure diethylamine were added slowly to the calculated quantity of 5N-hydrochloric acid contained in a 250-ml. distilling flask, followed by 39 g. of sodium nitrite (assumed of 90% purity). The contents of the flask were rapidly distilled to dryness. The upper yellow layer of the distillate was removed, and the lower layer was saturated with A.R. potassium carbonate whereupon more of the nitrosoamine separated and was added to the upper layer. The crude nitrosoamine was dried (K_2CO_3) during 24 hours and distilled. The yield of diethylnitrosoamine, b. p. 174·5°/777 mm., was 44 g.

*Di-*n*-propylnitrosoamine.*—This was prepared from 29 g. of di-*n*-propylamine (Eastman Kodak), 58 ml. of 5N-hydrochloric acid, and 22 g. of sodium nitrite, as for the diethyl compound. The yield of product, b. p. 89°/13 mm., was 31 g. (compare Schmidt, *Z. physikal. Chem.*, 1907, **58**, 513).

*Di-*n*-butylnitrosoamine.*—26 G. of Sharples's di-*n*-butylamine were added to 41 ml. of 5N-hydrochloric acid; some hydrochloride separated out and the mixture was transferred with the aid of 20 ml. of water to a 200-ml. distilling flask containing 15·5 g. of sodium nitrite (assumed of 90% purity). Upon warming, an upper layer appeared; the mixture was rapidly distilled to dryness, and the nitrosoamine isolated as for the diethyl analogue. The yield was 26 g.; b. p. 125—125·5°/21 mm.

Nitromethane.—About 150 g. of highly purified nitromethane, kindly supplied by Imperial Chemical Industries Ltd., were dried ($CaSO_4$) and distilled through a three-section Pyrex Young and Thomas column. Most of it passed over at 101°/762 mm.

Nitroethane.—A highly purified sample, presented by Imperial Chemical Industries Ltd., was dried and distilled as for nitromethane; b. p. 130·5°/761 mm.

2-*Nitro*-n-*propane.*—The I.C.I. product was purified as for nitromethane; b. p. 119·5°/752 mm.

1-*Nitro*-n-*butane.*—Commercially pure silver nitrite (Johnson and Matthey) was washed with absolute alcohol and then with sodium-dried ether, and dried by heating at 100° for 20 minutes, followed by keeping in a vacuum desiccator for 24 hours. In a 200-ml. distilling flask, fitted with a reflux condenser and with the side arm closed by a cork, were placed 64 g. of dry *n*-butyl bromide and 80 g. of the purified silver nitrite. No reaction occurred in the cold. After standing for 2 hours, the mixture was heated successively on a steam-bath for 4 hours (some brown fumes were evolved) and in an oil-bath at 110° for 8 hours. The mixture was distilled and the fraction, b. p. 150—151·5°/780 mm. (18 g.), was collected separately. This was dried ($CaSO_4$) and distilled: pure 1-nitro-*n*-butane was collected at 151·5—152·5°/780 mm., as a colourless liquid.

1-*Nitro*-n-*pentane.*—A mixture of 56 g. of dry silver nitrite and 50 g. of *n*-amyl bromide was heated, as for 1-nitro-*n*-butane, in a bath at 110° for 2 hours, at 115—125° for 2·5 hours, kept at room temperature for 12 hours, and then at 120—130° for 2·5 hours. Distillation yielded 15 g. of a fraction, b. p. 170—173°/775 mm., which was yellow. Redistillation gave pure 1-nitro-*n*-pentane, b. p. 66°/16 mm., as a colourless liquid. Distillation at atmospheric pressure yields a yellow product, evidently due to slight decomposition.

1-*Nitro*-n-*hexane.*—A mixture of 41 g. of dry silver nitrite, 51 g. of *n*-hexyl iodide, and 100 ml. of sodium-dried ether was refluxed for 8 hours, the ethereal solution was decanted, and the solid thoroughly washed with dry ether. After removal of the ether, the residue was distilled and the following fractions were collected, all of which were colourless: 100—160°, 9 g.; 160—189°, 4·5 g.; 190—193°, 13 g. The last fraction was dried ($CaSO_4$) and distilled; b. p. 81·5°/15 mm. The silver nitrite–*n*-hexyl bromide procedure was less satisfactory.

n-*Butyl Nitrite.*—This was prepared from *n*-butyl alcohol and nitrous acid (*Org. Synth.*, 1936, **16**, 7) and was collected as a pale yellow liquid, b. p. 27°/88 mm. The physical measurements for all alkyl nitrites were carried out immediately after distillation because of their comparative instability.

n-*Amyl Nitrite.*—A solution of 95 g. of sodium nitrite in 375 ml. of water was placed in a 1-l. three-necked flask, equipped with a mechanical stirrer, a thermometer, and a dropping funnel with stem extending to the bottom of the flask, and cooled to 0°. A mixture of 25 ml. of water, 62·5 g. of concentrated sulphuric acid, and 110 g. of redistilled *n*-amyl alcohol (Sharples, b. p. 137°/766 mm.), cooled to 0°, was added with stirring during 1 hour; the temperature was maintained at ± 1° throughout. After standing at 0° for 1·5 hours, the mixture was filtered, the yellow amyl nitrite layer was separated and washed twice with 25 ml. portions of a solution containing 1 g. of sodium hydrogen carbonate and 12·5 g. of sodium chloride in 50 ml. of water, and then dried ($CaSO_4$). The crude nitrite (107 g.) upon distillation passed over largely at 104—105°/763 mm.; a middle fraction, b. p. 104·5°/763 mm., had $d_{4^\circ}^{20^\circ}$ 0·8816, $n_D^{20^\circ}$ 1·3892. The compound was distilled under reduced pressure for the physical measurements; b. p. 29°/40 mm.

n-*Hexyl Nitrite.*—This was prepared similarly to *n*-amyl nitrite with the substitution of 127·5 g. of *n*-hexyl alcohol (Carbon and Carbide Corporation, b. p. 156—157°/752 mm.) for the *n*-amyl alcohol. The yield of crude nitrite was 125 g.; this boiled at 129—130°/761 mm. and a middle fraction, immediately after distillation, had $d_{4^\circ}^{20^\circ}$ 0·8810, $n_D^{20^\circ}$ 1·3986, and after 24 hours $d_{4^\circ}^{20^\circ}$ 0·8810, $n_D^{20^\circ}$ 1·3992. The systematic physical measurements were carried out with a sample which was distilled under reduced pressure; b. p. 52°/44 mm.

Nitrobenzene.—The A.R. product (B.D.H.) was distilled from an all-glass apparatus and a middle fraction was collected; b. p. 207·5°/760 mm.

Ethyl Nitrate.—An Eastman Kodak preparation was washed twice with water, dried ($MgSO_4$) and distilled through a fractionating column in an all-glass apparatus; b. p. 88°/757 mm.

n-*Propyl Nitrate.*—100 G. of pure concentrated nitric acid were boiled with 2 g. of urea until effervescence ceased (20 minutes) and then cooled to 0°. A solution of 12·5 g. of urea in 60 g. of pure *n*-propyl alcohol, cooled to 0°, was introduced during 15 minutes, allowed to stand for 15 minutes, and then distilled in an all-glass apparatus from a bath at 110—115°. The distillate (100 ml.) was well washed with brine (a few drops of sodium hydroxide solution were added to the final wash solution to remove the last traces of acid), then washed with water and dried ($MgSO_4$). Fractional distillation through an all-glass apparatus from an oil-bath yielded 30 ml. of *n*-propyl alcohol (b. p. 95—105°, mainly 95—97°), followed by 25 g. of *n*-propyl nitrate at 109—110°. Refractionation of the *n*-propyl nitrate gave the pure compound, b. p. 110°/762 mm.

n-*Butyl Nitrate.*—This was prepared from 100 g. of nitrous acid-free nitric acid and 74 g. of pure *n*-butyl alcohol as described for *n*-propyl nitrate. The yield of *n*-butyl nitrate, b. p. 135—135·5°/762 mm., was 24 g.

Dimethyl Carbonate.—100 G. of the commercial product (B.D.H.) were washed successively with 10% sodium carbonate solution, saturated calcium chloride solution, and water, dried by shaking mechanically for 1 hour with anhydrous calcium chloride (compare *Org. Synth.*, 1931, **11**, 99, Note 3), and fractionated; b. p. 89·5°/755 mm.

Diethyl carbonate (Hopkin and Williams), di-*n*-propyl carbonate (Eastman Kodak), di-*n*-butyl carbonate (Eastman Kodak) and di*iso*butyl carbonate (Eastman Kodak) were similarly purified and had b. p. 125·5°/758 mm., 165°/752 mm., 204·5°/758 mm., and 187·5°/763 mm., respectively.

Methyl Thiocyanate.—The Eastman Kodak product was dried ($CaSO_4$) and fractionated; b. p. 130·5°/765 mm.

