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

By ARTHUR I. VOGEL.

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.	$R_{\mathbf{C}}$.	$R_{\mathbf{D}}$.	$R_{\mathbf{F}}$.	$R_{\mathbf{G}'}$.	$Mn_{\mathbf{D}}^{20^{\bullet}}$.
5-Membered carbon ring	$4 \cdot 6$	-0.19	-0.19	-0.19	-0.22	-4.56
6-Membered carbon ring	1.4	-0.12	-0.12	-0.16	-0.12	-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.	$R_{\mathbf{C}}$.	$R_{\mathbf{D}}$.	$R_{\mathbf{F}}$.	$R_{\mathbf{G}'}$.	$Mn_{\mathbf{D}}^{20}$.
Methylcyclopentane (I)	$243 \cdot 8$	27.63	27.77	28.07	28.24	118.67
Methylcyclopentane (II)		27.79	27.90	28.12	28.46	118.54
Methylcyclopentane (III)	$243 \cdot 9$	27.69	27.82	28.12	28.36	118.57
cycloHexane	241.8	27.63	27.75	28.05	28.27	120.06
Methylcyclohexane	280.9	32.36	32.53	32.87	33.12	139.82
cycloHeptane	278.9	32.01	32.18	32.53	32.76	141.73
1 -Methyl- Δ^2 -cyclopentene	$232 \cdot 9$	27.10	27.25	27.51	27.86	117.03
cycloHexene	230.4	29.96	27.11	27.47	27.74	118.82
\mathbf{I} -Methyl- Δ^1 -cyclohexene	269.4	31.66	31.84	32.26	32.57	139.51
cycloHeptene	268.2	31.58	31.75	$32 \cdot 17$	32.49	140.16
3-Methylcyclopentanol	255.0	29.22	29.37	29.66	29.89	144.97
cycloHexanol (supercooled)	253.3	29.04	29.16	29.48	29.71	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 :

$$[CH_2]_{x} \bigvee_{CH_2}^{CR_1R_2} + 2H - [CH_2]_{x} \bigvee_{CH_3}^{CHR_1R_2}$$

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 $5 \times CH_2$. 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 o .	$R_{\mathbf{D}}.$	$R_{\mathbf{F}}$.	$R_{\mathbf{G}'}$.	$Mn_{\mathbf{D}}^{20}$ °.
cycloPentane	$4 \cdot 9$	-0.12	-0.12	-0·14	-0.12	-4.30
Methylcyclopentane	$4 \cdot 3$	0.11	-0.10	-0.09	-0.12	-4.94
cycloPentene	4.5	-0.38	-0.37	-0.39	-0.43	-4.89
1 -Methyl- Δ^2 -cyclopentene	3.7	-0.13	-0.13	-0.14	-0.14	-5.22
cycloPentanol	$5 \cdot 0$	-0.21	-0.21	-0.22	-0.22	-4.25
cycloPentyl methyl ether	4.0	-0.16	-0.12	-0.18	-0.21	-4.59
cycloPentyl ethyl ether	4 ·1	-0.50	-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	$5 \cdot 9$	-0.13	-0.14	-0.14	-0.16	-4.16
Mean	4 ·6	-0.19	-0.19	-0.19	-0.522	-4.56
cycloPentanone	7.5	0.11	0.12	0.12	0.10	-4.01
3-Methylcyclopentanone	5.7	0.10	0.07	0.11		-4.73
cycloPentyl chloride	$5 \cdot 2$	-0.06	-0.04	-0.05	-0.03	-3.85
cycloPentyl bromide	6.3	0.07	0.06	0.08	0.05	-1.56
cycloPentyl iodide	$7 \cdot 9$	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).

ТΑ	BLE	II.

Values for the six-carbon ring from cyclohexane compounds.

