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

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\begin{abstract}
New experimental data are provided for the calculation of the refractivities at $20^{\circ}$ 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 :

|  | $P$. | $R_{\text {c }}$. | $R_{\text {D }}$. | $R_{\text {F }}$. | $R_{\mathbf{G}^{\prime}}$. | $M n^{20}{ }^{2}$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5-Membered carbon ring | $4 \cdot 6$ | $-0 \cdot 19$ | $-0 \cdot 19$ | $-0 \cdot 19$ | $-0.22$ | $-4.56$ |
| 6 -Membered carbon ring | 1.4 | -0.15 | -0.15 | $-0 \cdot 16$ | $-0 \cdot 17$ | $-3.53$ |

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 $\mathrm{CH}_{2}$ for the D line of $4 \cdot 62$; the correct value is, however, $4 \cdot 647$ (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 $\mathrm{CH}_{2}$ of $39 \cdot 0$ was employed. A comparison of the physical properties of the following isomeric compounds suggests that the contributions of

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-l-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

## 1810 Vogel: Physical Properties and Chemical Constitution.

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 2 H 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 $5 \times \mathrm{CH}_{2}$. All the results for the cyclopentane ring are collected in Table I.

Table I.
Values for the five-carbon ring from cyclopentane compounds.

|  | $P$. | $R_{\mathbf{0}}$. | $R_{\text {D }}$. | $R_{\text {F }}$. | $R_{\mathrm{G}^{\prime}}$. | $M n_{\text {D }}^{20}{ }^{\circ}$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| cycloPentane | $4 \cdot 9$ | $-0.15$ | $-0.15$ | -0.14 | $-0.17$ | $-4.30$ |
| Methylcyclopentane | $4 \cdot 3$ | -0.11 | $-0 \cdot 10$ | $-0.09$ | $-0.15$ | $-4 \cdot 94$ |
| cycloPentene | $4 \cdot 5$ | -0.38 | $-0.37$ | -0.39 | -0.43 | -4.89 |
| 1-Methyl- $\Delta^{2}$-cyclopentene | $3 \cdot 7$ | $-0.13$ | $-0.13$ | -0.14 | -0.14 | $-5 \cdot 22$ |
| cycloPentanol | $5 \cdot 0$ | -0.21 | -0.21 | -0.22 | -0.22 | -4.25 |
| cycloPentyl methyl ether | $4 \cdot 0$ | -0.16 | $-0 \cdot 17$ | -0.18 | -0.21 | -4.59 |
| cycloPentyl ethyl ether.. | $4 \cdot 1$ | $-0.20$ | $-0 \cdot 19$ | -0.19 | $-0.23$ | $-4.53$ |
| cycloPentyl formate .. | $5 \cdot 2$ | -0.22 | -0.22 | $-0.22$ | $-0.25$ | $-4 \cdot 25$ |
| cycloPentyl acetate.................... | $5 \cdot 9$ | $-0 \cdot 13$ | $-0 \cdot 14$ | $-0 \cdot 14$ | $-0 \cdot 16$ | -4.16 |
| Mean $\mid>\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots .$. | $4 \cdot 6$ | $-0 \cdot 19$ | $-0 \cdot 19$ | $-0 \cdot 19$ | -0.22 | $-4.56$ |
| cycloPentanone ....................... | $7 \cdot 5$ | $0 \cdot 11$ | $0 \cdot 12$ | $0 \cdot 12$ | $0 \cdot 10$ | $-4.01$ |
| 3-Methylcyclopentanone ........... | $5 \cdot 7$ | $0 \cdot 10$ | 0.07 | $0 \cdot 11$ | - | $-4.73$ |
| cycloPentyl chloride ................. | $5 \cdot 2$ | $-0.06$ | $-0.04$ | -0.02 | $-0.03$ | $-3 \cdot 85$ |
| cycloPentyl bromide ................. | $6 \cdot 3$ | 0.07 | $0 \cdot 06$ | 0.08 | 0.05 | $-1.56$ |
| cycloPentyl iodide | $7 \cdot 9$ | $0 \cdot 19$ | $0 \cdot 21$ | $0 \cdot 24$ | $0 \cdot 23$ | 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 cyclohexane 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 -methylcyclohexanone 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.

