365. Physical Properties and Chemical Constitution. Part XIX. Five-membered and Six-membered Carbon Rings.

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New experimental data are provided for the calculation of the refractivities at 20° and the parachors of a number of cyclopentane and cyclohexane derivatives. These and those described in Part III (J., 1938, 1338) have been employed in the computation of the constants for the 5-membered and 6-membered carbon rings respectively. The mean values, excluding ketones and halides, are as follows:

	P.	$R_{\mathbf{C}}$.	$R_{\mathbf{D}}$.	$R_{\mathbf{F}}$.	$R_{\mathbf{G'}}$.	$Mn_{\mathbf{D}}^{20}$.
5-Membered carbon ring	$4 \cdot 6$	-0.19	-0.19	-0.19	-0.22	-4.56
6-Membered carbon ring	1.4	-0.15	-0.15	-0.16	-0.17	-3.53

The view seems generally accepted (see, e.g., Eisenlohr, "Spektrochemie organischer Verbindungen: Molekularrefraktion und -dispersion", Ferdinand Enke, 1912, 86) that the contributions of the 5- and 6-membered carbon rings to the molecular refraction are zero. Ruzicka and Boekenoogen (Helv. Chim. Acta, 1931, 14, 1323; compare Ruzicka et al., ibid., 1930, 13, 1158) find the ring increments for 5-, 7-, 8-, and 15-rings to be + 0.04, - 0.10, - 0.47, and - 0.62 respectively, that for the 6-ring being assumed to be zero. They use Eisenlohr's value for CH₂ for the D line of 4.62; the correct value is, however, 4.647 (Part IX, J., 1946, 133). Sugden (J., 1924, 125, 1180) assigns values of 8.5 and 6.1 (compare Sugden and Wilkins, J., 1927, 142) to the 5- and 6-membered rings respectively; the data from which these constants were calculated were not stated, but a value for CH₂ of 39.0 was employed. A comparison of the physical properties of the following isomeric compounds suggests that the contributions of

	P.	$R_{\mathbf{C}}$.	$R_{\mathbf{D}}$.	$R_{\mathbf{F}}.$	$R_{\mathbf{G'}}$.	$Mn_{\bf D}^{20}$ °.
Methylcyclopentane (I)	243.8	27.63	$27 \cdot 77$	28.07	28.24	118.67
Methylcyclopentane (II)		27.79	27.90	$28 \cdot 12$	28.46	118.54
Methylcyclopentane (III)	$243 \cdot 9$	27.69	27.82	$28 \cdot 12$	28.36	118.57
cycloHexane	241.8	27.63	$27 \cdot 75$	28.05	28.27	120.06
Methyl <i>cyclo</i> hexane	280.9	$32 \cdot 36$	$32 \cdot 53$	$32 \cdot 87$	$33 \cdot 12$	$139 \cdot 82$
cycloHeptane	278.9	32.01	$32 \cdot 18$	32.53	32.76	141.73
$I-Methyl-\Delta^2$ -cyclopentene	232.9	$27 \cdot 10$	$27 \cdot 25$	27.51	27.86	117.03
cycloHexene	$230 \cdot 4$	29.96	$27 \cdot 11$	$27 \cdot 47$	27.74	118.82
I-Methyl- Δ^1 -cyclohexene	$269 \cdot 4$	31.66	31.84	$32 \cdot 26$	32.57	139.51
cycloHeptene	$268 \cdot 2$	31.58	31.75	$32 \cdot 17$	$32 \cdot 49$	$140 \cdot 16$
3-Methyl <i>cyclo</i> pentanol	255.0	$29 \cdot 22$	29.37	29.66	29.89	144.97
cycloHexanol (supercooled)	$253 \cdot 3$	29.04	$29 \cdot 16$	$29 \cdot 48$	$29 \cdot 71$	146.83

the rings to the molecular refractivity, although small, are not zero. The data are extracted from Part III (J., 1938, 1323); under methylcyclopentane, I was prepared from 3-methylcyclopentanone, II from 1-methylcyclopentan-1-ol (Eisenlohr, "Fortschritte der Chemie, Physik und physikalischen Chemie", 1925, Band 18, Heft 9, p. 23), and III by heating cyclohexane with aluminium chloride (Wibaut et al., Rec. Trav. chim., 1939, 58, 365). The results for the methylene hydrocarbons (Part III, loc. cit.) have been omitted since the compounds were by-products in thermal decomposition reactions and consequently their absolute purity is doubtful.