Ethyl Thiocyanate.—The Eastman Kodak product was dried (Na_2SO_4) and fractionated; b. p. 145·5°/765 mm.

n-*Propyl Thiocyanate.*—In a 1-l. three-necked flask, fitted with a dropping funnel, a mercury-sealed mechanical stirrer, and a reflux condenser, was placed a mixture of 133 g. of A.R. potassium thiocyanate and 312 g. of rectified spirit. The stirrer was set in motion, the mixture heated on a ring burner, and 154 g. of *n*-propyl bromide added during 20 minutes; potassium bromide separated and the mixture was refluxed for 5 hours with vigorous stirring in order to avoid bumping. After the mixture had been kept overnight, the potassium bromide were filtered off and washed with 75 ml. of rectified spirit. The combined filtrate and washings were distilled on a water-bath through a four-section Pyrex Young and Thomas column to separate most of the alcohol. The residue was treated with 125 ml. of water, the upper layer separated, and the aqueous phase extracted with two 50-ml. portions of ether. The combined upper layer and ether extracts were dried and distilled from a 250-ml. flask through a well-lagged three-section Pyrex Young and Thomas column. After the ether and a little alcohol had passed over at 78°, the temperature rose sharply to 164·5—165°/762 mm. and 93 g. passed over at this temperature. Upon redistillation, the *n*-propyl thiocyanate boiled constantly at 164·5°/760 mm. The above procedure is superior to that described in *Org. Synth.*, 1931, **11**, 92, for *iso*propyl thiocyanate since it gives a pure product (b. p. range $<1°$) in one operation.

n-*Butyl Thiocyanate.*—This was prepared, as for the *n*-propyl compound, from 133 g. of A.R. potassium thocyanate, 312 g. of rectified spirit, and 172 g. of *n*-butyl bromide. The yield of crude ester, b. p. 183°, was 126 g. This was further dried ($CaSO_4$) and redistilled; b. p. 184°/770 mm.

Ethyl iso*Thiocyanate.*—The Eastman Kodak product was dried (Na_2SO_4) and distilled from a Claisen flask with fractionating side arm; b. p. 132—132·5°/762 mm.

Allyl iso*Thiocyanate.*—The B.D.H. pure product was fractionated as for the ethyl compound; b. p. 151—151·5°/768 mm.

Potassium Ethyl Xanthate.—42 G. of potassium hydroxide pellets were dissolved in 120 g. of absolute ethyl alcohol (refluxing was necessary) and the cold solution decanted from the undissolved impurities. 57 G. of A.R. carbon disulphide were added slowly and with constant shaking; the mixture set almost solid. The solid was filtered off and washed twice with ether (*d* 0·720) and once with anhydrous ether; the yield was 110 g. The ester was dried by leaving it for 3 days in a vacuum desiccator over silica gel; the yield of the dry compound was 74 g.

Diethyl Xanthate.—A mixture of 32 g. of potassium ethyl xanthate, 50 ml. of absolute ethyl alcohol, and 32 g. of ethyl iodide was refluxed for 3 hours: no reaction occurred in the cold but within 15 minutes of heating the yellow mixture became white owing to separation of potassium iodide. Excess of water was added, and the lower layer separated, washed with water and dried ($CaSO_4$). The crude dry compound (29·5 g.) had b. p. 196—198°/761 mm. This was redistilled for the physical measurements; b. p. 70·2°/4·9 mm.

*Di-*n-*propyl Xanthate.*—A mixture of 42 g. of potassium *n*-propyl xanthate, 50 ml. of absolute alcohol, and 41·5 g. of *n*-propyl iodide was warmed gently on a water-bath until reaction commenced; after 1 hour the vigorous reaction subsided and the mixture was refluxed for 3 hours. The crude *ester* (36 g.) was isolated as for the ethyl compound and had b. p. 91·1°/4·5 mm. (Found: S, 35·9. $C_7H_{14}OS_2$ requires S, 36·0%).

Potassium n-*Propyl Xanthate.*—28 G. of potassium hydroxide pellets were refluxed with 100 g. of *n*-propyl alcohol for 2 hours, and then cooled to room temperature. The solution was decanted from the little solid which had separated, and 38 g. of A.R. carbon disulphide were added slowly. After cooling in ice, the solid was filtered off, washed twice with ether (*d* 0·720) and once with anhydrous ether, and dried over silica gel in a vacuum desiccator to constant weight. The yield of dry xanthate was 42 g.

Ethyl S-n-*Butylxanthate.*—This was prepared from 32 g. of potassium ethyl xanthate, 50 ml. of absolute alcohol, and 37 g. of *n*-butyl iodide as detailed for diethyl xanthate and the product was isolated directly after saturation of the diluted reaction mixture with salt. The crude dry *xanthate* weighed 35 g., and on distillation boiled constantly at 90·3°/4·0 mm. (Found: S, 35·8. $C_7H_{14}OS_2$ requires S, 36·0%).

Potassium n-*Butyl Xanthate.*—20 G. of potassium hydroxide pellets were refluxed with 100 g. of *n*-butyl alcohol until dissolved and then allowed to cool to room temperature. The solution was decanted from the impurities and the little solid potassium hydroxide which had separated, and then 36 g. of A.R. carbon disulphide were slowly added. After cooling in ice, the potassium derivative was filtered off, washed successively with ether (*d* 0·720) and sodium-dried ether, and dried in a vacuum desiccator over silica gel and anhydrous calcium chloride for 3 days. The yield of dry potassium *n*-butyl xanthate was 42 g. It crystallises well from absolute ethyl alcohol.

n-*Butyl* S-*Ethylxanthate.*—The crude product, prepared from 47 g. of potassium *n*-butyl xanthate, 50 ml. of absolute ethyl alcohol, and 39 g. of ethyl iodide as detailed for ethyl *S*-*n*-butylxanthate, weighed 42 g. The pure *ester* boiled at 91·0°/4·3 mm. (Found: S, 35·0. $C_7H_{14}OS_2$ requires S, 36·0%).

*Di-*n-*butyl Xanthate.*—This was prepared in the usual manner from 31·5 g. of potassium *n*-butyl xanthate, 50 ml. of absolute ethyl alcohol, and 30 g. of *n*-butyl iodide. The yield of *xanthate*, b. p. 117·0°/4·0 mm., was 29 g. (Found: S, 31·3. $C_9H_{18}OS_2$ requires S, 31·1%).

545. *Methyl dichloroacetate.* B. p. 143°/763 mm.; M 142·95; n_C 1·44034, n_D 1·44275, n_F 1·44864, $n_{G'}$ 1·45302; R_C 27·38, R_D 27·52, R_F 27·83, $R_{G'}$ 28·07; $Mn_D^{20°}$ 206·25. Densities determined: $d_{4°}^{20°}$ 1·3767, $d_{4°}^{41·2°}$ 1·3481, $d_{4°}^{60·4°}$ 1·3221, $d_{4°}^{85·0°}$ 1·2858. Apparatus *D*.

(These headings apply to all the succeeding tables in this paper).

t.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	H.	$d_{4°}^{t°}$.	γ.	P.
18·0°	10·24	1·3784	34·86	252·0	60·8°	9·06	1·3216	29·57	252·2
21·0	10·13	1·3753	34·41	251·7	86·3	8·35	1·2840	26·48	252·6
41·4	9·60	1·3478	31·95	252·2				Mean	252·1

546. *Ethyl dichloroacetate.* B. p. 155·5°/764 mm.; *M* 157·00; n_{C} 1·43608, n_{D} 1·43841, n_{F} 1·44420, $n_{\mathrm{G'}}$ 1·44853; R_{C} 32·01, R_{D} 32·16, R_{F} 32·53, $R_{\mathrm{G'}}$ 32·80; $Mn_{\mathrm{D}}^{20^\circ}$ 225·83. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2826, $d_{4^\circ}^{41\cdot3}$ 1·2553, $d_{4^\circ}^{61\cdot4^\circ}$ 1·2298, $d_{4^\circ}^{86\cdot6^\circ}$ 1·1959. Apparatus *D*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
19·9°	10·36	1·2827	32·74	292·9	61·4°	9·09	1·2298	27·61	292·6
27·2	10·07	1·2733	31·67	292·5	87·4	8·43	1·1949	24·88	293·4
41·6	9·70	1·2549	30·06	293·0				Mean	292·9

547. n-*Propyl dichloroacetate.* B. p. 174·5—175°/769 mm.; *M* 171·02; n_{C} 1·43759, n_{D} 1·43993, n_{F} 1·44572, $n_{\mathrm{G'}}$ 1·45000; R_{C} 36·68, R_{F} 36·85, R_{F} 37·27, $\mathrm{R}_{\mathrm{G'}}$ 37·58; $Mn_{\mathrm{D}}^{20^\circ}$ 246·25. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2230, $d_{4^\circ}^{41\cdot5^\circ}$ 1·1975, $d_{4^\circ}^{60\cdot9^\circ}$ 1·1740, $d_{4^\circ}^{86\cdot6^\circ}$ 1·1425. Apparatus *A*.