|  | $P$. | $R_{\text {c }}$. | $R_{\text {D }}$. | $R_{\text {F }}$. | $R_{\text {G }}$. | $M n^{20}{ }^{\circ}$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| cycloHexane. | $1 \cdot 8$ | -0.12 | -0.11 | $-0 \cdot 12$ | $-0 \cdot 12$ | $-3.72$ |
| Methylcyclohexane | $1 \cdot 3$ | $-0.03$ | -0.01 | -0.01 | -0.04 | $-4 \cdot 34$ |
| Dicyclohexyl | $0 \cdot 8$ | -0.18 | -0.19 | -0.19 | $-0.20$ | $-3 \cdot 20$ |
| cycloHexene. | 1.5 | -0.27 | -0.27 | -0.28 | $-0.30$ | $-3 \cdot 43$ |
| cycloHexanol * | - | -0.16 | -0.17 | -0.16 | $-0.17$ | $-3 \cdot 19$ |
| cycloHexyl methyl ether | 1.5 | $-0.18$ | $-0.18$ | $-0.18$ | $-0.20$ | $-3 \cdot 66$ |
| cycloHexyl ethyl ether | $0 \cdot 5$ | $-0.13$ | $-0.16$ | -0.18 | $-0.15$ | $-3.54$ |
| cycloHexyl formate | $1 \cdot 3$ | -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 | $1 \cdot 4$ | $-0.15$ | $-0 \cdot 15$ | $-0 \cdot 16$ | $-0 \cdot 17$ | $-3.53$ |
| cycloHexanone | $6 \cdot 1$ | $-0 \cdot 10$ | -0.11 | $-0 \cdot 10$ | $-0.12$ | $-3 \cdot 13$ |
| 2-Methylcyclohexanone | $4 \cdot 7$ | $0 \cdot 08$ | $0 \cdot 08$ | 0.09 | 0.07 | $-3.85$ |
| 3-Methylcyclohexanone | $\left\{\begin{array}{l}2 \cdot 6 \\ 6.6\end{array}\right.$ | -0.08 0.19 | -0.07 0.21 | -0.06 0.22 | -0.08 0.21 | -3.79 -3.60 |
| 4-Methylcyclohexanone | $5 \cdot 4$ | $0 \cdot 22$ | $0 \cdot 22$ | $0 \cdot 23$ | $0 \cdot 23$ | $-3.88$ |
| cycloHexyl chloride | $5 \cdot 8$ | $0 \cdot 31$ | $0 \cdot 31$ | $0 \cdot 31$ | $0 \cdot 29$ | $-2.95$ |
| cycloHexyl bromide | 2.7 | 0.06 | $0 \cdot 07$ | $0 \cdot 08$ | 0.06 | $-0.28$ |
| cycloHexyl iodide ........ | $2 \cdot 7$ | $0 \cdot 22$ | $0 \cdot 24$ | $0 \cdot 29$ | $0 \cdot 30$ | $3 \cdot 46$ |

* The experimental data for cyclohexanol (Part III, J., 1938, 1331) require revision as follows : $M 100 \cdot 16 ; M n_{\mathrm{D}}^{20^{\circ}} 146 \cdot 83 ; d_{4^{\circ}}^{20^{\circ}} 0.9515$ (supercooled), $d_{4^{\circ}}^{25^{\circ}} 0.9475, d_{4^{6}}^{61 \cdot 8^{\circ}} 0.9178, d_{4^{\circ}}^{85 \cdot 3^{\circ}} 0.8975$.

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

|  | $P$. | $R_{0}$. | $R_{\text {D }}$. | $R_{\text {F }}$. | $R_{G^{\prime}}$. | $M n_{\text {D }}^{20}{ }^{\circ}$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| cycloHeptane | $-1.3$ | $-0.36$ | $-0.35$ | -0.34 | $-0.39$ | $-2 \cdot 40$ |
| cycloHeptene | -0.4 | -0.29 | $-0 \cdot 30$ | -0.28 | -0.30 | $-3.02$ |