	P.	$R_{\mathbf{c}}.$	$R_{\mathbf{D}}$. ·	$R_{\mathbf{F}}$.	$R_{\mathbf{G}'}$.	$Mn_{\mathbf{D}}^{20}$ °.
cycloHexane	1.8	-0.15	-0.11	-0.15	-0.15	-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	-0.522	-0.21	-0.28	-0.30	-3.43
cycloHexanol *		-0.16	-0.17	-0.16	-0.12	-3.19
cycloHexyl methyl ether	1.5	-0.18	-0.18	-0.18	-0.50	-3.66
cycloHexyl ethyl ether	0.5	0.13	-0.16	-0.18	-0.12	-3.54
cycloHexyl formate	1.3	-0.22	• -0.22	-0.21	-0.25	-3.34
cycloHexyl acetate	$2 \cdot 7$	-0.01	-0.08	-0.02	-0.08	-3.34
Mean	1.4	-0.12	-0.12	-0.16	-0.17	-3.53
cycloHexanone	6.1	-0.10	-0.11	-0.10	-0.15	-3.13
2-Methylcyclohexanone	4.7	0.08	0.08	0.09	0.07	-3.85
9 Mathulaudahawanana	∫ 2·6	-0.08	-0.02	-0.06	-0.08	-3.79
5-Methylcyclonexanone	ે6.6	0.19	0.21	0.22	0.21	-3.60
4-Methylcyclohexanone	5.4	0.22	0.22	0.23	0.23	-3.88
cycloHexyl chloride	$5 \cdot 8$	0.31	0.31	0.31	0.29	-2.95
cycloHexyl bromide	2.7	0.06	0.07	0.08	0.06	-0.58
cycloHexyl iodide	2.7	0.22	0.24	0.29	0.30	3.46

* The experimental data for cyclohexanol (Part III, J., 1938, 1331) require revision as follows: $M \ 100 \cdot 16$; $Mn_{D}^{90^{\circ}} \ 146 \cdot 83$; $d_{4^{\circ}}^{20^{\circ}} \ 0.9515$ (supercooled), $d_{4^{\circ}}^{22^{\circ}} \ 0.9475$, $d_{4^{\circ}}^{81 \cdot 8^{\circ}} \ 0.9178$, $d_{4^{\circ}}^{85 \cdot 9^{\circ}} \ 0.8975$.

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

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	P.	$R_{\mathbf{C}}$.	$R_{\mathbf{D}}$.	$R_{\mathbf{F}}$.	$R_{G'}$.	$Mn_{\mathbf{D}}^{20}$ °.
cycloHeptane	-1.3	-0.36	-0.35	-0.34	-0.39	-2.40
cycloHeptene	-0.4	-0.53	-0.30	-0.58	-0.30	-3.05

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%). cycloHexyl 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.

cyclo*Hexyl 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.

cycloHexyl 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°. The fractionation of B.D.H. "pure" cyclohexyl acetate yielded a middle fraction, b. p. 161°/770 mm., d_1^{20} 0.9609, n_2^{00} 1.4435, whence $R_{\rm D}$ 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 $(MgSO_4)$, and fractionated. The yield of *cyclo*hexyl 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. 172.5°/772 mm., d_2^{20} 0.9872, n_D^{20} 1.4437, whence R_D 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 *cyclo*pentyl 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. cyclo*Hexyl chloride*. A mixture of 150 g. of pure *cyclo*hexanol, 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 $141-142^{\circ}/755$ mm.

cyclonextene) had passed over, 102 g. of cyclonexyl chloride were collected at 141—142°/155 mm. cycloPentyl 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 wached successively with concentrated hydrochloric acid

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 *cyclo*hexyl bromide collected at $164^{\circ}/766$ 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°/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 *cyclo*hexyl 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 $81-83^{\circ}/20$ mm. : a middle fraction, b. p. $81.5^{\circ}/20$ mm., was used for the physical measurements. The pale colour was readily removed by shaking with pure silver powder.

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. $58^{\circ}/22$ 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 $(CaCl_2)$, 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. cycloPentyl methyl ether. B. p. $105^{\circ}/763 \text{ mm.}$; $M 100 \cdot 16$; $n_{0} 1 \cdot 41828$, $n_{D} 1 \cdot 42036$, $n_{F} 1 \cdot 42543$, $n_{G'} 1 \cdot 42916$; $R_{0} 29 \cdot 29$, $R_{D} 29 \cdot 42$, $R_{F} 29 \cdot 72$, $R_{G'} 29 \cdot 95$; $Mn_{20}^{20^{\circ}} 142 \cdot 27$. Densities determined : $d_{40}^{20^{\circ}} 0 \cdot 8624$, $d_{40}^{4^{\circ},0^{\circ}} 0 \cdot 8430$, $d_{40}^{4^{\circ},5^{\circ}} 0 \cdot 8240$, $d_{40}^{8^{\circ},8^{\circ}} 0 \cdot 7972$. Apparatus A.

