98. *Physical Properties and Chemical Constitution. Part XXIV.* Aliphatic Aldoximes, Ketoximes, and Ketoxime* O-*Alkyl Ethers,* NN-*Dialkylhydrazines, Aliphatic Ketazines, Mono- and Di-alkylaminopropionitriles, Alkoxypropionitriles, Dialkyl Azodiformates, and Dialkyl Carbonates. Bond Parachors, Bond Refractions, and Bond-refraction Coefficients.*

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New measurements have been made of the refractivities at 20°, and the parachors of aliphatic aldoximes, ketoximes, and ketoxime *O*-alkyl ethers, *NN*-dialkylhydrazines, aliphatic ketazines, β-mono- and β-di-alkylaminopropionitriles, β-alkoxypropionitriles, dialkyl azodiformates and dialkyl carbonates, and the contributions of the :N·OH, :NO, N·NH$_2$, :N·N:, NH, N (tertiary), N:N, and CO$_3$ groups, and of O (from alkoxypropionitriles) have been evaluated. The bond refractions, as well as the bond parachors and the bond-refraction coefficients, have been computed for a large number of links with the aid of the experimental data given in this and previous papers of this series. The bond constants of several links have been deduced by a number of independent methods, and the results are in satisfactory agreement. The comprehensive table of bond refractions and bond parachors may be employed for the computation of "theoretical" refractions and parachors. The bond-refraction coefficients permit of the calculation of the refractive index (n_D^{20}) of a liquid compound from its chemical formula.

The structures of the esters of oxy-acids and of related compounds are discussed.

THE determination of atomic, group, and structural parachors and refractivities has been extended to a number of series of nitrogen-containing compounds (compare Eisenlohr, *Z. physikal. Chem.*, 1912, **79**, 412). New measurements of the densities and surface tensions over a range of temperatures as well as the refractive indices at 20° for the C, D, F, and G′ lines have been made and the constants calculated as in previous papers of this series.

TABLE 1. *Values for the* :N·OH *group from aldoximes and ketoximes.*

	P	R_C	R_D	R_F	$R_{G'}$	Mn_D^{20}
Aldoximes						
CHMe:N·OH	65·0	6·42	6·44	6·48	6·67	42·92
CHEt:N·OH	64·5	6·37	6·43	6·56	6·66	42·62
CHPr^n:N·OH	63·1	6·41	6·48	6·60	6·71	42·71
Mean :N·OH	64·2	6·400	6·450	6·546	6·680	42·75
Ketoximes						
CMeEt:N·OH	61·3	6·41	6·47	6·62	6·78	43·16
CMePr^n:N·OH	59·3	6·39	6·46	6·60	6·70	43·12
CEt$_2$:N·OH	58·5	6·33	6·41	6·53	6·64	43·16
CEtPr^n:N·OH	57·3	6·23	6·32	6·44	6·55	42·97
CPr^n:N·OH	54·9	6·22	6·29	6·42	6·53	42·81
Mean :N·OH	58·3	6·316	6·390	6·522	6·640	43·04

The constants for :NOH in aldoximes and ketoximes are collected in Table 1, and for :NO in ketoxime *O*-alkyl ethers in Table 2.

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* Part XXIII, *J.*, 1948, 1833.

TABLE 2. *Values for the* $\mathrm{{:}NO}$ *group from ketoxime* O-*alkyl ethers.*

	P	R_{C}	R_{D}	R_{F}	$R_{\mathrm{G'}}$	Mn_{D}^{20}
$\mathrm{CMe_2{:}NOMe}$	53·5	5·67	5·74	5·87	6·01	41·91
$\mathrm{CMe_2{:}NOEt}$	53·1	5·85	5·91	6·06	6·29	41·35
$\mathrm{CMe_2{:}NOPr^n}$	52·2	5·70	5·78	5·91	6·04	41·52
$\mathrm{CMeEt{:}NOEt}$	54·8	5·75	5·83	5·97	6·09	41·28
$\mathrm{CMeEt{:}NOPr^n}$	47·7	5·53	5·60	5·74	5·89	41·52
$\mathrm{CEt_2{:}NOEt}$	48·3	5·66	5·73	5·88	6·00	41·41
$\mathrm{CEt_2{:}NOPr^n}$	48·1	5·58	5·64	5·80	5·92	41·50
$\mathrm{CMePr^n{:}NOEt}$	49·3	5·79	5·85	5·99	6·12	41·45
$\mathrm{CMePr^n{:}NOPr^n}$	48·6	5·64	5·70	5·84	5·98	41·48
$\mathrm{CEtPr^n{:}NOEt}$	48·7	5·79	5·84	6·01	6·12	41·66
$\mathrm{CEtPr^n{:}NOPr^n}$	47·8	5·71	5·76	5·93	6·03	41·42
$\mathrm{CPr^n_2{:}NOEt}$	46·1	5·78	5·83	5·99	6·07	41·37
$\mathrm{CPr^n_2{:}NOPr^n}$	46·0	5·78	5·82	5·98	6·10	40·56
Mean $\mathrm{{:}NO}$	49·2	5·710	5·792	5·921	6·058	41·48

Four *NN*-dialkylhydrazines were prepared by the reduction of the appropriate dialkylnitrosamines. Zinc and acetic acid are satisfactory only for diethylnitrosamine (compare Fischer, *Annalen*, 1879, **199**, 287); the higher members of the series are most conveniently prepared by reduction of the nitrosamine with lithium aluminium hydride in dry ethereal solution. The constants for the $\mathrm{N{\cdot}NH_2}$ grouping are given in Table 3.

TABLE 3. *Values for the* $\mathrm{N{\cdot}NH_2}$ *group from* NN-*dialkylhydrazines,* $\mathrm{R_2N{\cdot}NH_2}$.

	P	R_{C}	R_{D}	R_{F}	$R_{\mathrm{G'}}$	Mn_{D}^{20}
$\mathrm{NEt_2{\cdot}NH_2}$	56·1	7·33	7·41	7·54	7·68	47·87
$\mathrm{NPr^n_2{\cdot}NH_2}$	54·6	7·30	7·36	7·50	7·62	47·29
$\mathrm{NBu^n_2{\cdot}NH_2}$	53·6	7·30	7·37	7·50	7·61	48·29
$\mathrm{NAm^n_2{\cdot}NH_2}$	54·3	7·21	7·26	7·39	7·50	47·81
Mean $\mathrm{N{\cdot}NH_2}$	54·7	7·285	7·350	7·483	7·602	47·82

Two more dialkylnitrosamines have been investigated and the constants for the $\mathrm{N{\cdot}NO}$ grouping evaluated: these are in fair agreement with those found in Part XXIII (*J.*, 1948, 1838).

Values for the $\mathrm{N{\cdot}NO}$ *group from nitrosamines,* $\mathrm{R_2N{\cdot}NO}$.

	P	R_{C}	R_{D}	R_{F}	$R_{\mathrm{G'}}$	Mn_{D}^{20}
$\mathrm{NAm^n_2{\cdot}NO}$	60·8	7·61	7·70	7·94	8·22	69·44
$\mathrm{N(\mathit{n}\text{-}C_6H_{13})_2{\cdot}NO}$	59·6	7·74	7·83	8·12	8·36	69·29

The constants for the conjugated grouping $\mathrm{{:}N{\cdot}N{:}}$, evaluated from measurements on aliphatic ketazines, are collected in Table 4.

TABLE 4. *Values for the* $\mathrm{{:}N{\cdot}N{:}}$ *group from aliphatic ketazines,* $\mathrm{CRR'{:}N{\cdot}N{:}CRR'}$.

	P	R_{C}	R_{D}	R_{F}	$R_{\mathrm{G'}}$	Mn_{D}^{20}
$\mathrm{CMe_2{:}N{\cdot}N{:}CMe_2}$	63·8	8·09	8·25	8·57	8·86	39·11
$\mathrm{CMeEt{:}N{\cdot}N{:}CMeEt}$	61·4	8·06	8·21	8·55	8·83	38·80
$\mathrm{CEt_2{:}N{\cdot}N{:}CEt_2}$	55·9	7·90	8·08	8·39	8·69	38·83
$\mathrm{CMePr^n{:}N{\cdot}N{:}CMePr^n}$	58·6	8·09	8·21	8·56	8·87	39·02
$\mathrm{CEtPr^n{:}N{\cdot}N{:}CEtPr^n}$	53·0	7·99	8·18	8·50	8·91	38·91
$\mathrm{CPr^n_2{:}N{\cdot}N{:}CPr^n_2}$	49·2	8·13	8·30	8·61	8·91	39·06
Mean $\mathrm{{:}N{\cdot}N{:}}$	57·0	8·065	8·205	8·530	8·845	38·96

A series of β-monoalkylaminopropionitriles $\mathrm{NHR{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$ has been prepared by the cyanoethylation of primary aliphatic amines. By subtracting the results for the corresponding nitriles $\mathrm{R{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$ (Part XVII, *J.*, 1948, 674; *n*-heptyl and *n*-octyl cyanides in the present paper) the constants for the NH grouping are obtained directly: these are given in Table 5. The agreement, apart from the Mn_{D}^{20} figures which are somewhat higher, with the constants deduced from secondary aliphatic amines is reasonably satisfactory.

The constants for N (tertiary) were obtained in a similar manner from β-dialkylaminopropionitriles, prepared by the cyanoethylation of secondary aliphatic amines. The results are given in Table 6; the refractivities are slightly lower and the molecular-refraction coefficients slightly higher than those already found for N from tertiary aliphatic amines (Part XXII, *J.*, 1948, 1827); the parachor contributions appear to decrease with increase in the molecular weight of the alkyl group.

TABLE 5. *Values for the* NH *group from* β-*alkylaminopropionitriles,* $\mathrm{NHR{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$.

	P	R_C	R_D	R_F	$R_{G'}$	Mn^{20}_D
$\mathrm{NHEt{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	27·4	3·64	3·67	3·75	3·80	24·50
$\mathrm{NHPr^n{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	26·2	3·65	3·68	3·75	3·81	24·30
$\mathrm{NHBu^n{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	25·7	3·60	3·62	3·69	3·73	24·26
$\mathrm{NHAm^n{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	22·8	3·60	3·62	3·69	3·75	24·09
$n\text{-}\mathrm{C_6H_{13}{}^n{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	23·4	3·58	3·62	3·69	3·72	24·10
Mean NH	25·1	3·614	3·642	3·714	3·762	24·25
Mean NH (from $\mathrm{NHR_2}$; *J.*, 1948, 1826)	28·4	3·572	3·610	3·667	3·732	23·34

TABLE 6. *Values for the* N (*tertiary*) *group from* β-*dialkylaminopropionitriles,* $\mathrm{NR_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$.

	P	R_C	R_D	R_F	$R_{G'}$	Mn^{20}_D
$\mathrm{NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	7·0	2·67	2·71	2·79	2·86	26·07
$\mathrm{NPr^n{}_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	4·1	2·58	2·60	2·69	2·78	25·63
$\mathrm{NBu^n{}_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	2·8	2·65	2·68	2·75	2·83	25·74
$\mathrm{NAm^n{}_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	1·0	2·59	2·62	2·69	2·76	25·53
Mean N (tertiary)	?	2·623	2·653	2·730	2·808	25·74
Mean N (from $\mathrm{NR_3}$; *J.*, 1948, 1827)	7·2	2·698	2·744	2·820	2·914	24·37

The β-alkoxypropionitriles, prepared by the cyanoethylation of alcohols, may be employed to determine the constants for oxygen ($\mathrm{RO{\cdot}CH_2{\cdot}CH_2{\cdot}CN - R{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$). The results are given in Table 7 : it will be noted that they are in reasonable agreement with those obtained for O in aliphatic ethers (Part XII, *J.*, 1948, 617).

TABLE 7. *Values for the* O *group from alkoxypropionitriles,* $\mathrm{RO{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$.

	P	R_C	R_D	R_F	$R_{G'}$	Mn^{20}_D
$\mathrm{MeO{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	22·1	1·66	1·68	1·69	1·77	23·77
$\mathrm{EtO{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	19·9	1·74	1·77	1·77	1·83	23·41
$\mathrm{Pr^nO{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	20·0	1·74	1·75	1·79	1·83	23·22
$\mathrm{Bu^nO{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	20·6	1·76	1·76	1·78	1·83	23·15
$\mathrm{Am^nO{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	20·0	1·76	1·76	1·78	1·83	23·27
$n\text{-}\mathrm{C_6H_{13}{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$	20·7	1·71	1·73	1·75	1·80	23·14
Mean O	20·4	1·73	1·74	1·76	1·81	23·33
Mean O (from $\mathrm{R_2O}$; *J.*, 1948, 616)	19·8	1·753	1·764	1·786	1·805	22·74

The dialkyl azodiformates were used to compute the constants of the azo-group, $\mathrm{N{:}N}$, by subtraction of the experimental figures for dialkyl oxalates (Part XIII, *J.*, 1948, 624). The refractive indices for the F and G′ lines could not be determined because of the deep colour of the liquids. The results are shown in Table 8.

TABLE 8. *Values for the* $\mathrm{N{:}N}$ *group from dialkyl azodiformates,* $\mathrm{RO_2C{\cdot}N{:}N{\cdot}CO_2R}$.

	P	R_C	R_D	R_F	$R_{G'}$	Mn^{20}_D
$\mathrm{EtO_2C{\cdot}N{:}N{\cdot}CO_2Et}$	54·0	6·13	6·19	—	—	41·57
$\mathrm{Pr^nO_2C{\cdot}N{:}N{\cdot}CO_2Pr^n}$	52·8	5·93	5·98	—	—	41·83
$\mathrm{Bu^nO_2C{\cdot}N{:}N{\cdot}CO_2Bu^n}$	49·8	5·62	5·68	—	—	42·25
Mean $\mathrm{N{:}N}$	52·2	5·893	5·950	—	—	41·88

Experimental data for a large number of dialkyl carbonates were required in connexion with the evaluation of certain bond constants (see below). The study of dialkyl carbonates (Part XXIII, *J.*, 1948, 1839) has therefore been extended to include a number of mixed alkyl carbonates as well as di-*n*-amyl and di-*n*-hexyl carbonates : all of these were synthesised from the pure chlorocarbonate and the appropriate alcohol. The constants for the $\mathrm{CO_3}$ grouping are given in Table 9, and the mean values take into account *all* the carbonates investigated. The constants for the $>$CO grouping, derived with the aid of the data for acetals $\mathrm{CH_2(OR)_2}$ (Part XII, *J.*, 1948, 617) are presented in Table 10 : the new mean values, calculated for all the dialkyl carbonates, are in satisfactory agreement with the constants for the $>\mathrm{C{:}O}$ group for ketones (Part XI, *J.*, 1948, 611 ; Part XX, *J.*, 1948, 1816).

The comprehensive experimental data provided in this series of investigations have been employed to calculate bond constants. The advantages of the bond system as applied to refractions have been pointed out by Vickery and Denbigh (*Trans. Faraday Soc.*, 1949, **45**, 62) : these include (*a*) the assimilation into the bonds of the constitutive effects of the atomic system, which gives a neater scheme, and (*b*) the number of parameters is less for compounds containing more than one multivalent element, *e.g.*, for aliphatic amines, the atomic system uses five parameters (the atomic refractions of C and H, together with the three different values of N corresponding to primary, secondary, and tertiary amines) whereas the bond system employs only four parameters (the bond refractions of the C–C, C–H, C–N, and N–H bonds). We find that the bond system may be extended to include parachors and, rather unexpectedly, the molecular-refraction coefficients (Mn_D^{20}), leading to values for *bond parachors* and *bond-refraction coefficients.* The bond system may therefore be employed to evaluate the " calculated " parachors and the refractivities of compounds for the C, D, F, and G′ lines. The bond-refraction coefficients enable one to compute the refractive indices (n_D^{20}) of liquid organic compounds from their constitutional formulæ with an accuracy in most cases of 1% or better : the numerous practical applications of this facility are obvious (compare Vogel *et al.*, *Chem. and Ind.*, 1951, 376 ; Warrick, *J. Amer. Chem. Soc.*, 1946, **68**, 2455).

TABLE 9. *Values for the* CO$_3$ *group from dialkyl carbonates,* RR′CO$_3$.

	P	R_C	R_D	R_F	$R_{G'}$	Mn_D^{20}
EtPr^{n}CO$_3$	83·1	7·71	7·74	7·82	7·87	86·21
EtBu^{n}CO$_3$	83·8	7·72	7·75	7·82	7·87	86·51
EtAm^{n}CO$_3$	81·3	7·74	7·79	7·86	7·92	86·35
Et(n-C$_6$H$_{13}$)CO$_3$	82·0	7·77	7·81	7·88	7·93	86·37
Pr^{n}Bu^{n}CO$_3$	82·6	7·69	7·71	7·78	7·82	86·64
Am$^n_2$CO$_3$	79·4	7·66	7·68	7·74	7·79	86·45
(n-C$_6$H$_{13}$)$_2$CO$_3$	79·3	7·95	7·98	8·06	8·08	86·57
Mean CO$_3$ (including data in *J.*, 1948, 1839)	82·0	7·712	7·745	7·811	7·864	86·40

TABLE 10. *Values for the* >CO *group from dialkyl carbonates,* CO(OR)(OR′).

	P	R_C	R_D	R_F	$R_{G'}$	Mn_D^{20}
EtPr^{n}CO$_3$	45·4	4·47	4·49	4·54	4·56	41·25
EtBu^{n}CO$_3$	44·9	4·49	4·51	4·56	4·58	41·24
EtAm^{n}CO$_3$	44·1	4·50	4·53	4·58	4·61	41·29
Et(n-C$_6$H$_{13}$)CO$_3$	44·3	4·55	4·58	4·60	4·64	41·32
Pr^{n}Bu^{n}CO$_3$	44·1	4·48	4·50	4·55	4·57	41·35
Am$^n_2$CO$_3$	43·0	4·43	4·45	4·49	4·53	41·27
(n-C$_6$H$_{13}$)$_2$CO$_3$	41·9	4·76	4·79	4·83	4·85	41·41
Mean >CO (including data in *J.*, 1948, 1840)	44·3	4·480	4·505	4·545	4·574	41·26
Mean >C:O (ketones)	44·4	4·579	4·601	4·654	4·702	42·41

The fundamental bond constants (C–C) and (C–H),* deduced from the mean values for CH$_2$ derived from normal aliphatic hydrocarbons (Part IX, *J.*, 1946, 133 ; compare Part X, *J.*, 1948, 607), are :

	(P)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
(C–C)	4·30	1·286	1·296	1·301	1·328	12·86
(C–H)	17·85	1·669	1·676	1·693	1·704	3·87

Vickery and Denbigh (*loc. cit.*) have carried out an exhaustive analysis of the literature data on normal alkanes and find the refractions for the D-line to be (C–C) 1·296 and (C–H) 1·674.

To facilitate the calculation of the various bond constants, it is convenient to have available the constants of the alkyl groups. These have been computed from the data in Part IX (*loc. cit.*) and are collected in Table 11 [compare Table 1 in Part XI (*loc. cit.*)]. The bond constants for CH$_3$ were the mean values obtained by subtracting (n − 2)CH$_2$ + (C–C) from the normal alkanes; (C$_2$H$_5$) from (CH$_3$) + CH$_2$; (C$_3$H$_7{}^n$) to (C$_8$H$_{17}{}^n$) from {C$_n$H$_{2n+2}$ − (C–C)}/2 ; (C$_9$H$_{19}{}^n$) to (C$_{16}$H$_{33}{}^n$) from C$_n$H$_{2n+2}$ − (C–H) ;

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* Throughout the remainder of this paper, quantities in parentheses refer to bond constants.

$(C_4H_9{}^s)$, $(C_5H_{11}{}^i)$. $(CHMePr^n)$, and $(CHEt_2)$ as for $(C_3H_7{}^n)$ from the appropriate hydrocarbons; and $(C_3H_7{}^i)$ from 2:5-dimethylhexane, $(CH_2Pr^i)_2 - 2CH_2 - (C{-}C)$.

TABLE 11. *Bond constants for alkyl groups.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
(CH_3)	53·30	4·993	5·004	5·070	5·084	11·70
(C_2H_5)	93·30	9·617	9·651	9·765	9·819	32·99
$(C_3H_7{}^n)$	133·3	14·25	14·32	14·48	14·57	52·82
$(C_3H_7{}^i)$	131·6	14·27	14·33	14·50	14·60	52·48
$(C_4H_9{}^n)$	173·1	18·86	18·94	19·15	19·29	73·38
$(C_4H_9{}^i)$	171·6	18·89	18·97	19·19	19·33	73·11
$(C_4H_9{}^s)$	169·0	18·69	18·77	18·97	19·11	73·78
$(C_5H_{11}{}^n)$	212·8	23·50	23·60	23·87	24·04	94·03
$(C_5H_{11}{}^i)$ *	210·4	23·45	23·55	23·81	23·99	93·87
$(C_5H_{11}{}^i)$ †	210·9	23·53	23·63	23·89	24·07	93·78
$(CHMePr^n)$	207·6	23·25	23·35	23·65	23·78	94·40
$(CHEt_2)$	206·4	23·17	23·28	23·52	23·69	94·52
$(C_6H_{13}{}^n)$	252·9	28·08	28·21	28·51	28·72	114·67
$(C_7H_{15}{}^n)$	293·6	32·75	32·90	33·26	33·51	135·32
$(C_8H_{17}{}^n)$	333·5	37·32	37·49	37·89	38·17	156·00
$(C_9H_{19}{}^n)$	372·9	41·99	42·17	42·64	42·90	176·37
$(C_{10}H_{21}{}^n)$	412·1	46·61	46·82	47·34	47·70	197·04
$(C_{11}H_{23}{}^n)$	452·8	51·25	51·47	52·03	52·43	217·64
$(C_{12}H_{25}{}^n)$	492·2	55·78	56·03	56·63	57·07	238·32
$(C_{13}H_{27}{}^n)$	532·7	60·47	60·73	61·40	61·86	258·90
$(C_{14}H_{29}{}^n)$	573·6	65·12	65·42	66·12	66·64	279·63
$(C_{15}H_{31}{}^n)$	613·5	69·68	69·99	70·75	71·32	300·30
$(C_{16}H_{33}{}^n)$	653·5	74·25	74·59	75·38	75·96	320·99

* From di*iso*amyl prepared from *iso*amyl bromide (from Sharples synthetic *iso*amyl alcohol) and sodium.

† From di*iso*amyl prepared from *iso*amyl bromide (from Bisol fermentation *iso*amyl alcohol) and sodium.

The bond constants for the keto-group, (C=O), in aliphatic ketones RR′CO (Part XI, *J.*, 1948, 611) were deduced from the relation

$$(C{=}O) = E - \{(R) + (R') + 2(C{-}C)\}$$

where E is the observed parachor, molecular refractivity, or molecular-refraction coefficient. The results are collected in Table 12 : the constants for the methyl ketones are slightly higher than those for the other ketones.

TABLE 12. *Values for* (C=O) *from aliphatic ketones,* RR′CO.

