THE VARIATION OF THE
REFRACTIVE INDEX AND DISPERSION
WITH TEMPERATURE OF THE
CIS AND TRANS ISOMERS
OF DECAHYDRONAPHTHALENE

by

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It is, indeed, a pleasure to acknowledge the assistance of Dr. W. F. Seyer, under whose general guidance this work was performed.
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I INTRODUCTION

For several years considerable work has been carried out in these laboratories on the physical properties of decahydronaphthalene (C_{10}H_{18}) or decalin under the direction of Dr. W. F. Seyer.\(^1\) This naphthene is believed to exist in five stereo-isomeric forms, the cis and trans forms being the limiting positions and, therefore, of greater stability.

\[\text{cis}\]

\[\text{trans}\]

In previous investigations of the temperature effect on the physical properties such as specific heats\(^2\) and surface tension\(^3\), the trans form has shown no abnormalities, but the cis form has revealed definite discontinuities. These discontinuities are probably due to transformations of isomeric forms. The purpose of the following research is, therefore, twofold: first, to find the temperature coefficient of the refractive indices and dispersion, secondly, to note if these observations also show the discontinuities in the cis form.

2. Davies, G. F. M.A. Sc. Thesis 1939
II PREPARATION

the first successful separation of the two isomers was accomplished in 1936-37 by Dr. W. F. Seyer and R. D. Walker. The following preparation and purification is essentially that of the original workers with some minor changes.

Commercial decalin obtained from Eastman Kodak Co. was used. This was treated first with an acid wash, then an alkali wash, followed with a water wash until neutral. The separation of the two isomers was obtained by repeated low pressure rectification (approximately 10 m.m. of Hg.)

The final purification of the isomers obtained by rectification is accomplished by repeated fractional crystallization. The procedure is to save that fraction which crystallizes out before an eutectic is formed. By repeated operations, the fraction retained eventually reaches a constant freezing point which shows it to be of great purity.

The following table shows a comparison of the values obtained for freezing points and refractive indices of the various workers.

### III APPARATUS

(a) Refractometer

The apparatus used is a Pulfrich refractometer, the optical principle of which is:

\[ n_r \sin \varepsilon = n_o \sin (\frac{\pi}{2} - r) \]

let \( \varepsilon \to 0 \) (the limiting angle)

\[ \sin \varepsilon \to 1 \]

\[ \therefore n_r = n_o \sin (\frac{\pi}{2} - r) \]

for the emergence of the light ray from the prism.

---

5. International Critical Tables
6. Huckel, W. Annalen der Chemie 441-1-1925
7. Loc. cit.
\[ n_0 \sin r = n_0 \sin i = \sin i \quad \text{(2)} \]
\[ n_0 = 1 \quad \text{(for air)} \]

Square & combine (1) & (2)
\[ n_i = \sqrt{n_0^2 - \sin^2 i} \quad \text{(3)} \]

Since \( n_0 \) is given for the prism and angle \( i \) is observed, \( n_i \) can be calculated. The instrument is set in such a manner that only the grazing ray is refracted, that is, the light source is at A. The angle of emergence, \( i \), is read on a circle by a vernier correct to 30" of arc which corresponds to ±0.00005 for \( n_i \), or less than .003% error.

(b) Temperature Correction

The value of the refractive index was obtained by the use of tables calculated from the above formula. The tables assumed \( n_0 \) to be constant (the value of \( n_0 \) used is \( n_D^{15} \)), therefore, there must be a correction applied for deviations from 15°C.

Let \( n_o \) = refractive index of the prism at 15°C
\[ \Delta n_o = " " \quad \text{"correction per degree rise} \]
\( n_t \) = corrected refractive index.