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

<i>t</i> .	H_{\bullet}	d_{4}^{t} .	γ.	P.	t.	H.	d4°.	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	$263 \cdot 4$	60.1	14.15	0.8253	21.86	262.7
$24 \cdot 4$	16.13	0.8583	25.92	$263 \cdot 3$				Mea	n 263·2

439. cycloPentyl ethyl ether. B. p. $122 \cdot 5^{\circ}/766 \text{ mm.}$; $M \, 114 \cdot 18$; $n_{\rm C} \, 1 \cdot 42102$, $n_{\rm D} \, 1 \cdot 42316$, $n_{\rm F} \, 1 \cdot 42831$, $n_{\rm G'} \, 1 \cdot 43207$; $R_{\rm O} \, 33 \cdot 95$, $R_{\rm D} \, 34 \cdot 11$, $R_{\rm F} \, 34 \cdot 47$, $R_{\rm G'} \, 34 \cdot 73$; $M n_{20}^{20^{\circ}} \, 162 \cdot 50$. Densities determined : $d_{40}^{20^{\circ}} \, 0 \cdot 8528$, $d_{4^{\pm}}^{4 \pm 0^{\circ}} \, 0 \cdot 8334$, $d_{40}^{60^{\circ}} \, 0 \cdot 8146$, $d_{40}^{26^{\circ}} \, 3^{\circ} \, 0 \cdot 7899$. Apparatus D.

17·2° 21·3	$12.55 \\ 12.34$	$0.8554 \\ 0.8516$	$26.51 \\ 25.95$	$302 \cdot 9 \\ 302 \cdot 6$	40·9° 61·1	$11.57 \\ 10.81$	$0.8335 \\ 0.8141$	$23.82 \\ 21.73$	$302.6 \\ 302.8$
23.7	12.27	0.8493	25.74	$302 \cdot 8$	86.7	9.78	0.7895	19.07	302.2
								Mea	n 302·7

440. cyclo*Pentyl formate.* B. p. 138°/762 mm.; *M* 114·14; n_0 1·42990, n_D 1·43209, n_F 1·43741, n_6 · 1·44127; R_0 29·40, R_D 29·53, R_F 29·43, $R_{G'}$ 30·08; $Mn_D^{20^\circ}$ 163·46. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0026, $d_{4^{+3}}^{41\cdot3^\circ}$ 0·9819, $d_{4^{\circ}}^{60\cdot4^\circ}$ 0·9624, $d_{4^{\circ}}^{45\cdot3^\circ}$ 0·9368. Apparatus *A*.

15.8° 19.3	$17.08 \\ 17.02$	$1.0068 \\ 1.0034$	$32.20 \\ 31.98$	$270 \cdot 1 \\ 270 \cdot 5$	60·7° 85·6	$15.03 \\ 13.81$	$0.9621 \\ 0.9365$	$27.08 \\ 24.22$	$270 \cdot 6$ $270 \cdot 4$
41.5	15.90	0.9817	29.23	$270 \cdot 2$				Mean	270.4

441. cycloPentyl acetate. B. p. $153^{\circ}/760 \text{ mm.}$; $M 128 \cdot 17$; $n_0 1 \cdot 42962$, $n_D 1 \cdot 43178$, $n_F 1 \cdot 43708$, $n_{G'} 1 \cdot 44094$; $R_0 33 \cdot 92$, $R_D 34 \cdot 07$, $R_F 34 \cdot 43$, $R_{G'} 34 \cdot 70$; $Mn_D^{20^{\circ}} 183 \cdot 51$. Densities determined : $d_{4^{\circ}}^{20^{\circ}} 0 \cdot 9753$, $d_{4^{\circ}}^{40^{\circ}} ^{\circ} 0 \cdot 9540$, $d_{4^{\circ}}^{40^{\circ}} ^{\circ} 0 \cdot 9350$, $d_{4^{\circ}}^{40^{\circ}} ^{\circ} 0 \cdot 9086$. Apparatus D.