16·5°	13·52	1·2272	31·07	329·0	41·2°	12·64	1·1979	28·35	329·4
21·4	13·41	1·2213	30·67	329·5	61·9	11·95	1·1728	26·24	330·0
29·9	13·12	1·2111	29·75	329·8	86·3	11·06	1·1429	23·67	330·7
								Mean	329·6

548. n-*Butyl dichloroacetate.* B. p. 192°/749 mm.; *M* 185·05; n_{C} 1·44009, n_{D} 1·44245, n_{F} 1·44823, $n_{\mathrm{G'}}$ 1·45249; R_{C} 41·21, R_{D} 41·40, R_{F} 41·86, $R_{\mathrm{G'}}$ 42·21; $Mn_{\mathrm{D}}^{20^\circ}$ 266·93. Densities determined: $d_{4^\circ}^{20}$ 1·1848, $d_{4^\circ}^{41\cdot5^\circ}$ 1·1600, $d_{4^\circ}^{60\cdot9^\circ}$ 1·1384, $d_{4^\circ}^{85\cdot6^\circ}$ 1·1102. Apparatus *D*.

19·8°	10·46	1·1850	30·61	367·3	60·9°	9·36	1·1384	26·31	368·2
27·5	10·24	1·1764	29·75	367·4	86·7	8·74	1·1090	23·94	369·0
41·6	9·86	1·1599	28·24	367·8				Mean	367·9

549. *Methyl trichloroacetate.* B. p. 152°/758 mm.; *M* 177·43; n_{C} 1·45448, n_{D} 1·45707, n_{F} 1·46337, $n_{\mathrm{G'}}$ 1·46808; R_{C} 32·31, R_{D} 32·47, R_{F} 32·86, $R_{\mathrm{G'}}$ 33·14; $Mn_{\mathrm{D}}^{20^\circ}$ 258·53. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·4884, $d_{4^\circ}^{41\cdot6^\circ}$ 1·4564, $d_{4^\circ}^{60\cdot1\cdot}$ 1·4290, $d_{4^\circ}^{85\cdot7^\circ}$ 1·3901. Apparatus *A*.

13·3°	12·09	1·4984	33·92	285·8	61·2°	10·53	1·4274	28·14	286·3
18·3	11·95	1·4909	33·36	286·0	86·3	9·74	1·3892	25·34	286·5
41·5	11·22	1·4565	30·60	286·5				Mean	286·2

550. *Ethyl trichloroacetate.* B. p. 166°/755; *M* 191·46; n_{C} 1·44747, n_{D} 1·44997, n_{F} 1·45608, $n_{\mathrm{G'}}$ 1·46059; R_{C} 37·11, R_{D} 37·28, R_{F} 37·72, $R_{\mathrm{G'}}$ 38·04; $Mn_{\mathrm{D}}^{20^\circ}$ 277·62. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3800, $d_{4^\circ}^{41\cdot2^\circ}$ 1·3512, $d_{4^\circ}^{59\cdot4^\circ}$ 1·3266, $d_{4^\circ}^{86\cdot5^\circ}$ 1·2883. Apparatus *D*.

15·3°	9·16	1·3864	31·36	326·8	41·4°	8·52	1·3509	28·42	327·2
18·9	9·08	1·3815	30·98	327·0	60·8	8·04	1·3247	26·30	327·2
23·1	9·00	1·3757	30·58	327·1	86·5	7·48	1·2883	23·80	328·2
								Mean	327·3

551. n-*Propyl trichloroacetate.* B. p. 68°/8·5 mm.; *M* 205·49; n_{C} 1·44810, n_{D} 1·45057, n_{F} 1·45666, $n_{\mathrm{G'}}$ 1·46113; R_{C} 41·60, R_{D} 41·80, R_{F} 42·29, $R_{\mathrm{G'}}$ 42·64; $Mn_{\mathrm{D}}^{20^\circ}$ 298·08. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3225, $d_{4^\circ}^{41\cdot9^\circ}$ 1·2936, $d_{4^\circ}^{61\cdot7^\circ}$ 1·2685, $d_{4^\circ}^{85\cdot6^\circ}$ 1·2385. Apparatus *A*.

17·9°	12·39	1·3252	30·75	365·1	42·0°	11·54	1·2935	27·95	365·3
21·5	12·25	1·3205	30·29	365·1	62·9	10·88	1·2669	25·81	365·6
25·8	12·12	1·3150	29·84	365·2	87·8	10·08	1·2356	23·32	365·5
								Mean	365·3

552. n-*Butyl trichloroacetate.* B. p. 81·5°/7·5 mm.; *M* 219·51; n_{C} 1·44941, n_{D} 1·45187, n_{F} 1·45792, $n_{\mathrm{G'}}$ 1·46250; R_{C} 46·23, R_{D} 46·45, R_{F} 46·98, $R_{\mathrm{G'}}$ 47·39; $Mn_{\mathrm{D}}^{20^\circ}$ 318·70. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2747, $d_{4^\circ}^{40\cdot1^\circ}$ 1·2505, $d_{1^\circ}^{59\cdot5^\circ}$ 1·2278, $d_{4^\circ}^{84\cdot8^\circ}$ 1·1979. Apparatus *A*.

13·3°	12·85	1·2827	30·79	403·4	40·8°	12·06	1·2497	28·22	404·8
17·1	12·74	1·2782	30·49	403·6	61·1	11·37	1·2259	26·10	404·7
22·8	12·62	1·2720	30·06	404·1	86·9	10·56	1·1954	23·64	404·9
								Mean	404·3

553. *Methylene chloride.* B. p. 40°/763 mm.; *M* 84·95; n_{C} 1·42214, n_{D} 1·42456, n_{F} 1·43034, $n_{\mathrm{G'}}$ 1·43470; R_{C} 16·30, R_{D} 16·38, R_{F} 16·58, $R_{\mathrm{G'}}$ 16·72; $Mn_{\mathrm{D}}^{20^\circ}$ 120·80. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3247, $d_{4^\circ}^{25\cdot0^\circ}$ 1·3169. Apparatus *A*.

19·3°	11·27	1·3258	27·98	147·5	26·9°	10·97	1·3139	26·99	147·6
23·3	11·07	1·3195	27·35	147·4				Mean	147·5

554. *Methylene bromide.* B. p. 97°/760 mm.; *M* 173·86; n_{C} 1·53707, n_{D} 1·54119, n_{F} 1·55177, $n_{\mathrm{G'}}$ 1·55996; R_{C} 21·76, R_{D} 21·90, R_{F} 22·25; $R_{\mathrm{G'}}$ 22·53; $Mn_{\mathrm{D}}^{20^\circ}$ 267·95. Densities determined: $d_{4^\circ}^{20^\circ}$ 2·4956, $d_{4^\circ}^{42\cdot0^\circ}$ 2·4405, $d_{4^\circ}^{61\cdot6^\circ}$ 2·3911, $d_{4^\circ}^{86\cdot1^\circ}$ 2·3266. Apparatus *A*.

18·4°	8·55	2·4997	40·02	174·9	60·5°	7·50	2·3939	33·61	175·0
41·0	8·04	2·4430	36·78	175·3	85·4	6·91	2·3284	30·13	175·2
								Mean	175·1

555. *Methylene iodide.* B. p. 80°/25 mm.; *M* 267·87. Densities determined: $d_{4^\circ}^{20^\circ}$ 3·3240, $d_{4^\circ}^{41\cdot3^\circ}$ 3·2692, $d_{4^\circ}^{60\cdot9^\circ}$ 3·2204, $d_{4^\circ}^{86\cdot3^\circ}$ 3·1550. The results for the surface-tension measurements were unsatisfactory and the refractive indices were outside the range of the prisms available for the Pulfrich refractometer. The $d_{4^\circ}^{20^\circ}$ value was in good agreement with the figure interpolated from the results of Timmermans and Hennaut-Roland (*J. Chim. physique*, 1932, **29**, 529); their values for the refractive indices, interpolated to 20°, are n_{C} 1·73098, n_{D} 1·74108, n_{F} 1·76826 and give R_{C} 32·20, R_{D} 32·54, R_{F} 33·43, $Mn_{\mathrm{D}}^{20^\circ}$ 466·39.

556. *Ethylidene chloride.* B. p. 57·5°/761 mm.; *M* 98·97; n_{C} 1·41369, n_{D} 1·41596, n_{F} 1·42157, $n_{\mathrm{G'}}$ 1·42572; R_{C} 20·99, R_{D} 21·09, R_{F} 21·34, $R_{\mathrm{G'}}$ 21·52; $Mn_{\mathrm{D}}^{20^\circ}$ 140·14. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1776, $d_{4^\circ}^{41\cdot4^\circ}$ 1·1535. Apparatus *A*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
17·1°	11·33	1·1809	25·05	187·6	41·1°	10·26	1·1538	22·17	187·9
23·3	11·01	1·1739	24·20	187·3				Mean	187·6

557. s-*Tetrachloroethane.* B. p. 147°/770 mm.; *M* 167·88; n_{C} 1·49165, n_{D} 1·49437, n_{F} 1·50128, $n_{\mathrm{G'}}$ 1·50645; R_{C} 30·46, R_{D} 30·60, R_{F} 30·96, $R_{\mathrm{G'}}$ 31·23; $Mn_{\mathrm{D}}^{20^\circ}$ 250·88. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·5984, $d_{4^\circ}^{42\cdot3^\circ}$ 1·5640, $d_{4^\circ}^{61\cdot6^\circ}$ 1·5349, $d_{4^\circ}^{87\cdot6^\circ}$ 1·4954. Apparatus *A*.