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
Methyl ketones						
Me_2CO	46·4	3·48	3·51	3·56	3·60	29·88
MeEtCO	44·3	3·39	3·43	3·45	3·51	29·70
$MePr^nCO$	42·8	3·33	3·34	3·38	3·42	29·50
$MeBu^nCO$	42·5	3·48	3·51	3·56	3·59	29·49
$MeBu^iCO$	43·0	3·56	3·59	3·63	3·66	29·25
$MeAm^nCO$	44·4	3·55	3·59	3·62	3·67	29·38
n-$C_6H_{13}{\cdot}COMe$	40·9	3·46	3·49	3·54	3·55	29·38
n-$C_7H_{15}{\cdot}COMe$	38·9	3·43	3·45	3·49	3·53	29·37
n-$C_9H_{19}{\cdot}COMe$	—	3·44	3·46	3·50	3·58	29·57
Mean C=O (methyl ketones)	42·6	3·46	3·49	3·53	3·57	29·50
Dialkyl ketones						
Et_2CO	42·2	3·30	3·32	3·36	3·40	29·61
$EtPr^nCO$	42·1	3·37	3·40	3·43	3·56	29·47
$Pr^n{}_2CO$	39·9	3·27	3·27	3·30	3·36	29·28
$EtBu^nCO$	40·6	3·29	3·31	3·35	3·37	29·47
$EtAm^nCO$	40·0	3·23	3·25	3·28	3·30	29·43
n-$C_6H_{13}{\cdot}COEt$	40·5	3·28	3·29	3·35	3·37	29·54
n-$C_7H_{15}{\cdot}COEt$	40·3	3·29	3·31	3·34	3·38	29·37
$Bu^n{}_2CO$	39·2	3·27	3·29	3·32	3·34	29·42
$Bu^i{}_2CO$	39·8	3·40	3·43	3·47	3·48	28·90
$Am^n{}_2CO$	38·2	3·32	3·33	3·36	3·38	29·36
Mean (C=O)	40·3	3·30	3·32	3·36	3·39	29·39

The bond constants (C–O) for aliphatic ethers (Part XII, *J.*, 1948, 617) were readily computed from the expression :

$$2(\text{C–O}) = \text{RR'O} - (\text{R}) - (\text{R'})$$

those in aliphatic acetals (Part XII, *loc. cit.*) were obtained from the ethers derived from $CH_2(OR)_2$ and $CH_3{\cdot}CH(OR)_2$ by obvious methods. The results are given in Tables 13 and 14, respectively.

TABLE 13. *Values of* (C–O) *from aliphatic ethers*, RR'O.

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
Et_2O	12·7	1·58	1·60	1·62	1·64	17·84
$Pr^n{}_2O$	11·9	1·50	1·52	1·54	1·56	17·73
$Pr^i{}_2O$	13·0	1·52	1·53	1·53	1·55	17·42
$Bu^n{}_2O$	12·1	1·49	1·51	1·52	1·54	17·72
$Am^n{}_2O$	12·4	1·47	1·48	1·49	1·51	17·72
$Am^i{}_2O$ *	12·5	1·57	1·59	1·60	1·62	17·10
$Am^i{}_2O$ †	12·2	1·50	1·51	1·52	1·54	17·64
$(n\text{-}C_6H_{13})_2O$	12·1	1·53	1·53	1·55	1·57	17·67
$(n\text{-}C_7H_{15})_2O$	11·8	1·50	1·50	1·52	1·54	17·70
$(n\text{-}C_8H_{17})_2O$	12·1	1·56	1·56	1·58	1·61	17·67
$MeBu^nO$	12·2	1·53	1·54	1·55	1·58	18·00
$EtBu^nO$	12·1	1·55	1·57	1·58	1·60	17·76
$MeAm^nO$	12·3	1·51	1·52	1·53	1·56	18·01
$EtAm^nO$	12·2	1·54	1·55	1·56	1·59	17·76
$n\text{-}C_6H_{13}{\cdot}OMe$	12·0	1·51	1·53	1·54	1·56	17·99
$n\text{-}C_6H_{13}{\cdot}OEt$	11·8	1·54	1·55	1·57	1·60	17·73
$(CH_2Cl{\cdot}CH_2)_2O$	13·1	1·54	1·55	1·57	1·58	17·56
Mean (C–O) $_{\text{ethers}}$	12·4	1·53	1·54	1·55	1·57	17·71
$(CH_2{\cdot}CH_2{\cdot}OEt)_2O$	11·9	1·52	1·53	1·55	1·56	17·98
$(MeO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2)_2O$	12·3	1·51	1·52	1·54	1·55	18·17

* From Bisol fermentation *iso*amyl alcohol. † From Sharples synthetic *iso*amyl alcohol.

TABLE 14. *Values of* (C–O) *from aliphatic acetals*, $CH_2(OR)_2$ *and* $CH_3{\cdot}CH(OR)_2$.

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
$CH_2(OMe)_2$	12·0	1·45	1·46	1·47	1·49	17·96
$CH_2(OEt)_2$	11·7	1·46	1·47	1·48	1·50	17·66
$CH_2(OPr^n)_2$	11·5	1·45	1·45	1·46	1·48	17·65
$CH_2(OPr^i)_2$	11·8	1·44	1·45	1·45	1·47	17·56
$CH_2(OBu^n)_2$	11·4	1·46	1·47	1·47	1·49	17·70
$CH_2(OBu^i)_2$	11·3	1·46	1·46	1·47	1·49	17·62
$CH_2(OAm^n)_2$	11·3	1·45	1·46	1·46	1·48	17·73
$CH_2(O{\cdot}C_6H_{13}{}^n)_2$	11·5	1·44	1·45	1·46	1·47	17·72
$CH_3{\cdot}CH(OMe)_2$	11·5	1·42	1·44	1·44	1·46	17·83
$CH_3{\cdot}CH(OEt)_2$	11·1	1·46	1·47	1·48	1·50	17·53
$CH_3{\cdot}CH(OPr^n)_2$	11·0	1·44	1·44	1·45	1·47	17·55
$CH_3{\cdot}CH(OBu^n)_2$	10·8	1·45	1·46	1·46	1·48	17·58
$CH_3{\cdot}CH(OBu^i)_2$	10·7	1·45	1·46	1·47	1·48	17·46
Mean (C–O)$_{\text{acetals}}$	11·3	1·45	1·46	1·46	1·48	17·66

The preliminary values for (C–O) in trialkyl orthoformates $HC(OR)_3$ (Part XXIII, *J.*, 1948, 1835) are collected in Table 15 : these do not differ appreciably from (C–O) from acetals.

TABLE 15. *Values of* (C–O) *from trialkyl orthoformates*, $HC(OR)_3$.

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
$HC(OEt)_3$	11·3	1·43	1·45	1·45	1·47	17·54
$HC(OPr^n)_3$	10·9	1·44	1·44	1·45	1·47	17·57
$HC(OBu^n)_3$	10·5	1·45	1·45	1·46	1·47	17·58
Mean (C–O)$_{\text{orthoformates}}$	10·9	1·44	1·45	1·45	1·47	17·56

An independent determination of (C–O)$_{\text{ethers}}$ is obtained by the comparison of the experimental figures for β-alkoxypropionitriles $RO{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (this paper) and those for nitriles $R{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (Part XVII, *loc. cit.*). The results are given in Table 16 : these are in reasonable agreement with those deduced from dialkyl ethers (Table 13).

The large volume of experimental results for aliphatic carboxylic esters (Part XIII, *J.*, 1948, 624), and dialkyl carbonates (Part XXIII, *J.*, 1948, 1839) have been analysed as follows. The (C–O) constants in dialkyl carbonates may be evaluated directly by comparison with the appropriate aliphatic carboxylic esters [no assumption is necessary as to the character of the bond between carbon and oxygen only, $\mathrm{C}\overset{?}{\sim}\mathrm{O}$, although for dialkyl carbonates this has been shown to be (C=O)—Part XXIII, *J.*, 1948, 1840, and also Table 10 of the present paper]:

TABLE 16. *Values of* (C–O) *from alkoxypropionitriles,* RO·CH$_2$·CH$_2$·CN, *and nitriles,* R·CH$_2$·CH$_2$·CN.

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
MeO·CH$_2$·CH$_2$·CN	13·2	1·48	1·49	1·50	1·54	18·32
EtO·CH$_2$·CH$_2$·CN	12·1	1·52	1·54	1·54	1·58	18·14
Pr^{n}O·CH$_2$·CH$_2$·CN	12·2	1·52	1·53	1·55	1·58	18·04
Bu^{n}O·CH$_2$·CH$_2$·CN	11·9	1·53	1·53	1·54	1·58	18·01
Am^{n}O·CH$_2$·CH$_2$·CN	12·2	1·53	1·53	1·54	1·58	18·07
n-C$_6$H$_{13}$O·CH$_2$·CH$_2$·CN	12·5	1·52	1·52	1·53	1·57	18·00
Mean (C–O)	12·4	1·52	1·53	1·53	1·57	18·10

$$\mathrm{RO{\cdot}CO{\cdot}OR' - R{\cdot}CO{\cdot}OR' = (R) + (R') + 4(C{-}O) + (C\overset{?}{\sim}O)}$$
$$\mathrm{- [(R) + (R') + 2(C{-}O) + (C\overset{?}{\sim}O) + (C{-}C)]}$$

or
$$\mathrm{2(C{-}O) = RO{\cdot}CO{\cdot}OR' - R{\cdot}CO{\cdot}OR' + (C{-}C)}$$

The results of these calculations, the experimental figures for R·CO·OR′ of Part XIII (*loc. cit.*) being used, are presented in Table 17 : for some unsymmetrical dialkyl carbonates, the experimental data for two isomeric esters were employed in the computations. The mean bond refractions for the C–O link suggest that it is of the acetal type.

TABLE 17. *Values of* (C–O) *from dialkyl carbonates,* RO·CO·OR′, *and aliphatic carboxylic esters,* R·CO·OR′.

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
MeO·CO·OMe	11·3	1·38	1·39	1·39	1·40	17·63
EtO·CO·OEt	12·0	1·41	1·42	1·42	1·43	17·53
Pr^{n}O·CO·OPr^n	11·7	1·39	1·40	1·40	1·42	17·71
Bu^{n}O·CO·OB^n	11·2	1·39	1·39	1·40	1·40	17·70
EtO·CO·OPr^n	12·2	1·43	1·43	1·46	1·46	17·61
	12·3	1·40	1·41	1·42	1·43	17·66
EtO·CO·OBu^n	11·7	1·40	1·41	1·42	1·43	17·63
	11·9	1·40	1·40	1·41	1·42	17·67
EtO·CO·OAm^n	11·3	1·42	1·44	1·45	1·46	17·73
EtO·CO·OC$_6$H$_{13}$^{n}	11·8	1·46	1·47	1·47	1·48	17·75
Pr^{n}O·CO·OBu^n	11·2	1·40	1·40	1·42	1·42	17·74
	11·3	1·41	1·41	1·42	1·43	17·72
Mean (C–O)	11·6	1·41	1·41	1·42	1·43	17·67
(C–O)$_{\text{acetals}}$	11·3	1·45	1·46	1·46	1·48	17·66
(C–O)$_{\text{ethers}}$	12·4	1·53	1·54	1·55	1·57	17·71

The constants for *both* the C–O and the $\mathrm{C}\overset{?}{\sim}\mathrm{O}$ link in aliphatic carboxylic esters may be deduced from the experimental data for these esters and those for the dialkyl carbonates. For dialkyl carbonates

$$\mathrm{RO{\cdot}CO{\cdot}OR' = (R) + (R') + (C\overset{?}{\sim}O) + 4(C{-}O)}$$

or
$$\mathrm{(C\overset{?}{\sim}O) + 4(C{-}O) = RO{\cdot}CO{\cdot}OR' - [(R) + (R')]} \quad . \quad . \quad . \quad . \quad (1)$$

for aliphatic monocarboxylic esters

$$\mathrm{R{\cdot}CO{\cdot}OR' = (R) + (R') + (C\overset{?}{\sim}O) + (2C{-}O) + (C{-}C)}$$

or
$$\mathrm{(C\overset{?}{\sim}O) + 2(C{-}O) = R{\cdot}CO{\cdot}OR' - [(R) + (R') + (C{-}C)]} \quad . \quad . \quad . \quad . \quad (2)$$

and for aliphatic dicarboxylic esters

$$\mathrm{RO{\cdot}OC{\cdot}[CH_2]_{\mathit{n}}{\cdot}CO{\cdot}OR} = 2(\mathrm{R}) + n(\mathrm{CH_2}) + 2(\mathrm{C}\overset{?}{\sim}\mathrm{O}) + 4(\mathrm{C{-}O}) + 2(\mathrm{C{-}C})$$

or $$2(\mathrm{C}\overset{?}{\sim}\mathrm{O}) + 4(\mathrm{C{-}O}) = \mathrm{RO{\cdot}OC{\cdot}[CH_2]_{\mathit{n}}{\cdot}CO{\cdot}OR} - [2(\mathrm{R}) + n(\mathrm{CH_2}) + 2(\mathrm{C{-}C})] \qquad (2')$$

The simultaneous equations (1) and (2) enable $(\mathrm{C}\overset{?}{\sim}\mathrm{O})$ and (C–O) to be calculated.

The mean values deduced from all the data for carboxylic esters (excluding formates, acetates, oxalates, and malonates) in Part XIII (62 esters) and for all the dialkyl carbonates (Part XXIII and present paper—12 esters), together with the values for the two bond constants, are tabulated below.

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
Mean $(\mathrm{C}\overset{?}{\sim}\mathrm{O})$ + 4(C–O)	86·16	9·008	9·051	9·116	9·198	99·30
Mean $(\mathrm{C}\overset{?}{\sim}\mathrm{O})$ + 2(C–O)	63·51	6·162	6·189	6·248	6·308	64·13
Mean (C–O)	11·3	1·42	1·43	1·43	1·45	17·56
Mean $(\mathrm{C}\overset{?}{\sim}\mathrm{O})$	40·9	3·32	3·33	3·38	3·42	29·01
$(\mathrm{C{-}O})_{\mathrm{acetals}}$	11·3	1·45	1·46	1·46	1·48	17·65
$(\mathrm{C{-}O})_{\mathrm{ethers}}$	12·4	1·53	1·54	1·55	1·57	17·71
$(\mathrm{C{=}O})_{\mathrm{ketones}}$	40·3	3·30	3·32	3·36	3·39	29·39

These results support the view that in the $\mathrm{CO_2R}$ group of aliphatic carboxylic esters, the bond constants are $(\mathrm{C{-}O})_{\mathrm{acetals}}$ and $(\mathrm{C{=}O})_{\mathrm{ketones}}$.

The bond constants (C–Cl), (C–Br), and (C–I) were computed from the data given in Part VIII (*J.*, 1943, 636; see also Part XIV, *J.*, 1948, 645) from alkyl halides, polymethylene dihalides, and alkyl monohalogenoacetates. Preliminary figures for (C–F) were obtained from alkyl fluorides (Part XIV, *loc. cit.*). The results are tabulated below.

TABLE 18. *Values for* (C–Cl) *from aliphatic monochloro-compounds.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(M_D^{20})
From alkyl chlorides						
$\mathrm{Pr^nCl}$	58·4	6·51	6·53	6·61	6·68	56·21
$\mathrm{Pr^iCl}$ *	60·3	6·62	6·66	6·73	6·81	55·77
$\mathrm{Bu^nCl}$	57·2	6·44	6·48	6·55	6·63	56·37
$\mathrm{Bu^iCl}$	56·6	6·37	6·41	6·48	6·55	56·62
$\mathrm{Bu^sCl}$ *	60·5	6·70	6·74	6·83	6·89	55·55
$\mathrm{Am^nCl}$	57·4	6·42	6·46	6·51	6·57	56·48
$\mathrm{Am^iCl}$ (from synthetic alcohol)	58·8	6·65	6·69	6·77	6·83	56·27
$\mathrm{Am^iCl}$ (from fermentation alcohol) ...	57·9	6·52	6·56	6·63	6·69	56·43
$\mathrm{CHMePr^nCl}$ *	60·8	6·72	6·76	6·80	6·91	55·68
$\mathrm{CHEt_2Cl}$ *	63·0	6·85	6·88	6·98	7·04	55·60
n-$\mathrm{C_6H_{13}Cl}$	57·6	6·50	6·53	6·62	6·69	56·60
n-$\mathrm{C_7H_{15}Cl}$	57·1	6·41	6·43	6·54	6·57	56·65
n-$\mathrm{C_8H_{17}Cl}$	56·7	6·44	6·47	6·55	6·61	56·70
n-$\mathrm{C_9H_{19}Cl}$....................................	57·5	6·52	6·54	6·63	6·70	56·94
n-$\mathrm{C_{10}H_{21}Cl}$	59·9	6·50	6·54	6·60	6·66	56·99
n-$\mathrm{C_{11}H_{23}Cl}$	59·1	6·43	6·49	6·55	6·61	57·04
n-$\mathrm{C_{12}H_{25}Cl}$	57·5	6·49	6·52	6·59	6·67	57·10
From polymethylene dihalides.						
$\mathrm{Cl{\cdot}[CH_2]_2{\cdot}Cl}$	56·5	6·48	6·50	6·58	6·64	57·34
$\mathrm{Cl{\cdot}[CH_2]_3{\cdot}Cl}$	56·8	6·40	6·43	6·51	6·56	57·40
From alkyl monochloroacetates and dialkyl succinates.						
$\mathrm{CH_2Cl{\cdot}CO_2Me}$	55·9	6·46	6·49	6·57	6·62	57·03
$\mathrm{CH_2Cl{\cdot}CO_2Et}$	56·5	6·52	6·56	6·65	6·69	56·99
$\mathrm{CH_2Cl{\cdot}CO_2Pr^n}$	56·4	6·51	6·54	6·61	6·64	57·00
$\mathrm{CH_2Cl{\cdot}CO_2Bu^n}$	56·4	6·46	6·50	6·56	6·62	57·11
Mean (excluding *)	57·4	6·48	6·51	6·58	6·64	56·80

TABLE 19. *Values for* (C–Br) *from aliphatic monobromo-compounds.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
From alkyl bromides						
EtBr	72·1	9·31	9·38	9·53	9·67	123·18
Pr^{n}Br	70·6	9·31	9·37	9·52	9·66	123·69
Pr^{i}Br *	73·5	9·56	9·63	9·79	9·93	122·86
Bu^{n}Br	70·7	9·33	9·39	9·55	9·68	123·93
Bu^{i}Br	72·5	9·48	9·55	9·70	9·82	123·50
Bu^{s}Br *	74·5	9·73	9·80	9·97	10·12	123·08
Am^{n}Br	70·3	9·31	9·39	9·52	9·66	124·27
Am^{i}Br (from fermentation alcohol)	69·7	9·27	9·34	9·50	9·63	124·08
Am^{i}Br (from synthetic alcohol)	72·2	9·50	9·57	9·72	9·92	123·96
CHMePr^{n}Br *	73·3	9·55	9·62	9·74	9·92	123·41
$CHEt_2Br$ *	75·3	9·73	9·79	9·97	10·11	123·49
n-$C_6H_{13}Br$	70·4	9·34	9·39	9·56	9·70	124·33
n-$C_7H_{15}Br$	69·9	9·30	9·36	9·51	9·64	124·48
n-$C_8H_{17}Br$	70·3	9·35	9·41	9·57	9·70	124·57
n-$C_9H_{19}Br$	71·2	9·25	9·32	9·45	9·64	124·91
n-$C_{10}H_{21}Br$	72·5	9·45	9·52	9·66	9·80	124·86
n-$C_{11}H_{23}Br$	70·9	9·22	9·30	9·45	9·58	125·06
n-$C_{12}H_{25}Br$	74·1	9·43	9·49	9·65	9·77	125·10
n-$C_{14}H_{29}Br$	71·3	9·23	9·29	9·44	9·56	123·35
n-$C_{16}H_{33}Br$	72·2	9·31	9·38	9·53	9·66	125·45
From polymethylene dibromides						
$Br·[CH_2]_2·Br$	69·8	9·42	9·48	9·65	9·78	[130·41]
$Br·[CH_2]_3·Br$	70·4	9·18	9·24	9·40	9·51	[129·34]
From alkyl monobromoacetates and dialkyl succinates						
$CH_2Br·CO_2Pr^n$	69·3	9·32	9·39	9·54	9·65	125·14
$CH_2Br·CO_2Bu^n$	68·3	9·16	9·23	9·37	9·50	125·30
Mean (excluding *)	70·9	9·32	9·39	9·54	9·68	124·51

TABLE 20. *Values for* (C–I) *from aliphatic monoiodo-compounds.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
From alkyl iodides						
MeI *	93·6	14·11	14·25	14·58	14·88	205·70
EtI	93·3	14·45	14·55	14·89	15·21	203·82
Pr^{n}I	92·9	14·48	14·62	14·97	15·29	203·10
Pr^{i}I *	94·3	14·84	15·00	15·38	15·67	202·40
Bu^{n}I	91·5	14·41	14·55	14·90	15·21	202·63
Bu^{i}I	93·1	14·44	14·59 †	14·93	15·24	202·18
Bu^{s}I *	97·6	14·02	14·08	14·57	14·91	202·10
Am^{n}I	92·3	14·49	14·63	14·97	15·28	202·15
Am^{i}I (from fermentation alcohol)	91·8	14·52	14·66	15·01	15·31	201·86
Am^{i}I (from synthetic alcohol)	93·9	14·51	14·65	15·00	15·31	202·01
CHMePr^{n}I *	94·2	13·83	13·98	14·32	14·69	201·92
$CHEt_2I$ *	95·7	14·01	14·16	14·56	14·91	202·13
n-$C_6H_{13}I$	92·9	14·53	14·66	15·02	15·32	201·88
n-$C_7H_{15}I$	93·0	14·54	14·67	15·02	15·33	201·52
n-$C_8H_{17}I$	92·2	14·49	14·62	14·99	15·30	201·55
$I·[CH_2]_3·I$	90·7	14·30	14·43	14·79	—	[218·54]
From alkyl monoiodoacetates and dialkyl succinates						
$CH_2I·CO_2Pr^n$	93·3	14·41	14·54	14·90	15·19	203·82
$CH_2I·CO_2Bu^n$	92·7	14·59	14·74	15·09	15·39	202·97
Mean (excluding *)	92·4	14·47	14·61	14·96	15·28	202·46

† R_D for Bu^{i}I in Part VIII, *J.*, 1943, 637, should be 33·56, not 33·66.

TABLE 21. *Values for* (C–F) *from alkyl fluorides.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
Am^{n}F	28·8	1·38	1·39	1·36	1·36	28·32
n-$C_6H_{13}F$	29·1	1·48	1·47	1·47	1·48	28·15
n-$C_7H_{15}F$	27·1	1·37	1·37	1·35	1·36	28·24
n-$C_8H_{17}F$	27·8	1·57	1·58	1·58	1·58	28·37
Mean	28·2	1·45	1·44	1·44	1·45	28·27

The bond constants for the C=C bond were derived from the experimental figures for vinylacetates and for undecylenates, unsaturated aliphatic hydrocarbons, allylmalonates, and allyl esters of aliphatic acids (Part XVI, *J.*, 1948, 659). The method of calculation is essentially an application of that employed in Part XVI (*loc. cit.*) :

$$╒ = CR^1R^2{:}CR^3R^4 + 2H - CHR^1R^2{\cdot}CHR^3R^4\,;$$

For bond constants this may be written :

$$(C{=}C) = CR^1R^2{:}CR^3R^4 + 2(C{-}H) + (C{-}C) - CHR^1R^2{\cdot}CHR^3R^4$$

The results are collected in Table 22.