## Experimental

cycloPentyl 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 cyclopentanol (b. p. $141-142^{\circ} / 769 \mathrm{~mm}$.) 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 $120-130^{\circ}$ ( 45 g .). Repeated distillation from sodium to constant physical properties yielded 26 g . of pure cyclopentyl ethyl ether, b. p. $122 \cdot 5^{\circ} / 763 \mathrm{~mm}$.
cycloPentyl methyl ether. This was prepared similarly, 97 g . of methyl iodide being used. The yield of the pure cyclopentyl methyl ether, b. p. $105^{\circ} / 763 \mathrm{~mm}$., was 21 g . (Found: C, $72 \cdot 0 ; \mathrm{H}, 12 \cdot 1 . \mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}$ requires $\mathrm{C}, 72 \cdot 2 ; \mathrm{H}, 11.9 \%$ ).
cycloHexyl methyl ether. The yield of this ether, b. p. $133.5^{\circ} / 762 \mathrm{~mm}$., 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. $148 \cdot 5-149 \cdot 5^{\circ} / 763 \mathrm{~mm}$., 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. $160-195^{\circ}$. The fractionation of B.D.H. "pure" cyclohexyl acetate yielded a middle fraction, b. p. $161^{\circ} / 770 \mathrm{~mm}$., $d_{4 .}^{20^{\circ}} 0.9609, n_{\mathrm{D}}^{20^{\circ}} 1.4435$, whence $R_{\mathrm{D}} 39.27$; 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 $\left(\mathrm{MgSO}_{4}\right)$, and fractionated. The yield of cyclohexyl acetate, b. p. $172^{\circ} / 752 \mathrm{~mm}$., 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. $160-170^{\circ}$. Fractionation of B.D.H. "pure" cyclohexyl formate gave a large middle fraction of b. p. $172.5^{\circ} / 772 \mathrm{~mm}$., $d_{40^{20}}{ }^{\circ} 0.9872$, $n_{\mathrm{D}}^{20^{\circ}} \mathrm{I} \cdot 4437$, whence $R_{\mathrm{D}} 34 \cdot 47$. 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 $159 \cdot 5-\mathrm{I} 60^{\circ} / 757 \mathrm{~mm}$. ; yield, 57 g .
cycloPentyl formate. This was prepared by refluxing a mixture of 43 g . of distilled cyclopentanol containing l 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. $138^{\circ} / 762 \mathrm{~mm}$., were obtained.
cycloPentyl 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. $152 \cdot 5-153^{\circ} / 760 \mathrm{~mm}$., 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 $141-142^{\circ} / 755 \mathrm{~mm}$.
cycloPentyl chloride. In a $500-\mathrm{ml}$. three-necked flask, equipped with a mechanical stirrer and reflux condenser, were placed 43 g . of cyclopentanol (b. p. $140 \cdot 5-141 \cdot 5^{\circ} / 769 \mathrm{~mm}$.), 125 ml . of concentrated hydrochloric acid, and 50 g . of anhydrous calcium chloride. The mixture was heated, with stirring, at $100^{\circ}$ for 1 hour and the product was isolated as for the cyclohexyl compound. The yield of cyclopentyl chloride, b. p. $114-115^{\circ} / 777 \mathrm{~mm}$., 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 $500-\mathrm{ml}$. 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 ( $\mathrm{CaCl}_{2}$ ). The resulting crude bromide ( 69 g .) was fractionated and the pure cyclohexyl bromide collected at $164^{\circ} / 766 \mathrm{~mm}$.
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. $136 \cdot 5^{\circ} / 763 \mathrm{~mm}$.
cycloHexyl iodide. Vogel's procedure (B.P. 565,452 , 1944) was adopted. The flask was charged with 81 g . of pure cyclohexanol and $10 \cdot 2 \mathrm{~g}$. 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

## 1812 Vogel: Physical Properties and Chemical Constitution.

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 $\left(\mathrm{CaCl}_{2}\right)$, was 145 g . Upon distillation under reduced pressure, the cyclohexyl iodide passed over at $81-83^{\circ} / 20 \mathrm{~mm}$. : a middle fraction, b. p. $81 \cdot 5^{\circ} / 20 \mathrm{~mm}$., 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 $500-\mathrm{ml}$. 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. $58^{\circ} / 22 \mathrm{~mm}$.

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 $\left(\mathrm{CaCl}_{2}\right)$, and heated for 5 hours with excess of sodium at $110^{\circ}$. After filtration, the hydrocarbon was distilled. It boiled constantly at $233^{\circ} / 750 \mathrm{~mm}$. and had m. p. $4^{\circ}$.
438. cycloPentyl methyl ether. B. p. $105^{\circ} / 763 \mathrm{~mm}$; $M 100 \cdot 16 ; n_{\mathrm{O}} \mathrm{I} \cdot 41828, n_{\mathrm{D}} \mathrm{I} \cdot 42036, n_{\mathrm{F}} 1 \cdot 42543$, $n_{G^{\prime}} 1 \cdot 42916 ; \quad R_{\mathrm{C}} 29 \cdot 29, R_{\mathrm{D}} 29 \cdot 42, R_{\mathrm{F}} 29 \cdot 72, R_{G^{\prime}} 29.95 ; \quad M n_{\mathrm{D}}^{20^{\circ}} 142 \cdot 27$. Densities determined : $d_{4^{\circ}}^{20^{\circ}}$ $0.8624, d_{4}^{41 \cdot 0^{\circ}} 0.8430, d_{4^{\circ}}^{61 \cdot 5^{\circ}} 0.8240, d_{4}^{87.8^{\circ}} 0.7972$. Apparatus $A$.
(These headings apply to all subsequent tables in this paper.)

| $t$. | H. | $d_{4}^{\text {i }}$. | $\gamma$. | $P$. | $t$. | $H$. | $d_{4}^{t^{\circ}}$. | $\gamma$. | $P$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $16.9^{\circ}$ | 16.51 | $0 \cdot 8653$ | 26.75 | $263 \cdot 2$ | $41.5{ }^{\circ}$ | $15 \cdot 23$ | $0 \cdot 8425$ | 24.03 | $263 \cdot 2$ |
| $19 \cdot 1$ | $16 \cdot 43$ | $0 \cdot 8632$ | $26 \cdot 56$ | $263 \cdot 4$ | $60 \cdot 1$ | 14.15 | $0 \cdot 8253$ | 21.86 | $262 \cdot 7$ |
| $24 \cdot 4$ | 16•13 | $0 \cdot 8583$ | 25.92 | $263 \cdot 3$ |  |  |  |  | $263 \cdot 2$ |