17·2°	12·21	1·6027	36·64	257·7	60·3°	10·75	1·5369	30·91	257·6
20·9	12·09	1·5970	36·15	257·8	86·2	9·97	1·4975	27·96	257·8
40·4	11·43	1·5669	33·54	257·8				Mean	257·7

558. *Chloroform.* B. p. 61·5°/765 mm.; *M* 119·40; n_{C} 1·44353, n_{D} 1·44611, n_{F} 1·45232, $n_{\mathrm{G'}}$ 1·45700; R_{C} 21·26, R_{D} 21·37, R_{F} 21·63, $R_{\mathrm{G'}}$ 21·82; $Mn_{\mathrm{D}}^{20^\circ}$ 172·66. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·4904, $d_{4^\circ}^{40\cdot3^\circ}$ 1·4521. Apparatus *A*.

15·3°	9·93	1·4993	27·88	183·0	26·2°	9·62	1·4787	26·64	183·4
17·5	9·87	1·4951	27·63	183·1	40·1	9·07	1·4525	24·67	183·4
								Mean	183·2

559. *Methylchloroform.* B. p. 73·5°/758 mm.; *M* 133·42; n_{C} 1·43574, n_{D} 1·43832, n_{F} 1·44433, $n_{\mathrm{G'}}$ 1·44851; R_{C} 26·06, R_{D} 26·20, R_{F} 26·51, $R_{\mathrm{G'}}$ 26·73; $Mn_{\mathrm{D}}^{20^\circ}$ 191·90. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3376, $d_{4^\circ}^{40\cdot8^\circ}$ 1·3031, $d_{4^\circ}^{62\cdot3^\circ}$ 1·2684. Apparatus *E*.

21·0°	8·25	1·3360	25·67	224·8	40·9°	7·60	1·3029	23·06	224·8
28·3	8·03	1·3239	24·76	224·8	60·6	7·00	1·2712	20·72	224·5
								Mean	224·7

560. *Carbon tetrachloride.* B. p. 76·5°/766 mm.; *M* 153·84; n_{C} 1·45763, n_{D} 1·46025, n_{F} 1·46706, $n_{\mathrm{G'}}$ 1·47194; R_{C} 26·31, R_{D} 26·45, R_{F} 26·86, $R_{\mathrm{G'}}$ 27·08; $Mn_{\mathrm{D}}^{20^\circ}$ 224·65. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·5941, $d_{4^\circ}^{40\cdot8^\circ}$ 1·5551, $d_{4^\circ}^{57\cdot8^\circ}$ 1·5228. Apparatus *A*.

20·1°	9·25	1·5939	27·61	221·2	40·8°	8·44	1·5551	24·58	220·5
24·9	9·16	1·5848	27·18	221·1	59·5	7·92	1·5196	22·54	221·0
								Mean	221·0

561. *Ethylidene bromide.* B. p. 108°/771 mm.; *M* 187·89; n_{C} 1·50849, n_{D} 1·51223, n_{F} 1·52167, $n_{\mathrm{G'}}$ 1·52917; R_{C} 26·67, R_{D} 26·63, R_{F} 27·25, $R_{\mathrm{G'}}$ 27·58; $Mn_{\mathrm{D}}^{20^\circ}$ 284·13. Densities determined: $d_{4^\circ}^{20^\circ}$ 2·1018, $d_{4^\circ}^{42\cdot4^\circ}$ 2·0540, $d_{4^\circ}^{60\cdot0^\circ}$ 2·0129. Apparatus *A*.

16·3°	8·64	2·1100	34·14	215·2	62·4°	7·49	2·0076	28·16	215·6
41·2	8·04	2·0562	30·96	215·5				Mean	215·4

562. s-*Tetrabromoethane.* B. p. 124°/19 mm.; *M* 345·70; n_{C} 1·63011, n_{D} 1·63533, n_{F} 1·64847; R_{C} 41·70, R_{D} 41·97, R_{F} 42·66; $Mn_{\mathrm{D}}^{20^\circ}$ 565·32. Densities determined: $d_{4^\circ}^{20^\circ}$ 2·9501, $d_{4^\circ}^{42\cdot0^\circ}$ 2·9036, $d_{4^\circ}^{61\cdot1^\circ}$ 2·8625, $d_{4^\circ}^{87\cdot5^\circ}$ 2·8066. The results of the surface-tension measurements by the capillary rise method were not entirely satisfactory; it is hoped to repeat them by the method of maximum bubble pressure.

563. *Bromoform.* B. p. 148·5°/761 mm.; *M* 252·77; n_{C} 1·59256, n_{D} 1·59763, n_{F} 1·61059, $n_{\mathrm{G'}}$ 1·62084; R_{C} 29·65, R_{D} 29·86, R_{F} 30·38, $R_{\mathrm{G'}}$ 30·79; $Mn_{\mathrm{D}}^{20^\circ}$ 403·83. Densities determined: $d_{4^\circ}^{20^\circ}$ 2·8870, $d_{4^\circ}^{40\cdot0^\circ}$ 2·8400, $d_{4^\circ}^{59\cdot0^\circ}$ 2·7935, $d_{4^\circ}^{85\cdot9^\circ}$ 2·7251. Apparatus *D*.

24·8°	6·35	2·8755	45·10	227·8	60·1°	5·87	2·7909	40·46	228·4
41·7	6·04	2·8359	42·30	227·3				Mean	227·8

564. 1 : 2 : 3-*Tribromopropane.* B. p. 102°/18 mm.; *M* 280·83; n_{C} 1·58191, n_{D} 1·58633, n_{F} 1·59728, $n_{\mathrm{G'}}$ 1·60551; R_{C} 38·69, R_{D} 38·93, R_{F} 39·52, $R_{\mathrm{G'}}$ 39·96; $Mn_{\mathrm{D}}^{20^\circ}$ 445·48. Densities determined: $d_{4^\circ}^{20^\circ}$ 2·4222, $d_{4^\circ}^{41\cdot4^\circ}$ 2·3861, $d_{4^\circ}^{60\cdot9^\circ}$ 2·3457, $d_{4^\circ}^{86\cdot5^\circ}$ 2·2919. Apparatus *A*.

17·5°	10·07	2·4271	45·77	301·7	62·0°	9·19	2·3437	40·33	302·0
41·5	9·54	2·3859	42·62	301·5	87·7	8·58	2·2897	36·79	302·8
								Mean	302·0

565. *Ethyl orthoformate.* B. p. 143°/765 mm.; *M* 148·20; n_{C} 1·38792, n_{D} 1·38979, n_{F} 1·39428, $n_{\mathrm{G'}}$ 1·39738; R_{C} 39·13, R_{D} 39·30, R_{F} 39·71, $R_{\mathrm{G'}}$ 39·98; $Mn_{\mathrm{D}}^{20^\circ}$ 205·97. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8934, $d_{4^\circ}^{41\cdot1^\circ}$ 0·8722, $d_{4^\circ}^{60\cdot7^\circ}$ 0·8530, $d_{4^\circ}^{87\cdot3^\circ}$ 0·8245. Apparatus *D*.

17·1°	10·81	0·8963	23·93	365·7	60·7°	9·26	0·8530	19·50	365·2
21·9	10·68	0·8915	23·51	366·1	85·6	8·44	0·8262	17·22	365·4
40·7	9·91	0·8726	21·36	365·1				Mean	365·5

566. n-*Propyl orthoformate*. B. p. 91°/17 mm.; *M* 190·28; n_C 1·40512, n_D 1·40711, n_F 1·41188, $n_{G'}$ 1·41534; R_C 53·05, R_D 53·28, R_F 53·83, $R_{G'}$ 54·22; $Mn_D^{20^\circ}$ 267·74. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8794, $d_{4^\circ}^{41\cdot4^\circ}$ 0·8605, $d_{4^\circ}^{61\cdot0^\circ}$ 0·8427, $d_{4^\circ}^{85\cdot9^\circ}$ 0·8204. Apparatus *D*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
13·4°	11·64	0·8853	25·45	482·7	41·4°	10·72	0·8605	22·78	483·1
17·4	11·50	0·8817	25·04	482·8	61·0	10·09	0·8427	21·00	483·4
20·0	11·41	0·8794	24·78	482·8	86·8	9·25	0·8196	18·72	482·9
								Mean	483·0

567. n-*Butyl orthoformate*. B. p. 127°/16 mm.; *M* 232·35; n_C 1·41603, n_D 1·41806, n_F 1·42302, $n_{G'}$ 1·42654; R_C 66·92, R_D 67·21, R_F 67·90, $R_{G'}$ 68·40; $Mn_D^{20^\circ}$ 329·50. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8713, $d_{4^\circ}^{41\cdot4^\circ}$ 0·8540, $d_{4^\circ}^{61\cdot7^\circ}$ 0·8382, $d_{4^\circ}^{85\cdot1^\circ}$ 0·8188. Apparatus *D*.