TABLE 22. *Values for* (C=C) *from aliphatic ethylenic compounds.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
Vinylacetates, $CH_2{:}CH{\cdot}CH_2{\cdot}CO_2R$						
R = H	28·2	4·11	4·16	4·27	4·37	20·03
R = Me	29·0	4·11	4·16	4·27	4·35	19·97
R = Et	28·3	4·06	4·12	4·23	4·32	19·93
R = Pr^n	28·4	4·10	4·16	4·26	4·36	19·76
R = Bu^n	28·1	4·12	4·18	4·30	4·38	19·73
R = Am^n	27·6	4·09	4·15	4·26	4·34	19·66
Undecylenates, $CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CO_2R$						
R = Me	29·6	4·19	4·24	4·36	4·44	19·70
R = Et	29·1	4·11	4·14	4·26	4·35	19·79
R = Pr^n	29·2	4·13	4·18	4·30	4·40	19·79
R = Bu^n	28·3	4·13	4·18	4·28	4·40	19·98
Unsaturated aliphatic hydrocarbons						
C_5H_{10}	26·9	4·16	4·20	4·33	4·45	19·23
C_6H_{12}	29·7	4·11	4·16	4·29	4·39	19·23
C_8H_{16}	28·3	4·17	4·24	4·35	4·46	19·08
$C_{10}H_{20}$	28·8	4·08	4·11	4·24	4·37	18·99
$C_{12}H_{24}$	28·8	4·12	4·16	4·30	4·40	19·12
$C_{14}H_{28}$	28·0	4·06	4·10	4·23	4·34	19·20
$C_{16}H_{32}$	29·0	4·13	4·17	4·32	4·40	19·19
Diallyl	28·9	4·16	4·20	4·32	4·41	18·94
Allylmalonates, $C_3H_5{\cdot}CH(CO_2R)_2$						
R = Me	28·4	4·12	4·18	4·29	4·38	20·07
R = Et	27·7	4·07	4·11	4·22	4·32	19·90
R = Pr^n	26·5	4·07	4·12	4·24	4·33	19·79
R = Bu^n	28·1	4·13	4·18	4·28	4·40	19·75
Allyl esters of aliphatic acids						
$CH_3{\cdot}CO_2{\cdot}C_3H_5$	29·2	4·03	4·09	4·20	4·28	19·75
$CH_3{\cdot}CH_2{\cdot}CO_2{\cdot}C_3H_5$	29·0	4·13	4·18	4·30	4·39	19·76
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_3H_5$	27·6	4·10	4·16	4·27	4·38	19·86
$(CH_2{\cdot}CO_2{\cdot}C_3H_5)_2$	29·3	4·20	4·25	4·36	4·44	20·34
Mean (C=C)	28·5	4·12	4·17	4·28	4·38	19·39

The experimental data for but-3-yne-1-carboxyates and dec-9-yne-1-carboxylates (Part XVII, *J.*, 1948, 674) were used to determine the constants of the terminal C≡C bond. The relation

$$(C{\equiv}C)_{\text{terminal}} = HC{:}CR + 4(C{-}H) + (C{-}C) - CH_3{\cdot}CH_2R$$

was used for calculating the constants given in Table 23.

TABLE 23. *Values for* (C≡C) *from acetylenic esters.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
But-3-yne-1-carboxylates, $CH{\vdots}C{\cdot}[CH_2]_2{\cdot}CO_2R$						
R = Me	53·6	5·83	5·88	5·98	6·07	25·31
R = Et	53·1	5·84	5·89	5·98	6·10	25·18
R = Pr^n	53·0	5·87	5·92	6·01	6·11	24·87
R = Bu^n	52·5	5·91	5·95	6·05	6·15	24·77
Dec-9-yne-1-carboxylates, $CH{\vdots}C{\cdot}[CH_2]_8{\cdot}CO_2R$						
R = Me	55·1	5·78	5·83	5·95	6·03	25·10
R = Et	53·6	5·73	5·77	5·87	5·97	25·05
R = Pr^n	53·4	5·76	5·81	5·93	6·02	25·03
Mean $(C{\equiv}C)_{\text{terminal}}$	53·5	5·82	5·87	5·97	6·07	25·04

The literature data for d_4^{20} and n_D^{20} (Henne and Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 484; Hennion and Banigan, *ibid.*, 1946, **68**, 1380; Campbell and O'Connor, *ibid.*, 1939, **61**, 2898; Campbell and Eby, *ibid.*, 1941, **63**, 2684) for acetylenic hydrocarbons were employed in the compilation of Tables 24 and 25. It will be noted that the mean bond refraction (D line) for (C≡C) (non-terminal) is appreciably higher than for (C≡C) (terminal).

TABLE 24. *Values for* (C≡C) *(terminal) from acetylenic hydrocarbons (literature data).*

	(R_D)	(Mn_D^{20})		(R_D)	(Mn_D^{20})
Pent-1-yne	5·84	23·71	Hepta-1 : 6-diyne	5·85	24·26
Hex-1-yne	5·84	23·76	Nona-1 : 8-diyne	5·84	24·30
Hept-1-yne	5·84	23·78	Mean $(C{\equiv}C)_{terminal}$	5·85	24·02
Oct-1-yne	5·89	23·75			

TABLE 25. *Values for* (C≡C) *(non-terminal) from acetylenic hydrocarbons (literature data).*

	(R_D)	(Mn_D^{20})		(R_D)	(Mn_D^{20})
Pent-2-yne	6·16	24·98	Non-3-yne	6·24	24·67
Hex-3-yne	6·27	24·79	Dec-5-yne	6·25	24·56
Oct-2-yne	6·14	25·06	Undec-5-yne	6·16	24·49
Oct-3-yne	6·29	24·75	Nona-2 : 7-diyne	6·36	25·40
Oct-4-yne	6·34	24·73	Mean $(C{\equiv}C)_{non\text{-}terminal}$	6·24	24·83

The constants for the C≡N bond have been deduced from the experimental data for aliphatic cyanides (Part XVII, *J.*, 1948, 676 : *n*-heptyl and *n*-octyl cyanides, this paper) and are presented in Table 26.

TABLE 26. *Values for* (C≡N) *from aliphatic cyanides.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
MeCN	64·5	4·76	4·79	4·84	4·88	30·71
EtCN	63·8	4·78	4·81	4·86	4·89	30·16
Pr^nCN	62·8	4·81	4·82	4·88	4·91	29·98
Bu^nCN	61·3	4·79	4·81	4·86	4·89	29·88
Am^nCN	60·9	4·80	4·82	4·87	4·90	29·80
Am^iCN (ex Sharples synthetic alcohol)	61·8	4·85	4·88	4·93	4·97	29·87
n-$C_6H_{13}CN$	59·4	4·78	4·81	4·86	4·90	29·65
n-$C_7H_{15}CN$	58·1	4·75	4·77	4·82	4·84	29·62
n-$C_8H_{17}CN$	58·0	4·88	4·89	4·95	4·98	29·39
Mean (C≡N)	61·4	4·80	4·82	4·87	4·91	29·91
$[CH_2]_2(CN)_2$	63·9	4·66	4·68	4·71	4·71	29·99
$CH_2{:}CH{\cdot}CH_2{\cdot}CN$	61·4	4·49	4·50	4·54	4·55	30·29

The constants (C–C) in three-, four-, five-, and six-membered carbon rings were evaluated from the experimental data given in Part XVIII (*J.*, 1948, 1804) and Part XIX (*J.*, 1948, 1809) by appropriate adaptation of the relation :

$$\text{Ring constant} = \underline{CH_2{\cdot}[CH_2]_{n-2}{\cdot}CR^1R^2} + 2H - CH_3{\cdot}[CH_2]_{n-2}{\cdot}CHR^1R^2$$

viz., n(C–C) for a ring of n carbon atoms

$$= \underline{CH_2{\cdot}[CH_2]_{n-2}{\cdot}CR^1R^2} - CH_3{\cdot}[CH_2]_{n-2}{\cdot}CHR^1R^2 + [n-1](C{-}C) + 2(C{-}H)$$

Tables 27—30 contain the results of these calculations.

TABLE 27. *Values for* (C–C) *from three-carbon rings.*

	(P)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
*cyclo*Propanecarboxylic acid	9·0	1·48	1·50	1·52	1·55	11·38
Methyl *cyclo*propyl ketone	8·9	1·52	1·54	1·56	1·59	11·19
Methyl *cyclo*propanecarboxylate	8·8	1·48	1·50	1·52	1·54	11·26
Ethyl *cyclo*propanecarboxylate	8·5	1·47	1·49	1·50	1·53	11·30
n-Propyl *cyclo*propanecarboxylate	8·4	1·49	1·50	1·52	1·55	11·33
n-Butyl *cyclo*propanecarboxylate	8·3	1·49	1·50	1·52	1·55	11·25
n-Amyl *cyclo*propanecarboxylate	8·1	1·45	1·47	1·49	1·51	11·24
Dimethyl *cyclo*propane-1 : 1-dicarboxylate	8·4	1·50	1·50	1·53	1·54	11·37
Diethyl *cyclo*propane-1 : 1-dicarboxylate	8·0	1·48	1·49	1·52	1·53	11·22
Di-*n*-propyl *cyclo*propane-1 : 1-dicarboxylate	7·8	1·44	1·44	1·47	1·49	11·26
Mean (C–C) for three-carbon rings	8·4	1·48	1·49	1·52	1·54	11·28

TABLE 28. *Values for* (C–C) *from four-carbon rings.*

	(P)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
*cyclo*Butanecarboxylic acid	7·1	1·38	1·39	1·40	1·42	11·51
Methyl *cyclo*butanecarboxylate	6·8	1·36	1·38	1·38	1·41	11·45
Ethyl *cyclo*butanecarboxylate	6·9	1·36	1·37	1·38	1·41	11·44
n-Propyl *cyclo*butanecarboxylate	6·8	1·37	1·38	1·39	1·42	11·41
n-Butyl *cyclo*butanecarboxylate	6·9	1·38	1·39	1·40	1·42	11·43
n-Amyl *cyclo*butanecarboxylate	6·8	1·35	1·37	1·37	1·40	11·45
Dimethyl *cyclo*butane-1 : 1-dicarboxylate	6·9	1·37	1·38	1·39	1·41	11·49
Diethyl *cyclo*butane-1 : 1-dicarboxylate	6·7	1·35	1·36	1·37	1·40	11·47
Di-*n*-propyl *cyclo*butane-1 : 1-dicarboxylate	6·7	1·36	1·37	1·39	1·41	11·40
Di-*n*-butyl *cyclo*butane-1 : 1-dicarboxylate	6·6	1·35	1·36	1·37	1·39	11·43
Mean (C–C) for four-carbon rings	6·8	1·36	1·37	1·38	1·41	11·44

TABLE 29. *Values for* (C–C) *from five-carbon rings.*

	(P)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
*cyclo*Pentane	4·5	1·257	1·263	1·285	1·292	12·06
Methyl*cyclo*pentane	5·2	1·28	1·28	1·29	1·32	11·85
*cyclo*Pentene	5·4	1·20	1·21	1·22	1·24	[11·58]
3-Methyl*cyclo*pentene	5·2	1·26	1·26	1·29	1·29	[11·44]
*cyclo*Pentanol	5·3	1·24	1·25	1·26	1·28	12·01
Methyl *cyclo*pentyl ether	5·1	1·25	1·26	1·26	1·29	11·94
Ethyl *cyclo*pentyl ether	5·0	1·25	1·26	1·26	1·28	11·97
*cyclo*Pentyl formate	5·3	1·24	1·25	1·26	1·28	12·01
*cyclo*Pentyl acetate	5·5	1·26	1·27	1·27	1·30	12·02
Mean (C–C) for five-carbon rings	5·2	1·25	1·26	1·26	1·28	11·95
*cyclo*Pentanone	5·7	1·32	1·33	1·33	1·33	12·02
3-Methyl*cyclo*pentanone	5·6	1·31	1·31	1·30	1·35	11·91
*cyclo*Pentyl chloride	5·3	1·28	1·29	1·30	1·32	12·09
*cyclo*Pentyl bromide	5·6	1·30	1·31	1·32	1·34	12·54
*cyclo*Pentyl iodide	5·9	1·32	1·34	1·35	1·37	12·88

TABLE 30. *Values for* (C–C) *from six-carbon rings.*

	(P)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn_D^{20})
*cyclo*Hexane	4·6	1·267	1·273	1·289	1·304	12·27
Methyl*cyclo*hexane	4·4	1·28	1·29	1·30	1·32	12·04
Di*cyclo*hexyl	4·3	1·25	1·25	1·27	1·28	12·34
*cyclo*Hexene	4·7	1·23	1·24	1·25	1·26	12·10
*cyclo*Hexanol	—	1·26	1·27	1·27	1·30	12·33
*cyclo*Hexyl methyl ether	4·6	1·26	1·27	1·27	1·30	12·25
Ethyl *cyclo*hexyl ether	4·4	1·26	1·27	1·27	1·30	12·27
*cyclo*Hexyl formate	4·5	1·25	1·26	1·27	1·29	12·30
*cyclo*Hexyl acetate	4·8	1·27	1·28	1·29	1·32	12·30
Mean (C–C) for six-carbon rings	4·5	1·26	1·27	1·28	1·30	12·24
*cyclo*Hexanone	5·4	1·28	1·29	1·30	1·31	12·33
2-Methyl*cyclo*hexanone	5·1	1·30	1·31	1·32	1·34	12·22
3-Methyl*cyclo*hexanone	4·7	1·27	1·29	1·29	1·32	12·23
4-Methyl*cyclo*hexanone	5·2	1·32	1·33	1·34	1·37	12·21
*cyclo*Hexyl chloride	5·3	1·34	1·35	1·35	1·38	12·37
*cyclo*Hexyl bromide	4·8	1·30	1·31	1·31	1·34	12·81
*cyclo*Hexyl iodide	3·9	1·32	1·34	1·35	1·37	13·60

The constants (O–H) in alcohols are readily derived from the observations upon aliphatic alcohols ROH (Part XX, *J.*, 1948, 1815) and are given in Table 31.

TABLE 31. *Values for* (O–H) *from Aliphatic Alcohols.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
MeOH	22·7	1·66	1·68	1·68	1·70	13·14
EtOH	21·3	1·70	1·71	1·72	1·74	12·70
Pr^{n}OH	19·7	1·68	1·68	1·70	1·71	12·77
Bu^{n}OH	20·6	1·71	1·72	1·72	1·73	12·50
Bu^{i}OH	18·8	1·66	1·66	1·67	1·67	12·59
Am^{n}OH	19·2	1·70	1·70	1·71	1·72	12·53
Am^{n}OH (synthetic)	—	1·66	1·67	1·68	1·68	12·58
n-C_6H_{13}·OH	—	1·64	1·64	1·67	1·66	12·50
n-C_7H_{15}·OH	—	1·60	1·60	1·61	1·62	12·36
n-C_8H_{17}·OH *	—	1·64	1·64	1·67	1·69	12·39
n-C_9H_{19}·OH	—	1·62	1·63	1·64	1·69	12·65
n-$C_{10}H_{21}$·OH	—	1·64	1·64	1·64	1·65	12·59
n-$C_{11}H_{23}$·OH	—	1·62	1·63	1·64	1·65	12·60
CH_2:CH·CH_2·OH	—	1·57	1·57	1·57	1·58	13·15
Mean (O–H)$_{\text{alcohols}}$	20·3	1·65	1·66	1·67	1·68	12·65
MeO·CH_2·CH_2·OH	21·5	1·65	1·66	1·67	1·68	12·65
EtO·CH_2·CH_2·OH	19·7	1·62	1·62	1·63	1·63	13·05
Bu^{n}O·CH_2·CH_2·OH	—	1·59	1·58	1·60	1·59	12·85

* The data for *n*-octyl alcohol (**463**; Part XX, *J.*, 1948, 1818) partially duplicate those for *n*-nonyl alcohol, **464**. The correct figures are n_C 1·42711, n_D 1·42927, n_F 1·43459, $n_{G'}$ 1·43853, Mn^{20}_D 186·12.

In the calculations of the constants for the O–H bond in aliphatic carboxylic acids (Part XX, *loc. cit.*) the relation

$$(\mathrm{O{-}H}) = \mathrm{R{\cdot}CO_2H} - \{(\mathrm{R}) + (\mathrm{C{=}O}) + (\mathrm{C{-}O})_{\mathrm{acetals}}\}$$

was employed; the results are collected in Table 32.

TABLE 32. *Values for* (O–H) *from aliphatic carboxylic acids.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
Me·CO_2H *	20·0	1·74	1·74	1·77	1·77	10·68
Et·CO_2H	20·3	1·78	1·79	1·81	1·82	10·55
Pr^n·CO_2H	20·2	1·82	1·83	1·86	1·86	10·45
Pr^i·CO_2H	20·4	1·77	1·77	1·79	1·80	10·30
Bu^n·CO_2H	19·6	1·82	1·82	1·85	1·84	10·55
Bu^i·CO_2H	19·8	1·80	1·80	1·83	1·83	10·34
Am^n·CO_2H	—	1·81	1·80	1·83	1·83	10·62
n-C_6H_{13}·CO_2H	—	1·80	1·80	1·84	1·84	10·78
n-C_7H_{15}·CO_2H	—	1·81	1·81	1·85	1·84	10·71
Mean (O–H)$_{\text{acids}}$ (excluding *)	20·0	1·80	1·80	1·83	1·83	10·54

The constants (S–S) are readily deduced from the data on dialkyl disulphides (R·S·S·R — R·S·R : Part XXI, *J.*, 1948, 1820), those for (C–S) from dialkyl sulphides, and those for (S–H) from aliphatic thiols, with the aid of the previously determined values for (C–S). The results are in Tables 33—35.

TABLE 33. *Values for* (S–S) *from dialkyl disulphides.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
$(SMe)_2$	50·8	7·95	8·02	8·21	8·39	54·53
$(SEt)_2$	49·6	8·05	8·14	8·30	8·48	54·13
$(SPr^n)_2$	49·6	8·04	8·11	8·30	8·47	53·85
$(SPr^i)_2$	50·1	8·02	8·06	8·28	8·42	53·98
$(SBu^n)_2$	48·4	8·10	8·15	8·35	8·49	53·65
$(SBu^i)_2$	48·0	7·91	7·98	8·14	8·33	53·49
$(SAm^n)_2$	47·6	8·12	8·21	8·41	8·57	53·44
$(SAm^i)_2$	48·3	7·97	8·04	8·23	8·41	53·53
Mean (S–S)	49·0	8·02	8·11	8·28	8·45	53·83

TABLE 34. *Values for* (C–S) *from dialkyl sulphides.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	$(Mn)^{20}_D$
SMe_2	28·3	4·52	4·56	4·64	4·72	32·90
SMeEt	27·7	4·51	4·55	4·61	4·72	32·85
SEt_2	27·5	4·58	4·61	4·71	4·81	32·75
$SMeBu^n$	26·9	4·54	4·58	4·66	4·77	32·93
$SMeBu^i$	27·3	4·56	4·60	4·67	4·76	32·80
SPr^n_2	26·2	4·49	4·58	4·67	4·75	32·84
SPr^i_2 *	27·3	4·68	4·74	4·80	4·90	32·58
$SEtBu^n$	27·0	4·60	4·65	4·73	4·82	32·81
SBu^n_2	26·6	4·55	4·59	4·67	4·76	32·90
SBu^i_2 *	25·6	4·63	4·67	4·81	4·83	32·72
SBu^s_2 *	26·4	4·76	4·80	4·90	4·99	32·32
SAm^n_2	25·7	4·55	4·59	4·67	4·75	32·91
SAm^i_2	26·1	4·64	4·69	4·77	4·85	32·76
$S(n\text{-}C_6H_{13})_2$	25·4	4·62	4·66	4·75	4·83	32·94
$S(n\text{-}C_7H_{15})_2$	25·7	4·61	4·64	4·73	4·79	32·97
$S(n\text{-}C_8H_{17})_2$	25·5	4·56	4·59	4·69	4·76	32·98
Mean (C–S) (excluding *)	26·6	4·57	4·61	4·70	4·78	32·84

TABLE 35. *Values for* (S–H) *from aliphatic thiols.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
EtSH	44·1	4·73	4·76	4·84	4·92	23·82
Pr^nSH	42·6	4·76	4·79	4·87	4·94	23·70
Pr^iSH	43·7	4·54	4·57	4·63	4·88	22·69
Bu^nSH	41·8	4·81	4·84	4·90	4·99	23·87
Bu^iSH	41·6	4·77	4·80	4·86	4·93	23·75
Am^nSH	41·8	4·77	4·79	4·86	4·94	23·88
Am^iSH	42·5	4·76	4·80	4·86	4·93	23·80
$n\text{-}C_6H_{13}\cdot SH$	41·9	4·76	4·80	4·88	4·93	23·85
$n\text{-}C_7H_{15}\cdot SH$	—	4·72	4·74	4·82	4·85	23·66
$n\text{-}C_8H_{17}\cdot SH$	—	4·86	4·89	4·97	5·03	23·82
Mean (S–H) (excluding *)	42·1	4·77	4·80	4·87	4·94	23·79

The most trustworthy values for (C–N) and (N–H) in aliphatic amines are derived from the experimental data for primary and secondary aliphatic amines. Thus for primary amines

$$(C\text{–}N) + 2(N\text{–}H) = RNH_2 - (R)$$

and for secondary amines

$$2(C\text{–}N) + (N\text{–}H) = R_2NH - 2(R)$$

These two simultaneous equations give the values for the individual bond constants (C–N) and (N–H). The final results for primary and secondary aliphatic amines are given in Table 36.

TABLE 36. *Values for* (C–N) *and* (N–H) *from primary and secondary aliphatic amines.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
(C–N) + 2(N–H) *from primary aliphatic amines*						
NH_2Pr^n	46·3	5·11	5·13	5·21	5·28	29·24
$NH_2\cdot Bu^n$	45·5	4·99	5·02	5·09	5·15	29·08
$NH_2\cdot Bu^i$	45·0	4·98	5·01	5·07	5·13	29·07
$NH_2\cdot Am^n$	46·7	5·08	5·12	5·18	5·24	28·99
$NH_2\cdot Am^i$	46·6	5·05	5·09	5·17	5·21	28·97
$n\text{-}C_6H_{13}\cdot NH_2$	46·5	5·06	5·08	5·16	5·23	28·82
$n\text{-}C_7H_{15}\cdot NH_2$	—	5·04	5·06	5·12	5·19	28·81
$n\text{-}C_8H_{17}\cdot NH_2$	—	5·11	5·14	5·22	5·30	28·71
$CH_2{:}CH\cdot CH_2\cdot NH_2$	45·3	5·08	5·11	5·17	5·24	[29·94]
$NH_2\cdot CH_2\cdot CH_2\cdot NH_2$	47·8	5·11	5·13	5·19	5·26	29·57
Mean (C–N) + 2(N–H)	46·2	5·061	5·089	5·158	5·223	29·03

TABLE 36.—(*continued*)

2(C–N) + (N–H) *from secondary aliphatic amines, etc.*						
NHEt$_2$	33·7	4·95	5·00	5·07	5·19	36·82
NHPr$^n_2$	32·3	4·86	4·87	4·95	5·05	36·53
NHPr$^i_2$	33·2	4·96	4·98	5·04	5·17	35·87
NHBu$^n_2$	32·5	4·89	4·94	5·00	5·10	36·46
NHBu$^i_2$	32·4	4·85	4·89	4·96	5·04	35·88
NHAm$^n_2$	33·0	4·74	4·79	4·84	4·93	36·42
NHAm$^i_2$	31·7	4·71	4·76	4·83	4·90	36·30
NH(C$_6$H$_{11}$)$_2$	34·7	4·95	4·99	5·06	5·14	35·97
NHMe·CO$_2$Et	31·9	4·73	4·79	4·85	4·93	[38·30]
NHEt·CO$_2$Et	31·3	4·89	4·93	4·99	5·08	[38·05]
Mean 2(C–N) + (N–H)	32·67	4·853	4·894	4·959	5·053	36·28
(C–N)	6·4	1·548	1·566	1·587	1·628	14·51
(N–H)	19·9	1·757	1·762	1·786	1·798	7·26

The constants for the C–N link have also been computed from the data on tertiary aliphatic amines (Part XXII, *J.*, 1948, 1827) and on β-dialkylaminopropionitriles {3(C–N) = R$_2$N·CH$_2$·CH$_2$·CN − 2(R) − CH$_3$·CH$_2$·CN + (C–H)} and are tabulated in Tables 37 and 38, respectively. The results obtained directly from the tertiary amino-compounds are (apart from the parachors, which seem to lead to slightly lower constants) in satisfactory agreement with those given in Table 36.