The problem was systematically investigated with the aid of the experimental data given in

Part III (loc. cit.) and the new results are recorded in the experimental section. The ring contributions were computed from the relationship:

The constants for 2H were taken from Part IX (loc. cit.), and those for the other reference compounds from earlier papers of this series: for cyclopentane the constants are obtained directly by subtracting $5 \times \text{CH}_2$. All the results for the cyclopentane ring are collected in Table I.

Table I.

Values for the five-carbon ring from cyclopentane compounds.

	P.	$R_{\mathbf{C}}$.	$R_{\mathbf{D}}$.	$R_{\mathbf{F}}$.	$R_{\mathbf{G'}}$.	$Mn_{ m D}^{20}$ °.
cycloPentane	4.9	-0.15	-0.15	-0.14	-0.17	-4.30
Methylcyclopentane	$4 \cdot 3$	-0.11	-0.10	-0.09	-0.15	-4.94
cyclo Pentene	4.5	-0.38	-0.37	-0.39	-0.43	-4.89
I-Methyl- Δ^2 -cyclopentene	$3 \cdot 7$	-0.13	-0.13	-0.14	-0.14	-5.22
cycloPentanol	5.0	-0.21	-0.21	-0.22	-0.22	-4.25
cycloPentyl methyl ether	4.0	-0.16	-0.17	-0.18	-0.21	-4.59
cycloPentyl ethyl ether	$4 \cdot 1$	-0.20	-0.19	-0.19	-0.23	-4.53
cycloPentyl formate	$5\cdot 2$	-0.22	-0.22	-0.22	-0.25	-4.25
cycloPentyl acetate	5.9	-0.13	-0.14	-0.14	-0.16	-4.16
Mean \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	4.6	-0.19	-0.19	-0.19	-0.22	-4.56
cycloPentanone	7.5	0.11	0.12	0.12	0.10	-4.01
3-Methyl <i>cyclo</i> pentanone	5.7	0.10	0.07	0.11		-4.73
cycloPentyl chloride	5.2	-0.06	-0.04	-0.02	-0.03	-3.85
cycloPentyl bromide	6.3	0.07	0.06	0.08	0.05	-1.56
cycloPentyl iodide	7.9	0.19	0.21	0.24	0.23	1.99

In the calculation of the mean values, the results for the cyclic ketones and cyclic halides have been omitted. No definite explanation can be offered of the apparently anomalous refractivities of these compounds; whether these are in fact real and are characteristic of the compounds or whether the differences are due to experimental error is an open question. The latter explanation is the more probable, since the preparation of perfectly pure cyclic halides is extremely difficult; this would suggest that ketones prepared by the decomposition of the pure semicarbazones with aqueous oxalic acid are not as pure as is generally supposed.

The results for the *cyclo*hexane compounds are summarised in Table II: the constants for the ketones and halides are not included in the calculation of the mean values; the two sets of figures for 3-methyl*cyclo*hexanone were obtained by the use of the two alternative reference compounds, methyl *n*-amyl ketone and di-*n*-propyl ketone, respectively (Part V, *J.*, 1940, 171).

TABLE II.

Values for the six-carbon ring from cyclohexane compounds.

	P.	$R_{\mathbf{C}}.$	$R_{\mathbf{D}}$. ·	$R_{\mathbf{F}}$.	$R_{\mathbf{G'}}$.	$Mn_{\bf D}^{20}$ °.
cycloHexane	1.8	-0.12	-0.11	-0.12	-0.12	-3.72
Methylcyclohexane	1.3	-0.03	-0.01	-0.01	-0.04	-4.34
Dicyclohexyl	0.8	-0.18	-0.19	-0.19	-0.20	-3.20
cycloHexene	1.5	-0.27	-0.27	-0.28	-0.30	-3.43
cycloHexanol *		-0.16	-0.17	-0.16	-0.17	-3.19
cycloHexyl methyl ether	1.5	-0.18	-0.18	-0.18	-0.20	-3.66
cycloHexyl ethyl ether	0.5	-0.13	-0.16	-0.18	-0.15	-3.54
cycloHexyl formate	1.3	-0.22	-0.22	-0.21	-0.25	-3.34
cycloHexyl acetate	$2 \cdot 7$	-0.07	-0.08	-0.07	-0.08	-3.34
Mean	1.4	-0.15	-0.15	-0.16	-0.17	-3.53
cycloHexanone	$6 \cdot 1$	-0.10	-0.11	-0.10	-0.12	-3.13
2 -Methyl <i>cyclo</i> hexanone	4.7	0.08	0.08	0.09	0.07	-3.85
	∫ 2·6	-0.08	-0.07	-0.06	-0.08	-3.79
3-Methyl <i>cyclo</i> hexanone	∖ 6.6	0.19	0.21	0.22	0.21	-3.60
4-Methylcyclohexanone	$5 \cdot 4$	0.22	0.22	0.23	0.23	-3.88
cycloHexyl chloride	5.8	0.31	0.31	0.31	0.29	-2.95
cycloHexyl bromide	$2 \cdot 7$	0.06	0.07	0.08	0.06	-0.28
cycloHexyl iodide	$2 \cdot 7$	0.22	0.24	0.29	0.30	3.46