439. cycloPentyl ethyl ether. B. p. $122.5^{\circ} / 766 \mathrm{~mm} . ; M 114 \cdot 18 ; n_{\mathrm{C}} \mathrm{I} \cdot 42102, n_{\mathrm{D}} \mathrm{l} \cdot 42316, n_{\mathrm{F}} \mathrm{l} \cdot 42831$, $n_{G^{\prime}} \mathrm{I} \cdot 43207 ; R_{\mathrm{G}} 33 \cdot 95, R_{\mathrm{D}} 34 \cdot 11, R_{\mathrm{F}} 34 \cdot 47, R_{\mathrm{G}^{\prime}} 34 \cdot 73 ; M n_{\mathrm{D}}^{20^{\circ}} 162 \cdot 50$. Densities determined: $d_{4}^{200^{\circ}}$ $0.8528, d_{4}^{41} \cdot 0^{\circ}{ }_{0.8334} d_{4^{60} \cdot 6^{\circ}}^{0.8146}, d_{4}^{86 \cdot 3^{F}}{ }_{0.7899}$. Apparatus $D$.

| $17.2^{\circ}$ | 12.55 | $0 \cdot 8554$ | 26.51 | 302.9 | $40.9^{\circ}$ | 11.57 | 0.8335 | 23.82 | $302 \cdot 6$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $21 \cdot 3$ | $12 \cdot 34$ | $0 \cdot 8516$ | $25 \cdot 95$ | $302 \cdot 6$ | $61 \cdot 1$ | 10.81 | $0 \cdot 8141$ | 21.73 | $302 \cdot 8$ |
| $23 \cdot 7$ | $12 \cdot 27$ | $0 \cdot 8493$ | 25.74 | $302 \cdot 8$ | 86.7 | 9.78 | $0 \cdot 7895$ | 19.07 | $302 \cdot 2$ |
|  |  |  |  |  |  |  |  |  | 302.7 |

440. cycloPentyl formate. B. p. $138^{\circ} / 762 \mathrm{~mm}$; $M 114 \cdot 14$; $n_{\mathrm{C}} \mathrm{I} \cdot 42990, n_{\mathrm{D}} \mathrm{l} \cdot 43209$, $n_{\mathrm{F}} 1 \cdot 43741$ $n_{G^{\prime}} 1.44127 ; R_{\mathrm{C}} 29 \cdot 40, R_{\mathrm{D}} 29 \cdot 53, R_{\mathrm{F}} 29 \cdot 43, R_{\mathrm{G}^{\prime}} 30 \cdot 08 ; M n_{\mathrm{D}}^{20^{\circ}} 163 \cdot 46$. Densities determined: $d_{4^{\circ}}^{20^{\circ}}$


| $15 \cdot 8^{\circ}$ | 17.08 | 1.0068 | 32.20 | $270 \cdot 1$ | $60.7^{\circ}$ | 15.03 | 0.9621 | 27.08 | 270.6 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 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 | 270.2 |  |  |  | Mean 270.4 |  |

441. cycloPentyl acetate. B. p. $153^{\circ} / 760 \mathrm{~mm} . ; M 128 \cdot 17$; $n_{\mathrm{O}} \mathrm{l} \cdot 42962, n_{\mathrm{D}} \mathrm{l} \cdot 43178, n_{\mathrm{F}} \mathrm{l} \cdot 43708, n_{G^{\prime}}$ I.44094; $R_{\mathrm{C}} 33.92, R_{\mathrm{D}} 34.07, R_{\mathrm{F}} 34.43, R_{\mathrm{G}^{\prime}} 34 \cdot 70 ; M n_{\mathrm{D}}^{20^{\circ}} 183.5 \mathrm{I}$. Densities determined: $d_{4^{\circ}}^{20^{\circ}} 0.9753$, $d_{4}^{40 \cdot 7^{\circ}} 0.9540, d_{4^{6.1}}{ }^{6}{ }^{\circ} \cdot 9350, d_{4}^{86 \cdot 6^{\circ}}{ }_{0.9086 \text {. }}$ Apparatus $D$.

| $20.4^{\circ}$ | 12.74 | 0.9749 | 30.67 | 309.4 | $60.9^{\circ}$ | $11 \cdot 24$ | 0.9342 | $25 \cdot 93$ | 309.6 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 41.4 | II.92 | 0.9533 | 28.06 | $309 \cdot 4$ | $86 \cdot 1$ | 10.30 | 0.9091 | $23 \cdot 12$ | $309 \cdot 2$ |
|  |  |  |  |  |  |  |  |  | Mean $309 \cdot 4$ |