TABLE 37. *Values for* (C–N) *from tertiary aliphatic amines.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
NEt$_3$	5·6	1·59	1·61	1·64	1·69	14·97
NPr$^n_3$	4·4	1·56	1·57	1·60	1·66	14·86
NBu$^n_3$	4·2	1·54	1·56	1·59	1·63	14·95
NAm$^n_3$	4·5	1·48	1·50	1·52	1·56	14·88
NAm$^i_3$	3·8	1·46	1·48	1·51	1·54	14·81
Mean (C–N)	4·5	1·53	1·54	1·57	1·62	14·89

TABLE 38. *Values for* (C–N) *from* β-*dialkylaminopropionitriles.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
NEt$_2$·CH$_2$·CH$_2$·CN	4·1	1·54	1·56	1·59	1·63	15·07
NPr$^n_2$·CH$_2$·CH$_2$·CN	3·2	1·51	1·52	1·55	1·59	14·92
NBu$^n_2$·CH$_2$·CH$_2$·CN	2·8	1·53	1·55	1·57	1·61	14·96
NAm$^n_2$·CH$_2$·CH$_2$·CN	2·1	1·51	1·53	1·55	1·59	14·89
Mean (C–N)	3·1	1·52	1·54	1·57	1·61	14·96

We have also obtained values of the (N–H) constants from monoalkylaminopropionitriles, R·NH·CH$_2$·CH$_2$·CN, and alkyl cyanides, R·CH$_2$·CH$_2$·CN. The constants for the C–N bond employed in the calculations were those determined from the β-dialkylaminopropionitriles (Table 38); these are slightly lower than those deduced from primary and secondary aliphatic amines (Table 36) and since two C–N bonds are involved, the differences will be expected to be larger. The results are given in Table 39.

TABLE 39. *Values for* (N–H) *from* β-*alkylaminopropionitriles.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn^{20}_D)
NHEt·CH$_2$·CH$_2$·CN	25·5	1·89	1·89	1·91	1·91	7·44
NHPr^n·CH$_2$·CH$_2$·CN	24·3	1·90	1·90	1·91	1·92	7·24
NHBu^n·CH$_2$·CH$_2$·CN	23·8	1·85	1·84	1·85	1·84	7·20
NHAm^n·CH$_2$·CH$_2$·CN	20·9	1·85	1·84	1·85	1·86	7·03
n-C$_6$H$_{13}$·NH·CH$_2$·CH$_2$·CN	21·5	1·83	1·84	1·85	1·84	7·04
Mean (N–H)	23·2	1·86	1·86	1·87	1·87	7·19

The (N–O) constants were deduced from the data on alkyl nitrates, R·CH$_2$·O·NO$_2$, and aliphatic nitro-compounds R·CH$_2$·NO$_2$ (Part XXIII, *J.*, 1948, 1833): the constants (C–O)$_{\text{acetals}}$ (Table 14) and (C–N) (Table 36) were used in the calculations. The resulting (N–O) constants and (C–O)$_{\text{acetals}}$ were used in the evaluation of the (N=O) constants from alkyl nitrites R·O·N:O (Part XXIII, *loc. cit.*). Tables 40 and 41 give the various values obtained.

TABLE 40. *Values for* (N–O) *from alkyl nitrates and nitroparaffins.*

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
$EtNO_3$	13·4	2·35	2·37	2·40	2·45	18·56
Pr^nNO_3	13·4	2·51	2·50	2·56	2·55	18·89
Bu^nNO_3	15·5	2·42	2·46	2·46	2·50	19·00
Mean (N–O)	14·1	2·42	2·43	2·49	2·51	18·82

TABLE 41. *Values for* (N=O) *from alkyl nitrites.*

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
Bu^nNO_2	52·5	4·00	4·04	4·11	4·21	32·16
Am^nNO_2	51·8	3·91	3·95	4·01	4·12	32·29
n-C_6H_{13}·NO_2	52·2	3·97	4·00	4·08	4·18	32·33
Mean (N=O)	52·2	3·96	4·00	4·07	4·17	32·26

The (N=O) constants were employed to compute those for (N→O) from the data for nitroparaffins, RN(→O):O (Table 42). An independent determination is possible from alkyl nitrates RO·N(→O):O, and alkyl nitrites RO·N:O; the figures for R = Bu^n (Part XXIII, *loc. cit.*), the only experimental observations available at present, are :

(*P*) 17·2, (R_C) 1·76, (R_D) 1·77, (R_F) 1·77, ($R_{G'}$) 1·76, and (Mn^{20}_D) 25·56.

TABLE 42. *Values for* (N→O) *from nitroparaffins.*

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
$MeNO_2$	20·7	1·79	1·79	1·81	1·81	25·08
$EtNO_2$	19·1	1·80	1·80	1·82	1·80	25·43
Pr^nNO_2	17·4	1·74	1·75	1·75	1·78	25·27
Pr^iNO_2	19·3	1·71	1·69	1·71	1·69	24·94
Bu^nNO_2	16·1	1·83	1·82	1·84	1·81	25·61
Am^nNO_2	15·5	1·80	1·79	1·81	1·78	25·26
n-C_6H_{13}·NO_2	15·1	1·82	1·81	1·84	1·82	25·29
Mean (N→O)	17·6	1·78	1·78	1·80	1·78	25·27

The observations on aliphatic ketoxime *O*-alkyl ethers CRR′:NOR″ were employed to evaluate the (C=N) constants with the aid of the values of (C–C), $(C–O)_{ethers}$, and (N–O) (Table 43). These are slightly higher than the (C=N) constants deduced from aliphatic aldoximes CHR:N·OH [$(O–H)_{alcohols}$ being used: Table 44] and aliphatic ketoximes CRR′:N·OH (Table 45).

TABLE 43. *Values for* (C=N) *from aliphatic ketoxime* O-*alkyl ethers.*

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
CMe_2:N·OMe	33·5	3·65	3·72	3·78	3·91	24·64
CMe_2:N·OEt	32·9	3·82	3·89	3·96	4·09	24·08
CMe_2:N·OPr^n	32·3	3·68	3·75	3·81	3·94	24·25
CMeEt:N·OEt	33·2	3·74	3·81	3·88	4·00	24·01
CMeEt:N·OPr^n	27·8	3·51	3·58	3·64	3·76	24·25
CEt_2:N·OEt	28·3	3·64	3·71	3·78	3·90	24·14
CEt_2:N·OPr^n	28·2	3·57	3·62	3·70	3·83	24·23
$CMePr^n$:N·OEt	29·4	3·77	3·83	3·89	4·03	24·18
$CMePr^n$:N·OPr^n	28·8	3·63	3·67	3·74	3·89	24·21
$CEtPr^n$:N·OEt	28·8	3·78	3·82	3·91	4·03	24·09
$CEtPr^n$:N·OPr^n	28·0	3·69	3·73	3·83	3·94	24·15
CPr^n_2:N·OEt	27·3	3·76	3·80	3·89	3·98	24·10
CPr^n_2:N·OPr^n	26·3	3·77	3·79	3·88	4·01	23·29
Mean (C=N)	29·6	3·69	3·76	3·82	3·95	24·13

TABLE 44. *Values for* (C=N) *from aliphatic aldoximes.*

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
CHMe:N·OH	36·0	3·63	3·64	3·72	3·81	24·36
CHEt:N·OH	34·0	3·58	3·63	3·70	3·80	24·06
$CHPr^n$:N·OH	33·2	3·62	3·67	3·74	3·85	24·15
Mean $(C=N)_{aldoximes}$	34·4	3·61	3·65	3·72	3·82	24·19

TABLE 45. *Values for* (C=N) *from aliphatic ketoximes.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
CMeEt:N·OH	31·1	3·63	3·68	3·75	3·85	24·54
CEt$_2$:N·OH	28·4	3·55	3·62	3·67	3·78	24·54
CMePr^n:N·OH	29·3	3·61	3·67	3·74	3·84	24·50
CEtPr^n:N·OH	27·3	3·45	3·53	3·57	3·68	24·35
CPr$^n_2$:N·OH	24·1	3·44	3·49	3·55	3·67	24·19
Mean (C=N)$_{\text{ketoximes}}$	28·0	3·54	3·60	3·66	3·76	24·42

The most accurate values for (N–N) were obtained from the data on *NN*-dialkylhydrazines, $NR_2{\cdot}NH_2$, and secondary amines, NHR_2 :

$$(\text{N–N}) = \text{NR}_2{\cdot}\text{NH}_2 - \text{NHR}_2 - (\text{N–H})$$

Another procedure, from dialkyl nitrosamines, utilises the previously determined values for (N=O) (Table 41) :

$$(\text{N–N}) = \text{NR}_2{\cdot}\text{NO} - \text{NR}_2 + (\text{N–H}) - (\text{N=O})$$

Both series of results are given in Table 46 : the divergences for (P) and (Mn_D^{20}) are noteworthy.

TABLE 46. *Values for* (N–N) *from* NN-*dialkylhydrazines.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
NEt$_2$·NH$_2$	6·7	1·91	1·95	1·98	2·02	16·65
NPr$^n_2$·NH$_2$	6·8	1·97	2·02	2·05	2·10	18·16
NBu$^n_2$·NH$_2$	5·6	1·93	1·96	2·01	2·03	16·43
NAm$^n_2$·NH$_2$	5·8	1·99	2·01	2·05	2·11	16·99
Mean (N–N)	6·2	1·95	1·99	2·02	2·08	16·81
Values for (N–N) *from dialkylnitrosamines*						
NEt$_2$·NO	7·2	1·87	1·89	2·03	2·12	20·47
NPr$^n_2$·NO	6·6	1·94	1·98	2·12	2·22	20·79
NBu$^n_2$·NO	2·4	1·89	1·92	2·08	2·13	20·83
NAm$^n_2$·NO	0	1·95	1·97	2·11	2·24	20·88
(n-C$_6$H$_{13}$)$_2$N·NO	−2·4	2·04	2·05	2·22	2·33	20·61
Mean (N–N)	?	1·94	1·96	2·11	2·21	20·72

The constants for the N=N bond, recorded in Table 47, were deduced from the observations on dialkyl azodiformates, $RO_2C{\cdot}N{:}N{\cdot}CO_2R$, and dialkyl oxalates, $RO_2C{\cdot}CO_2R$ (Part XIII, *J.*, 1948, 639) : $(\text{N=N}) = \text{RO}_2\text{C}{\cdot}\text{N}{:}\text{N}{\cdot}\text{CO}_2\text{R} - \text{RO}_2\text{C}{\cdot}\text{CO}_2\text{R} - 2(\text{C–N}) + (\text{C–C})$.

TABLE 47. *Values for* (N=N) *from dialkyl azodiformates.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
EtO$_2$C·N:N·CO$_2$Et	45·6	4·33	4·36	—	—	25·41
Pr^{n}O$_2$C·N:N·CO$_2$Pr^n	44·4	4·13	4·15	—	—	25·67
Bu^{n}O$_2$C·N:N·CO$_2$Bu^n	41·4	3·82	3·85	—	—	26·09
Mean (N=N)	44·8	4·09	4·12	—	—	25·72

Some experimental data on azohydrocarbons are given by Barrick, Drake, and Lochte (*J. Amer. Chem. Soc.*, 1936, **58**, 160). We have used their figures to calculate the constants for the N=N bond and have employed our own constants for the alkyl groups (Table 11) and for (C–N) (Table 26). The results are given below and, having regard to the instability of these aliphatic azohydrocarbons, the agreement with our own constants is moderately satisfactory.

	(P)	(R_C)	(R_D)	(R_F)
Pr^{i}N:NPr^i	42·2	4·22	4·31	4·32
Bu^{s}N:NBu^s	44·7	4·76	4·78	4·88

The constants for the C=S bond were determined from the data on alkyl xanthates CS(OR)·SR′ (Part XXIII, *J.*, 1948, 1840) by using the expression :

$$(\text{C=S}) = \text{CS(OR)}{\cdot}\text{SR}' - 2(\text{C–S}) - 2(\text{C–O})_{\text{acetals}} - (\text{R}) - (\text{R}')$$

The results are given in Table 48.

TABLE 48. *Values for* (C=S) *from dialkyl xanthates.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
CS(OEt)·SEt	73·6	11·41	11·62	12·19	12·72	64·88
CS(OPr^n)·SPr^n	70·9	11·75	11·95	12·56	13·13	65·17
CS(OEt)·SBu^n	71·0	11·75	11·97	12·58	13·14	65·09
CS(OBu^n)·SEt	71·1	11·74	11·96	12·57	—	65·09
CS(OBu^n)·SBu^n	68·0	11·83	12·06	12·68	13·21	64·87
Mean (C=S)	70·9	11·70	11·91	12·52	13·05	65·02

The literature data for carbon disulphide (see *J.*, 1948, 1841) give for (C=S) (P) 71·8, (R_C) 10·56, (R_D) 10·70, (R_F) 11·03, $(R_{G'})$ 11·32, and (Mn_D^{20}) 61·97.

TABLE 49. *Values for* (S–O) *from alkyl sulphates and alkyl sulphites.*

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
R = Me	36·2	4·77	4·81	4·90	4·98	36·23
R = Et	34·9	4·85	4·92	5·00	5·10	37·63
R = Pr^n	34·8	4·99	5·04	5·13	5·21	37·55
R = Bu^n	33·2	4·93	4·99	5·07	5·14	35·04
Mean (S–O)	34·8	4·88	4·94	5·03	5·11	37·13

TABLE 50. *Values for* (S→O) *from* $R_2SO_4 - R_2SO_3$.

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
R = Me	18·2	−0·07	−0·08	−0·15	−0·19	19·79
R = Et	18·8	−0·11	−0·14	−0·20	−0·26	19·37
R = Pr^n	16·8	−0·30	−0·33	−0·40	−0·46	20·80
R = Bu^n	17·4	−0·21	−0·25	−0·32	−0·36	23·40
Mean (S→O)	17·8	−0·17	−0·20	−0·27	−0·32	20·84

TABLE 51. *Bond parachors, bond refractions* (*at* 20°) *and bond-refraction coefficients* (*at* 20°).

	(P)	(R_C)	(R_D)	(R_F)	$(R_{G'})$	(Mn_D^{20})
(C-H)	17·85	1·669	1·676	1·693	1·704	3·87
(C-C)	4·30	1·286	1·296	1·301	1·328	12·86
(C=C)	28·5	4·12	4·17	4·28	4·38	9·39
(C≡C)$_{\text{terminal}}$	53·5	5·82	5·87	5·97	6·07	25·04
(C≡C)$_{\text{non-terminal}}$ *	—	—	6·24	—	—	24·83
(C-C)$_{cyclo\text{propane}}$	8·4	1·48	1·49	1·52	1·54	11·28
(C-C)$_{cyclo\text{butane}}$	6·8	1·36	1·37	1·38	1·41	11·44
(C-C)$_{cyclo\text{pentane}}$	5·2	1·25	1·26	1·26	1·28	11·95
(C-C)$_{cyclo\text{hexane}}$	4·5	1·26	1·27	1·28	1·30	12·24
(C_{ar}–C_{ar})	16·5	2·660	2·688	2·760	2·822	15·67
(C-F) *	28·2	1·45	1·44	1·44	1·45	28·27
(C-Cl)	57·4	6·48	6·51	6·58	6·64	56·80
(C-Br)	70·9	9·32	9·39	9·54	9·68	124·51
(C-I)	92·4	14·47	14·61	14·96	15·28	202·46
(C-O)$_{\text{ethers}}$	12·4	1·53	1·54	1·55	1·57	17·71
(C-O)$_{\text{acetals}}$	11·3	1·45	1·46	1·47	1·48	17·46
(C=O)	40·3	3·30	3·32	3·36	3·39	29·39
(C=O)$_{\text{methyl ketones}}$	42·6	3·46	3·49	3·53	3·57	29·50
(C-S)	26·6	4·57	4·61	4·70	4·78	32·84
(C=S)	70·9	11·70	11·91	12·52	13·05	65·02
(C-N)	6·4	1·55	1·57	1·59	1·63	14·51
(C=N)	29·3	3·69	3·76	3·82	3·95	24·13
(C≡N)	61·4	4·80	4·82	4·87	4·91	29·91
(O-H)$_{\text{alcohols}}$	20·3	1·65	1·66	1·67	1·68	13·15
(O-H)$_{\text{acids}}$	20·0	1·80	1·80	1·83	1·83	10·54
(S-H)	42·1	4·77	4·80	4·87	4·94	23·79
(S-S)	49·0	8·02	8·11	8·28	8·45	53·83
(S-O)	34·8	4·88	4·94	5·03	5·11	37·13
(S→O)	17·8	−0·17	−0·20	−0·27	−0·32	20·84
(N-H)	19·9	1·76	1·76	1·79	1·80	7·26
(N-O)	14·1	2·42	2·43	2·49	2·51	18·82
(N→O)	17·6	1·78	1·78	1·80	1·78	25·27
(N=O)	52·2	3·96	4·00	4·07	4·17	32·26
(N-N)	6·2	1·95	1·99	2·02	2·08	16·81
(N=N)	44·8	4·09	4·12	—	—	25·72

* Preliminary values.

The experimental data for alkyl sulphates and sulphites (Part VII, *J.*, 1943, 16; Part XXIII, *J.*, 1948, 1836) may be employed to calculate the constants of the S–O bond :

$$2(\mathrm{S{-}O}) = 2(\mathrm{RO})_2\mathrm{SO} - (\mathrm{RO})_2\mathrm{SO}_2 - 2(\mathrm{R}) - 2(\mathrm{C{-}O})_{\mathrm{acetals}}$$

The results are collected in Table 49. The constants for the S→O bond (Table 50) (strictly speaking, this is the bond in which oxygen is attached only to sulphur) are obtained directly from alkyl sulphates and alkyl sulphites :

$$(\mathrm{S{\rightarrow}O}) = \mathrm{R_2SO_4} - \mathrm{R_2SO_3}$$

The bond parachors, bond refractions for the C, D, F, and G′ lines at 20°, and the bond-refraction coefficients 20° so far deduced are summarised in Table 51.

The bond constants (C_{ar}–C_{ar}) were determined from our own measurements of d_4^{20} and the refractive indices of pure benzene : the parachor (206·23) was computed from Sugden's figures for the surface tension at various temperatures (*J.*, 1924, **125**, 31) and the relation for the variation of density with temperature given in " International Critical Tables." The values obtained, our own values being used for (C–H), are : (P) 16·52, (R_C) 2·660, (R_D) 2·688, (R_F) 2·760, ($R_{G'}$) 2·822, and (Mn_D^{20}) 15·67.

A large number of monosubstituted benzenes have been studied in the present series, and an attempt has been made to investigate the character of the bond between the aromatic ring and the substituent element or group (C_{ar}–X) with the aid of the bond refractions for the D line. Table 52 gives the ratios of the bond refractions (D line) for the single and the double bonds so far investigated.

TABLE 52. *Single : double bond ratios for bond refractions* (D *line*).

Elements in bond	Bond refraction		Ratio
	single	double	
Carbon–carbon	1·296	4·17	1 : 3·2
Carbon–oxygen	1·54 (ethers)	3·32	1 : 2·2
	1·46 (acetals)	3·32	1 : 2·3
Carbon–nitrogen	1·57	3·75	1 : 2·4
Carbon–sulphur	4·61	11·91	1 : 2·6
Nitrogen–oxygen	2·43	4·00	1 : 1·65
Nitrogen–nitrogen	1·99	4·12	1 : 2·1
		Mean	1 : 2.3

The ratio 1 : 2·3 is employed for computing the refractions of double bonds which have not yet been investigated or cannot be determined by the usual methods, *e.g.*, (C=Cl) from (C–Cl), etc. This is, of course, only a rough approximation and it may well be that the derived figures, *e.g.*, for Ph–X where X is halogen, are too low. The results of the calculations of the bond refractions (for the D line) and the percentage double-bond character p_d of the (C_{ar}–X) link are collected in Table 53; (C_6H_5) was computed from C_6H_6 – (C–H) : p_d was obtained from the expression

$$p_d = 100\,(r_{\mathrm{obs}} - r_{\mathrm{single}})/(r_{\mathrm{double}} - r_{\mathrm{single}})$$

where r_{single} and r_{double} are the bond refractions of the single- and double-bond links, respectively (cf. Cresswell, Jeffery, Leicester, and Vogel, *Research*, 1949, **2**, 46). The alkyl cinnamates (Part XVI, *J.*, 1948, 661) and phenylpropiolates (Part XVII, *J.*, 1948, 676) contain conjugated systems and are therefore too complex to be investigated by this simple procedure.

It is of interest to investigate the bond constants when two or more halogens are attached to the same carbon atom. The values for 2(C–Cl) were computed from the experimental data (Part XXIII, *J.*, 1948, 1834) for alkyl dichloroacetates and alkyl succinates, the known values for (C–C) and (C–H) being used. The results are collected in

TABLE 53. *Bond refractions and the percentage double-bond character of links between* X *and the aromatic ring in* C_6H_5X.

	R_D	bond	(C$_{ar}$–X)	p_d
PhMe	31·10	(C$_{ar}$–C)	1·59	10
PhEt	35·75	,,	1·59	10
PhPr^n	40·43	,,	1·60	10·5
PhBu^n	45·08	,,	1·63	11·5
PhAm^n	49·73	,,	1·62	11
n-C$_6$H$_{13}$·Ph	54·29	,,	1·57	10
PhCOMe	36·27	(C$_{ar}$–COR)	1·97	23
PhCOEt	40·83	,,	2·06	26
PhCOPr^n	49·62	,,	2·16	30
PhCH$_2$·COMe	40·48	(C$_{ar}$–CH$_2$·COR)	1·54	8
PhCH$_2$·COEt	44·99	,,	1·58	10
PhCH$_2$·COPr^n	49·62	,,	1·47	6
PhCH$_2$·CH$_2$·COMe	45·07	(C$_{ar}$–CH$_2$·CH$_2$·COR)	1·57	9
PhCH$_2$·CH$_2$·COEt	49·58	,,	1·54	8
PhCH$_2$·CH$_2$·COPr^n	54·20	,,	1·41	4
PhCO$_2$Et	42·57	(C$_{ar}$–CO$_2$R)	1·93	22
PhCO$_2$Pr^n	47·22	,,	1·88	20
PhCO$_2$Bu^n	51·90	,,	1·94	22
PhCH$_2$·CO$_2$Me	41·84	(C$_{ar}$–CH$_2$·CO$_2$R)	1·49	7
PhCH$_2$·CO$_2$Et	46·55	,,	1·54	8
PhCH$_2$·CO$_2$Pr^n	51·22	,,	1·54	8
PhCH$_2$·CO$_2$Bu^n	55·89	,,	1·59	9
PhCH$_2$·CH$_2$·CO$_2$Me	46·52	(C$_{ar}$–CH$_2$·CH$_2$·CO$_2$R)	1·57	9
PhCH$_2$·CH$_2$·CO$_2$Et	51·14	,,	1·51	8
PhCH$_2$·CH$_2$·CO$_2$Pr^n	55·81	,,	1·54	8
PhCH$_2$·CH$_2$·CO$_2$Bu^n	60·48	,,	1·58	10
PhOMe	32·88	(C$_{ar}$–OR)	1·83	16
PhOEt	37·70	,,	1·94	23
PhOPr^n	42·28	,,	1·93	22
PhOPr^i	42·39	,,	1·93	22
PhOBu^n	47·06	,,	2·11	32
PhOAm^n	51·64	,,	2·05	31
n-C$_6$H$_{13}$·OPh	56·38	,,	2·13	33
PhCH$_2$·OH	32·47	(C$_{ar}$–CH$_2$·OH)	1·42	4
PhCH$_2$·CH$_2$·OH	37·12	(C$_{ar}$–CH$_2$·CH$_2$·OH)	1·39	3
PhF	25·98	(C$_{ar}$–F)	1·48	2
PhCl	31·14	(C$_{ar}$–Cl)	6·64	2
CH$_2$Cl	36·03	(C$_{ar}$–CH$_2$Cl)	1·66	12
PhBr	33·99	(C$_{ar}$–Br)	9·49	1
PhCH$_2$·CH$_2$Br	43·81	(C$_{ar}$–CH$_2$·CH$_2$·Br)	1·98	21
PhI	39·15	(C$_{ar}$–I)	14·61	0·2
PhCH$_2$·CH$_2$I	48·78	(C$_{ar}$–CH$_2$·CH$_2$I)	1·72	15
PhCN	31·58	(C$_{ar}$–CN)	2·26	33
PhCH$_2$·CN	35·22	(C$_{ar}$–CH$_2$·CN)	1·30	0
PhNO$_2$	32·72	(C$_{ar}$–NO$_2$)	2·44	40
PhNH$_2$	30·56	(C$_{ar}$–NH$_2$)	2·54	44
PhCH$_2$·NH$_2$	34·45	(C$_{ar}$–CH$_2$·NH$_2$)	1·50	7
PhNHMe	35·67	(C$_{ar}$–NHR)	2·83	58
PhNHEt	40·45	,,	2·96	64
PhNHPr^n	44·72	,,	2·96	64
PhNHBu^n	49·80	,,	3·10	70
PhNMe$_2$	40·81	(C$_{ar}$–NR$_2$)	3·16	73
PhNEt$_2$	50·20	,,	3·15	72
PhNPr$^n{}_2$	59·56	,,	3·30	79
PhNBu$^n{}_2$	68·84	,,	3·27	78
PhSH	34·52	(C$_{ar}$–SH)	5·22	8
SPh$_2$	59·77	(C$_{ar}$–SPh)	5·38	11
PhSMe	39·42	(C$_{ar}$–SR)	5·35	10
PhSEt	44·19	,,	5·42	11
PhSPr^n	48·85	,,	5·45	11
PhSPr^i	48·98	,,	5·42	11
PhSBu^n	53·59	,,	5·56	13
PhSAm^n	58·23	,,	5·36	10
n-C$_6$H$_{13}$·SPh	62·96	,,	5·59	13

Table 54; those for methylene chloride, ethylidene dichloride, and acetylene tetrachloride are also included, but are less trustworthy owing to the difficulty of preparing and storing these polyhalogenated hydrocarbons in a state of purity.