Then \( n_t = n_o + K \)

where \( K \) = correction value
\[ n_i^2 = n_o^2 - \sin^2 i \]
\[ n_t^2 = [n_o + (t-15)\Delta n_o]^2 - \sin^2 i \]
\[ K = \frac{n_o \Delta n_o (t-15)}{n_i^2} \]
Values given for the prism used:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>D</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δn₀</td>
<td>0.00024</td>
<td>0.00028</td>
<td>0.00039</td>
</tr>
<tr>
<td>n₁₅</td>
<td>1.61829</td>
<td>1.62533</td>
<td>1.63573</td>
</tr>
</tbody>
</table>

The refractometer and liquid is kept at a constant temperature by circulating water through it from a large constant temperature bath. The method used gives a constancy of ±0.01°C, but the thermometer reading can be read only to ±0.02°C accuracy.

(c) Source of Light

The source of H\(\alpha\) and H\(\beta\) lines is a Guild type of hydrogen discharge tube. It was filled and evacuated repeatedly with hydrogen gas which was generated electrolytically, and then purified by absorption of impurities. The final pressure of the hydrogen in the tube is of the order of 0.01 m.m. of mercury. The excitation of the hydrogen atoms is effected by a 6 volt high tension vibratory coil generating 5 to 10 thousand volts in the secondary circuit.

\[ H_\alpha = \lambda = 6562 \text{Å} \]
\[ H_\beta = \lambda = 4861 \text{Å} \]

The sodium D line was obtained by burning fused sodium chloride with a bunsen burner. This gave a sharp, intense line.

NOTE. There were a few difficulties encountered in the making of the tube, the major one being the determination of the optimum pressure. Since the intensity of the illumination is a function of the pressure and voltage, during
evacuation the secondary circuit was completed, and at the point of maximum intensity evacuation was stopped. But at the maximum intensity, the pressure being very low, the mean free path of the excited atoms is so large that it caused "burning" of the glass at the end of the capillary which causes a diminution of the available light. The burning will eventually cause a leak at the "burnt" point. However, after many trials, an optimum condition was attained. Another difficulty was encountered in the making of electrodes. They were made of the purest aluminium available and were held by tungsten wire fused to the glass wall of the tube.

IV GENERAL OBSERVATIONS ON REFRACTION

The law of Gladstone and Dale states that the specific and molecular refractivities are nearly constant with temperature variations

\[ r_G = \frac{(n-1)^2}{d} \]

\[ R_d = \frac{(n-1)}{d} M \]

\[ d = \text{density} \]

\[ M = \text{molecular weight} \]

A greater constancy is obtained by using the formula of Lorentz and Lorentz.

\[ r_L = \frac{(n^2-1)}{(n+2)} \frac{1}{d} \]

\[ R_L = \frac{(n^2-1)}{(n^2+2)} \frac{M}{d} \]
The purely empirical formula found by Eykman to fit organic liquids has shown a greater constancy than the Gladstone--Dale and Lorentz-Lorentz formulae in the measurements of temperature--pressure effect on the refractivity of benzene.\(^9\)

\[
\begin{align*}
\text{r}_E &= \frac{(n^2 - 1)}{(n + 0.4)} \frac{1}{d} \\
\text{r}_F &= \frac{(n^2 - 1)}{(n + 0.4)} \frac{M}{d}
\end{align*}
\]

Previous investigators have shown, that, in general, the molecular refractivity is the sum of the atomic refractivities; but in the case of isomers the laws of addition are very complex and cannot be applied according to the table given by Eisenlohr.\(^10\)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>D</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon</td>
<td>2.413</td>
<td>2.418</td>
<td>2.438</td>
</tr>
<tr>
<td>hydrogen</td>
<td>1.092</td>
<td>1.100</td>
<td>1.115</td>
</tr>
</tbody>
</table>