^{*} The experimental data for cyclohexanol (Part III, J., 1938, 1331) require revision as follows: M 100·16; $Mn_D^{20^\circ}$ 146·83; $d_4^{20^\circ}$ 0·9515 (supercooled), $d_4^{20^\circ}$ 0·9475, $d_4^{61\cdot8^\circ}$ 0·9178, $d_4^{86\cdot3^\circ}$ 0·8975.

The data for cycloheptane and cycloheptene (Part III, loc. cit.) provide the following preliminary values for the constants of the seven-carbon ring:

	P.	$R_{\mathbf{C}}.$	$R_{\mathbf{D}}.$	$R_{\mathbf{F}}$.	$R_{\mathbf{G'}}$.	$Mn_{\mathbf{D}}^{20}$ °.
cycloHeptane	-1.3	-0.36	-0.35	-0.34	-0.39	$-2 \cdot 40$
cycloHeptene	-0.4	-0.29	-0.30	-0.28	-0.30	-3.02

Experimental.

cyclo*Pentyl ethyl ether.* 15.5 G. of sodium were "molecularised" under xylene, the xylene replaced by 150 ml. of anhydrous ether, and a solution of 57 g. of *cyclo*pentanol (b. p. 141—142°/769 mm.) in 75 ml. of dry ether added with stirring during 3 hours, and the whole allowed to stand for 12 hours. 103 G. of pure ethyl iodide were added during 2 hours to the resulting solid sodio-compound: the ether boiled gently. After standing overnight, the ether was removed on a water-bath, and the residue distilled from an air-bath; the crude ether was collected at 120—130° (45 g.). Repeated distillation from sodium to constant physical properties yielded 26 g. of pure cyclopentyl ethyl ether, b. p. 122·5°/763 mm. cycloPentyl methyl ether. This was prepared similarly, 97 g. of methyl iodide being used. The yield of the pure cyclopentyl methyl ether, b. p. 105°/763 mm., was 21 g. (Found: C, 72·0; H, 12·1. C₆H₁₂O

requires C, 72.2; H, 11.9%).

cyclo Hexyl methyl ether. The yield of this ether, b. p. 133.5°/762 mm., from 15.5 g. of "molecular" sodium in 100 ml. of dry ether, 66 g. of pure cyclohexanol in 200 ml. of dry ether, and 97 g. of methyl iodide was 20 g.

cycloHexyl ethyl ether. This was prepared as for the methyl ether but from 108 g. of ethyl iodide;
b. p. 148·5—149·5°/763 mm., yield, 27 g.

cyclo Hexyl acetate. Attempts to prepare this ester by refluxing a mixture of 50 g. of cyclohexanol, 90 g. of glacial acetic acid, and 4 g. of concentrated sulphuric acid gave a product of b. p. $160-195^{\circ}$. The fractionation of B.D.H. "pure" cyclohexyl acetate yielded a middle fraction, b. p. $161^{\circ}/770$ mm., $d_{s}^{20^{\circ}} 0.9609$, $n_{D}^{20^{\circ}} 1.4435$, whence $R_{D} 39.27$; this was evidently impure and contained free cyclohexanol. The pure ester was readily prepared by making use of the experimental fact that hydrogen chloride dissolves in cyclohexanol without the formation of any appreciable quantity of cyclohexyl chloride. 75 G. of pure cyclohexanol were treated with dry hydrogen chloride until 1.5 g. were absorbed, 135 g. of A.R. glacial acetic acid were added, and the mixture was refluxed for 14 hours. The product was poured into excess of water, the ester layer separated and washed successively with water, saturated sodium hydrogen carbonate solution, and water, dried (MgSO₄), and fractionated. The yield of cyclohexyl acetate, b. p. 172°/752 mm., was 57 g.