TABLE 54. *Values for* 2(C–Cl) *from compounds containing the* —CCl_2 *Group.*

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
$CHCl_2\cdot CO_2Me$	111·3	13·27	13·35	13·50	13·63	112·82
$CHCl_2\cdot CO_2Et$	113·7	13·26	13·34	13·49	13·62	112·47
$CHCl_2\cdot CO_2Pr^n$	111·6	13·28	13·35	13·51	13·63	112·43
$CHCl_2\cdot CO_2Bu^n$	110·3	13·20	13·28	13·42	13·56	112·58
Mean 2(C–Cl)	111·7	13·25	13·33	13·48	13·61	112·58
CH_2Cl_2	111·8	12·96	13·03	13·19	13·31	113·06
$CH_3\cdot CHCl_2$	112·2	13·04	13·12	13·26	13·40	111·72
$CHCl_2\cdot CHCl_2$	108·9	12·92	12·98	13·19	13·25	115·15
Mean (C–Cl) from monohalogeno-compounds	57·4	6·48	6·51	6·58	6·64	56·80

The bond constants for 3(C–Cl) were similarly determined from the experimental data (Part XXIII, *loc. cit.*) for alkyl trichloroacetates and alkyl succinates. These, as well as those for the comparatively unstable chloroform and methylchloroform, are presented in Table 55.

TABLE 55. *Values for* 3(C–Cl) *from compounds containing the* CCl_3 *group.*

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
$CCl_3\cdot CO_2Me$	163·3	19·87	19·98	20·22	20·40	168·97
$CCl_3\cdot CO_2Et$	166·0	20·03	20·14	20·37	20·56	168·13
$CCl_3\cdot CO_2Pr^n$	165·2	19·87	19·98	20·22	20·39	168·13
$CCl_3\cdot CO_2Bu^n$	164·6	19·89	20·01	20·23	20·44	168·22
Mean 3(C–Cl)	164·8	19·91	20·03	20·26	20·45	168·36
$CHCl_3$	165·3	19·59	19·69	19·94	20·12	168·79
$CH_3\cdot CCl_3$	171·4	21·07	21·20	21·44	21·65	180·20

The bond constants for (C–Cl) in carbon tetrachloride are : (*P*) 55·3, (R_C) 6·58, (R_D) 6·61, (R_F) 7·72, ($R_{G'}$) 6·77, and (Mn^{20}_D) 56·16.

The few polybromo-compounds so far investigated give the following results :

	(*P*)	(R_C)	(R_D)	(R_F)	($R_{G'}$)	(Mn^{20}_D)
2(C–Br) from CH_2Br_2	139·3	18·42	18·54	18·87	19·13	260·21
2(C–Br) from $CHBr_2\cdot CHBr_2$	—	18·54	18·67	18·99	—	272·37
3(C–Br) from $CHBr_3$	209·9	27·98	28·18	28·69	29·09	409·96
Mean (C–Br) from monobromo-compounds	70·9	9·32	9·39	9·54	9·68	124·51

It is difficult to draw any trustworthy conclusions from these few results, particularly from bromoform which is known to be unstable when pure.

The Structures of The Esters of Oxy-acids and of Related Compounds.—In Part XXIII (*J.*, 1948, 1841) the structures of the nitro-group, alkyl nitrates, thionyl chloride, sulphuryl chloride, alkyl sulphites, alkyl sulphates, phosphorus oxychloride, and trialkyl orthophosphates were considered from the view-point of atomic and structural parachors and refractions, and it was suggested that the results indicate the presence of co-ordinate links in these compounds. It seems appropriate to consider the subject again by using the bond constants. Particular attention will be paid to the values of the bond refractions, since these are the most sensitive to changes of structure; the results for bond parachors and bond-refraction coefficients will, however, be included for completeness.

The presence of a co-ordinate link in nitro-compounds and alkyl nitrates seems to be generally accepted. The bond constants deduced above for the various nitrogen–oxygen links are :

	(*P*)	(R_D)	(Mn^{20}_D)
(N–O)	14·1	2·43	18·82
(N→O)	17·6	1·78	25·27
(N=O)	52·2	4·00	32·26

It will be noted that the refraction of the N→O link is less than that of the normal covalent bond N–O and very much less than that of the double bond N=O.

The constants for the two types of bonds in alkyl sulphites and alkyl sulphates, represented as (S–O) and (S→O) are :

	(*P*)	(R_D)	(Mn^{20}_D)		(*P*)	(R_D)	(Mn^{20}_D)
(S–O)	34·8	4·94	37·13	(S→O)	17·8	−0·20	17·80

The refraction is very much less for the $S \rightarrow O$ link, but no explanation can at present be offered for the negative value : the parachor differences between the two links are particularly noteworthy. It will be recalled that in the deduction of the constants for the S–O link (Table 49), it was assumed that the link between sulphur and oxygen only in alkyl sulphites was identical with the two such links in alkyl sulphates : a rigid proof of the validity of this assumption is desirable. New measurements are in progress on compounds containing the S–O link only (*e.g.*, RO·S·S·OR) and further discussion must be postponed until these have been completed. The following facts, however, do not support the presence of the $S{=}O$ link, as has recently been postulated (see below) :

(i) R_D for SO_2Cl_2 is 21·43 and for $SOCl_2$ 22·12 : the molecular refractions of the alkyl sulphates are slightly *less* than those of the alkyl sulphites (Part XXIII, *J.*, 1948, 1835).

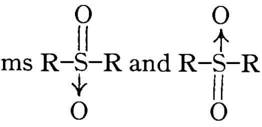
(ii) By subtracting R_D for the alkyl sulphides (Part VII, *J.*, 1943, 16) from R_{He} for the alkyl sulphoxides (Strecker and Spitaler, *Ber.*, 1926, **59**, 1755), the refractions for the sulphur to oxygen link are obtained; they are 0·90, 0·71, and 0·73 for R = Me, Et, and Pr^n, severally. New experiments on sulphoxides are in progress in order to determine the constants with greater accuracy.

(iii) Strecker and Spitaler (*loc. cit.*) have determined R_{He} for dimethyl, diethyl, and di-*n*-propyl sulphones at 50—100° and find R_{He} to be substantially the same as for the corresponding sulphoxides. The molecular refractions at 25° for allyl phenyl sulphide, sulphoxide, and sulphone are 48·46, 49·13, and 48·72, respectively; for crotyl phenyl sulphide and sulphone 53·50 and 53·34, respectively; and for *sec.*-butyl phenyl sulphide and sulphone, 53·36 and 53·63, respectively (Cope, Morrison, and Field, *J. Amer. Chem. Soc.*, 1951, **72**, 64). Experiments on liquid sulphones are in progress in order to confirm these highly significant results.

Note. The constants given for sulphones in *J.*, 1948, 1845 refer to the $C–SO_2–C$ results and *not* to the O_2 grouping : they were obtained from $R_2SO_2 - R_2$.

The observations on trialkyl orthophosphates (Part VII, *J.*, 1943, 17) do not support the view that the phosphorus to oxygen link is a double bond. Jones, Davies, and Dyke's data (*J. Phys. Chem.*, 1933, **37**, 583) for triethyl, tri-*iso*-butyl, and tri-*n*-amyl phosphites lead to the following values for the P–O link for the D-line : 3·22, 3·22, and 3·13, or a mean of 3·19. The less accurate experimental figures on cyclic phosphorus compounds given by Lucas, Mitchell, and Scully (*J. Amer. Chem. Soc.*, 1951, **72**, 5491) when combined with our own results for phosphorus trichloride (Part XXIII, *loc. cit.*) give a mean value of 3·00 for the (P–O) link. The bond refractions for the $(P \rightarrow O)$ link in trialkyl orthophosphates, computed with (P–O) 3·19 and $(C–O)_{acetals}$ are : R = Me, −1·21 ; R = Et, −1·13 ; R = Pr^n, −1·25 ; R = Pr^i, −1·15 ; R = Bu^n, −1·20 ; R = Bu^i and R = Am^n, −1·51. The mean value is −1·26. The figure obtained directly from $POCl_3 - PCl_3$ (*J.*, 1948, 1835) is −1·22.

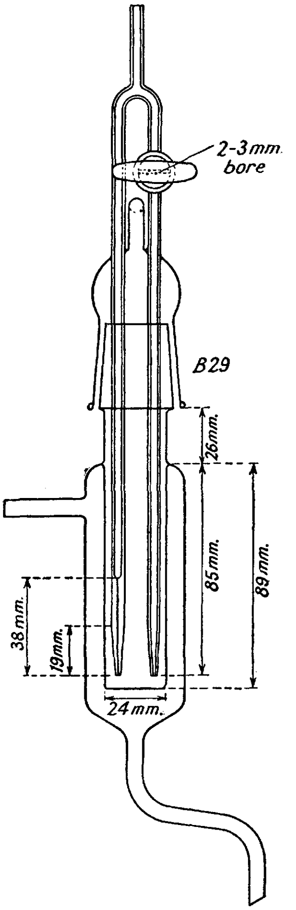
The general conclusion may be drawn that bond-refraction data do not support the view that alkyl sulphites, alkyl sulphates, alkyl orthophosphates, and related compounds, and sulphoxides and sulphones, contain double bonds. The detailed arguments, based on many approximations, put forward by Phillips, Hunter, and Sutton (*J.*, 1945, 146) in support of the double-bond theory have been adversely criticised by Wells (*J.*, 1949, 55); in particular, he has shown that the abnormal shortness of many bond lengths cannot at present be explained satisfactorily. The authors feel that a knowledge of the physical constants of unequivocal examples of single bonds (S–O), (P–O), etc., or of double bonds ($S{=}O$), etc., would materially assist the solution of the problem. Infra-red studies appear to have led to different results in deciding between various alternative structures. Barnard, Fabian, and Koch (*J.*, 1949, 2442) conclude from infra-red studies of selected sulphoxides and sulphones that "it is unambiguously demonstrated that the sulphur–oxygen link is nearly a covalent double bond and contains a minor proportion of the polar co-ordinate single-bond structure which is relatively more important in the sulphoxides than in the sulphones." Koch and Moffitt (*Trans. Faraday Soc.*, 1951, **47**, 8) conclude "that the double-bonded structure of the S–O linkages in sulphones is no longer in doubt." On the other hand infra-red spectrum studies by Amstutz, Hundsberger, and Chessick (*J. Amer. Chem. Soc.*, 1951, **73**, 1220) lead to the conclusions "that in sulphoxides the bond between sulphur and oxygen has considerable double-bond character with possible minor contributions from a semi-ionic structure, $-\overset{\oplus}{\mathrm{S}}-\overset{\ominus}{\mathrm{O}}$; and that sulphones are a resonance hybrid of the two forms R–S–R and R–S–R."



$$\mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\downarrow}}{S}}{-}R} \text{ and } \mathrm{R{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\|}}{S}}{-}R}$$

EXPERIMENTAL

Physical Measurements.—Surface tensions were usually measured by the capillary-rise method (Part VII, *J.*, 1943, 18); the constant K of the apparatus used was 2·3282. Densities were determined with a " Phœnix " or " Pyrex " glass pycnometer (Part III, *J.*, 1938, 1325; Part VII, *loc. cit.*). In the tabulated results t is the temperature, $H = h - 0{\cdot}24$, where h is the observed difference in height (in mm.) in the two arms of the U-tube, d_4^t the density at $t°$ (calculated from the observed densities by assuming a linear variation with temperature), γ the surface tension (dynes/cm.) computed from the equation $\gamma = Khd$, and P is the parachor.



For those liquids which did not appear to wet glass and for those cases where an independent check was required, the maximum bubble pressure method (compare Sugden, *J.*, 1922, **121**, 864; 1924, **125**, 28) was employed. The apparatus, shown in the figure, is an improved version of that described by Sugden (*loc. cit.*). It was constructed of " Pyrex " or " Hysil " glass; the standard ground-glass joint (B29) was external; the tubes comprising the actual bubbler were entirely of precision bore (" Hysil Veridia," 2—3 mm. in diameter), the narrow precision bore capillary (0·1—0·2 mm. in diameter and *ca.* 4 cm. long) being sealed to that of the wider bore; both capillaries were ground externally to conical form. (The wider capillary is shown of conical bore in the figure for the sake of clarity, but was in fact of uniform bore throughout.) The outer vessel of the bubbler was surrounded by a sealed-on glass jacket through which suitable vapours (redistilled methylene chloride, chloroform, trichloroethylene, etc.) could be passed for measurements at various temperatures; the temperature was read on a standardised Anschütz-type thermometer (with sealed-in glass scale) dipping directly in the liquid. The gauge consisted of a water-jacketed U-tube (40 cm. long and 4 mm. bore) filled with absolute alcohol tinted with a little magenta; the liquid levels were viewed against an illuminated glass screen placed at a distance of 2—3 cm. in order to eliminate heating effects; a thermometer was immersed in the water jacket. The difference in heights in the two arms of the U-tube was determined by means of a Pye " universal reading cathetometer," fitted with a vernier reading to 0·05 mm.: suitable precautions were taken that both the U-tube and the cross-wire in the eyepiece of the telescope objective were vertical. The mercury aspirator was similar to that described by Sugden (*loc. cit.*). The density of the tinted alcohol was determined at several temperatures between 10° and 30°, and a graph was drawn relating temperature and (density × g) (g = 981 cm./sec.^{2}). The difference between the pressures required to liberate bubbles from the two tubes, Δp (dynes/cm.^{2}), was obtained from the expression :

Δp = difference in pressure on gauge (cm. of alcohol) × {density of alcohol at temperature of gauge × g}

The correction factor ϕ was computed from the equation :

$$\phi = 1 + 0{\cdot}69 r_2 g d_4^t / \Delta p$$

where r_2 is the radius of the wide tube in cm. (0·126 cm.) and d_4^t is the density of the liquid at the temperature of observation. The constant of the apparatus A was deduced from the expression $\gamma = A\phi\Delta p$, pure benzene being used, γ being the surface tension. The surface tensions of benzene at various temperatures were those determined by Sugden (*J.*, 1924, **125**, 31; "The Parachor and Valency," 1930, p. 211). The value of A found in this manner was 0·005393. In the tabulated results, the above symbols are used with the addition of the parachor P calculated in the usual manner: allowance was made for the density of the vapour (computed as described by Sugden, Reed, and Wilkins, *J.*, 1925, **127**, 1540) when the temperature of measurement was within 60° of the b. p. of the sample.

Most of the refractive-index measurements were made at 20° ± 0·02° in a Zeiss Pulfrich refractometer. Some determinations (including those on benzene) were made with a Hilger–Chance refractometer, precision model, for liquids. The results with the two instruments agreed to within 0·0001 for the C, D, and F lines, but differences as high as 0·0004 were sometimes found for the G′ line. Where 20° is used, 20·0° is to be understood; n_C, n_D, n_F, and n_G are to be taken as referring to $n_C^{20·0}$, etc., and R_C, etc., to $[R_L]_C$, etc.

Unless otherwise stated, all b. p.s are corrected. All the compounds were distilled immediately before the measurements were made. Analyses are by Drs. Weiler and Strauss. The numbering of compound in Clarendon type follows from Part XXIII (*J.*, 1948, 1855). References to compounds, the preparation of which is described in previous Parts of this series, will be abbreviated, *e.g.*, XXIII, **605**.

Preparation of pure compounds

Aliphatic Aldoximes and Ketoximes.—Acetaldoxime. This was prepared from redistilled acetaldehyde (b. p. 22·5°), hydroxylamine hydrochloride and sodium carbonate solution. The dried product was distilled in an all-glass apparatus through a Widmer column; a middle fraction, b. p. 115·2°/766 mm., was collected for the physical measurements.

Propaldoxime. This was prepared from freshly distilled propaldehyde (B.D.H.) (b. p. 49—49·5°); b. p. 134°/761 mm.

n-*Butaldoxime.* Pure butaldehyde was obtained by drying the commercial product (anhydrous magnesium sulphate) and distilling it through a Widmer column; it had b. p. 73°/755 mm. This was converted into the oxime, b. p. 151°/750 mm., in the usual manner.

Diethyl ketoxime. This was prepared by the method described in *Org. Synth.*, 1931, **11**, 54 for *n*-heptaldoxime (on $\frac{1}{10}$th scale); 33 g. of diethyl ketoxime, b. p. 165—166°/763 mm., were obtained from 34·4 g. of diethyl ketone. Redistillation gave the pure compound, b. p. 165·5°/765 mm.

Similarly prepared were: ethyl methyl ketoxime (28 g. from 28·8 g. of ketone), b. p. 151·5°/770 mm.; methyl *n*-propyl ketoxime (27 g. from 34·8 g. of ketone), b. p. 168°/754 mm.; ethyl *n*-propyl ketoxime (27 g. from 40 g. of ketone), b. p. 180°/753 mm.; and di-*n*-propyl ketoxime (26·5 g. from 45·6 g. of ketone), b. p. 194·5—195°/755 mm.

Ketoxime O-Alkyl Ethers.—General. Only the *O*-methyl ether of acetoxime can be prepared by methylation with methyl sulphate and alkali since acetone, formed as a by-product by the hydrolysis of the ketoxime, can be readily removed by washing with water. With higher ketoximes the ketone is not easily separated by fractionation without considerable sacrifice of yield. The *O*-ethyl ethers of ketoximes were readily prepared by ethylation with ethyl sulphate and alkali (compare Ponzio and Charrier, *Gazzetta*, 1907, **37**, 506); the *O*-*n*-propyl ethers were obtained by treatment in methanol solution with sodium methoxide and *n*-propyl iodide (compare Dunstan and Goulding, *J.*, 1906, **79**, 628).

Acetoxime O-*methyl ether.* Acetoxime (100 g.) was dissolved in a solution of sodium hydroxide (220 g.) in water (730 ml.), and methyl sulphate (252 g.) was added with stirring during 40 minutes with occasional water cooling; stirring was continued for a further 30 minutes, and the upper layer was separated, dried (anhydrous $MgSO_4$), and fractionated through a 10″ vacuum-jacketed Widmer column. The yield of acetoxime *O*-methyl ether, b. p. 72—73°/760 mm., was 40 g.; on redistillation, it boiled mostly at 73°/760 mm.

Acetoxime O-*ethyl ether.* Prepared as for the methyl ether, but at 60—70°, acetoxime *O*-ethyl ether (34 g. from 50 g. of acetoxime) was collected at 91—93°; on redistillation, it boiled largely at 93°/760 mm.

Similarly prepared were: *ethyl methyl ketoxime* O-*ethyl ether* (36 g. from 60 g. of ketoxime), b. p. 113°/761 mm. (Found: C, 63·0; H, 11·6; N, 11·9. $C_6H_{13}ON$ requires C, 62·6; H, 11·4; N, 12·2%); *diethyl ketoxime* O-*ethyl ether* (20 g. from 30 g. of ketoxime), b. p. 132·5°/764 mm. (Found: C, 65·3; H, 11·7; N, 11·1. $C_7H_{15}ON$ requires C, 65·0; H, 11·6; N, 10·8%); *methyl* n-*propyl ketoxime* O-*ethyl ether* (32 g. from 50·5 g. of ketoxime), b. p. 134°/754 mm. (Found : C, 65·2; H, 11·8; N, 10·5%); and *ethyl* n-*propyl ketoxime* O-*ethyl ether* (32 g. from 57·5 g. of ketoxime), b. p. 152°/770 mm. (Found : C, 67·5; H, 12·2. $C_8H_{17}ON$ requires C, 67·1; H, 11·9%).

Acetoxime O-n-*propyl ether*. To a solution of sodium methoxide [from sodium (23 g.) in absolute methanol (300 ml.)] acetoxime (73 g.) dissolved in absolute methanol (100 ml.) was added, followed by *n*-propyl iodide (171 g.). The mixture became hot, and was kept for 2 days at the laboratory temperature, and then refluxed for 3 hours. About two-thirds of the methanol was distilled off, and excess of water was added to the distillate; the ethereal layer was separated, dried, and fractionated through a lagged Widmer or Dufton column. The yield of acetoxime *O-n*-propyl ether, b. p. 114—116°/747 mm., was 33 g.; on redistillation, most boiled at 116°/750 mm.

Similarly prepared were : *ethyl methyl ketoxime* O-n-*propyl ether* (34 g. from 80 g. of ketoxime), b. p. 136°/756 mm. (Found : C, 65·4; H, 11·6; N, 10·4%); *diethyl ketoxime* O-n-*propyl ether*, b. p. 153·5—154°/766 mm. (Found : C, 66·7; H, 12·0; N, 10·2%); *methyl* n-*propyl ketoxime* O-n-*propyl ether* (70 g. from 132 g. of ketoxime), b. p. 154°/755 mm. (Found : C, 67·4; H, 11·8%); *ethyl* n-*propyl ketoxime* O-n-*propyl ether* (28 g. from 140 g. of ketoxime), b. p. 170·5°/765 mm. (Found : C, 68·4; H, 12·2. $C_9H_{19}ON$ requires C, 68·7; H, 12·2%); and *di*-n-*propyl ketoxime* O-n-*propyl ether* (17 g. from 144 g. of ketoxime), b. p. 187°/749 mm. (Found : C, 69·8; H, 12·5. $C_{10}H_{21}ON$ requires C, 70·1; H, 12·3%).

NN-*Dialkylhydrazines*.—NN-*Diethylhydrazine*. (i) The following modification of Fischer's method (*Annalen*, 1879, **199**, 287) was employed. Diethylnitrosamine (XXIII, **574**) (102 g.), zinc dust (95%; 255 g.), and water (900 ml.) were stirred mechanically and the temperature was maintained at 25—30° whilst 85% acetic acid (370 ml.) was added during 2 hours. Stirring was continued, and the mixture was heated to and kept at 60° for 1 hour and then filtered hot. Next morning the zinc acetate crystals were filtered off and 50% sodium hydroxide solution was added to the filtrate at such a rate that a precipitate was just visible and steam distillation was continued until the distillate was no longer basic to litmus. The distillate was neutralised with concentrated hydrochloric acid (85 ml.) and a further 5 ml. of acid were added, and the liquid was evaporated on a steam-bath under diminished pressure to a thick viscous syrup. The latter was poured on twice its weight of sodium hydroxide pellets in a Claisen flask; when warmed gently the crude diethylhydrazine passed over at 85—100°. It was dried first over potassium hydroxide pellets (2 days) then over fused barium oxide. The dried product was distilled through a vacuum-jacketed Widmer column in an all-glass apparatus, and the fraction, b. p. 95—99° (50 g.), was collected, set aside for several days over fused barium oxide, and then fractionated as before; pure diethylhydrazine, b.p. 99·5—100°/762 mm., was the sole product and was collected in a receiver fitted with a barium oxide guard tube. It had d_4^{20} 0·7988, n_D^{20} 1·4214.