442. cycloPentyl chloride. B. p. 114.5-115 $/ 777 \mathrm{~mm} . ; \quad M 104.58 ; n_{\mathrm{O}} 1 \cdot 44894, n_{\mathrm{D}} 1 \cdot 45127, n_{\mathrm{F}}$ $1.45703, n_{G^{\prime}} 1.46125 ; R_{\mathrm{O}} 27.83, R_{\mathrm{D}} 27.96, R_{\mathrm{F}} 28 \cdot 27, R_{\mathrm{G}^{\prime}} 28.50 ; M n_{\mathrm{D}}^{20^{\circ}}$ 151.78. Densities determined:


| $15 \cdot 0^{\circ}$ | $16 \cdot 40$ | $1 \cdot 0103$ | $31 \cdot 03$ | $244 \cdot 3$ | $40 \cdot 7^{\circ}$ | $15 \cdot 14$ | 0.9849 | 27.92 | $244 \cdot 1$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $20 \cdot 5$ | $16 \cdot 08$ | 1.0048 | $30 \cdot 25$ | $244 \cdot 1$ | $61 \cdot 3$ | $14 \cdot 12$ | 0.9650 | $25 \cdot 51$ | $243 \cdot 7$ |
| $26 \cdot 6$ | $15 \cdot 89$ | 0.9987 | $29 \cdot 72$ | $244 \cdot 5$ | $87 \cdot 0$ | $12 \cdot 83$ | 0.9381 | 22.54 | $243 \cdot 3$ |
|  |  |  |  |  |  |  |  | Mean $244 \cdot 0$ |  |

443. cycloPentyl bromide. B. p. $136 \cdot 5^{\circ} / 753 \mathrm{~mm}$.; $M 149 \cdot 04$; $n_{\mathrm{O}} \mathrm{l} \cdot 48565, n_{\mathrm{D}} \mathrm{I} \cdot 48858, n_{\mathrm{F}} 1 \cdot 49590$, $n_{\mathrm{G}^{\prime}} \mathrm{I} \cdot 50142 ; R_{\mathrm{C}} 30.83, R_{\mathrm{D}} 30 \cdot 99, R_{\mathrm{F}} 31.38, R_{\mathrm{G}^{\prime}} 31 \cdot 67 ; M n_{\mathrm{D}}^{20^{\circ}} 221.86$. Densities determined : $d_{4}^{20^{\circ}}$ $\mathrm{I} \cdot 3873$, $d_{4}^{40 \cdot 8^{\circ}}{ }^{\circ} \cdot 3603$, $d_{4}^{60 \cdot 8^{\circ}}{ }^{\circ} \cdot 3348$, $d_{4}^{88 \cdot \cdot^{\circ}}{ }^{\mathrm{F}} \cdot 2983$. Apparatus $D$.

| $16.9^{\circ}$ | $9 \cdot 84$ | 1-3913 | $33 \cdot 81$ | $258 \cdot 3$ | $61.1^{\circ}$ | $8 \cdot 62$ | 1-3343 | $28 \cdot 40$ | 257.9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 20.5 | $9 \cdot 70$ | 1.3866 | $33 \cdot 22$ | $258 \cdot 0$ | 86.5 | $7 \cdot 97$ | I-3004 | 25.60 | $257 \cdot 8$ |
| $40 \cdot 5$ | 9-17 | $1 \cdot 3608$ | $30 \cdot 82$ | $258 \cdot 1$ |  |  |  |  | 258 |

444. cycloPentyl iodide. B. p. $58^{\circ} / 22 \mathrm{~mm}$.; $M 196.04$; $n_{\mathrm{C}} \mathrm{l} \cdot 54268, n_{\mathrm{D}} \mathrm{l} \cdot 54705, n_{\mathrm{F}} \mathrm{I} \cdot 55817$, $n_{\mathrm{G}^{\prime}}$, I.56700; $R_{\mathrm{C}} 36 \cdot 13, R_{\mathrm{D}} 36 \cdot 38, R_{\mathrm{F}} 36 \cdot 99, R_{\mathbf{G}^{\prime}} 37 \cdot 47$; $M n_{\mathrm{D}}^{20^{\circ}} 303 \cdot 29$. Densities determined : $d_{4^{\circ}}^{20^{\circ}} \mathrm{I} \cdot 7092$, $d_{4}^{4 \cdot \cdot 6^{\circ}} 1 \cdot 6794, d_{4}^{6 \cdot 5^{\circ}} \mathrm{I} \cdot 6498, d_{4}^{86 \cdot 9^{\circ}} 1 \cdot 6117$. Apparatus $D$.

| $14.9^{\circ}$ | 8.68 | 1.7166 | $36 \cdot 80$ | 281.3 | $61 \cdot 1^{\circ}$ | 7.74 | 1.6489 | $31 \cdot 52$ | $281 \cdot 7$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 20.0 | 8.58 | 1.7092 | $36 \cdot 21$ | 281.4 | $85 \cdot 6$ | 7.23 | 1.6097 | 28.74 | $282 \cdot 0$ |
| 42.0 | 8.12 | 1.6771 | 33.63 | 281.5 |  |  |  | Mean 281.6 |  |