These values were calculated from the Lorentz-Lorentz formula and the values of \(R_L^C\), \(R_L^D\), & \(R_L^F\) do not allow for isomers or variations with temperature. This would give for decalin:

\[
\begin{align*}
\text{R}_L^C &= (2.413)(10) + (1.092)(18) = 32.79 \\
\text{R}_L^D &= (2.418)(10) + (1.100)(18) = 33.98 \\
\text{R}_L^F &= (2.438)(10) + (1.115)(18) = 44.45
\end{align*}
\]

9. Gibson & Kincaid J.A.C.S. 60-511-1938

10. Eisenlohr, Z. Physikal Chemie. 1911-75-585
Moreover, later workers\(^\text{11}\) have shown that the refractive index is a function of density which is a function of temperature and pressure. Apparently, their researches have led them to the conclusion that all saturated compounds have a specific dispersion of approximately 0.0099 irrespective of their boiling point. Therefore, by the use of Cauchy equations

\[
\begin{align*}
    n_c^t &= n_B^t - 0.292(n_F - n_c) \\
    n_F^t &= n_D^t - 0.708(n_F - n_c)
\end{align*}
\]

and when the density is known, the refractive indices can be calculated. In effect, if the refractive indices are plotted against density, the result will be a straight line. The line was determined by these investigators and was given in the form.

\[
\Delta n = 0.60 \Delta d
\]

or

\[
\Delta n = f(r, d) \Delta d
\]

which on integration gives \(f(n,d) = \text{constant}\). Since the formulae of Gladstone—Dale, Lorentz—Lorentz, and Eykman are of this form, it should be possible to differentiate them to find the slope of the refractive-index density curve. Therefore, it now remains to find the value of the function \(f(n,d)\).

For Gladstone—Dale equation

\[
R_G = \frac{n-1}{d} M
\]

\[
\Delta n = \frac{n-1}{d} \Delta d
\]

For Lorentz-Lorentz equation:
\[ F_L = \frac{n^2 - 1}{n^2 + 2} \frac{M^2}{d} \]
\[ \Delta n = \frac{(n^2 - 1)(n^2 + 2)}{2 \cdot n} \Delta d \]

For Eykman equation:
\[ F_E = \frac{n^2 - 1}{n^2 + 0.4} \frac{M^2}{d} \]
\[ \Delta n = \frac{(n^2 - 1)(n^2 + 0.4)}{2.8 \cdot n} \Delta d \]

As a first approximation, which is substantiated by unpublished data on high boiling point compounds, the specific dispersion varies linearly with temperature\(^1\). This is to be expected since density varies linearly with temperature (to a first approximation) and the refractive index is directly connected with density. However, the temperature coefficient of specific dispersion is small.

\[ \delta = \frac{n_F^t - n_C^t}{d_C^t} \]
\[ \delta = \text{specific dispersion} \]
\[ \Delta \delta = \frac{n_F^t - n_C^t}{d_C^t} \]
\[ \Delta \delta = \text{molecular dispersion} \]

The advantage of measuring mean dispersion\(^2\) rather than a refractive index is that the former varies less with temperature: it is also possible that molecular dispersion and specific dispersion have a larger temperature coefficient than the mean specific dispersion.

\[ \delta_M = \frac{n_F^t - n_C^t}{d_C^t} \]