17·1°	12·02	0·8732	25·92	600·4	41·0°	11·25	0·8543	23·68	600·3
22·0	11·85	0·8697	25·45	600·1	60·9	10·60	0·8388	21·96	599·6
27·8	11·72	0·8651	25·04	600·8	86·8	9·88	0·8174	19·94	600·7
								Mean	600·3

568. *Thionyl chloride*. B. p. 76·5°/768 mm.; *M* 118·97; n_C 1·51593, n_D 1·52048, n_F 1·53310, $n_{C'}$ 1·5432 (somewhat doubtful); R_C 21·95, R_D 22·12, R_F 22·56, $R_{G'}$ 22·98; $Mn_D^{20^\circ}$ 180·06. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·6366, $d_{4^\circ}^{41\cdot6^\circ}$ 1·5972, $d_{4^\circ}^{58\cdot9^\circ}$ 1·5645. Apparatus *E*.

18·3°	8·78	1·6397	33·53	174·6	40·8°	8·19	1·5987	30·49	175·0
20·8	8·68	1·6351	33·05	174·5	59·1	7·59	1·5641	27·65	174·7
								Mean	174·7

[Sugden, Reed, and Wilkins (*loc. cit.*) find $d_{4^\circ}^{20^\circ}$ (extrap.) 1·645 and *P* 174·5.]

569. *Sulphuryl chloride*. B. p. 69·5°/775 mm.; *M* 134·97; n_C 1·44049, n_D 1·44325, n_F 1·45005, $n_{G'}$ 1·45508; R_C 21·31, R_D 21·43, R_F 21·71, $R_{G'}$ 21·92; $Mn_D^{20^\circ}$ 194·80. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·6708, $d_{4^\circ}^{41\cdot8^\circ}$ 1·6217. Apparatus *A*.

16·1°	9·63	1·6796	30·29	188·5	26·6°	9·22	1·6560	28·59	188·6
17·9	9·59	1·6755	30·09	188·7	41·6	8·69	1·6221	26·39	187·7
								Mean	188·4

Sugden, Reed, and Wilkins (*loc. cit.*) give $d_{4^\circ}^{20^\circ}$ (extrap.) 1·682, *P* 193·3 for a specimen prepared from chlorosulphonic acid. In view of the disparity in density and large difference in surface tension from the author's results, another specimen of pure sulphuryl chloride was prepared from an independent source of commercially pure material by careful fractionation through a Widmer column in an all-glass apparatus; the sample for the surface-tension measurements was collected directly in the surface-tension apparatus and the usual precautions against exposure to the atmosphere were taken throughout. The original results were adequately confirmed and it would appear that Sugden, Reed, and Wilkins's sample was impure. The results for the highly purified sample were as follows: b. p. 69°/763 mm.; n_C 1·44065, n_D 1·44340, n_F 1·45024, $n_{G'}$ 1·45533; R_C 21·31, R_D 21·43, R_F 21·71, $R_{G'}$ 21·93; $Mn_D^{20^\circ}$ 194·82. Densities determined: $d_{4^\circ}^{20}$ 1·6712, $d_{4^\circ}^{40\cdot6^\circ}$ 1·6264. Apparatus *F*.

18·7°	7·65	1·6740	29·82	188·4	40·5°	7·08	1·6266	26·81	189·0
25·3	7·36	1·6596	28·44	187·9				Mean	188·4

570. *Phosphorus trichloride*. B. p. 75°/772 mm.; M 137·35; n_C 1·51039, n_D 1·51473, n_F 1·52576, $n_{G'}$ 1·53467; R_C 26·08, R_D 26·27, R_F 26·74, $R_{G'}$ 27·11; $Mn_D^{20^\circ}$ 208·04. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·5761, $d_{4^\circ}^{43\cdot5^\circ}$ 1·5332, $d_{4^\circ}^{61\cdot5^\circ}$ 1·5008. Apparatus *E*.

15·3°	7·92	1·5847	29·23	201·5	41·6°	7·23	1·5367	25·88	201·8
19·2	7·83	1·5776	28·77	201·7	60·3	6·72	1·5030	23·52	201·7
25·5	7·62	1·5660	27·79	201·5				Mean	201·6

571. *Phosphorus oxychloride*. B. p. 106·5°/775 mm.; *M* 153·35; n_C 1·45917, n_D 1·46085, n_F 1·46746, $n_{G'}$ 1·47240; R_C 24·97, R_D 25·05, R_F 25·36, $R_{G'}$ 25·59; $Mn_D^{20^\circ}$ 224·03. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·6795, $d_{4^\circ}^{40\cdot7^\circ}$ 1·6414, $d_{4^\circ}^{60\cdot8^\circ}$ 1·6045, $d_{4^\circ}^{85\cdot1^\circ}$ 1·5580. Apparatus *A*.

14·9°	10·54	1·6890	33·33	218·2	61·9°	9·09	1·6025	27·28	218·9
20·5	10·40	1·6786	32·69	218·4	86·4	8·33	1·5556	24·26	219·2
41·2	9·72	1·6405	29·86	218·5				Mean	218·6

[Sugden, Reed, and Wilkins (*loc. cit.*) give $d_{4^\circ}^{20^\circ}$ (extrap.) 1·680, *P* 217·6.]

572. *Phosphorus tribromide*. B. p. 171·5°/763 mm.; *M* 270·73; n_D 1·69632; R_D 36·07; $Mn_D^{20^\circ}$ 459·24. Densities determined: $d_{4^\circ}^{20^\circ}$ 2·8903, $d_{4^\circ}^{41\cdot0^\circ}$ 2·8420, $d_{4^\circ}^{60\cdot0^\circ}$ 2·7965, $d_{4^\circ}^{85\cdot0^\circ}$ 2·7364. Apparatus *A*.

15·6°	7·97	2·9006	43·29	239·4	59·5°	7·18	2·7977	37·61	239·7
41·4	7·55	2·8411	40·17	239·8				Mean	239·7

[Sugden, Reed, and Wilkins (*loc. cit.*) give $d_{4^\circ}^{20^\circ}$ (extrap.) 2·893, *P* 242·9.]

573. *Dimethylnitrosoamine*. B. p. 151°/767 mm.; *M* 74·09; n_{C} 1·43210, n_{D} 1·43580, n_{F} 1·44544, $n_{\text{G'}}$ 1·45360 (line faint); R_{C} 19·12, R_{D} 19·27, R_{F} 19·64, $R_{\text{G'}}$ 19·95; $Mn_{\text{D}}^{20°}$ 106·38. Densities determined: $d_{4°}^{20°}$ 1·0050, $d_{4°}^{42·6°}$ 0·9837, $d_{4°}^{60·0°}$ 0·9668, $d_{4°}^{85·6°}$ 0·9408. Apparatus *D*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
16·3°	15·55	1·0086	38·73	183·3	60·8°	13·96	0·9660	33·29	184·2
21·9	15·44	1·0031	38·25	183·7	86·8	12·97	0·9396	30·10	184·7
40·8	14·69	0·9854	35·75	183·8				Mean	183·9

574. *Diethylnitrosoamine*. B. p. 174·5°/777 mm.; *M* 102·14; n_{C} 1·43468, n_{D} 1·43791, n_{F} 1·44640, $n_{\text{G'}}$ 1·45347; R_{C} 28·25, R_{D} 28·43, R_{F} 28·91, $R_{\text{G'}}$ 29·31; $Mn_{\text{D}}^{20°}$ 146·87. Densities determined: $d_{4°}^{20°}$ 0·9428, $d_{4°}^{40·3°}$ 0·9255, $d_{4°}^{60·0°}$ 0·9082, $d_{4°}^{86·7°}$ 0·8842. Apparatus *D*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
16·4°	14·30	0·9459	33·40	259·6	63·0°	12·81	0·9108	28·81	259·8
21·2	14·16	0·9417	32·93	259·8	87·8	11·95	0·8832	26·06	261·3
41·8	13·52	0·9242	30·86	260·5				Mean	259·8

575. *Di*-n-*propylnitrosoamine*. B. p. 89°/13 mm.; *M* 130·19; n_{C} 1·44059, n_{D} 1·44365, n_{F} 1·45155, $n_{\text{G'}}$ 1·45804; R_{C} 37·50, R_{D} 37·73, R_{F} 38·31, $R_{\text{G'}}$ 38·78; $Mn_{\text{D}}^{20°}$ 187·96. Densities determined: $d_{4°}^{20°}$ 0·9160, $d_{4°}^{41·6°}$ 0·8992, $d_{4°}^{61·1°}$ 0·8830, $d_{4°}^{86·9°}$ 0·8624. Apparatus *A*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
19·1°	18·46	0·9167	31·69	337·0	61·2°	16·69	0·8829	27·59	338·0
25·0	18·25	0·9120	31·17	337·3	86·5	15·76	0·8627	25·46	339·0
41·9	17·58	0·8990	29·59	337·8				Mean	337·8

576. *Di*-n-*butylnitrosoamine*. B. p. 125—125·5°/21 mm.; *M* 158·24; n_{C} 1·44454, n_{D} 1·44746, n_{F} 1·45497, $n_{\text{G'}}$ 1·46109; R_{C} 46·70, R_{D} 46·98, R_{F} 47·66, $R_{\text{G'}}$ 48·21; $Mn_{\text{D}}^{20°}$ 229·05. Densities determined: $d_{4°}^{20°}$ 0·9009, $d_{4°}^{41·9°}$ 0·8838, $d_{4°}^{61·7°}$ 0·8686, $d_{4°}^{86·5°}$ 0·9498. Apparatus *D*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
17·3°	13·72	0·9030	30·60	412·1	62·3°	12·45	0·8682	26·69	414·3
21·0	13·61	0·9001	30·25	412·3	88·0	11·67	0·8487	24·46	414·6
42·0	13·06	0·8837	28·46	413·6				Mean	413·4