445. Dicyclohexyl. B. p. $233^{\circ} / 750 \mathrm{~mm} .$, m. p. $4^{\circ} ; M 166 \cdot 30 ; n_{\mathrm{C}} \mathrm{l} \cdot 47696, n_{\mathrm{D}} 1 \cdot 47954, n_{\mathrm{F}} 1 \cdot 48538$, $n_{G^{\prime}} 1.48993 ; R_{\mathrm{C}} 52.99, R_{\mathrm{D}} 53.22, R_{\mathrm{F}} 53.78, R_{\mathrm{G}^{\prime}} 54 \cdot 21 ; M n_{\mathrm{D}}^{20^{\circ}} 246.04$. Densities determined: $d_{4^{\circ}}^{20^{\circ}}$ $0.8868, d_{4 \circ}^{40 \cdot 11^{\circ}} 0.8727, d_{4^{\circ}}^{60 \cdot 7^{\circ}} 0.8585, d_{4^{8}}^{8.0^{\circ}}{ }_{0.8420}$. Apparatus $E$.

| $t$. | $H$. | $d_{4^{\circ} \cdot}^{\iota^{\circ}}$ | $\gamma$. | $P$. | $t$. | $H$. | $d_{4^{\circ} \cdot}$ | $\gamma$. | $P$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $15 \cdot 9^{\circ}$ | $16 \cdot 04$ | $0 \cdot 8897$ | $33 \cdot 24$ | $448 \cdot 8$ | $60 \cdot 4^{\circ}$ | $14 \cdot 46$ | $0 \cdot 8587$ | $28 \cdot 92$ | $449 \cdot 1$ |
| $20 \cdot 5$ | $15 \cdot 83$ | $0 \cdot 8864$ | $32 \cdot 68$ | $448 \cdot 6$ | $86 \cdot 7$ | $13 \cdot 50$ | $0 \cdot 8408$ | $26 \cdot 44$ | $\mathbf{4 4 8 \cdot 5}$ |
| $41 \cdot 2$ | $15 \cdot 05$ | $0 \cdot 8720$ | $30 \cdot 56$ | $448 \cdot 4$ |  |  |  | Mean $448 \cdot 7$ |  |

446. cycloHexyl methyl ether. B. p. $133 \cdot 5^{\circ} / 763 \mathrm{~mm} . ; M 114 \cdot 18 ; n_{\mathrm{C}} 1 \cdot 43248, n_{\mathrm{D}} 1 \cdot 43470, n_{\mathrm{F}} 1 \cdot 44004$, $n_{G^{\prime}} \mathrm{I} \cdot 44398 ; R_{\mathrm{C}} 33 \cdot 87, R_{\mathrm{D}} 34 \cdot 02, R_{\mathrm{F}} 34 \cdot 38, R_{G^{\prime}} 34 \cdot 65 ; M n_{\mathrm{D}}^{20^{\circ}} 163 \cdot 81$. Densities determined: $d_{4}^{20^{\circ}}$ $0 \cdot 8752, d_{4^{\circ}}^{40 \cdot 5^{\circ}} 0.8574, d_{4^{\circ}}^{61 \cdot 9^{\circ}} 0.8395, d_{4^{8} \cdot 7^{\circ}}^{86} 0.8168$. Apparatus $D$.

| $14 \cdot 7^{\circ}$ | 13.26 | 0.8798 | 28.81 | 300.7 | $41 \cdot 3^{\circ}$ | $12 \cdot 19$ | 0.8567 | $25 \cdot 79$ | $300 \cdot 4$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $17 \cdot 9$ | $13 \cdot 14$ | 0.8770 | 28.46 | 300.7 | $60 \cdot 8$ | 11.42 | 0.8404 | 23.70 | $299 \cdot 8$ |
| $27 \cdot 4$ | 12.77 | 0.8688 | $27 \cdot 40$ | 300.7 | $86 \cdot 0$ | 10.41 | 0.8162 | $20 \cdot 98$ | $299 \cdot 4$ |
|  |  |  |  |  |  |  |  | Mean $300 \cdot 3$ |  |

447. cycloHexyl ethyl ether. B. p. 148.5-149.5 $/ 763 \mathrm{~mm}$.; $M 128 \cdot 21 ; n_{\mathrm{C}} \mathrm{I} \cdot 43284, n_{\mathrm{D}} 1 \cdot 43505$, $n_{\mathrm{F}} \mathrm{I} \cdot 44042, n_{\mathrm{G}^{\prime}} 1 \cdot 44506 ; R_{\mathrm{G}} 38 \cdot 55, R_{\mathrm{D}} 38 \cdot 73, R_{\mathrm{F}} 39 \cdot 14, R_{\mathrm{G}^{\prime}} 39 \cdot 50 ; M n_{\mathrm{D}}^{20^{\circ}} 183 \cdot 99$. Densities determined : $d_{4}^{20^{\circ}} 0 \cdot 8640, d_{4^{4}}^{4} \cdot 6^{\circ} 0 \cdot 8466, d_{4^{\circ}}^{6 \cdot 1^{\circ}}{ }^{\circ} 0 \cdot 8295, d_{4^{8 .}}{ }^{85} 3^{\circ} 0.8074$. Apparatus $A$.