cycloHexyl formate. When a mixture of 50 g. of pure cyclohexanol and 70 g. of A.R. 98/100% formic acid was refluxed for 6 hours, the product, isolated in the usual way, had b. p. 160-170°. Fractionation of B.D.H. "pure" cyclohexyl formate gave a large middle fraction of b. p. $172 \cdot 5^{\circ}/772 \text{ mm.}$, $d_{\rm s}^{20^{\circ}}$ 0.9872, $n_{\rm b}^{20^{\circ}}$ 1.4437, whence $R_{\rm b}$ 34.47. The pure ester was prepared by refluxing a mixture of 75 g. of pure cyclohexanol containing 1.5 g. of dissolved hydrogen chloride and 103 g. of A.R. 98/100% formic acid for 14 hours, pouring the mixture into excess of concentrated calcium chloride solution (to facilitate separation of the crude ester), and working up as for cyclohexyl acetate. After about 6 g. of cyclohexene

had passed over, pure cyclohexyl formate distilled at 159·5—160°/757 mm.; yield, 57 g. cycloPentyl formate. This was prepared by refluxing a mixture of 43 g. of distilled cyclopentanol containing 1 g, of dissolved hydrogen chloride and 69 g, of pure A.R. formic acid for 14 hours; after working up as detailed for cyclohexyl formate and fractionating through a Widmer column 26 g. of the pure ester, b. p. 138°/762 mm., were obtained.

cyclo Pentyl acetate. This was prepared as for cyclopentyl formate, 90 g. of A.R. glacial acetic acid

being used instead of formic acid; the yield of ester, b. p. 152.5—153 760 mm., was 27 g. cycloHexyl chloride. A mixture of 150 g. of pure cyclohexanol, 375 ml. of concentrated hydrochloric acid, and 150 g. of anhydrous calcium chloride was refluxed for 16 hours with frequent shaking. The crude chloride layer was separated, washed successively with water, saturated sodium hydrogen carbonate solution, and water, and dried for 24 hours over excess of calcium chloride. The crude dry product was fractionated through a Widmer column: after a low b. p. fraction (ca. 6 g.; mainly cyclohexene) had passed over, 102 g. of cyclohexyl chloride were collected at 141—142°/755 mm.

cyclo Pentyl chloride. In a 500-ml. three-necked flask, equipped with a mechanical stirrer and reflux condenser, were placed 43 g. of cyclopentanol (b. p. 140·5—141·5°/769 mm.), 125 ml. of concentrated hydrochloric acid, and 50 g. of anhydrous calcium chloride. The mixture was heated, with stirring, at

100° for 1 hour and the product was isolated as for the cyclohexyl compound. The yield of cyclopentyl chloride, b. p. 114—115°/777 mm., was 30 g. cycloHexyl bromide. A mixture of 50 g. of pure cyclohexanol and 260 g. of A.R. 47% hydrobromic acid was slowly distilled during 6 hours from a 500-ml. distilling flask. The distillate was diluted with a little water, and the lower layer separated and washed successively with concentrated hydrochloric acid (to remove unchanged alcohol), water, saturated sodium hydrogen carbonate solution, and water, and dried (CaCl₂). The resulting crude bromide (69 g.) was fractionated and the pure cyclohexyl bromide collected at 164°/766 mm.

cycloPentyl bromide. This was prepared from 43 g. of pure cyclopentanol and 260 g. of constant b. p. hydrobromic acid. The crude, dry bromide (60 g.) upon fractionation afforded pure cyclopentyl bromide, b. p. $136.5^{\circ}/763$ mm.

cycloHexyl iodide. Vogel's procedure (B.P. 565,452, 1944) was adopted. The flask was charged with 81 g. of pure cyclohexanol and 10·2 g. of purified red phosphorus, and the special apparatus with 100 g. of iodine. The cyclohexanol was kept at the b. p. until a few ml. of the solution of iodine in the alcohol had collected; the latter was slowly added to the cyclohexanol-phosphorus mixture. Heat was liberated in the subsequent formation of cyclohexyl iodide and only a minute flame was necessary beneath

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the flask to maintain the reaction. After all the iodine had been introduced into the flask, most of the iodide was distilled into the special apparatus. About 70 ml. of water were then added to the contents of the flask, and the distillation continued to remove the remaining iodide. The yield of crude cyclohexyl iodide, after washing successively with water, concentrated hydrochloric acid, water, saturated sodium hydrogen carbonate solution, and water, and drying (CaCl₂), was 145 g. Upon distillation under reduced pressure, the *cyclo*hexyl iodide passed over at 81—83°/20 mm.: a middle fraction, b. p. 81·5°/20 mm., was used for the physical measurements. The pale colour was readily removed by shaking with pure

cycloPentyl iodide. A mixture of 43 g. of pure cyclopentanol and 340 g. of constant b. p. hydriodic acid was slowly distilled during 6 hours from a 500-ml. distilling flask. The crude iodide layer (89 g.) was separated, washed with a little sodium hydrogen sulphite solution to remove the dark colour, and then washed and dried as for the preceding iodide. Distillation of the dry product (83 g.) gave colourless

cyclopentyl iodide, b. p. 58°/22 mm.