577. *Nitromethane*. B. p. 101°/762 mm.; *M* 61·04; n_{C} 1·37895, n_{D} 1·38152, n_{F} 1·38778, $n_{\text{G'}}$ 1·39270; R_{C} 12·29, R_{D} 12·36, R_{F} 12·54, $R_{\text{G'}}$ 12·69; $Mn_{\text{D}}^{20°}$ 83·55. Densities determined: $d_{4°}^{20°}$ 1·1371, $d_{4°}^{41·1°}$ 1·1081, $d_{4°}^{60·9°}$ 1·0815. Apparatus *A*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
17·3°	17·43	1·1408	37·23	132·2	41·2°	16·24	1·1080	33·69	133·0
20·7	17·26	1·1361	36·72	132·3	60·9	15·25	1·0815	30·88	133·1
25·9	17·06	1·1290	36·07	132·5				Mean	132·6

578. *Nitroethane*. B. p. 114°/765 mm.; *M* 75·08; n_{C} 1·38936, n_{D} 1·39173, n_{F} 1·39765, $n_{\text{G'}}$ 1·40212; R_{C} 16·93, R_{D} 17·02, R_{F} 17·25, $R_{\text{G'}}$ 17·42; $Mn_{\text{D}}^{20°}$ 104·49. Densities determined: $d_{4°}^{20°}$ 1·0497, $d_{4°}^{41°}$ 1·0250, $d_{4°}^{59·8°}$ 1·0026, $d_{4°}^{85·0°}$ 0·9726. Apparatus *D*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
20·2°	12·42	1·0477	32·14	170·7	61·4°	10·98	1·0007	27·14	171·2
25·0	12·29	1·0437	31·68	170·7	87·3	10·03	0·9699	24·02	171·6
41·3	11·66	1·0247	29·50	170·8				Mean	171·0

579. 1-*Nitro*-n-*propane*. B. p. 130·5°/761 mm.; *M* 89·10; n_{C} 1·39816, n_{D} 1·40130, n_{F} 1·40639, $n_{\text{G'}}$ 1·41083; R_{C} 21·50, R_{D} 21·64, R_{F} 21·89, $R_{\text{G·}}$ 22·15; $Mn_{\text{D}}^{20°}$ 124·86. Densities determined: $d_{4°}^{20°}$ 1·0009, $d_{4°}^{41·1°}$ 0·9794, $d_{4°}^{61·5°}$ 0·9573, $d_{4°}^{87·0°}$ 0·9296. Apparatus *A*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
17·1°	16·31	1·0039	30·66	208·8	61·7°	14·34	0·9571	25·70	209·6
20·1	16·13	1·0008	30·23	208·8	86·7	13·25	0·9299	23·07	210·0
41·3	15·32	0·9792	28·09	209·5				Mean	209·3

580. 2-*Nitro*-n-*propane*. B. p. 119·5°/752 mm.; *M* 89·10; n_{C} 1·39196, n_{D} 1·39426, n_{F} 1·39992, $n_{\text{G'}}$ 1·40418; R_{C} 21·48, R_{D} 21·59, R_{F} 21·87, $R_{\text{G'}}$ 22·08; $Mn_{\text{D}}^{20°}$ 124·23. Densities determined: $d_{4°}^{20°}$ 0·9876, $d_{4°}^{41·6°}$ 0·9652, $d_{4°}^{60·3°}$ 0·9453, $d_{4°}^{86·8°}$ 0·9162. Apparatus *A*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
21·0°	15·74	0·9865	29·08	209·7	61·1°	13·87	0·9445	24·53	209·9
29·1	15·40	0·9781	28·20	209·9	86·0	12·73	0·9170	21·86	210·1
41·2	14·80	0·9656	26·76	209·7				Mean	209·8

581. 1-*Nitro*-n-*butane*. B. p. 151·5—152·5°/780 mm.; *M* 103·12; n_{C} 1·40975, n_{D} 1·41028, n_{F} 1·41613, $n_{\text{G'}}$ 1·42048; R_{C} 26·20, R_{D} 26·33, R_{F} 26·65, $R_{\text{G'}}$ 26·90; $Mn_{\text{D}}^{20°}$ 145·43. Densities determined: $d_{4°}^{20°}$ 0·9710, $d_{4°}^{41·2°}$ 0·9514, $d_{4°}^{60·0°}$ 0·9335, $d_{4°}^{87·0°}$ 0·9067. Apparatus *A*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
15·4°	16·34	0·9753	29·84	247·1	41·6°	15·29	0·9510	27·23	247·7
20·3	16·15	0·9707	29·35	247·3	62·1	14·52	0·9312	25·32	248·4
25·9	16·05	0·9654	29·01	247·9	87·5	13·43	0·9062	22·79	248·6
								Mean	247·8

582. 1-*Nitro*-n-*pentane*. B. p. 66°/16 mm.; *M* 117·15; n_C 1·41516, n_D 1·41751, n_F 1·42329, $n_{G'}$ 1·42771; R_C 30·81, R_D 30·96, R_F 31·34, $R_{G'}$ 31·62; $Mn_D^{20^\circ}$ 166·06. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9525, $d_{4^\circ}^{41·6^\circ}$ 0·9330, $d_{4^\circ}^{63·0^\circ}$ 0·9137, $d_{4^\circ}^{88·0^\circ}$ 0·8912. Apparatus *D*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
17·0°	12·53	0·9552	29·55	286·0	62·3°	11·19	0·9143	25·27	287·3
25·3	12·36	0·9477	28·93	286·7	88·3	10·40	0·8901	22·86	287·8
41·5	11·81	0·9331	27·21	286·8				Mean	286·9

583. 1-*Nitro*-n-*hexane*. B. p. 81·5°/15 mm.; *M* 131·18; n_C 1·42111, n_D 1·42346, n_F 1·42930, $n_{G'}$ 1·43366; R_C 35·41, R_D 35·59, R_F 36·01, $R_{G'}$ 36·34; $Mn_D^{20^\circ}$ 186·73. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9396, $d_{4^\circ}^{41·3^\circ}$ 0·9219, $d_{4^\circ}^{62·6^\circ}$ 0·9043, $d_{4^\circ}^{85·5^\circ}$ 0·8845. Apparatus *D*.

20·5°	12·77	0·9392	29·62	325·8	62·5°	11·53	0·9044	25·75	326·7
42·2	12·07	0·9212	27·46	326·0	86·7	10·90	0·8835	23·78	327·9
								Mean	326·6

584. *Nitrobenzene*. B. p. 207·5°/760 mm.; *M* 123·13; n_C 1·54559, n_D 1·55246, n_F 1·57086, $n_{G'}$ 1·58972 (line faint); R_D 32·38, R_D 32·72, R_F 33·62, $R_{G'}$ 34·44; $Mn_D^{20^\circ}$ 191·13. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2031, $d_{4^\circ}^{1·5^\circ}$ 1·1829, $d_{4^\circ}^{61·7^\circ}$ 1·1641, $d_{4^\circ}^{86·6^\circ}$ 1·1402. Apparatus *A*.

16·3°	19·72	1·2066	44·55	263·6	60·5°	17·94	1·1652	39·14	264·3
19·5	19·56	1·2036	44·08	263·6	86·5	16·86	1·1403	36·00	264·4
40·9	18·69	1·1834	41·42	263·9				Mean	263·9

585. n-*Butyl nitrite*. B. p. 27°/88 mm.; *M* 103·12; n_C 1·37463, n_D 1·37683, n_F 1·38241, $n_{G'}$ 1·38678; R_C 26·73, R_D 26·87, R_F 27·22; $R_{G'}$ 27·50; $Mn_D^{20^\circ}$ 141·98. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8823, $d_{4^\circ}^{40·9^\circ}$ 0·8575. Apparatus *A*.

13·5°	13·07	0·8900	21·78	250·3	23·6°	12·76	0·8780	20·98	251·4
17·7	12·96	0·8850	21·48	250·8	41·3	11·76	0·8570	18·87	251·1
								Mean	250·9

586. n-*Amyl nitrite*. B. p. 104·5°/763 mm. and 29°/40 mm.; *M* 117·15; n_C 1·38707, n_D 1·38931, n_C 1·39498, $n_{G'}$ 1·39935; R_C 31·28, R_D 31·44, R_F 31·84, $R_{G'}$ 32·16; $Mn_D^{20^\circ}$ 162·76. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8820, $d_{4^\circ}^{40·7^\circ}$ 0·8603, $d_{4^\circ}^{63·7^\circ}$ 0·8352. Apparatus *A*.