| $17 \cdot 3^{\circ}$ | 16.92 | 0.8663 | 27.45 | $338 \cdot 7$ | $40 \cdot 6^{\circ}$ | $15 \cdot 91$ | 0.8475 | $25 \cdot 25$ | $339 \cdot 1$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | ---: |
| $20 \cdot 7$ | $16 \cdot 85$ | 0.8634 | $27 \cdot 24$ | $339 \cdot 2$ | $60 \cdot 9$ | $14 \cdot 84$ | 0.8288 | 23.03 | $338 \cdot 9$ |
| $27 \cdot 6$ | 16.55 | 0.8585 | 26.60 | $339 \cdot 2$ | $85 \cdot 4$ | 13.63 | 0.8073 | $20 \cdot 60$ | $338 \cdot 4$ |
|  |  |  |  |  |  |  |  | Mean $338 \cdot 9$ |  |

448. cycloHexyl formate. B. p. $160^{\circ} / 757 \mathrm{~mm}$.; $M 128 \cdot 17$; $n_{\mathrm{D}} \mathrm{l} \cdot 44073$, $n_{\mathrm{D}} \mathrm{l} \cdot 44305, n_{\mathrm{F}} 1 \cdot 44857$, $n_{\mathrm{G}^{\prime}} \mathrm{I} \cdot 45263 ; R_{\mathrm{C}} 34 \cdot 03, R_{\mathrm{D}} 34 \cdot 19, R_{\mathrm{F}} 34 \cdot 56, R_{\mathrm{G}^{\prime}} 34 \cdot 82 ; M n_{\mathrm{D}}^{20^{\circ}} 184 \cdot 96$. Densities determined: $d_{4}^{20}{ }^{\circ}$ $0.9941, d_{4^{\circ}}^{41.3^{\circ}} 0.9735, d_{4^{\circ}}^{61 \cdot 1^{\circ}} 0.9552, d_{4^{\circ}}^{87 \cdot 1^{\circ}} 0.9317$. Apparatus $A$.

| $13 \cdot 0^{\circ}$ | $17 \cdot 62$ | $1 \cdot 0007$ | $33 \cdot 02$ | 307.0 | $61 \cdot 3^{\circ}$ | $15 \cdot 38$ | 0.9550 | $27 \cdot 50$ | $307 \cdot 3$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $19 \cdot 0$ | $17 \cdot 39$ | 0.9950 | $32 \cdot 40$ | $307 \cdot 3$ | $87 \cdot 1$ | $14 \cdot 25$ | 0.9317 | $24 \cdot 86$ | $307 \cdot 2$ |
| $41 \cdot 0$ | 16.35 | 0.9738 | $29 \cdot 81$ | $307 \cdot 6$ |  |  |  | Mean $307 \cdot 3$ |  |

449. cycloHexyl acetate. B. p. $172^{\circ} / 752 \mathrm{~mm} . ; M 142 \cdot 19$; $n_{\mathrm{O}} \mathrm{l} \cdot 43950, n_{\mathrm{D}} \mathrm{l} \cdot 44174, n_{\mathrm{F}} \mathrm{l} \cdot 44718, n_{\mathrm{G}^{\prime}}$ $1.45118 ; R_{\mathrm{C}} 38 \cdot 61, R_{\mathrm{D}} 38 \cdot 77, R_{\mathrm{F}} 39 \cdot 19, R_{\mathrm{G}^{\prime}} 39 \cdot 50 ; M n_{\mathrm{D}}^{20^{\circ}} 205 \cdot 00$. Densities determined: $d_{4}^{20^{\circ}} 0.9697$, $d_{4}^{40 \cdot 6^{\circ}} 0.9501, d_{4}^{62 \cdot 3^{\circ}} 0.9298, d_{4}^{86} 6^{\circ}{ }^{\circ} 0.9072$. Apparatus $D$.

| $20 \cdot 3^{\circ}$ | 13.08 | 0.9694 | 31.31 | $347 \cdot 0$ | $61 \cdot 5^{\circ}$ | $11 \cdot 57$ | 0.9306 | 26.59 | $347 \cdot 0$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $41 \cdot 1$ | 12.31 | 0.9496 | 28.87 | $347 \cdot 1$ | 87.1 | 10.66 | 0.9067 | 23.87 | $346 \cdot 6$ |
|  |  |  |  |  |  |  |  | Mean $346 \cdot 9$ |  |