Dicyclohexyl. The Eastman Kodak product was shaken mechanically with half its volume of concentrated sulphuric acid, but the latter did not darken. The acid was separated and the hydrocarbon was washed repeatedly with water, dried (CaCl₂), and heated for 5 hours with excess of sodium at 110°. After filtration, the hydrocarbon was distilled. It boiled constantly at 233°/750 mm. and had m. p. 4°.

438. cyclo*Pentyl methyl ether*. B. p. $105^\circ/763$ mm.; M $100\cdot16$; $n_{\rm C}$ $1\cdot41828$, $n_{\rm D}$ $1\cdot42036$, $n_{\rm F}$ $1\cdot42543$, $n_{\rm G'}$ $1\cdot42916$; $R_{\rm C}$ $29\cdot29$, $R_{\rm D}$ $29\cdot42$, $R_{\rm F}$ $29\cdot72$, $R_{\rm G'}$ $29\cdot95$; $Mn_{\rm D}^{20^\circ}$ $142\cdot27$. Densities determined: $d_4^{20^\circ}$ $0\cdot8624$, $d_4^{41\cdot0^\circ}$ $0\cdot8430$, $d_4^{61\cdot5^\circ}$ $0\cdot8240$, $d_4^{87\cdot8^\circ}$ $0\cdot7972$. Apparatus A.

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

t.	H_ullet	$d_{4}^{\mathbf{t}^{\mathbf{o}}}$	γ.	P.	t.	H.	$d_{4}^{t^{\circ}}$.	γ.	P.
16.9°	16.51	0.8653	26.75	$263 \cdot 2$	41.5°	15.23	0.8425	24.03	$263 \cdot 2$
19.1	16.43	0.8632	26.56	$263 \cdot 4$	$60 \cdot 1$	$14 \cdot 15$	0.8253	21.86	$262 \cdot 7$
$24 \cdot 4$	16.13	0.8583	25.92	263.3				Mea	n 263·2

439. cyclo Pentyl ethyl ether. B. p. $122\cdot5^{\circ}/766$ mm.; M $114\cdot18$; $n_{\rm C}$ $1\cdot42102$, $n_{\rm D}$ $1\cdot42316$, $n_{\rm F}$ $1\cdot42831$, $n_{\rm G'}$ $1\cdot43207$; $R_{\rm C}$ $33\cdot95$, $R_{\rm D}$ $34\cdot11$, $R_{\rm F}$ $34\cdot47$, $R_{\rm G'}$ $34\cdot73$; $Mn_{\rm D}^{20^{\circ}}$ $162\cdot50$. Densities determined: $d_4^{20^{\circ}}$ $0\cdot8528$, $d_4^{4^{\circ}-0^{\circ}}$ $0\cdot8334$, $d_4^{6^{\circ}-0^{\circ}}$ $0\cdot8146$, $d_4^{68-3^{\circ}}$ $0\cdot7899$. Apparatus D.

$17 \cdot 2^{\circ}$	12.55	0.8554	26.51	$302 \!\cdot\! 9$	40.9°	11.57	0.8335	23.82	$302 \cdot 6$
21.3	12.34	0.8516	25.95	$302 \cdot 6$	$61 \cdot 1$	10.81	0.8141	21.73	$302 \cdot 8$
$23 \cdot 7$	$12 \cdot 27$	0.8493	25.74	$302 \cdot 8$	86.7	9.78	0.7895	19.07	$302 \cdot 2$
								Mea	n 302·7

440. cyclo Pentyl formate. B. p. 138°/762 mm.; M 114·14; n_0 1·42990, $n_{\rm D}$ 1·43209, $n_{\rm F}$ 1·43741, $n_{\rm G'}$ 1·44127; R_0 29·40, $R_{\rm D}$ 29·53, $R_{\rm F}$ 29·43, $R_{\rm G'}$ 30·08; $Mn_{\rm D}^{20^{\circ}}$ 163·46. Densities determined: $d_4^{20^{\circ}}$ 1·0026, $d_4^{41\cdot3^{\circ}}$ 0·9819, $d_4^{40\cdot4^{\circ}}$ 0·9624, $d_4^{45\cdot3^{\circ}}$ 0·9368. Apparatus A.