(ii) The compound could also be prepared by the reduction of diethylnitrosamine with lithium aluminium hydride. Finely-powdered lithium aluminium hydride (10 g.) was stirred for several minutes with sodium-dried ether (600 ml.) and a solution of diethylnitrosamine (23·5 g.) in anhydrous ether (135 ml.) was then added, with stirring, at a rate of about 2 drops per second; refluxing of the ether began after 20 minutes, and the rate of addition was adjusted so as to keep the reaction under control. A white solid was deposited gradually, the addition was complete in 1 hour, and stirring was continued for 15 minutes more. Water (25 ml.) was then added very cautiously with vigorous stirring during 1 hour; this was followed by 10N-sodium hydroxide (50 ml.) and, after being stirred for a further 10 minutes, the mixture was filtered and the residue was washed with ether (2 × 50 ml.). The combined filtrate and washings were dried (KOH pellets, followed by anhydrous $CaSO_4$) and fractionated through a 10″ vacuum-jacketed Widmer column; the diethylhydrazine (10 g.) was collected at 98·5—99·5°/760 mm. The crude product had d_4^{20} 0·7998, n_D^{20} 1·4201, and was evidently of high purity.

NN-*Di*-n-*propylhydrazine*. (i) Di-*n*-propylnitrosamine (41 g.) (XXIII, **575**) was dissolved in glacial acetic acid (210 ml.) and zinc powder (95%; 83 g.) added in small portions, with stirring, during 4 hours whilst the temperature was kept at 20—25°. Stirring was continued at 45—50° for 1 hour, and the mixture was filtered hot and washed with a little cold water. The filtrate was treated with 50% sodium hydroxide solution until the precipitate just redissolved, and the upper layer was separated. The preparation was repeated and the combined upper layers were dried (KOH pellets, 1 day; fresh KOH pellets, 1 week; fused BaO, 2 days) and distilled through a lagged Widmer column : the crude di-*n*-propylhydrazine (41 ml.), b. p. 135—140°, was dried (fused BaO, 8 weeks) and again fractionated. The pure *di*-n-*propylhydrazine* passed over at 140·5—141°/760 mm. and had d_4^{20} 0·8011, n_D^{20} 1·4265 (Found : C, 62·3; H, 13·9; N, 24·0. $C_6H_{16}N_2$ requires C, 62·1; H, 13·8; N, 24·1%). For the physical measurements the sample was distilled under diminished pressure in dry nitrogen; it had b. p. 31·5°/7 mm., d_4^{20} 0·7997, and n_D^{20} 1·4266.

(ii) Di-*n*-propylnitrosamine (29·5 g.) in anhydrous ether (200 ml.) was reduced with powdered lithium aluminium hydride (10 g.) in anhydrous ether (600 ml.) as detailed under diethylhydrazine. Stirring was continued for 8 hours after the nitrosamine had been added and the mixture was kept overnight. After decomposition of the excess of lithium aluminium hydride with water (35 ml.), and working up as before, pure di-*n*-propylhydrazine (20 g.), b. p. 140·5—141°/768 mm., d_4^{20} 0·8011, n_D^{20} 1·4266, was obtained.

NN-*Di*-n-*butylhydrazine.* The reduction of di-*n*-butylnitrosamine (XXIII, **576**) with zinc and acetic acid always gave mixtures of di-*n*-butylamine and di-*n*-butylhydrazine (the former predominating), which could not be separated satisfactorily by fractional distillation. The presence of di-*n*-butylhydrazine in the mixture was established by the addition of ethyl oxalate whereupon oxalic acid bis-*NN*-di-*n*-butylhydrazide slowly separated as needles, in poor yield (cf. Franchimont and van Erp, *Rec. Trav. chim.*, 1895, **14**, 318): these melted at 170° after recrystallisation from rectified spirit (Found: C, 63·1; H, 11·5. Calc. for $C_{18}H_{38}O_2N_4$: C, 63·1; H, 11·8%).

The compound was readily obtained by reduction of di-*n*-butylnitrosamine (36 g.) in anhydrous ether (205 ml.) with lithium aluminium hydride (10 g.) in anhydrous ether (600 ml.) for 5 hours as detailed for di-*n*-propylhydrazine. *Di*-n-*butylhydrazine* (15 g.), b. p. 60—62°/11 mm., d_4^{20} 0·8029, n_D^{20} 1·4325, was obtained; it boiled largely at 61°/8 mm. on redistillation (Found: C, 66·8; H, 13·8; N, 19·1. $C_8H_{20}N_2$ requires C, 66·6; H, 14·0; N, 19·4%).

NN-*Di*-n-*amylhydrazine.* Di-*n*-amylnitrosamine (30 g.; for preparation, see below) was reduced with lithium aluminium hydride (7·1 g.) as described above. The pure *hydrazine*, b. p. 87°/7 mm. (18 g.), was obtained as a colourless liquid on rapid distillation under reduced pressure (Found: C, 70·0; H, 14·3. $C_{10}H_{24}N_2$ requires C, 69·7; H, 14·0%) and its physical properties were determined immediately. After 1 day in a vacuum desiccator over fused barium oxide, it acquired a pale yellow colour and had d_4^{20} 0·8148, n_D^{20} 1·4390.

Di-n-*amylnitrosamine.* Redistilled di-*n*-amylamine (Light) (30 g.) was mixed with absolute ethyl alcohol (12 ml.), and 5N-hydrochloric acid was added, with stirring, until the solution was neutral to methyl orange; warming may be necessary to prevent crystallisation of the hydrochloride. The solution of the hydrochloride was added to one of sodium nitrite (22·5 g.) in water (25 ml.), and the mixture was heated, with vigorous stirring, to the boiling point and then refluxed gently for 45 minutes. After cooling, the upper oily layer was separated and heated rapidly over a gauze; about 5 ml. of impure alcohol distilled at 80—100° and a little solid (probably salt) appeared. The heating was discontinued and the solid separated; the residual yellow oil was distilled under reduced pressure giving *di*-n-*amylnitrosamine* (20 g.), b. p. 130—133°/10 mm. On redistillation from an all-glass apparatus this boiled largely at 130·5°/12 mm. (Found: C, 64·5; H, 11·9; N, 15·1. $C_{10}H_{22}ON_2$ requires C, 64·5; H, 11·8; N, 15·4%).

Di-n-*hexylnitrosamine.* Prepared similarly this *nitrosamine* had b. p. 155°/11 mm. (Found: C, 67·3; H, 12·2; N, 13·4. $C_{12}H_{26}ON_2$ requires C, 67·7; H, 12·2; N, 13·2%).

Aliphatic Ketazines.—Dimethyl, ethyl methyl, diethyl, methyl *n*-propyl, ethyl *n*-propyl, and di-*n*-propyl ketazine were prepared by heating the corresponding ketone under reflux with a 49% solution of hydrazine hydrate; alcohol was used to effect dissolution in the preparation of all except the first-named ketazine. The reaction mixture was subsequently treated with excess of potassium carbonate, whereupon the crude ketazine either separated or was obtained by ether extraction, and was purified by distillation.

Diethyl ketazine had b. p. 196°/757 mm. (Curtius and Thun, *J. pr. Chem.*, 1891, **44**, 161, give b. p. 190—195°; Mailhe, *Bull. Soc. chim.*, 1920, **27**, 541, erroneously gives b. p. 160—163°).

β-*Monoalkylaminopropionitriles.*—Redistilled acrylonitrile was treated with an excess of the corresponding monoalkylamine with stirring at <30°. After a further period of stirring, the mixture was heated at 100° for 1—2 hours and then treated with anhydrous potassium carbonate, the oil so obtained was distilled. The following propionitriles were so obtained: β-ethylamino-, b. p. 78—79°/11 mm. (cf. Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 725, who give b. p. 92—95° (30 mm.); β-*n*-propylamino-, b. p. 91—92°/11—12 mm. (cf. Tarbell, Shakespeare, Claus, and Burnett, *ibid.*, 1946, **68**, 127, who give b. p. 119—121°/30 mm.); β-*n*-butylamino-, b. p. 100°/9 mm.; β-*n*-amylamino-, b. p. 114°/10 mm. (cf. Burckhalter, Jones, Holcomb, and Sweet, *ibid.*, 1943, **65**, 2012, who give b. p. 112—113°/10 mm.); and β-n-*hexylamino-propionitrile*, b. p. 126°/9 mm. (25 g. from 11·2 g. of acrylonitrile and 32 g. of *n*-hexylamine) (Found: C, 69·6; H, 11·9; N, 18·2. $C_9H_{18}N_2$ requires C, 70·0; H, 11·8; N, 18·2%).

β-*Dialkylaminopropionitriles.*—Heating a mixture of redistilled acrylonitrile with an excess of dialkylamine at 50° for 24 hours, followed by storage for 2 days at laboratory temperature, removal of the excess of amine, and distillation of the residue at reduced pressure gave the following β-dialkylaminopropionitriles: β-diethylamino-, b. p. 76°/11 mm. (cf. Whitmore *et al.*, *loc. cit.*, who give b. p. 104—106°/35 mm.); β-di-*n*-propylamino-, b. p. 105—106°/11 mm. (cf. Whitmore *et al.*, *loc. cit.*, who give b. p. 116°/20 mm.); β-di-*n*-butylamino-, b. p. 120°/10 mm.; and β-di-*n*-amylamino-propionitrile, b. p. 149°/8 mm. (Holcomb and Hamilton, *J. Amer. Chem. Soc.*, 1942, **64**, 1309, give b. p. 136°/6 mm.).

β-*Alkoxypropionitriles.*—β-*Methoxy-* (b. p. 165·5°/759 mm.) *and* β-*ethoxy-propionitrile* (b. p. 173°/756 mm.; 58°/10 mm.). These were prepared by MacGregor and Pugh's method (*J.*, 1945, 535).

β-n-*Propoxypropionitrile.* Acrylonitrile (26·5 g.) was added at <45° to a solution of potassium hydroxide (0·15 g.) in *n*-propyl alcohol (33 g.), with stirring during 25 minutes. The mixture was heated under reflux at 100° for 1 hour and then allowed to cool. After the removal of a small quantity of brown solid, distillation gave the required nitrile (36·5 g.), which had b. p. 73·5°/10 mm. when pure (Christian and Hixon, *J. Amer. Chem. Soc.*, 1948, **70**, 133, give b. p. 87—89°/24 mm.).

β-n-*Butoxy-*, β-n-*amyloxy-*, *and* β-n-*hexyloxy-propionitrile.* These were prepared in a manner similar to that described for the *n*-propoxy-compound. β-n-*Hexyloxypropionitrile* [32 g.; from *n*-hexyl alcohol (67 g.), acrylonitrile (35 g.), and sodium (0·05 g.), under reflux for 18 hours] had b. p. 115·5°/9 mm. after redistillation (Found: C, 69·9; H, 11·2. $C_9H_{17}ON$ requires C, 69·9; H, 11·0%).

All the above nitriles remained colourless after several months' storage.

Dialkyl Azodiformates.—*Diethyl azodiformate.* This was prepared as detailed in *Org. Synth.*, 1948, **28**, 58.

Di-n-*propyl azodiformate.* This was prepared similarly from 90% hydrazine hydrate (11·5 g.) in alcohol (102 ml.), *n*-propyl chloroformate (b. p. 113—115°; 49·2 g.), and a solution of sodium carbonate (21·4 g.) in water (100 ml.) except that, after all the reactants had been added, stirring was continued for 7 hours. The upper oily layer was then separated, and the aqueous layer was extracted with ether (4 × 50 ml.). The combined extracts and upper layer were dried ($MgSO_4$), and the solvents removed first on a steam-bath and then under reduced pressure. The residue (32 g.) solidified on cooling and melted at 58—59°; the m. p. was raised to 63—64° on recrystallisation from benzene–light petroleum (b. p. 60—80°) (Boehm and Mehta, *Ber.*, 1938, **71**, 1797, give m. p. 63—64°).

This hydrazodiformate (28 g.), suspended in a mixture of water (150 ml.) and benzene (150 ml.), was oxidised with chlorine following the procedure used for the diethyl compound. *Di*-n-*propyl azodiformate* (23 g.), a red liquid, b. p. 121—123°/11 mm., was obtained (Found: C, 47·8; H, 7·1. $C_8H_{14}O_4N_2$ requires C, 47·5; H, 7·0%). A middle fraction, b. p. 122°/11 mm., was employed for the physical measurements.

Di-n-*butyl azodiformate.* This was prepared from *n*-butyl chloroformate (b. p. 136—138°, rapid distillation; 45·5 g.) as described for the di-*n*-propyl compound. The resulting hydrazodiformate (33 g.; m. p. 46°) was oxidised with chlorine and gave *di*-n-*butyl azodiformate* (22 g.), b. p. 142—144°/11 mm. (Found: C, 51·8; H, 8·1. $C_{10}H_{18}O_4N_2$ requires C, 52·1; H, 7·9%). Redistillation gave a main fraction, b. p. 142°/11 mm.

Dialkyl Carbonates.—These were prepared by heating alkyl chloroformates and the appropriate alcohols under reflux (for the times given below in parentheses). Ethyl, *n*-propyl, and *n*-butyl chloroformate were obtained from Messrs. Light, and *n*-amyl and *n*-hexyl chloroformate from Eastman Kodak. They were all purified by fractional distillation immediately before use: two rapid distillations gave better results than one slow, careful fractionation (cf. Chattaway and Saerens, *J.*, 1920, **117**, 708).

Di-n-*butyl carbonate.* *n*-Butyl chloroformate (47 g.) and anhydrous *n*-butyl alcohol (51 g.) were refluxed for 3 hours. Hydrogen chloride was freely evolved during the first 2 hours and then slackened. Upon distillation a fraction (33 g.), b. p. 115—140°, composed of mixed reactants, passed over first, followed by the di-*n*-butyl carbonate at 202—205°/750 mm. (46 g.). Redistillation gave the pure product, b. p. 204·5°/755 mm., d_4^{20} 0·9249, n_D^{20} 1·4118. The Eastman Kodak product when purified (XXIII, **594**) had b. p. 204·5°/758 mm., d_4^{20} 0·9251, n_D^{20} 1·4117.

Di-n-*amyl carbonate.* *n*-Amyl chloroformate (50 g.; b. p. 39—40°/9 mm., d_4^{20} 1·0241, n_D^{20} 1·4180) and pure *n*-amyl alcohol (51 g.) were refluxed for 3 hours, by which time the smell of the former could no longer be detected. On distillation, di-*n*-amyl carbonate (41 g.), b. p. 237—239°/754 mm., was collected. Redistillation gave a main fraction of b. p. 238·5°/757 mm.

*Di-*n*-hexyl carbonate.* *n*-Hexyl chloroformate (49·3 g.; b. p. 64—65°/10 mm., d_4^{20} 1·0113, n_D^{20} 1·4236) and pure *n*-hexyl alcohol (61·2 g.) gave, on distillation after 12 hours' refluxing, di-*n*-hexyl carbonate (55 g.), b. p. 266—269°/762 mm. and 146·5°/9 mm. on redistillation.

Ethyl n*-propyl carbonate.* Ethyl chloroformate (54·3 g.; b. p. 93°/753 mm., d_4^{20} 1·1356, n_D^{20} 1·3952) was heated to gentle boiling and treated during 1 hour with anhydrous *n*-propyl alcohol (30 g.). Refluxing was continued for 2·5 hours by which time the evolution of hydrogen chloride had slackened considerably. The mixture was fractionated through a Dufton column, giving a low-boiling fraction (20 g.) and then ethyl *n*-propyl carbonate (40·5 g.), b. p. 146°/758 mm. Redistillation gave the pure compound, b. p. 145·5°/760 mm.

n*-Butyl ethyl carbonate.* Anhydrous *n*-butyl alcohol (37 g.) was added during 90 minutes to ethyl chloroformate, (54·3 g.) and the mixture was refluxed for 2 hours. Fractionation gave *n*-butyl ethyl carbonate (31 g.), b. p. 166—167°/759 mm.; this boiled largely at 167°/759 mm. on redistillation (Chattaway and Saerens, *loc. cit.*, give b. p. 168·5°/748 mm.).

n*-Amyl ethyl carbonate.* Anhydrous *n*-amyl alcohol (44 g.) was added during 60 minutes to boiling ethyl chloroformate (53·4 g.) and the mixture was refluxed for 2 hours. Fractionation gave n*-amyl ethyl carbonate* (36 g.) b. p. 187—189°/760 mm. (Found: C, 60·2; H, 10·0. $C_8H_{16}O_3$ requires C, 60·0; H, 10·0%). This boiled largely at 188°/760 mm. on redistillation.

Ethyl n*-hexyl carbonate.* Pure *n*-hexyl alcohol (51 g.) was added during 90 minutes to boiling ethyl chloroformate (54·3 g.), and the mixture was refluxed for 4 hours. Fractionation gave *ethyl* n*-hexyl carbonate* (32 g.), b. p. 205—207°/764 mm. (Found: C, 62·3; H, 10·4. $C_9H_{18}O_3$ requires C, 62·1; H, 10·4%). This boiled largely at 206·5°/764 mm. on redistillation.

n*-Butyl* n*-propyl carbonate.* *n*-Butyl chloroformate (68·3 g.; b. p. 46—47°/28 mm., d_{40}^{2} 1·0558, n_D^{20} 1·4118) was added during 90 minutes to boiling anhydrous *n*-propyl alcohol (30 g.). After refluxing for a further 3 hours, the mixture was fractionated through a Dufton column whereupon *n*-butyl *n*-propyl carbonate (49 g.), b. p. 186—187°/764 mm., was obtained. On redistillation, the main fraction of b. p. 187°/764 mm. was collected (Chattaway and Saerens, *loc. cit.*, give b. p. 187·5°/752 mm.).

n*-Heptyl cyanide.* A mixture of sodium cyanide (15·2 g.) in water (20 ml.) and *n*-heptyl iodide (57 g.) in methanol (75 ml.) was refluxed for 28 hours, and methanol (60 ml.) then removed by fractionation. The residue was treated with water, and the upper layer of crude nitrile washed twice with half its volume of concentrated hydrochloric acid by shaking it for 0·5 and 2 hours, thrice with water, then with saturated sodium hydrogen carbonate solution, and finally with water; it was then dried (anhydrous $MgSO_4$) and distilled (yield 29 g.). The high density of a middle fraction suggested the presence of a little iodide; the product in methanol (100 ml.) was accordingly heated under reflux for 12 hours with sodium cyanide (10 g.) in water (15 ml.), and the *n*-heptyl cyanide then isolated as before; b. p. 82·5°/10 mm., d_4^{20} 0·8141, n_D^{20} 1·4206 (Merckx, Verhulst, and Bruylants, *Bull. Soc. chim. Belg.*, 1933, **42**, 177, found b. p. 82°/10 mm., d_4^{20} 0·8136, n_D^{20} 1·4202, interpolated from values at 15° and 30°).

n*-Octyl cyanide.* This was prepared from *n*-octyl bromide (65 g.) and sodium cyanide (20·1 g.) as described for n-heptyl cyanide. The product was redistilled from phosphoric oxide (10 g.), then refluxed with thionyl chloride (20 g.) for 1 hour, and again treated with aqueous sodium cyanide for 11 hours; the alcohol was distilled off and the residue dissolved in ether. The ethereal solution was shaken with concentrated hydrochloric acid (2 × 20 ml.) for 1-hour periods, washed with water, sodium hydrogen carbonate solution and water, and dried ($MgSO_4$). The residue left when the ether was removed was refluxed for 1 hour with thionyl chloride (20 g.), the excess of the latter distilled off at atmospheric pressure, and the residual liquid distilled under reduced pressure, giving *n*-octyl cyanide (14 g.), a middle fraction of which had b. p. 100°/11 mm., d_4^{20} 0·8164, n_D^{20} 1·4258 (Merckx, Verhulst, and Bruylants, *loc. cit.*, find b. p. 98·5°/10 mm., d_4^{20} 0·8169, n_D^{20} 1·4252, interpolated).

607. *Acetaldoxime.* B. p. 115°/762 mm.; M 59·07; n_C 1·42452, n_D 1·42636, n_F 1·43340, $n_{G'}$ 1·43884; R_C 15·65, R_D 15·71, R_F 15·94, $R_{G'}$ 16·11; Mn_D^{20} 84·26. Densities determined: d_4^{20} 0·9640, $d_4^{39·7}$ 0·9462, $d_4^{59·5}$ 0·9278.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
22·2°	14·20	0·9620	31·80	145·8	60·2°	12·72	0·9272	27·46	145·8
40·0	13·42	0·9459	29·55	145·6				Mean	145·7

608. *Propaldoxime.* B. p. 134°/761 mm.; M 73·10; n_C 1·42750, n_D 1·43028, n_F 1·43703, $n_{G'}$ 1·44228; R_C 20·23, R_D 20·35, R_F 20·62, $R_{G'}$ 20·84; Mn_D^{20} 104·55. Densities determined: d_4^{20} 0·9286, $d_4^{40·6}$ 0·9091, $d_4^{60·2}$ 0·8912, $d_4^{85·3}$ 0·8664.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
14·9°	13·97	0·9324	30·36	183·8	41·7°	13·08	0·9081	27·65	184·6
19·8	13·77	0·9288	29·78	183·9	61·4	12·24	0·8901	25·37	184·3
								Mean	184·2

609. n-*Butaldoxime*. B. p. 151°/750 mm.; M 87·12; n_{C} 1·43358, n_{D} 1·43670, n_{F} 1·44303, $n_{\mathrm{G'}}$ 1·44830; R_{C} 24·90, R_{D} 25·06, R_{F} 25·37, $R_{\mathrm{G'}}$ 25·64; Mn_{D}^{20} 125·17. Densities determined: d_4^{20} 0·9103, $d_4^{40\cdot4}$ 0·8927, $d_4^{60\cdot2}$ 0·8762, $d_4^{85\cdot1}$ 0·8534.

21·4°	13·63	0·9081	28·82	222·8	60·5°	12·34	0·8759	25·16	222·8
40·4	12·97	0·8927	26·96	222·4	85·8	11·54	0·8528	22·86	223·5
								Mean	222·9

610. *Ethyl methyl ketoxime*. B. p. 151·5°/770 mm.; M 87·12; n_{C} 1·44027, n_{D} 1·44310, n_{F} 1·44997, $n_{\mathrm{G'}}$ 1·45530; R_{C} 24·88, R_{D} 25·01, R_{F} 25·35, R_{G} 25·60; Mn_{D}^{20} 125·72. Densities determined: d_4^{20} 0·9238, $d_4^{41\cdot0}$ 0·9055, $d_4^{60\cdot5}$ 0·8887, $d_4^{86\cdot5}$ 0·8645.

16·0°	14·03	0·9273	30·29	220·4	60·4°	12·43	0·8888	25·72	220·7
19·1	13·93	0·9246	29·99	220·5	85·3	11·51	0·8656	23·20	220·9
41·2	13·08	0·9053	27·57	220·5				Mean	220·6

611. *Methyl* n-*propyl ketoxime*. B. p. 168°/754 mm.; M 101·15; n_{C} 1·44252, n_{D} 1·44546, n_{F} 1·45205, n_{G} 1·45278; R_{C} 29·49, R_{D} 29·67, R_{F} 30·05, $R_{\mathrm{G'}}$ 30·34; Mn_4^{20} 146·21. Densities determined: d_4^{20} 0·9083, $d_4^{41\cdot0}$ 0·8905, $d_4^{60\cdot9}$ 0·8738, $d_4^{86\cdot3}$ 0·8517.