$309.6 \\ 309.2$	$25.93 \\ 23.12$	$0.9342 \\ 0.9091$	$11 \cdot 24 \\ 10 \cdot 30$	$\begin{array}{c} 60 \cdot 9^{\circ} \\ 86 \cdot 1 \end{array}$	$\begin{array}{c} \mathbf{309\cdot 4} \\ \mathbf{309\cdot 4} \end{array}$	$30.67 \\ 28.06$	$\begin{array}{c} 0.9749 \\ 0.9533 \end{array}$	$12.74 \\ 11.92$	20·4° 41·4
309.4	Mean								

442. cycloPentyl 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: $d_{4^\circ}^{20^\circ}$ 1·0053, $d_{4^\circ}^{1\circ}$ 0·9855, $d_{4^\circ}^{61.7^\circ}$ 0·9646, $d_{4^\circ}^{861^\circ}$ 0·9390. Apparatus A.

15·0° 20·5 26·6	16.40 16.08 15.89	$1.0103 \\ 1.0048 \\ 0.9987$	$31.03 \\ 30.25 \\ 29.72$	$244 \cdot 3 \\ 244 \cdot 1 \\ 244 \cdot 5$	40.7° 61.3 87.0	$15 \cdot 14 \\ 14 \cdot 12 \\ 12 \cdot 83$	0·9849 0·9650 0·9381	$27.92 \\ 25.51 \\ 22.54$	$244 \cdot 1 \\ 243 \cdot 7 \\ 243 \cdot 3$
								Mea	n 244·0

443. cycloPentyl bromide. B. p. $136 \cdot 5^{\circ}/753 \text{ mm.}$; $M \cdot 149 \cdot 04$; $n_{\rm C} \cdot 1\cdot 48565$, $n_{\rm D} \cdot 1\cdot 48588$, $n_{\rm F} \cdot 1\cdot 49590$, $n_{\rm G'} \cdot 1\cdot 50142$; $R_{\rm C} \cdot 30 \cdot 83$, $R_{\rm D} \cdot 30 \cdot 99$, $R_{\rm F} \cdot 31 \cdot 38$, $R_{\rm G'} \cdot 31 \cdot 67$; $Mn_{\rm D}^{20^{\circ}} \cdot 221 \cdot 86$. Densities determined: $d_4^{20^{\circ}} \cdot 1\cdot 3873$, $d_{4^{\circ}}^{40 \cdot 8^{\circ}} \cdot 1\cdot 33603$, $d_{4^{\circ}}^{60 \cdot 8^{\circ}} \cdot 1\cdot 3348$, $d_{4^{\circ}}^{88 \cdot 1^{\circ}} \cdot 1\cdot 2983$. Apparatus D.

16·9°	9.84	1.3913	33.81	258.3	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	258.1				Mear	n 258·0

444. cyclo*Pentyl iodide*. B. p. 58°/22 mm.; M 196.04; $n_{\rm G}$ 1.54268, $n_{\rm D}$ 1.54705, $n_{\rm F}$ 1.55817, $n_{\rm G'}$ 1.56700; $R_{\rm O}$ 36.13, $R_{\rm D}$ 36.38, $R_{\rm F}$ 36.99, $R_{\rm G'}$ 37.47; $Mn_{\rm D}^{20^\circ}$ 303.29. Densities determined : $d_{4^\circ}^{20^\circ}$ 1.7092, $d_{4^\circ}^{40^\circ}$ 1.6794, $d_{4^\circ}^{60.5^\circ}$ 1.6498, $d_{4^\circ}^{30^\circ}$ 1.6117. Apparatus D.

14·9°	8.68	1.7166	36.80	281.3	61·1°	7.74	1.6489	31.52	281.7
20.0	8.58	1.7092	36.21	$281 \cdot 4$	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; $Mn_D^{20^\circ}$ 246·04. Densities determined : $d_{4^{\circ}}^{20^\circ}$ 0·8868, $d_{4^{\circ}}^{40^{\circ}}$ 0·8727, $d_{4^{\circ}}^{60^{\circ}}$ 0·8585, $d_{4^{\circ}}^{85\cdot0^\circ}$ 0·8420. Apparatus E.