15.8°	17.08	1.0068	$32 \cdot 20$	$270 \cdot 1$	$60 \cdot 7^{\circ}$	15.03	0.9621	27.08	$270 \cdot 6$
19.3	17.02	1.0034	31.98	270.5	85.6	13.81	0.9365	24.22	270.4
41.5	15.90	0.9817	29.23	$270 \cdot 2$				Mea	n 270.4

441. cyclo*Pentyl acetate*. B. p. 153°/760 mm.; M 128·17; n_0 1·42962, n_D 1·43178, n_F 1·43708, $n_{G'}$ 1·44094; R_0 33·92, R_D 34·07, R_F 34·43, $R_{G'}$ 34·70; $Mn_D^{20^\circ}$ 183·51. Densities determined : $d_4^{20^\circ}$ 0·9753, $d_4^{40^\circ}$ 7° 0·9540, $d_4^{60^{-1^\circ}}$ 0·9350, $d_4^{86^\circ}$ 0·9086. Apparatus D.

$20 \cdot 4^{\circ} \\ 41 \cdot 4$	 $0.9749 \\ 0.9533$	$\begin{array}{c} 30.67 \\ 28.06 \end{array}$	$309 \cdot 4 \\ 309 \cdot 4$	$60.9^{\circ} \\ 86.1$	$0.9342 \\ 0.9091$		$\substack{309.6\\309.2}$
						Mea	n 309·4

442. cyclo*Pentyl chloride.* B. p. 114·5—115°/777 mm.; M 104·58; $n_{\rm C}$ 1·44894, $n_{\rm D}$ 1·45127, $n_{\rm F}$ 1·45703, $n_{\rm G'}$ 1·46125; $R_{\rm C}$ 27·83, $R_{\rm D}$ 27·96, $R_{\rm F}$ 28·27, $R_{\rm G'}$ 28·50; $Mn_{\rm D}^{20^\circ}$ 151·78. Densities determined: $d_{\rm A'}^{20^\circ}$ 1·0053, $d_{\rm A'}^{40^{-1^\circ}}$ 0·9855, $d_{\rm A'}^{60^{-1^\circ}}$ 0·9846, $d_{\rm A'}^{86^{-1^\circ}}$ 0·9390. Apparatus A.

15.0°	16.40	1.0103	31.03	244.3	$40 \cdot 7^{\circ}$	15.14	0.9849	27.92	$244 \cdot 1$
20.5	16.08	1.0048	30.25	$244 \cdot 1$	61.3	$14 \cdot 12$	0.9650	25.51	243.7
26.6	15.89	0.9987	29.72	244.5	87.0	12.83	0.9381	22.54	$243 \cdot 3$
								Mes	n 944.0

443. cyclo Pentyl bromide. B. p. $136\cdot5^\circ/753$ mm.; M $149\cdot04$; $n_{\rm C}$ $1\cdot48565$, $n_{\rm D}$ $1\cdot48858$, $n_{\rm F}$ $1\cdot49590$, $n_{\rm G'}$ $1\cdot50142$; $R_{\rm C}$ $30\cdot83$, $R_{\rm D}$ $30\cdot99$, $R_{\rm F}$ $31\cdot38$, $R_{\rm G'}$ $31\cdot67$; $Mn_{\rm D}^{20^\circ}$ $221\cdot86$. Densities determined: $d_4^{20^\circ}$ $1\cdot3873$, $d_4^{40\cdot8^\circ}$ $1\cdot3603$, $d_4^{40\cdot8^\circ}$ $1\cdot3348$, $d_4^{80\cdot1^\circ}$ $1\cdot2983$. Apparatus D.

16·9°	9.84	1.3913	33.81	$258 \cdot 3$	61·1°	8.62	1.3343	28.40	257.9
20.5	9.70	1.3866	33.22	258.0	86.5	7.97	1.3004	25.60	257.8
40.5	9.17	1.3608	30.82	$258 \cdot 1$				Maa	n 950.0

444. cyclo*Pentyl iodide.* B. p. 58°/22 mm.; M 196·04; n_0 1·54268, n_D 1·54705, n_F 1·55817, n_{G} 1·56700; R_0 36·13, R_D 36·38, R_F 36·99, $R_{G'}$ 37·47; $Mn_D^{20°}$ 303·29. Densities determined: $d_4^{20°}$ 1·7092, $d_4^{40°}$ 1·6794, $d_4^{60°}$ 1·6498, $d_4^{60°}$ 1·6117. Apparatus D.