450. cycloHexyl chloride. B. p. $142^{\circ} / 755 \mathrm{~mm} . ; M 118.61 ; n_{\mathrm{C}} \mathrm{l} \cdot 45993, n_{\mathrm{D}} \mathrm{l} \cdot 46235, n_{\mathrm{F}} \mathrm{l} \cdot 46828$, $n_{\mathrm{G}^{\prime}}$ I.47266; $R_{\mathrm{C}} 32.84, R_{\mathrm{D}} 32.99, R_{\mathrm{F}} 33.35, R_{\mathrm{G}^{\prime}} 33.62$; $M n_{\mathrm{D}}^{20^{\circ}} 173 \cdot 46$. Densities determined: $d_{4^{\circ}}^{20} 0.9891$, $d_{4^{\circ}}^{40 \cdot 6^{\circ}} 0.9690, d_{4^{\circ}}^{61 \cdot 0^{\circ}} 0.9497, d_{4^{8}}^{8 \cdot 5} \cdot{ }^{\circ}{ }^{\circ} \cdot 9256$. Apparatus $A$.

| $15 \cdot 9^{\circ}$ | 17.34 | 0.9932 | $32 \cdot 25$ | $284 \cdot 6$ | $60 \cdot 9^{\circ}$ | $15 \cdot 24$ | 0.9498 | $27 \cdot 10$ | $284 \cdot 9$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $40 \cdot 0$ | $16 \cdot 20$ | 0.9696 | $29 \cdot 41$ | $284 \cdot 9$ | $86 \cdot 0$ | $14 \cdot 16$ | 0.9251 | $24 \cdot 53$ | $285 \cdot 3$ |
|  |  |  |  |  |  |  |  | Mean $284 \cdot 9$ |  |

451. cyclo Hexyl bromide. B. p. $164^{\circ} / 766 \mathrm{~mm}$.; $M 163 \cdot 07$; $n_{\mathrm{C}} \mathrm{I} \cdot 49226, n_{\mathrm{D}} \mathrm{I} \cdot 49526, n_{\mathrm{F}} \mathrm{I} \cdot 50269$, $n_{G^{\prime}} 1 \cdot 50830 ; R_{\mathrm{C}} 35 \cdot 43, R_{\mathrm{D}} 35 \cdot 61, R_{\mathrm{F}} 36 \cdot 06, R_{\mathrm{G}^{\prime}} 36 \cdot 40 ; M n_{\mathrm{D}}^{20^{\circ}} 243.84$. Densities determined : $d_{4^{2}} 0^{\circ}$ $1 \cdot 3360, d_{4}^{42 \cdot 50^{\circ}} 1 \cdot 3092, d_{4^{\circ}}^{61 \cdot 7^{\circ}} 1 \cdot 2875$, $d_{4}^{85 \cdot 7^{\circ}} 1 \cdot 2583$. Apparatus $A$.

| $23.1{ }^{\circ}$ | $13 \cdot 45$ | 1-3323 | 33.55 | 294.6 | $60 \cdot 6{ }^{\circ}$ | $12 \cdot 18$ | $1 \cdot 2888$ | $29 \cdot 39$ | 294.6 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 41.2 | 12.84 | 1-3107 | 31.51 | $294 \cdot 8$ | $86 \cdot 3$ | 11.27 | $1 \cdot 2577$ | $26 \cdot 48$ | $294 \cdot 4$ |
|  |  |  |  |  |  |  |  |  | $294 \cdot 6$ |

452. cycloHexyl iodide. B. p. $81.5^{\circ} / 20 \mathrm{~mm}$.; $M 210.07$; $n_{\mathrm{O}} \mathrm{I} .54333, n_{\mathrm{D}} \mathrm{I} \cdot 54765, n_{\mathrm{F}} 1.55856, n_{\mathrm{G}^{\prime}}$ $1.56730 ; R_{\mathrm{G}} 40 \cdot 78, R_{\mathrm{D}} 41 \cdot 05, R_{\mathrm{F}} 41 \cdot 73, R_{\mathbf{G}^{\prime}} 42 \cdot 26 ; M n_{\mathrm{D}}^{20^{\circ}} 325 \cdot 13$. Densities determined: $d_{4^{\circ}}^{20^{\circ}} 1 \cdot 6244$, $d_{4}^{41 \cdot 2^{\circ}} 1 \cdot 5968, d_{4}^{62 \cdot 2^{\circ}} 1 \cdot 5702, d_{4^{6}}^{86 \cdot 3^{\circ}} 1 \cdot 5403$. Apparatus $D$.

| $15 \cdot 2^{\circ}$ | $9 \cdot 17$ | $1 \cdot 6306$ | $36 \cdot 93$ | $317 \cdot 6$ | $61 \cdot 2^{\circ}$ | $8 \cdot 19$ | 1.5715 | $31 \cdot 06$ | $315 \cdot 6$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $25 \cdot 0$ | $8 \cdot 92$ | 1.6180 | $35 \cdot 64$ | $317 \cdot 2$ | $86 \cdot 8$ | 7.66 | 1.5397 | $29 \cdot 13$ | $317 \cdot 0$ |
| 40.5 | 8.65 | 1.5977 | $34 \cdot 13$ | 317.8 |  |  |  | Mean $317 \cdot 1$ |  |

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