t.	H.	$d_{\mathbf{A}^{\circ}}^{t^{\circ}}$.	γ.	P.	<i>t</i> .	H.	$d_{4^{\mathbf{a}}}^{\mathbf{a}}$.	γ.	P.
15.9°	16.04	0.8897	33.24	448 ·8	60·4°	14.46	0.8587	28.92	449.1
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. cycloHexyl methyl ether. B. p. $133 \cdot 5^{\circ}/763 \text{ mm.}$; M 114·18; $n_{\rm C} 1 \cdot 43248$, $n_{\rm D} 1 \cdot 43470$, $n_{\rm F} 1 \cdot 44004$, $n_{\rm G'} 1 \cdot 44398$; $R_{\rm C} 33 \cdot 87$, $R_{\rm D} 34 \cdot 02$, $R_{\rm F} 34 \cdot 38$, $R_{\rm G'} 34 \cdot 65$; $Mn_{\rm D}^{20^{\circ}} 163 \cdot 81$. Densities determined : $d_4^{20^{\circ}} 0 \cdot 8752$, $d_{4^{\circ}}^{40.5^{\circ}} 0 \cdot 83574$, $d_{4^{\circ}}^{40.5^{\circ}} 0 \cdot 8395$, $d_{4^{\circ}}^{46.7^{\circ}} 0 \cdot 8168$. Apparatus D.

14·7° 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° 60·8 86.0	12.19 11.42 10.41	$0.8567 \\ 0.8404 \\ 0.8162$	$25.79 \\ 23.70 \\ 20.98$	300·4 299·8 200.4
27.4	12.11	0.0000	21 10	500 1	000	10 11	0 0102	Mea	n 300.3

447. cycloHexyl 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; $R_{\rm C}$ 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 : $d_{4^\circ}^{20^\circ}$ 0.8640, $d_{4^\circ}^{1.6^\circ}$ 0.8466, $d_{4^\circ}^{60.1^\circ}$ 0.8295, $d_{4^\circ}^{85.3^\circ}$ 0.8074. Apparatus A.

17·3°	16.92	0.8663	27.45	338.7	40.6°	15.91	0.8475	$25 \cdot 25$	339.1
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	339.2	$85 \cdot 4$	13.63	0.8073	20.60	338·4
								Mea	n 338.9

448. cycloHexyl formate. B. p. $160^{\circ}/757 \text{ mm.}$; M 128·17; $n_{\rm C}$ 1·44073, $n_{\rm D}$ 1·44305, $n_{\rm F}$ 1·44857, $n_{\rm G'}$ 1·45263; $R_{\rm C}$ 34·03, $R_{\rm D}$ 34·19, $R_{\rm F}$ 34·56, $R_{\rm G'}$ 34·82; $Mn_{20}^{20^{\circ}}$ 184·96. Densities determined : $d_{4^{\circ}}^{20^{\circ}}$ 0·9941, $d_{4^{\circ}}^{41\cdot3^{\circ}}$ 0·9735, $d_{4^{\circ}}^{61\cdot1^{\circ}}$ 0·9552, $d_{4^{\circ}}^{87\cdot1^{\circ}}$ 0·9317. Apparatus A.

13·0°	17.62	1.0007	33.02	307.0	61.3°	15.38	0.9550	27.50	3 07· 3
19.0	17.39	0.9950	32.40	307.3	87.1	14.25	0.9317	$24 \cdot 86$	307.2
41.0	16.35	0.9738	29.81	307.6				Mean	307.3

449. cyclo*Hexyl acetate.* B. p. $172^{\circ}/752$ mm.; *M* 142·19; $n_{\rm C}$ 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 : $d_{4^{\circ}}^{20^{\circ}}$ 0·9697, $d_{4^{\circ}}^{40^{\circ}}$ 0·9501, $d_{4^{\circ}}^{42^{\circ}}$ 0·9298, $d_{4^{\circ}}^{46^{\circ}}$ 0·9072. Apparatus *D*.