14.9°	8.68	1.7166	36.80	281.3	$61 \cdot 1^{\circ}$	7.74	1.6489	31.52	281.7
20.0	8.58	1.7092	36.21	281.4	85.6	7.23	1.6097	28.74	282.0
42.0	8.12	1.6771	33.63	281.5				Mea	n 281·6

445. Dicyclohexyl. B. p. 233°/750 mm., m. p. 4°; M 166·30; $n_{\rm C}$ 1·47696, $n_{\rm D}$ 1·47954, $n_{\rm F}$ 1·48538, $n_{\rm G'}$ 1·48993; $R_{\rm C}$ 52·99, $R_{\rm D}$ 53·22, $R_{\rm F}$ 53·78, $R_{\rm G'}$ 54·21; $Mn_{\rm D}^{20^\circ}$ 246·04. Densities determined: $d_4^{20^\circ}$ 0·8868, $d_4^{40.1^\circ}$ 0·8727, $d_4^{60.7^\circ}$ 0·8585, $d_4^{85.0^\circ}$ 0·8420. Apparatus E.

t.	H.	$d_{f 4^{\circ}}^{f t^{\circ}}.$	γ.	P.	t.	H.	d_{4}^{i} .	γ.	P.
15.9°	16.04	0.8897	33.24	448.8	$60 \cdot 4^{\circ}$	14.46	0.8587	28.92	$449 \cdot 1$
20.5	15.83	0.8864	32.68	448.6	86.7	13.50	0.8408	26.44	448.5
41.2	15.05	0.8720	30.56	448.4				Mea	ın 448·7

446. cyclo*Hexyl methyl ether*. B. p. $133\cdot5^\circ/763$ mm.; M $114\cdot18$; $n_{\rm C}$ $1\cdot43248$, $n_{\rm D}$ $1\cdot43470$, $n_{\rm F}$ $1\cdot44004$, $n_{\rm G'}$ $1\cdot44398$; $R_{\rm C}$ $33\cdot87$, $R_{\rm D}$ $34\cdot02$, $R_{\rm F}$ $34\cdot38$, $R_{\rm G'}$ $34\cdot65$; $Mn_{\rm D}^{20^\circ}$ $163\cdot81$. Densities determined: $d_4^{20^\circ}$ $0\cdot8752$, $d_4^{40\cdot5^\circ}$ $0\cdot8574$, $d_4^{61\cdot5^\circ}$ $0\cdot8395$, $d_4^{86\cdot7^\circ}$ $0\cdot8168$. Apparatus D.

$14.7^{\circ} \\ 17.9 \\ 27.4$	13.26 13.14 12.77	$0.8798 \\ 0.8770 \\ 0.8688$	$28.81 \\ 28.46 \\ 27.40$	$300.7 \\ 300.7 \\ 300.7$	$41.3^{\circ} \\ 60.8 \\ 86.0$	$12 \cdot 19$ $11 \cdot 42$ $10 \cdot 41$	$0.8567 \\ 0.8404 \\ 0.8162$	$25.79 \\ 23.70 \\ 20.98$	300.4 299.8 299.4
								Mea	n 300·3

447. cyclo*Hexyl ethyl ether.* B. p. 148·5—149·5°/763 mm.; M 128·21; $n_{\rm C}$ 1·43284, $n_{\rm D}$ 1·43505, $n_{\rm F}$ 1·44042, $n_{\rm G}$ 1·44506; $R_{\rm G}$ 38·55, $R_{\rm D}$ 38·73, $R_{\rm F}$ 39·14, $R_{\rm G'}$ 39·50; $Mn_{\rm D}^{20^\circ}$ 183·99. Densities determined: $d_4^{20^\circ}$ 0·8640, $d_4^{41^\circ}$ 0·8466, $d_4^{60\cdot1^\circ}$ 0·8295, $d_4^{85\cdot3^\circ}$ 0·8074. Apparatus A.

$17 \cdot 3^{\circ}$	16.92	0.8663	$27 \cdot 45$	338.7	40·6°	15.91	0.8475	$25 \cdot 25$	$339 \cdot 1$
20.7	16.85	0.8634	27.24	339.2	60.9	14.84	0.8288	23.03	338.9
27.6	16.55	0.8585	26.60	$339 \cdot 2$	$85 \cdot 4$	13.63	0.8073	20·60	338·4
								Mea	n 338.9

448. cyclo*Hexyl formate.* B. p. $160^\circ/757$ mm.; M $128\cdot17$; n_0 $1\cdot44073$, $n_{\rm D}$ $1\cdot44305$, $n_{\rm F}$ $1\cdot44857$, $n_{\rm G'}$ $1\cdot45263$; $R_{\rm C}$ $34\cdot03$, $R_{\rm D}$ $34\cdot19$, $R_{\rm F}$ $34\cdot56$, $R_{\rm G'}$ $34\cdot82$; $Mn_{\rm D}^{20^\circ}$ $184\cdot96$. Densities determined: $d_4^{20^\circ}$ $0\cdot9941$, $d_4^{41\cdot3^\circ}$ $0\cdot9735$, $d_4^{61\cdot1^\circ}$ $0\cdot9552$, $d_4^{87\cdot1^\circ}$ $0\cdot9317$. Apparatus A.