18·9°	13·77	0·9092	29·15	258·5	61·0°	12·28	0·8737	24·98	258·8
41·7	12·90	0·8898	26·72	258·5	87·1	11·49	0·8511	22·77	259·6
								Mean	258·8

612. *Diethyl ketoxime*. B. p. 165·5°/765 mm.; M 101·15; n_{C} 1·44337, n_{D} 1·44651, n_{F} 1·45282, $n_{\mathrm{G'}}$ 1·45820; R_{C} 29·42, R_{D} 29·60, R_{F} 29·96, $R_{\mathrm{G'}}$ 30·26; Mn_{D}^{20} 146·31. Densities determined: d_4^{20} 0·9123, $d_4^{40\cdot2}$ 0·8962, $d_4^{60\cdot4}$ 0·8786, $d_4^{86\cdot1}$ 0·8567.

25·1°	13·62	0·9082	28·80	258·0	61·2°	12·33	0·8779	25·20	258·2
40·5	12·98	0·8960	27·08	257·5	85·7	11·44	0·8570	22·83	258·0
								Mean	257·9

613. *Ethyl* n-*propyl ketoxime*. B. p. 180°/753 mm.; M 115·17; n_{C} 1·44372, n_{D} 1·44701, n_{F} 1·45302, $n_{\mathrm{G'}}$ 1·45816; R_{C} 33·96, R_{D} 34·18, R_{F} 34·58, $R_{\mathrm{G'}}$ 34·92; Mn_{D}^{20} 166·65. Densities determined: d_4^{20} 0·9002, $d_4^{41\cdot4}$ 0·8829, $d_4^{60\cdot0}$ 0·8672, $d_4^{85\cdot1}$ 0·8466.

17·1°	13·80	0·9025	29·00	296·1	60·8°	12·39	0·8666	25·00	297·2
41·8	12·98	0·8826	26·67	296·5	86·3	11·53	0·8456	22·70	297·3
								Mean	296·8

614. *Di*-n-*propyl ketoxime*. B. p. 194·5—195°/755 mm.; M 129·20; n_{C} 1·44440, n_{D} 1·44746, n_{F} 1·45357, $n_{\mathrm{G'}}$ 1·45888; R_{C} 38·58, R_{D} 38·81, R_{F} 39·27, $R_{\mathrm{G'}}$ 39·66; Mn_{D}^{20} 187·02. Densities determined: d_4^{20} 0·8903, $d_4^{40\cdot0}$ 0·8748, $d_4^{85\cdot7}$ 0·8381.

19·4°	13·43	0·8908	27·85	333·2	61·1°	12·20	0·8581	24·37	334·5
40·4	12·80	0·8745	26·06	333·8	86·8	11·38	0·8372	22·18	333·0
								Mean	333·6

t	Δp	d_4^t	ϕ	γ	P	t	Δp	d_4^t	ϕ	γ	P
20·5°	5135	0·8899	1·0148	28·10	334·3	60·7°	4459	0·8584	1·0164	24·44	334·7
40·4	4775	0·8745	1·0156	26·15	334·1	85·7	4053	0·8381	1·0176	22·24	334·8
										Mean	334·5

615. *Acetoxime* O-*methyl ether*. B. p. 73°/760 mm.; M 87·12; n_{C} 1·39797, n_{D} 1·40052, n_{F} 1·40673, $n_{\mathrm{G'}}$ 1·41153; R_{C} 25·15, R_{D} 25·29, R_{F} 25·63, $R_{\mathrm{G'}}$ 25·90; Mn_{D}^{20} 122·01. Densities determined: d_4^{20} 0·8361, $d_4^{41\cdot1}$ 0·8126.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
17·9°	11·82	0·8385	23·07	227·9	42·3°	10·84	0·8113	20·48	228·7
								Mean	228·3

616. *Acetoxime* O-*ethyl ether*. B. p. 93°/760 mm.; M 101·15; n_{C} 1·40176, n_{D} 1·40420, n_{F} 1·41033, $n_{\mathrm{G'}}$ 1·41499; R_{C} 29·95, R_{D} 30·11, R_{F} 30·51, $R_{\mathrm{G'}}$ 30·82; Mn_{D}^{20} 142·04. Densities determined: d_4^{20} 0·8219, $d_4^{40\cdot5}$ 0·8010, $d_4^{60\cdot9}$ 0·7795.

t	*H*	d_4^t	γ	*P*	*t*	*H*	d_4^t	γ	*P*
21·4°	11·69	0·8205	22·33	268·0	60·2°	9·93	0·7802	18·04	267·6
41·0	10·83	0·8005	20·18	268·0				Mean	267·9

617. *Acetoxime* O-n-*propyl ether*. B. p. 116°/750 mm.; *M* 115·17; n_C 1·40920, n_D 1·41196, n_F 1·41784, $n_{G'}$ 1·42247; R_C 34·44, R_D 34·64, R_F 35·07, $R_{G'}$ 35·42; Mn_D^{20} 162·74. Densities determined: d_4^{20} 0·8272, $d_4^{41\cdot0}$ 0·8063, $d_4^{60\cdot9}$ 0·7865.

16·9°	12·39	0·8303	23·95	306·9	60·9°	10·53	0·7865	19·28	306·9
40·3	11·46	0·8070	21·53	307·4				Mean	307·1

618. *Ethyl methyl ketoxime* O-*ethyl ether*. B. p. 113°/761 mm.; *M* 115·17; n_C 1·40894, n_D 1·41152, n_F 1·41747, $n_{G'}$ 1·42198; R_C 34·48, R_D 34·67, R_F 35·12, $R_{G'}$ 35·45; Mn_D^{20} 162·56. Densities determined: d_4^{20} 0·8256, $d_4^{40\cdot2}$ 0·8045, $d_4^{60\cdot4}$ 0·7837, $d_4^{84\cdot2}$ 0·7585.

t	Δp	d_4^t	ϕ	γ	*P*	*t*	Δp	d_4^t	ϕ	γ	*P*
18·0°	4357	0·8269	1·0162	23·88	307·9	59·5°	3546	0·7846	1·0189	19·49	308·4
39·9	3927	0·8052	1·0175	21·55	308·2	85·2	3049	0·7574	1·0212	16·75	307·6
										Mean	308·0

619. *Ethyl methyl ketoxime* O-n-*propyl ether*. B. p. 136°/756 mm.; *M* 129·20; n_C 1·41637, n_D 1·41896, n_F 1·42504, $n_{G'}$ 1·42961; R_C 38·89, R_D 39·11, R_F 39·60, $R_{G'}$ 39·97; Mn_D^{20} 183·33. Densities determined: d_4^{20} 0·8343, $d_4^{40\cdot2}$ 0·8156, $d_4^{60\cdot7}$ 0·7968, $d_4^{86\cdot0}$ 0·7712.

17·8°	4422	0·8364	1·0161	24·23	342·7	61·0°	3659	0·7965	1·0186	20·10	343·5
40·6	3969	0·8152	1·0175	21·78	342·4	85·0	3130	0·7721	1·0210	17·23	341·7
										Mean	342·6

620. *Diethyl ketoxime* O-*ethyl ether*. B. p. 132·5°/764 mm.; *M* 129·20; n_C 1·41608, n_D 1·41861, n_F 1·42467, $n_{G'}$ 1·42931; R_C 39·01, R_D 39·22, R_F 39·72, $R_{G'}$ 40·10; Mn_D^{20} 183·28. Densities determined: d_4^{20} 0·8312, $d_4^{42\cdot2}$ 0·8106, $d_4^{61\cdot6}$ 0·7917, $d_4^{84\cdot7}$ 0·7692.

t	*H*	d_4^t	γ	*P*	*t*	*H*	d_4^t	γ	*P*
15·1°	12·54	0·8359	24·40	343·5	61·1°	10·66	0·7921	19·66	343·5
20·5	12·22	0·8307	23·63	342·9	86·9	9·55	0·7671	17·06	342·3
41·0	11·43	0·8117	21·60	343·2				Mean	343·1

621. *Diethyl ketoxime* O-n-*propyl ether*. B. p. 153·5—154°/760 mm.; *M* 143·23; n_C 1·42110, n_D 1·42361, n_F 1·42970, $n_{G'}$ 1·43437; R_C 43·57, R_D 43·80, R_F 44·35, $R_{G'}$ 44·77; Mn_D^{20} 203·90. Densities determined: d_4^{20} 0·8338, $d_4^{41\cdot6}$ 0·8143, $d_4^{60\cdot6}$ 0·7974, $d_4^{85\cdot9}$ 0·7737.

21·0°	12·67	0·8329	24·57	382·9	60·7°	11·18	0·7973	20·75	383·4
41·4	11·93	0·8145	22·62	383·5	85·8	10·10	0·7738	18·20	382·3
								Mean	383·0

622. *Methyl* n-*propyl ketoxime* O-*ethyl ether*. B. p. 134°/754 mm.; *M* 129·20; n_C 1·41582, n_D 1·41836, n_F 1·42441, $n_{G'}$ 1·42909; R_C 39·15, R_D 39·36, R_F 39·85, $R_{G'}$ 40·24; Mn_D^{20} 183·26. Densities determined: d_4^{20} 0·8279, $d_4^{40\cdot4}$ 0·8094, $d_4^{60\cdot8}$ 0·7893, $d_4^{85\cdot3}$ 0·7649.

t	Δp	d_4^t	ϕ	γ	*P*	*t*	Δp	d_4^t	ϕ	γ	*P*
18·4°	4424	0·8294	1·0160	23·69	343·7	60·0°	3569	0·7902	1·0189	19·61	344·1
39·5	3961	0·8103	1·0175	21·73	344·3	86·0	3132	0·7642	1·0208	17·24	344·5
										Mean	344·2

623. *Methyl* n-*propyl ketoxime* O-n-*propyl ether*. B. p. 155°/746 mm.; *M* 143·22; n_C 1·42055, n_D 1·42306, n_F 1·42912, $n_{G'}$ 1·43385; R_C 43·64, R_D 43·87, R_F 44·41, $R_{G'}$ 44·85; Mn_D^{20} 203·82. Densities determined: d_4^{20} 0·8315, $d_4^{40\cdot0}$ 0·8129, $d_4^{60\cdot8}$ 0·7962, $d_4^{86\cdot0}$ 0·7694.

17·8°	4561	0·8334	1·0156	24·99	384·1	60·7°	3741	0·7962	1·0182	20·53	382·8
39·5	4096	0·8130	1·0169	22·47	383·4	86·5	3293	0·7694	1·0199	18·11	384·0
										Mean	383·6

624. *Ethyl* n-*propyl ketoxime* O-*ethyl ether*. B. p. 152°/770 mm.; *M* 143·23; n_C 1·42010, n_D 1·42261, n_F 1·42870, $n_{G'}$ 1·43329; R_C 43·78, R_D 44·00, R_F 44·56, $R_{G'}$ 44·97; Mn_D^{20} 203·76. Densities determined: d_4^{20} 0·8282, $d_4^{40\cdot0}$ 0·8105, $d_4^{62\cdot2}$ 0·7905, $d_4^{86\cdot8}$ 0·7678.

t	*H*	d_4^t	γ	*P*	*t*	*H*	d_4^t	γ	*P*
17·3°	12·69	0·8306	24·54	383·8	61·5°	10·94	0·7911	20·15	383·6
41·0	11·77	0·8096	22·19	384·0	87·0	9·93	0·7676	17·75	383·1
								Mean	383·6

625. *Ethyl* n-*propyl ketoxime* O-n-*propyl ether.* B. p. 170·5°/760 mm.; *M* 157·25; n_C 1·42421, n_D 1·42671, n_F 1·43286, $n_{G'}$ 1·43733; R_C 48·33, R_D 48·58, R_F 49·20, $R_{G'}$ 49·64; Mn_D^{20} 224·35. Densities determined : d_4^{20} 0·8305, $d_4^{40\cdot0}$ 0·8135, $d_4^{60\cdot6}$ 0·7958, $d_4^{86\cdot3}$ 0·7734.

t	*H*	d_4^t	γ	*P*	*t*	*H*	d_4^t	γ	*P*
20·3°	12·86	0·8302	24·86	422·9	59·6°	11·33	0·7967	21·02	422·7
40·2	12·20	0·8133	23·10	423·9	86·7	10·24	0·7730	18·43	421·5
								Mean	422·8

626. *Di*-n-*propyl ketoxime* O-*ethyl ether.* B. p. 170·5°/765 mm.; *M* 157·25; n_C 1·42386, n_D 1·42636, n_F 1·43253, $n_{G'}$ 1·43638; R_C 48·40, R_D 48·65, R_F 49·26, $R_{G'}$ 49·68; Mn_D^{20} 224·30. Densities determined : d_4^{20} 0·8288, $d_4^{40\cdot0}$ 0·8121, $d_4^{61\cdot8}$ 0·7932, $d_4^{86\cdot3}$ 0·7718.

20·1°	12·72	0·8287	24·54	422·3	61·5°	11·13	0·7935	20·56	422·0
43·2	11·93	0·8094	22·48	423·0	86·6	10·13	0·7715	18·20	421·0
								Mean	421·1

627. *Di*-n-*propyl ketoxime* O-n-*propyl ether.* B. p. 187°/749 mm.; *M* 171·28; n_C 1·42824, n_D 1·43073, n_F 1·43683, $n_{G'}$ 1·44143; R_C 53·04, R_D 53·31, R_F 53·96, $R_{G'}$ 54·46; Mn_D^{20} 234·02. Densities determined : d_4^{20} 0·8312, $d_4^{41\cdot7}$ 0·8127, $d_4^{61\cdot0}$ 0·7963, $d_4^{86\cdot9}$ 0·7739.

21·0°	12·92	0·8303	24·98	461·2	61·0°	11·35	0·7963	21·04	460·7
40·6	12·14	0·8136	23·00	461·0	87·3	10·50	0·7739	18·92	461·6
								Mean	461·1

628. NN-*Diethylhydrazine.* B. p. 99·5—100°/762 mm.; *M* 88·16; n_C 1·41860, n_D 1·42136, n_F 1·42745, $n_{G'}$ 1·43225; R_C 27·85, R_D 28·01, R_F 28·37, $R_{G'}$ 28·64; Mn_D^{20} 125·31. Densities determined : d_4^{20} 0·7988, $d_4^{41\cdot3}$ 0·7791, $d_4^{59\cdot7}$ 0·7623.

24·4°	13·20	0·7947	24·42	246·6	60·6°	11·66	0·7615	20·67	247·2
41·8	12·45	0·7786	22·57	247·0				Mean	246·9

629. NN-*Di*-n-*propylhydrazine.* B. p. 31·5°/7 mm.; *M* 116·21; n_C 1·42412, n_D 1·42661, n_F 1·43267, $n_{G'}$ 1·43716; R_C 37·09, R_D 37·29, R_F 37·75, $R_{G'}$ 38·09; Mn_D^{20} 165·79. Densities determined : d_4^{20} 0·7997, $d_4^{41\cdot0}$ 0·7819, $d_4^{60\cdot7}$ 0·7644.

24·5°	13·31	0·7959	24·66	325·4	61·0°	11·80	0·7641	20·99	325·5
41·1	12·70	0·7818	23·12	326·0				Mean	325·6

No measurements were carried out at 86° because of the slight decomposition due to prolonged heating at this temperature (small bubbles seen in the capillary tube of the surface-tension apparatus and in the pycnometer).

630. NN-*Di*-n-*butylhydrazine.* B. p. 61°/8 mm.; *M* 144·26; n_C 1·43184, n_D 1·43430, n_F 1·44033, $n_{G'}$ 1·44481; R_C 46·30, R_D 46·54, R_F 47·10, $R_{G'}$ 47·51; Mn_D^{20} 206·91. Densities determined : d_4^{20} 0·8078, $d_4^{40\cdot0}$ 0·7924.

22·6°	13·82	0·8058	25·93	404·0	40·7°	13·17	0·7919	24·28	404·4
								Mean	404·2

631. NN-*Di*-n-*amylhydrazine.* B. p. 87°/7 mm.; *M* 172·31; n_C 1·43526, n_D 1·43771, n_F 1·44363, $n_{G'}$ 1·44818; R_C 55·49, R_D 55·76, R_F 56·42, $R_{G'}$ 56·92; Mn_D^{20} 247·73. Densities determined : d_4^{20} 0·8107, $d_4^{41\cdot0}$ 0·7948, $d_4^{60\cdot9}$ 0·7797.

16·1°	14·43	0·8137	27·34	484·2	61·1°	12·72	0·7795	23·08	484·5
41·0	13·46	0·7948	24·91	484·3				Mean	484·3

Slight decomposition occurred after prolonged heating at 60°; the measurements of surface tension and density were completed before decomposition was visible.

632. *Di*-n-*amylnitrosamine.* B. p. 130·5°/12 mm.; *M* 186·30; n_C 1·44831, n_D 1·45122, n_F 1·45839, $n_{G'}$ 1·46446; R_C 55·89, R_D 56·20, R_F 56·97, $R_{G'}$ 56·62; Mn_D^{20} 270·36. Densities determined : d_4^{20} 0·8930, $d_4^{40\cdot7}$ 0·8776, $d_4^{61\cdot0}$ 0·8627, $d_4^{87\cdot3}$ 0·8436.

20·2°	14·58	0·8929	30·31	489·6	61·7°	13·35	0·8622	26·80	491·6
41·0	13·87	0·8774	28·33	389·9	86·3	12·59	0·8443	24·75	492·2
								Mean	490·8

633. *Di-*n*-hexylnitrosamine.* B. p. 155°/11 mm.; M 214·35; n_{C} 1·45042, n_{D} 1·45322, n_{F} 1·46026, $n_{\mathrm{G'}}$ 1·46595; R_{C} 65·19, R_{D} 65·54, R_{F} 66·42, $R_{\mathrm{G'}}$ 67·13; Mn_{D}^{20} 311·49. Densities determined: d_4^{20} 0·8844, $d_4^{40\cdot9}$ 0·8693, $d_4^{61\cdot0}$ 0·8551, $d_4^{86\cdot1}$ 0·8380.

t	H	d_4^t	γ	P	t	H	d	γ	P
19·9°	14·62	0·8845	30·11	567·7	61·3°	13·38	0·8459	26·63	569·6
42·1	13·92	0·8685	28·15	568·4	86·7	12·59	0·8376	24·55	569·6
								Mean	569·6

634. *Di-*n*-hexylamine.* B. p. 236—236·5°/758 mm.; M 185·35; n_{C} 1·43209, n_{D} 1·43445, n_{F} 1·43999, $n_{\mathrm{G'}}$ 1·44418; R_{C} 60·95, R_{D} 61·25, R_{F} 61·92, $R_{\mathrm{G'}}$ 62·43; Mn_{D}^{20} 265·88. Densities determined: d_4^{20} 0·7889, $d_2^{41\cdot2}$ 0·7736, $d_4^{60\cdot1}$ 0·7596, $d_4^{84\cdot1}$ 0·7418.

t	Δp	d_4^t	ϕ	γ	P	t	Δp	d_4^t	ϕ	γ	P
23·5°	4958	0·7863	1·0135	27·10	537·8	60·4°	4328	0·7594	1·0150	23·69	538·5
40·5	4708	0·7741	1·0140	25·75	539·4	85·0	3957	0·7411	1·0160	21·68	539·7
										Mean	538·9

635. *Dimethyl ketazine.* B. p. 133°/763 mm.; M 112·18; n_{C} 1·44979, n_{D} 1·45347, n_{F} 1·46244, $n_{\mathrm{G'}}$ 1·46979; R_{C} 35·78, R_{D} 36·04, R_{F} 36·65, $R_{\mathrm{G'}}$ 37·15; Mn_{D}^{20} 163·05. Densities determined: d_4^{20} 0·8422, $d_4^{40\cdot1}$ 0·8242, $d_4^{60\cdot5}$ 0·8053.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
20·3°	13·58	0·8419	26·62	302·7	62·0°	11·77	0·8043	22·04	302·2
41·1	12·76	0·8233	24·46	303·0				Mean	302·6

636. *Ethyl methyl ketazine.* B. p. 169°/765 mm.; M 140·23; n_{C} 1·45081, n_{D} 1·45417, n_{F} 1·46203, $n_{\mathrm{G'}}$ 1·46930; $\mathrm{R_C}$ 45·00, R_{D} 45·30, R_{F} 46·02, $R_{\mathrm{G'}}$ 46·59; Mn_{D}^{20} 203·92. Densities determined: d_4^{20} 0·8387, $d_4^{40\cdot2}$ 0·8215, $d_4^{60\cdot6}$ 0·8042, $d_4^{84\cdot5}$ 0·7829.

17·6°	13·73	0·8409	26·88	379·7	61·3°	12·02	0·8036	22·49	380·0
42·0	12·78	0·8200	24·40	380·1	84·5	11·21	0·7829	20·43	380·8
								Mean	380·2

637. *Methyl* n-*propyl ketazine.* B. p. 202°/757 mm.; M 168·28; n_{C} 1·45390, n_{D} 1·45712, n_{F} 1·46529, $n_{\mathrm{G'}}$ 1·47175; R_{C} 54·30, R_{D} 54·63, R_{F} 55·47, $R_{\mathrm{G'}}$ 56·14; Mn_{D}^{20} 245·20. Densities determined: d_4^{20} 0·8391, $d_4^{41\cdot2}$ 0·8217, $d_4^{59\cdot6}$ 0·8067, $d_4^{85\cdot3}$ 0·7857.

18·9°	13·87	0·8400	27·13	457·2	61·8°	12·26	0·8409	22·97	457·7
40·8	13·09	0·8220	25·05	458·0	88·5	11·26	0·7831	20·53	457·4
								Mean	457·6

638. *Diethyl ketazine.* B. p. 196°/757 mm.; M 168·28; n_{C} 1·45301, n_{D} 1·45672, n_{F} 1·46436, $n_{\mathrm{G'}}$ 1·47104; R_{C} 54·08, R_{D} 54·46, R_{F} 55·25, $R_{\mathrm{G'}}$ 55·92; Mn_{D}^{20} 245·13. Densities determined: d_4^{20} 0·8412, $d_4^{40\cdot6}$ 0·8244, $d_4^{60\cdot6}$ 0·8081, $d_4^{85\cdot9}$ 0·7878.

20·7°	13·56	0·8406	26·54	454·4	61·3°	12·11	0·8075	22·77	455·2
40·5	12·80	0·8247	24·58	454·3	86·9	11·19	0·7870	20·50	455·0
								Mean	454·7

639. *Ethyl* n-*propyl ketazine.* B. p. 97°/9 mm.; M 196·33; n_{C} 1·45441, n_{D} 1·45811, n_{F} 1·46547, $n_{\mathrm{G'}}$ 1·47276; $\mathrm{R_C}$ 63·44, R_{D} 63·89, R_{F} 64·78, $R_{\mathrm{G'}}$ 65·65; Mn_{D}^{20} 286·27. Densities determined: d_4^{20} 0·8387, $d_4^{40\cdot7}$ 0·8229, $d_4^{60\cdot0}$ 0·8086, $d_4^{85\cdot9}$ 0·7889.

21·3°	13·57	0·8377	26·47	531·6	60·7°	12·25	0·8081	23·05	532·3
40·5	12·96	0·8231	24·84	532·5	86·1	11·31	0·7887	20·77	531·4
								Mean	532·0

640. *Di-*n*-propyl ketazine.* B. p. 118°/7 mm.; M 224·38; n_{C} 1·45581, n_{D} 1·45951, n_{F} 1·46660, $n_{\mathrm{G'}}$ 1·47284; R_{C} 72·85, R_{D} 73·34, R_{F} 74·31, $R_{\mathrm{G'}}$ 75·16; Mn_{D}^{20} 327·48. Densities determined: d_4^{20} 0·8372, $d_4^{40\cdot1}$ 0·8229, $d_4^{60\cdot0}$ 0·8088, $d_4^{85\cdot7}$ 0·7893.