$20.3^{\circ} \\ 41.1$	$13.08 \\ 12.31$	$0.9694 \\ 0.9496$	$31.31 \\ 28.87$	$347.0 \\ 347.1$	61.5° 87.1	$11.57 \\ 10.66$	$0.9306 \\ 0.9067$	$26.59 \\ 23.87$	$347.0 \\ 346.6$
								Mean	n 346·9

450. cycloHexyl chloride. B. p. $142^{\circ}/755 \text{ mm.}$; M 118.61; $n_0 1.45993$, $n_D 1.46235$, $n_F 1.46828$, $n_{G'} 1.47266$; $R_0 32.84$, $R_D 32.99$, $R_F 33.35$, $R_G 33.62$; $Mn_D^{20^{\circ}} 173.46$. Densities determined : $d_{4^{\circ}}^{20^{\circ}} 0.9891$, $d_{4^{\circ}}^{40^{\circ}} 0.9690$, $d_{4^{\circ}}^{61.0^{\circ}} 0.9497$, $d_{4^{\circ}}^{20^{\circ}} 0.9256$. Apparatus A.

15∙9° 40∙0	$17.34 \\ 16.20$	$0.9932 \\ 0.9696$	$32 \cdot 25 \\ 29 \cdot 41$	$284.6 \\ 284.9$	60·9° 86·0	$15.24 \\ 14.16$	$0.9498 \\ 0.9251$	$27 \cdot 10 \\ 24 \cdot 53$	$284.9 \\ 285.3$
								Mean	28 4 ·9

451. cyclo*Hexyl bromide.* B. p. $164^{\circ}/766 \text{ mm.}$; *M* $163 \cdot 07$; $n_0 \cdot 1.49226$, $n_D \cdot 1.49526$, $n_F \cdot 1.50269$, $n_{G'} \cdot 1.50830$; $R_0 \cdot 35 \cdot 43$, $R_D \cdot 35 \cdot 61$, $R_F \cdot 36 \cdot 06$, $R_{G'} \cdot 36 \cdot 40$; $Mn_D^{20^{\circ}} \cdot 243 \cdot 84$. Densities determined : $d_{4^{\circ}}^{20^{\circ}} \cdot 1.3360$, $d_{4^{\circ}}^{42 \cdot 5^{\circ}} \cdot 1.3092$, $d_{4^{\circ}}^{61 \cdot 7^{\circ}} \cdot 1.2875$, $d_{4^{\circ}}^{85 \cdot 7^{\circ}} \cdot 1.2583$. Apparatus *A*.

23·1° 41·2	$13.45 \\ 12.84$	$1.3323 \\ 1.3107$	$33.55 \\ 31.51$	$294.6 \\ 294.8$	60·6° 86·3	$12.18 \\ 11.27$	$1.2888 \\ 1.2577$	$29.39 \\ 26.48$	$294.6 \\ 294.4$
								Mea	n 294·6

452. cyclo*Hexyl iodide*. B. p. $81.5^{\circ}/20$ mm.; $M \ 210.07$; $n_{\rm C} \ 1.54333$, $n_{\rm D} \ 1.54765$, $n_{\rm F} \ 1.55856$, $n_{\rm G'} \ 1.56730$; $R_{\rm C} \ 40.78$, $R_{\rm D} \ 41.05$, $R_{\rm F} \ 41.73$, $R_{\rm G'} \ 42.26$; $Mn_{\rm D'}^{20} \ 325.13$. Densities determined : $d_{4^{\circ}}^{20^{\circ}} \ 1.6244$, $d_{4^{\circ}}^{41.2^{\circ}} \ 1.55968$, $d_{4^{\circ}}^{42.2^{\circ}} \ 1.5702$, $d_{4^{\circ}}^{42^{\circ}} \ 1.5403$. Apparatus D.

$15 \cdot 2^{\circ}$ 25 · 0 40 · 5	$9.17 \\ 8.92 \\ 8.65$	$1.6306 \\ 1.6180 \\ 1.5977$	$36.93 \\ 35.64 \\ 34.13$	$317.6 \\ 317.2 \\ 317.8$	$\begin{array}{c} 61 \cdot 2^{\circ} \\ 86 \cdot 8 \end{array}$	8·19 7·66	$1.5715 \\ 1.5397$	31·06 29·13 Mean	$315.6 \\ 317.0 \\ 317.1$
Woolw	-2° 9-17 1-6306 36-93 317 -0 8-92 1-6180 35-64 317 -5 8-65 1-5977 34-13 317 Woolwich Polytechnic, London, S.E.		S.E. 18.		[7	Received, D	ecember 4th,	1947.]	