13·4°	14·06	0·8890	23·41	289·8	41·5°	12·72	0·8595	20·47	289·9
16·5	13·90	0·8857	23·05	289·8	58·2	11·83	0·8410	18·63	289·4
22·1	13·76	0·8798	22·67	290·5				Mean	289·9

587. n-*Hexyl nitrite*. B. p. 129·5—130°/761 mm. and 52°/44 mm.; *M* 131·17; n_C 1·39619, n_D 1·39846, n_C 1·40412, $n_{G'}$ 1·40853; R_C 35·92, R_D 36·10, R_F 36·55, $R_{G'}$ 36·90; $Mn_D^{20^\circ}$ 183·44. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8778, $d_{4^\circ}^{41·4^\circ}$ 0·8572, $d_{4^\circ}^{61·7^\circ}$ 0·8371. Apparatus *D*.

16·3°	11·10	0·8814	24·16	329·9	42·1°	10·22	0·8565	21·62	331·0
19·2	11·02	0·8786	23·91	330·1	62·0	9·50	0·8368	19·63	330·0
24·7	10·90	0·8732	23·51	330·8				Mean	330·4

588. *Ethyl nitrate*. B. p. 88°/757 mm.; *M* 91·07; n_C 1·38294, n_D 1·38528, n_F 1·39091, $n_{G'}$ 1·39526; R_C 19·18, R_D 19·28, R_F 19·53, $R_{G'}$ 19·73; $Mn_D^{20^\circ}$ 126·16. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1076, $d_{4^\circ}^{40·6^\circ}$ 1·0809. Apparatus *F*.

18·3°	10·97	1·1098	28·34	189·3	41·5°	10·03	1·0797	25·21	189·1
31·3	10·47	1·0929	26·64	189·3				Mean	189·2

589. n-*Propyl nitrate*. B. p. 110°/762 mm.; *M* 105·10; n_C 1·39491, n_D 1·39725, n_F 1·40287, $n_{G'}$ 1·40706; R_C 23·91, R_D 24·03, R_F 24·33, $R_{G'}$ 24·56; $Mn_D^{20^\circ}$ 146·86. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0538, $d_{4^\circ}^{40·0^\circ}$ 1·0316, $d_{4^\circ}^{59·7^\circ}$ 1·0066. Apparatus *F*.

17·8°	11·16	1·0563	27·45	227·7	40·9°	10·19	1·0316	24·45	226·8
22·3	11·04	1·0512	27·02	227·9	58·4	9·60	1·0081	22·53	227·1
								Mean	227·5

590. n-*Butyl nitrate*. B. p. 135—135·5°/763 mm.; *M* 119·12; n_C 1·40413, n_D 1·40647, n_F 1·41211, $n_{G'}$ 1·41653; R_C 28·49, R_D 28·64, R_F 28·99, $R_{G'}$ 29·26; $Mn_D^{20^\circ}$ 167·54. Densities determined; $d_{4^\circ}^{20^\circ}$ 1·0228, $d_{4^\circ}^{40·0^\circ}$ 1·0018, $d_{4^\circ}^{60·7^\circ}$ 0·9791. Apparatus *F*.

13·9°	11·98	1·0293	28·71	267·9	41·8°	10·97	0·9999	25·54	267·8
18·5	11·80	1·0244	28·40	268·4	60·4	10·35	0·9794	23·60	268·1
								Mean	268·1

591. *Dimethyl carbonate*. B. p. 89·5°/755 mm.; *M* 90·07; n_C 1·36700, n_D 1·36874, n_F 1·37288, $n_{G'}$ 1·37568; R_C 18·89, R_D 18·97, R_F 19·16, $R_{G'}$ 19·29; $Mn_D^{20^\circ}$ 123·28. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0706, $d_{4^\circ}^{40·4^\circ}$ 1·0446, $d_{4^\circ}^{58·6^\circ}$ 1·0205. Apparatus *A*.

19·3°	14·63	1·0715	29·35	195·7	61·3°	12·45	1·0170	23·71	195·7
42·1	13·47	1·0424	26·29	195·7				Mean	195·5

592. *Diethyl carbonate.* B. p. 125·5°/758 mm.; *M* 118·13; n_C 1·38248, n_D 1·38433, n_F 1·38872, $n_{G'}$ 1·39183; R_C 28·19, R_D 28·31, R_F 28·59, $R_{G'}$ 28·80; $Mn_D^{20^\circ}$ 163·53. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9764, $d_{4^\circ}^{41\cdot5^\circ}$ 0·9521, $d_{4^\circ}^{61\cdot7^\circ}$ 0·9302, $d_{4^\circ}^{85\cdot7^\circ}$ 0·9024. Apparatus *D*.

t.	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*	*t.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*
13·2°	11·22	0·9840	27·27	274·3	41·6°	10·21	0·9520	24·00	274·7
16·4	11·03	0·9804	26·71	273·9	61·2	9·50	0·9309	21·79	274·2
23·1	10·88	0·9729	26·14	274·5	87·2	8·59	0·9007	19·11	274·2
								Mean	274·3

593. *Di-*n*-propyl carbonate.* B. p. 165°/752 mm.; *M* 146·18; n_C 1·39876, n_D 1·40072, n_F 1·40543, $n_{G'}$ 1·40885; R_C 37·48, R_D 37·64, R_F 38·03, $R_{G'}$ 38·32; $Mn_D^{20^\circ}$ 204·75. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9429, $d_{4^\circ}^{41\cdot0^\circ}$ 0·9232, $d_{4^\circ}^{61\cdot2^\circ}$ 0·9032, $d_{4^\circ}^{87\cdot1^\circ}$ 0·8769. Apparatus *D*.

19·3°	11·60	0·9436	27·03	353·2	60·8°	10·18	0·9036	22·72	353·2
21·9	11·52	0·9441	26·77	353·3	87·3	9·30	0·8767	20·14	353·2
41·2	10·81	0·9230	24·64	352·9				Mean	353·2

594. *Di-*n*-butyl carbonate.* B. p. 204·5°/758 mm.; *M* 174·23; n_C 1·40966, n_D 1·41167, n_F 1·41656, $n_{G'}$ 1·42000; R_C 46·64, R_D 46·84, R_F 47·33, $R_{G'}$ 47·66; $Mn_D^{20^\circ}$ 245·96. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9251, $d_{4^\circ}^{40\cdot8^\circ}$ 0·9057, $d_{4^\circ}^{61\cdot0^\circ}$ 0·8883, $d_{4^\circ}^{87\cdot0^\circ}$ 0·8638. Apparatus *A*.

16·8°	15·83	0·9280	27·51	430·0	61·5°	13·99	0·8878	23·26	431·0
23·0	15·61	0·9223	26·96	430·5	87·0	12·94	0·8638	20·93	431·4
41·4	14·81	0·9052	25·10	430·8				Mean	430·7

595. *Di*iso*butyl carbonate.* B. p. 187·5°/763 mm.; *M* 174·23; n_C 1·40529, n_D 1·40731, n_F 1·41212, $n_{G'}$ 1·41567; R_C 46·77, R_D 46·97, R_F 47·46, $R_{G'}$ 47·82; $Mn_D^{20^\circ}$ 245·19. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9137, $d_{4^\circ}^{40\cdot5^\circ}$ 0·8945, $d_{4^\circ}^{62\cdot1^\circ}$ 0·8744, $d_{4^\circ}^{85\cdot0^\circ}$ 0·8517. Apparatus *A*.

14·5°	15·00	0·9189	25·81	427·4	61·3°	13·12	0·8752	21·50	428·7
41·0	13·96	0·8940	23·37	428·5	86·3	12·02	0·8505	19·14	428·5
								Mean	428·3

596. *Methyl thiocyanate.* B. p. 130·5°/765 mm.; *M* 73·11; n_C 1·46523, n_D 1·46854, n_F 1·47658, n_G 1·48278; R_C 18·82, R_D 18·93, R_F 19·21, $R_{G'}$ 19·43; $Mn_D^{20^\circ}$ 107·36. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0744, $d_{4^\circ}^{40\cdot9^\circ}$ 1·0504, $d_{4^\circ}^{61\cdot3^\circ}$ 1·0281, $d_{4^\circ}^{86\cdot5^\circ}$ 0·9985. Apparatus *D*.

15·3°	14·39	1·0798	38·37	168·5	42·5°	13·43	1·0486	34·78	168·5
21·3	14·19	1·0729	37·60	168·7	60·9	12·77	1·0285	32·44	169·6
23·7	14·09	1·0702	27·24	168·8	85·2	11·83	1·0000	29·22	170·1
								Mean	169·0

597. *Ethyl thiocyanate.* B. p. 145·5°/765 mm.; *M* 87·14; n_C 1·45998, n_D 1·46304, n_F 1·47070, $n_{G'}$ 1·47656; R_C 23·59, R_D 23·72, R_F 24·06, $R_{G'}$ 24·30; $Mn_D^{20^\circ}$ 127·49. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0116, $d_{4^\circ}^{41\cdot1^\circ}$ 0·9896, $d_{4^\circ}^{60\cdot6^\circ}$ 0·9704, $d_{4^\circ}^{87\cdot0^\circ}$ 0·9426. Apparatus *A*.