24·1°	13·56	0·8342	26·34	609·3	61·7°	12·15	0·8076	22·85	607·4
40·8	12·89	0·8224	24·68	608·1	87·1	11·40	0·7883	20·87	608·8
								Mean	608·4

641. β-*Ethylaminopropionitrile.* B. p. 78·5°/11 mm.; *M* 98·15; n_C 1·43031, n_D 1·43269, n_F 1·43865, $n_{G'}$ 1·44284; R_C 28·57, R_D 28·71, R_F 29·06, $R_{G'}$ 29·30; Mn_D^{20} 140·62. Densities determined: d_4^{20} 0·8878, $d_4^{40\cdot2}$ 0·8711, $d_4^{61\cdot4}$ 0·8534, $d_4^{85\cdot5}$ 0·8338.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
24·1°	15·78	0·8844	32·49	265·0	61·3°	14·48	0·8535	28·77	266·3
40·6	15·27	0·8708	30·96	265·9	87·1	13·64	0·8325	26·44	267·0
								Mean	266·6

642. β-n-*Propylaminopropionitrile.* B. p. 91°/11 mm.; *M* 112·16; n_C 1·43292, n_D 1·43535, n_F 1·44107, $n_{G'}$ 1·44547; R_C 33·23, R_D 33·40, R_F 33·78, $R_{G'}$ 34·07; Mn_D^{20} 160·99. Densities determined: d_4^{20} 0·8771, $d_4^{42\cdot6}$ 0·8598, $d_4^{60\cdot8}$ 0·8450, $d_4^{85\cdot6}$ 0·8245.

t	Δp	d_4^t	ϕ	γ	P	t	Δp	d_4^t	ϕ	γ	P
18·8°	5776	0·8780	1·0130	31·56	302·8	60·7°	5062	0·8451	1·0142	27·69	304·5
40·2	5399	0·8617	1·0136	29·51	303·4	85·6	4688	0·8245	1·0150	25·66	306·2
										Mean	304·2

643. β-n-*Butylaminopropionitrile.* B. p. 100°/9 mm.; *M* 126·20; n_C 1·43567, n_D 1·43801, n_F 1·44376, $n_{G'}$ 1·44812; R_C 37·75, R_D 37·93, R_F 38·36, $R_{G'}$ 38·68; Mn_D^{20} 181·48. Densities determined: d_4^{20} 0·8736, $d_4^{40\cdot6}$ 0·8572, $d_4^{61\cdot6}$ 0·8407, $d_4^{85\cdot6}$ 0·8217.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
16·2°	15·26	0·8766	31·14	340·1	61·0°	13·98	0·8412	27·38	343·2
40·3	14·56	0·8574	29·06	341·8	86·0	13·27	0·8214	25·44	345·6
								Mean	342·7

t	Δp	d_4^t	ϕ	γ	P	t	Δp	d_4^t	ϕ	γ	P
18·6°	5613	0·8746	1·0133	30·67	339·6	60·8°	4974	0·8413	1·0144	27·21	342·6
40·2	5285	0·8575	1·0138	28·90	341·2	84·8	4592	0·8223	1·0153	25·14	343·7
										Mean	341·8

644. β-n-*Amylaminopropionitrile.* B. p. 114°/10 mm.; *M* 140·23; n_C 1·43787, n_D 1·44028, n_F 1·44600, $n_{G'}$ 1·45027; R_C 42·39, R_D 42·59, R_F 43·07, $R_{G'}$ 43·43; Mn_D^{20} 201·97. Densities determined: d_4^{20} 0·8683, $d_4^{41\cdot6}$ 0·8520, $d_4^{61\cdot0}$ 0·8376, $d_4^{85\cdot9}$ 0·8182.

22·2°	5385	0·8666	1·0137	29·44	376·9	60·0°	4843	0·8384	1·0148	26·50	379·5
40·6	5079	0·8528	1·0143	27·79	377·5	84·0	4507	0·8196	1·0155	24·68	381·4
										Mean	378·8

645. β-n-*Hexylaminopropionitrile.* B. p. 126°/9 mm.; *M* 154·25; n_C 1·44084, n_D 1·44325, n_F 1·44888, $n_{G'}$ 1·45314; R_C 47·07, R_D 47·30, R_F 47·83, $R_{G'}$ 48·20; Mn_D^{20} 222·63. Densities determined: d_4^{20} 0·8651, $d_4^{40\cdot0}$ 0·8508, $d_4^{59\cdot7}$ 0·8366, $d_4^{86\cdot1}$ 0·8168.

18·4°	5483	0·8663	1·0135	29·97	416·6	61·0°	4885	0·8357	1·0146	26·73	419·7
40·0	5182	0·8508	1·0140	28·34	418·3	86·2	4564	0·8167	1·0153	24·99	422·2
										Mean	419·2

646. β-*Diethylaminopropionitrile.* B. p. 76°/11 mm.; *M* 126·20; n_C 1·43292, n_D 1·43540, n_F 1·44136, $n_{G'}$ 1·43540; R_C 37·87, R_D 38·06, R_F 38·52, $R_{G'}$ 38·85; Mn_D^{20} 181·15. Densities determined: d_4^{20} 0·8659, $d_4^{40\cdot5}$ 0·8492, $d_4^{60\cdot5}$ 0·8336, $d_4^{86\cdot7}$ 0·8116.

	H	d_4^t	γ	P	t	H	d_4^t	γ	P
17·1°	15·09	0·8683	30·51	341·6	60·9°	13·52	0·8333	26·23	342·7
20·9	14·93	0·8652	30·08	341·6	86·6	12·64	0·8117	23·89	343·7
40·5	14·25	0·8492	28·17	342·4				Mean	342·4

647. β-*Di*-n-*propylaminopropionitrile.* B. p. 105·5°/11 mm., *M* 154·25; n_C 1·43524, n_D 1·43771, n_F 1·44361, $n_{G'}$ 1·44800; R_C 47·05, R_D 47·28, R_F 47·84, $R_{G'}$ 48·25; Mn_D^{20} 221·77. Densities determined: d_4^{20} 0·8558, $d_4^{41\cdot5}$ 0·8392, $d_4^{61\cdot4}$ 0·8249, $d_4^{86\cdot5}$ 0·8055.

14·1°	14·74	0·8603	29·52	417·9	61·5°	13·26	0·8248	25·46	420·1
41·3	13·90	0·8394	27·16	419·5	87·3	12·47	0·8049	23·37	421·3
								Mean	419·7

648. β-*Di*-n-*butylaminopropionitrile.* B. p. 120°/10 mm.; *M* 182·31; n_C 1·44009, n_D 1·44255, n_F 1·44844, $n_{G'}$ 1·45292; R_C 56·33, R_D 56·60, R_F 57·25, $R_{G'}$ 57·74; Mn_D^{20} 263·00. Densities determined: d_4^{20} 0·8532, $d_4^{40·9}$ 0·8380, $d_4^{59·9}$ 0·8244, $d_4^{85·8}$ 0·8063.

t	*H*	d_4^t	γ	*P*	*t*	*H*	d_4^t	γ	*P*
19·9°	14·70	0·8533	29·20	496·7	60·6°	13·42	0·8239	25·74	498·4
40·5	14·07	0·8383	27·46	497·8	85·9	12·63	0·8062	23·71	499·0
								Mean	498·0

649. β-*Di*-n-*amylaminopropionitrile.* B. p. 149°/8 mm.; *M* 210·36; n_C 1·44342, n_D 1·44586, n_F 1·45178, $n_{G'}$ 1·45632; R_C 65·55, R_D 65·87, R_F 66·62, $R_{G'}$ 67·19; Mn_D^{20} 304·09. Densities determined; d_4^{20} 0·8515, $d_4^{41·1}$ 0·8363, $d_4^{61·3}$ 0·8226, $d_4^{86·6}$ 0·8044.

t	Δ*p*	d_4^t	*ϕ*	γ	*P*	*t*	Δ*p*	d_4^t	*ϕ*	γ	*P*
21·0°	5238	0·8508	1·0139	28·64	572·0	60·2°	4701	0·8234	1·0149	25·73	575·4
39·5	4987	0·8374	1·0143	27·28	574·1	86·2	4338	0·8047	1·0158	23·77	577·2
										Mean	574·7

650. β-*Methoxypropionitrile,* B. p. 165·5°/759 mm.; *M* 85·11; n_C 1·40111, n_D 1·40317, n_F 1·40793, $n_{G'}$ 1·41260; R_C 22·01, R_D 22·11, R_F 22·34, $R_{G'}$ 22·58; Mn_D^{20} 119·43. Densities determined: d_4^{20} 0·9398, $d_4^{40·6}$ 0·9209, $d_4^{60·4}$ 0·9011, $d_4^{87·0}$ 0·8763.

13·2°	6747	0·9464	1·0120	36·82	221·5	59·9°	5676	0·9016	1·0136	31·03	222·8
40·1	6106	0·9214	1·0129	33·35	222·0	86·0	5156	0·8773	1·0145	28·21	223·6
										Mean	222·5

651. β-*Ethoxypropionitrile.* B. p. 58°/10 mm.; *M* 99·13; n_C 1·40513, n_D 1·40751, n_F 1·41216, $n_{G'}$ 1·41651; R_C 26·67, R_D 26·81, R_F 27·08, $R_{G'}$ 27·33; Mn_D^{20} 139·53. Densities determined: d_4^{20} 0·9112, $d_4^{42·0}$ 0·8913, $d_4^{59·5}$ 0·8749, $d_4^{86·5}$ 0·8512.

t	*H*	d_4^t	γ	*P*	*t*	*H*	d_4^t	γ	*P*
19·6°	14·90	0·9116	31·62	257·9	61·6°	13·44	0·8730	27·32	259·6
41·2	14·14	0·8920	29·37	258·7	86·9	12·60	0·8508	24·96	259·0
								Mean	258·6

652. β-n-*Propoxypropionitrile.* B. p. 73·5°/10 mm.; *M* 113·16; n_C 1·41082, n_D 1·41306, n_F 1·41820, $n_{G'}$ 1·42232; R_C 31·32, R_D 31·47, R_F 31·82, $R_{G'}$ 32·09; Mn_D^{20} 159·91. Densities determined: d_4^{20} 0·8967, $d_4^{42·4}$ 0·8772, $d_4^{62·5}$ 0·8601, $d_4^{85·7}$ 0·8391.

20·7°	14·57	0·8961	30·40	296·5	61·9°	13·20	0·8606	26·45	298·2
40·0	13·89	0·8793	28·44	297·2	84·5	12·52	0·8402	24·59	299·9
								Mean	298·0

653. β-n-*Butoxypropionitrile.* B. p. 91°/10 mm.; *M* 127·18; n_C 1·41607, n_D 1·41816, n_F 1·42317, $n_{G'}$ 1·42770; R_C 35·91, R_D 36·07, R_F 36·45, $R_{G'}$ 36·78; Mn_D^{20} 180·37. Densities determined: d_4^{20} 0·8890, $d_4^{39·3}$ 0·8734, $d_4^{59·7}$ 0·8570, $d_4^{85·6}$ 0·8353.

14·9°	14·64	0·8930	30·44	334·5	61·6°	13·18	0·8553	26·24	336·6
19·9	14·40	0·8891	29·81	334·3	86·8	12·48	0·8343	24·24	338·2
40·2	13·87	0·8727	28·18	335·8				Mean	335·9

654. β-n-*Amyloxypropionitrile.* B. p. 117°/18 mm.; *M* 141·21; n_C 1·42225, n_D 1·42446, n_F 1·42961, $n_{G'}$ 1·43337; R_C 40·55, R_D 40·73, R_F 41·16, $R_{G'}$ 41·51; Mn_D^{20} 201·15. Densities determined: d_4^{20} 0·8856, $d_4^{40·3}$ 0·8701, $d_4^{60·8}$ 0·8541, $d_4^{86·5}$ 0·8329.

t	Δ*p*	d_4^t	*ϕ*	γ	*P*	*t*	Δ*p*	d_4^t	*ϕ*	γ	*P*
15·6°	5624	0·8890	1·0135	30·74	374·1	60·2°	4906	0·8546	1·0149	26·85	376·2
40·5	5238	0·8699	1·0142	28·65	375·6	85·2	4538	0·8339	1·0157	24·86	378·1
										Mean	376·0

655. β-n-*Hexyloxypropionitrile.* B. p. 115·5°/9 mm.; *M* 155·24; n_C 1·42568, n_D 1·42787, n_F 1·43314, $n_{G'}$ 1·43726; R_C 45·20, R_D 45·41, R_F 45·89, $R_{G'}$ 46·28; Mn_D^{20} 221·67. Densities determined: d_4^{20} 0·8794, $d_4^{40·0}$ 0·8646, $d_4^{60·3}$ 0·8483, $d_4^{86·1}$ 0·8284.

19·0°	5562	0·8802	1·0135	30·40	414·1	60·4°	4939	0·8482	1·0147	27·03	417·3
40·3	5248	0·8644	1·0141	28·70	415·7	85·8	4562	0·8286	1·0155	24·98	418·9
										Mean	416·5

656. *Ethyl azodiformate.* B. p. 104·5°/12 mm.; *M* 174·16; n_C 1·41921, n_D 1·42176, n_F and $n_{G'}$ could not be determined; R_C 39·54, R_D 39·89; Mn_D^{20} 247·67. Densities determined: d_4^{20} 1·1129, $d_4^{44·7}$ 1·0876, $d_4^{61·4}$ 1·0703, $d_4^{85·9}$ 1·0450.

	H	d_4^t	γ	*P*	*t*	*H*	d_4^t	γ	*P*
22·1°	12·78	1·1107	33·05	376·0	61·7°	11·63	1·0700	28·97	377·6
42·1	12·22	1·0903	31·02	377·0	87·3	10·75	1·0437	26·12	377·2
								Mean	377·0

657. n-*Propyl azodiformate.* B. p. 122°/11 mm.; *M* 202·21; n_C 1·42459, n_D 1·42712; R_C 48·69, R_D 48·94; Mn_D^{20} 288·57. Densities determined: d_4^{20} 1·0610, $d_4^{40·0}$ 1·0418, $d_4^{60·2}$ 1·0234, $d_4^{86·5}$ 0·9978.

20·3°	13·07	1·0607	32·28	454·4	61·2°	11·75	1·0224	27·97	454·8
40·0	12·34	1·0418	29·93	454·0	87·6	10·94	0·9967	25·39	455·4
								Mean	454·7

658. n-*Butyl azodiformate.* B. p. 142°/11 mm.; *M* 230·26; n_C 1·43113, n_D 1·43370; R_C 57·58, R_D 57·88; Mn_D^{20} 330·12. Densities determined: d_4^{20} 1·0354, $d_4^{39·9}$ 1·0174, $d_4^{59·5}$ 1·0000, $d_4^{86·1}$ 0·9750.

16·8°	13·14	1·0383	31·76	529·5	60·0°	11·92	0·9995	27·74	528·8
40·1	12·41	1·0172	29·39	527·1	86·5	11·22	0·9752	25·47	530·5
								Mean	529·0

659. *Ethyl* n-*propyl carbonate.* B. p. 145·5°/760 mm.; *M* 132·16; n_C 1·39167, n_D 1·39357, n_F 1·39818, $n_{G'}$ 1·41043; R_C 32·87, R_D 33·01, R_F 33·36, $R_{G'}$ 33·59; Mn_D^{20} 184·18. Densities determined: d_4^{20} 0·9567, $d_4^{40·5}$ 0·9361, $d_4^{60·9}$ 0·9155, $d_4^{86·0}$ 0·8894.

16·9°	12·07	0·9598	26·97	313·8	61·9°	10·47	0·9145	22·29	314·0
21·9	11·87	0·9548	26·39	313·7	87·7	9·58	0·8877	19·84	314·0
41·0	11·25	0·9356	24·51	314·3				Mean	314·0

660. n-*Butyl ethyl carbonate.* B. p. 167°/759 mm.; *M* 146·18; n_C 1·39887, n_D 1·40082, n_F 1·40557, $n_{G'}$ 1·40886; R_C 37·51, R_D 37·67, R_F 38·07, $R_{G'}$ 38·34; Mn_D^{20} 204·77. Densities determined: d_4^{20} 0·9424, $d_4^{40·9}$ 0·9235, $d_4^{61·5}$ 0·9034, $d_4^{85·3}$ 0·8806.

18·8°	12·26	0·9435	26·93	352·9	61·4°	10·76	0·9035	22·69	352·9
40·9	11·49	0·9235	24·70	352·9	86·2	9·99	0·8797	20·46	353·4
								Mean	353·0

661. n-*Amyl ethyl carbonate.* B. p. 188°/760 mm.; *M* 160·21; n_C 1·40572, n_D 1·40771, n_F 1·41259, $n_{G'}$ 1·41598; R_C 42·14, R_D 42·34, R_F 42·79, $R_{G'}$ 43·10; Mn_D^{20} 225·53. Densities determined: d_4^{20} 0·9329, $d_4^{40·0}$ 0·9157, $d_4^{59·5}$ 0·8977, $d_4^{85·1}$ 0·8756.

23·9°	12·34	0·9295	26·70	391·8	60·7°	11·10	0·8966	23·17	392·0
40·7	11·76	0·9151	25·06	391·7	87·0	10·19	0·8739	20·73	391·1
								Mean	391·7

662. *Ethyl* n-*hexyl carbonate.* B. p. 206·5°/764 mm.; *M* 174·23; n_C 1·41093, n_D 1·41296, n_F 1·41784, $n_{G'}$ 1·42132; R_C 46·76, R_D 46·97, R_F 47·45, $R_{G'}$ 47·80; Mn_D^{20} 246·19. Densities determined: d_4^{20} 0·9250, $d_4^{40·2}$ 0·9070, $d_4^{60·1}$ 0·8892, $d_4^{86·1}$ 0·8663.

16·1°	13·01	0·9285	28·12	432·1	60·5°	11·48	0·8888	23·75	432·7
40·4	12·12	0·9068	25·59	432·1	87·1	10·57	0·8654	21·30	432·5
								Mean	432·4

663. n-*Butyl* n-*propyl carbonate.* B. p. 187°/764 mm.; *M* 160·21; n_C 1·40514, n_D 1·40711, n_F 1·41195, $n_{G'}$ 1·41527; R_C 42·12, R_D 42·30, R_F 42·75, $R_{G'}$ 43·05; Mn_D^{20} 225·43. Densities determined: d_4^{20} 0·9325, $d_4^{40·6}$ 0·9133, $d_4^{60·0}$ 0·8959, $d_4^{85·9}$ 0·8714.

16·1°	12·54	0·9361	27·33	391·3	61·0	11·04	0·8950	23·00	392·0
20·1	12·42	0·9324	26·96	391·5	86·7	10·21	0·8707	20·70	392·5
40·9	11·75	0·9130	24·92	392·3				Mean	391·9

664. *Di*-n-*amyl carbonate.* B. p. 238·5°/757 mm.; M 202·29; n_C 1·41847, n_D 1·42056, n_F 1·42561, $n_{G'}$ 1·42923; R_C 55·94, R_D 56·18, R_F 56·77, $R_{G'}$ 57·19; Mn_D^{20} 287·37. Densities determined: d_4^{20} 0·9123, $d_4^{40\cdot5}$ 0·8949, $d_4^{61\cdot0}$ 0·8788, $d_4^{86\cdot5}$ 0·8574.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
19·9°	13·10	0·9124	27·83	509·2	60·7°	11·66	0·8790	23·86	508·6
40·4	12·37	0·8950	25·77	509·3	86·7	10·96	0·8572	21·87	510·3
								Mean	509·4

665. *Di*-n-*hexyl carbonate.* B. p. 146·5°/9 mm.; M 230·34; n_C 1·42519, n_D 1·42727, n_F 1·43252, $n_{G'}$ 1·43619; R_C 65·40, R_D 65·69, R_F 66·38, $R_{G'}$ 66·85; Mn_D^{20} 328·77. Densities determined: d_4^{20} 0·9009, $d_4^{41\cdot0}$ 0·8850, $d_4^{61\cdot5}$ 0·8692, $d_4^{85\cdot6}$ 0·8501.

t	Δp	d_4^t	ϕ	γ	P	t	Δp	d_4^t	ϕ	γ	P
18·0°	5151	0·9024	1·0149	28·19	588·2	60·2°	4491	0·8702	1·0165	24·62	589·6
40·0	4821	0·8858	1·0157	26·41	589·5	86·0	4086	0·8498	1·0177	22·43	589·8
										Mean	589·3

666. n-*Heptyl cyanide.* B. p. 82·5°/10 mm.; M 125·21; n_C 1·41838, n_D 1·42056, n_F 1·42569, $n_{G'}$ 1·42935; R_C 38·79, R_D 38·97, R_F 39·38, $R_{G'}$ 39·68; Mn_D^{20} 177·88. Densities determined: d_4^{20} 0·8141, $d_4^{40\cdot4}$ 0·7985, $d_4^{60\cdot0}$ 0·7838, $d_4^{86\cdot5}$ 0·7630.

22·5°	5099	0·8122	1·0136	27·87	354·2	61·0°	4521	0·7830	1·0148	24·74	356·7
40·3	4805	0·7986	1·0142	26·28	355·0	86·1	4147	0·7633	1·0157	22·72	358·1
										Mean	356·0

667. n-*Octyl cyanide.* B. p. 100°/11 mm.; M 139·24; n_C 1·42356, n_D 1·42576, n_F 1·43088, $n_{G'}$ 1·43472; R_C 43·49, R_D 43·68, R_F 44·14, $R_{G'}$ 44·48; Mn_D^{20} 198·53. Densities determined: d_4^{20} 0·8164, $d_4^{41\cdot0}$ 0·8016, $d_4^{61\cdot7}$ 0·7866, $d_4^{85\cdot9}$ 0·7691.

23·1°	5206	0·8142	1·1033	28·21	395·0	61·0°	4584	0·7871	1·0146	25·08	395·9
40·2	4927	0·8022	1·0139	26·94	395·4	85·8	4227	0·7692	1·0155	23·15	397·0
										Mean	395·8

414. n-*Hexyl cyanide.* The sample of XVII, **414** was redistilled and the surface tensions determined by the method of maximum bubble pressure. Unlike those obtained by the capillary-rise method, the results were constant and reproducible.

19·1°	5117	0·8107	1·0135	27·97	316·1	61·2°	4384	0·7787	1·0152	24·00	316·0
40·0	4740	0·7949	1·0143	25·93	315·6	86·5	4050	0·7584	1·0160	22·19	318·2
										Mean	316·5

668. *Acrylonitrile.* A commercial sample (Light) was carefully fractionated. B. p. 76·5°/748 mm.; M 53·06; n_C 1·38836, n_D 1·39142, n_F 1·39890, $n_{G'}$ 1·40478; R_C 15·54, R_D 15·64, R_F 15·91, $R_{G'}$ 16·12; Mn_D^{20} 73·83. Densities determined: d_4^{20} 0·8064, $d_4^{41\cdot0}$ 0·7839.

t	H	d_4^t	γ	P	t	H	d_4^t	γ	P
15·1°	14·70	0·8117	27·76	150·1	40·6°	13·58	0·7843	24·80	151·1
17·8	14·62	0·8088	27·53	150·3				Mean	150·5

669. *Benzene.* "AnalaR" benzene was frozen twice and then twice distilled through a Widmer column. B. p. 80·2°/769 mm.; M 78·108; n_C 1·49622, n_D 1·50089, n_F 1·51298, $n_{G'}$ 1·52306; R_C 25·973, R_D 26·181, R_F 26·715, $R_{G'}$ 27·155; Mn_D^{20} 117·23; d_4^{20} 0·8788. $n_{G'}$ was determined with the Hilger–Chance refractometer since the value was outside the range of the Pulfrich refractometer.

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