13.0°	17.62	1.0007	33.02	307.0	$61 \cdot 3^{\circ}$	15.38	0.9550	27.50	$307 \cdot 3$
19.0	17.39	0.9950	$32 \cdot 40$	307.3	87.1	14.25	0.9317	24.86	$307 \cdot 2$
41.0	16.35	0.9738	29.81	307.6				Mea	an 307·3

449. cyclo*Hexyl acetate.* B. p. $172^{\circ}/752$ mm.; M 142·19; $n_{\rm 0}$ 1·43950, $n_{\rm D}$ 1·44174, $n_{\rm F}$ 1·44718, $n_{\rm G}$ 1·45118; $R_{\rm C}$ 38·61, $R_{\rm D}$ 38·77, $R_{\rm F}$ 39·19, $R_{\rm G}$ 39·50; $Mn_{\rm D}^{20^{\circ}}$ 205·00. Densities determined: $d_{\rm 4}^{20^{\circ}}$ 0·9697, $d_{\rm 4}^{40^{\circ}}$ 0·9501, $d_{\rm 4}^{62^{\circ}}$ 0·9298, $d_{\rm 4}^{86^{\circ}}$ 0·9072. Apparatus D.

				347.0					
41.1	12.31	0.9496	28.87	$347 \cdot 1$	87.1	10.66	0.9067	23.87	346.6
								Moo	n 246.0

450. cyclo*Hexyl chloride*. B. p. 142°/755 mm.; M 118·61; $n_{\rm C}$ 1·45993, $n_{\rm D}$ 1·46235, $n_{\rm F}$ 1·46828, $n_{\rm G}$ 1·47266; $R_{\rm C}$ 32·84, $R_{\rm D}$ 32·99, $R_{\rm F}$ 33·35, $R_{\rm G'}$ 33·62; $Mn_{\rm D}^{20^\circ}$ 173·46. Densities determined: $d_4^{20^\circ}$ 0·9891, $d_4^{40.6^\circ}$ 0·9690, $d_4^{61.0^\circ}$ 0·9497, $d_4^{85.5^\circ}$ 0·9256. Apparatus A.

15.9°		0.9932		284.6	60.9°		0.9498		284.9
40.0	16.20	0.9696	29.41	284.9	86.0	14.16	0.9251	24.53	$285 \cdot 3$
								Mea	n 284·9

451. cyclo*Hexyl bromide*. B. p. $164^{\circ}/766$ mm.; M $163\cdot07$; n_{0} $1\cdot49226$, n_{D} $1\cdot49526$, n_{F} $1\cdot50269$, $n_{G'}$ $1\cdot50830$; R_{0} $35\cdot43$, R_{D} $35\cdot61$, R_{F} $36\cdot06$, $R_{G'}$ $36\cdot40$; $Mn_{D}^{20^{\circ}}$ $243\cdot84$. Densities determined: $d_{4^{\circ}}^{20^{\circ}}$ $1\cdot3360$, $d_{4^{\circ}}^{4^{\circ}}$ $1\cdot3092$, $d_{4^{\circ}}^{61\cdot7^{\circ}}$ $1\cdot2875$, $d_{4^{\circ}}^{85\cdot7^{\circ}}$ $1\cdot2583$. Apparatus A.

		$294.6 \\ 294.8$			
				Mag	n 204.6

452. cyclo*Hexyl iodide*. B. p. $81\cdot5^{\circ}/20$ mm.; M $210\cdot07$; $n_{\rm C}$ $1\cdot54333$, $n_{\rm D}$ $1\cdot54765$, $n_{\rm F}$ $1\cdot55856$, $n_{\rm G}$ $1\cdot56730$; $R_{\rm C}$ $40\cdot78$, $R_{\rm D}$ $41\cdot05$, $R_{\rm F}$ $41\cdot73$, $R_{\rm G'}$ $42\cdot26$; $Mn_{\rm D}^{20^{\circ}}$ $325\cdot13$. Densities determined: $d_4^{20^{\circ}}$ $1\cdot6244$, $d_4^{41\cdot2^{\circ}}$ $1\cdot5968$, $d_4^{62\cdot2^{\circ}}$ $1\cdot5702$, $d_4^{86\cdot3^{\circ}}$ $1\cdot5403$. Apparatus D.

$15\cdot2^{\circ}$	9.17	1.6306	36.93	317.6	$61 \cdot 2^{\circ}$	8.19	1.5715	31.06	315.6
25.0	8.92	1.6180	35.64	317.2	86.8	7.66	1.5397	$29 \cdot 13$	317.0
40.5	8.65	1.5977	$34 \cdot 13$	317.8				Mea	n 317·1

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