14·4°	17·84	1·0174	33·99	206·8	41·1°	16·63	0·9896	30·82	207·4
19·9	17·53	1·0117	33·21	206·8	61·2	15·80	0·9698	28·69	208·0
27·2	17·30	1·0042	32·53	207·2	87·0	14·64	0·9426	25·84	208·4
								Mean	207·4

598. n-*Propyl thiocyanate.* B. p. 164·5°/760 mm.; *M* 101·17; n_C 1·46016, n_D 1·46314, n_F 1·47050, $n_{G'}$ 1·47621; R_C 28·24, R_D 28·39, R_F 28·78, $R_{G'}$ 29·08; $Mn_D^{20^\circ}$ 148·02. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9817, $d_{4^\circ}^{40\cdot6^\circ}$ 0·9627, $d_{4^\circ}^{60\cdot3^\circ}$ 0·9439, $d_{4^\circ}^{81\cdot9^\circ}$ 0·9233. Apparatus *D*.

17·9°	13·52	0·9837	32·84	246·2	60·9°	12·19	0·9433	28·40	247·6
25·4	13·41	0·9767	32·35	247·0	86·8	11·38	0·9187	25·82	248·2
41·5	12·83	0·9619	30·48	247·1				Mean	247·2

599. n-*Butyl thiocyanate.* B. p. 184°/770 mm.; *M* 115·19; n_C 1·46099, n_D 1·46389, n_F 1·47108, $n_{G'}$ 1·47660; R_C 32·89, R_D 33·07, R_F 33·51, $R_{G'}$ 33·84; $Mn_D^{20^\circ}$ 168·63. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9610, $d_{4^\circ}^{40\cdot5^\circ}$ 0·9433, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9252, $d_{4^\circ}^{85\cdot2^\circ}$ 0·9035. Apparatus *A*.

19·2°	17·81	0·9617	32·07	285·0	60·5°	16·21	0·9255	28·09	286·5
26·5	17·56	0·9553	31·41	285·5	85·1	15·25	0·9036	25·80	287·4
40·4	16·96	0·9434	29·96	285·7				Mean	286·0

600. *Ethyl* iso*thiocyanate.* B. p. 132—132·5°/762 mm.; *M* 87·14; n_C 1·49877, n_D 1·50435, n_F 1·51495, $n_{G'}$ 1·52432; R_C 25·69, R_D 25·92, R_F 26·38, $R_{G'}$ 26·78; $Mn_D^{20^\circ}$ 131·09. Densities determined: $d_{4^\circ}^{20}$ 0·9962, $d_{4^\circ}^{42\cdot0^\circ}$ 0·9740, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9545, $d_{4^\circ}^{87\cdot1^\circ}$ 0·9269. Apparatus *D*.

16·4°	13·49	0·9999	33·31	209·4	60·2°	12·00	0·9551	28·30	210·4
19·2	13·42	0·9970	33·04	209·6	86·3	11·08	0·9277	25·38	210·8
41·3	12·67	0·9747	30·50	210·1				Mean	210·1

601. *Allyl* iso*thiocyanate*. B. p. 151—151·5°/768 mm.; *M* 99·19, n_{C} 1·52179, n_{D} 1·52686, n_{F} 1·53970, $n_{\mathrm{G'}}$ 1·54982, R_{C} 29·89, R_{D} 30·13, R_{F} 30·74, $R_{\mathrm{G'}}$ 31·22; $Mn_{\mathrm{D}}^{20°}$ 151·45. Densities determined: $d_{4°}^{20°}$ 1·0118, $d_{4°}^{40\cdot0°}$ 0·9927, $d_{4°}^{60\cdot9°}$ 0·9723, $d_{4°}^{85\cdot5°}$ 0·9472. Apparatus *A*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
21·0°	17·95	1·0108	33·97	236·9	60·9°	16·12	0·9723	29·35	237·4
28·1	17·73	1·0039	33·36	237·2	85·6	15·11	0·9471	26·80	238·3
40·7	17·02	0·9920	31·61	237·1				Mean	237·4

602. *Diethyl xanthate*. B. p. 70·2°/4·9 mm.; *M* 150·25; n_{C} 1·52775, n_{D} 1·53325, n_{F} 1·54795, $n_{\mathrm{G'}}$ 1·56079; R_{C} 42·68, R_{D} 43·05, R_{F} 44·04, $R_{\mathrm{G'}}$ 44·88; $Mn_{\mathrm{D}}^{20°}$ 230·38. Densities determined: $d_{4°}^{20°}$ 1·0837, $d_{4°}^{41\cdot0°}$ 1·0647, $d_{4°}^{61\cdot7°}$ 1·0451, $d_{4°}^{86\cdot9°}$ 1·0213. Apparatus *D*.

19·2°	12·82	1·0844	34·33	335·4	60·2°	11·55	1·0446	29·80	336·1
25·4	12·68	1·0787	33·78	335·8	86·7	10·83	1·0215	27·32	336·3
41·9	12·14	1·0639	31·90	335·6				Mean	335·8

603. *Di*-n-*propyl xanthate*. B. p. 91·1°/4·5 mm.; *M* 178·30; n_{C} 1·51894, n_{D} 1·52396, n_{F} 1·53741, $n_{\mathrm{G'}}$ 1·54895; R_{C} 52·29, R_{D} 52·72, R_{F} 53·84, $R_{\mathrm{G'}}$ 54·80; $Mn_{\mathrm{D}}^{20°}$ 271·73. Densities determined: $d_{4°}^{20°}$ 1·0349, $d_{4°}^{41\cdot3°}$ 1·0165, $d_{4°}^{61\cdot9°}$ 0·9992, $d_{4°}^{87\cdot1°}$ 0·9767. Apparatus *A*.

20·9°	16·92	1·0341	32·76	412·5	61·5°	15·40	0·9995	28·82	413·3
28·0	16·68	1·0280	32·11	412·9	87·4	14·39	0·9764	26·31	413·6
40·8	16·18	1·0169	30·81	413·1				Mean	413·1

604. *Ethyl* S-n-*butylxanthate*. B. p. 90·3°/4·0 mm.; *M* 178·30; n_{C} 1·51865, n_{D} 1·52368, n_{F} 1·53710, $n_{\mathrm{G'}}$ 1·54872; R_{C} 52·27, R_{D} 52·69, R_{F} 53·82, $R_{\mathrm{G'}}$ 54·78; $Mn_{\mathrm{D}}^{20°}$ 271·68. Densities determined: $d_{4°}^{20}$ 1·0349, $d_{4°}^{42\cdot2°}$ 1·0162, $d_{4°}^{61\cdot4°}$ 1·0002, $d_{4°}^{87\cdot0°}$ 0·9774. Apparatus *D*.

18·0°	12·91	1·0366	33·05	412·4	60·6°	11·71	1·0007	28·94	413·3
23·6	12·73	1·0318	32·44	412·4	86·1	11·04	0·9783	26·67	414·2
42·3	12·20	1·0161	30·61	412·8				Mean	413·0

605. n-*Butyl* S-*ethylxanthate*. B. p. 91·0°/4·3 mm.; *M* 178·30; n_{C} 1·51869, n_{D} 1·52372, n_{F} 1·53718, $n_{\mathrm{G'}}$ not visible; R_{C} 52·26, R_{D} 52·68, R_{F} 53·81; $Mn_{\mathrm{D}}^{20°}$ 217·68. Densities determined: $d_{4°}^{20°}$ 1·0351, $d_{4°}^{42\cdot0°}$ 1·0164, $d_{4°}^{61\cdot7°}$ 1·0001, $d_{4°}^{87\cdot0°}$ 0·9777. Apparatus *A*.

18·3°	16·97	1·0365	32·94	412·1	61·1°	15·38	1·0006	28·82	412·9
29·8	16·79	1·0268	32·28	413·9	84·8	14·56	0·9796	26·71	413·8
40·9	16·12	1·0173	30·71	412·6				Mean	413·1

606. *Di*-n-*butyl xanthate*. B. p. 117°/4·0 mm.; *M* 206·35; n_{C} 1·50994, n_{D} 1·51456, n_{F} 1·52681, $n_{\mathrm{G'}}$ 1·53704; R_{C} 61·59, R_{D} 62·07, R_{F} 63·30, $R_{\mathrm{G'}}$ 64·32; $Mn_{\mathrm{D}}^{20°}$ 312·55. Densities determined: $d_{4°}^{20°}$ 1·0019, $d_{4°}^{41\cdot0°}$ 0·9855, $d_{4°}^{60\cdot8°}$ 0·9691, $d_{4°}^{87\cdot4°}$ 0·9475. Apparatus *A*.

15·9°	17·13	1·0052	32·24	489·2	41·3°	16·23	0·9852	29·94	490·0
20·3	17·03	1·0017	31·94	489·8	60·9	15·43	0·9690	28·00	489·9
24·9	16·83	0·9980	31·45	489·7	86·9	14·61	0·9479	25·93	491·3
								Mean	489·8

The author's thanks are due to Imperial Chemical Industries for the liberal grants in support of the investigations described in Parts XVIII—XXIII, and to Dr. G. H. Jeffery, F.R.I.C., for the preparation and purification of the alkyl nitrates.

WOOLWICH POLYTECHNIC, LONDON, S.E. 18. [*Received, December 4th*, 1947.]