### RESULTS

(a) for trans decahydronapthalene

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2°C</td>
<td>42°26'30&quot;</td>
<td>1.47096</td>
<td>10.°C</td>
<td>42°56'30&quot;</td>
<td>1.47345</td>
<td>9.2°C</td>
<td>44°15'30&quot;</td>
<td>1.47936</td>
</tr>
<tr>
<td>35.°C</td>
<td>44°11'</td>
<td>1.46068</td>
<td>30.°C</td>
<td>49°19'</td>
<td>1.46536</td>
<td>35.°C</td>
<td>46°03'</td>
<td>1.46885</td>
</tr>
<tr>
<td>45.°C</td>
<td>44°51'30&quot;</td>
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<td>35.°C</td>
<td>44°40'</td>
<td>1.46328</td>
<td>40.°C</td>
<td>46°23'30&quot;</td>
<td>1.46685</td>
</tr>
<tr>
<td>50.°C</td>
<td>45°12'</td>
<td>1.45479</td>
<td>45.°C</td>
<td>45°19'30&quot;</td>
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<td>45.°C</td>
<td>46°43'30&quot;</td>
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</tr>
<tr>
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<td>45°29'</td>
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<td>50.°C</td>
<td>45°40'30&quot;</td>
<td>1.45731</td>
<td>50.°C</td>
<td>47°03'30&quot;</td>
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</tr>
<tr>
<td>60.°C</td>
<td>45°51'30&quot;</td>
<td>1.45080</td>
<td>60.°C</td>
<td>46°19'</td>
<td>1.45349</td>
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<td>47°45'</td>
<td>1.45885</td>
</tr>
<tr>
<td>69.7°C</td>
<td>46°28'30&quot;</td>
<td>1.44702</td>
<td>69.7°C</td>
<td>46°59'30&quot;</td>
<td>1.44947</td>
<td>69.7°C</td>
<td>48°24'</td>
<td>1.45479</td>
</tr>
<tr>
<td>79.8°C</td>
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<td>1.44579</td>
<td>79.2°C</td>
<td>49°04'</td>
<td>1.45111</td>
</tr>
<tr>
<td>84.8°C</td>
<td>47°28'30&quot;</td>
<td>1.44103</td>
<td>84.6°C</td>
<td>47°55'</td>
<td>1.44366</td>
<td>84.7°C</td>
<td>49°28'</td>
<td>1.44879</td>
</tr>
</tbody>
</table>
Graph showing relationship between $T$ and $n^t$ of trans decalin.

Temperature ($^\circ$C)

Refractive Index ($n^t$)

Radius of circle

1.0°C and .0005 in $n^t$. 

Values along the horizontal axis range from 1440 to 1480.
(b) for cis decahydronapthalene

<table>
<thead>
<tr>
<th>temp.</th>
<th>angle</th>
<th>n_C</th>
<th>temp.</th>
<th>angle</th>
<th>n_D</th>
<th>temp.</th>
<th>angle</th>
<th>n_F</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1°C</td>
<td>40°26'</td>
<td>1.48274</td>
<td>10.0°C</td>
<td>40°59'30&quot;</td>
<td>1.48488</td>
<td>10.0°C</td>
<td>42°14'</td>
<td>1.49121</td>
</tr>
<tr>
<td>15.0°C</td>
<td>40°48'30&quot;</td>
<td>1.48056</td>
<td>15.0°C</td>
<td>41°18'</td>
<td>1.48310</td>
<td>15.0°C</td>
<td>42°38'</td>
<td>1.48892</td>
</tr>
<tr>
<td>20.0°C</td>
<td>41°10'30&quot;</td>
<td>1.47844</td>
<td>20.0°C</td>
<td>41°40'</td>
<td>1.48098</td>
<td>20.0°C</td>
<td>42°58'30&quot;</td>
<td>1.48694</td>
</tr>
<tr>
<td>25.0°C</td>
<td>41°30'30&quot;</td>
<td>1.47649</td>
<td>25.0°C</td>
<td>42°02'</td>
<td>1.47884</td>
<td>25.0°C</td>
<td>43°19'30&quot;</td>
<td>1.48479</td>
</tr>
<tr>
<td>30.0°C</td>
<td>41°58'30&quot;</td>
<td>1.47426</td>
<td>30.0°C</td>
<td>42°23'30&quot;</td>
<td>1.47675</td>
<td>30.0°C</td>
<td>43°44'</td>
<td>1.48252</td>
</tr>
<tr>
<td>35.0°C</td>
<td>42°15'30&quot;</td>
<td>1.47211</td>
<td>35.0°C</td>
<td>42°45'</td>
<td>1.47472</td>
<td>35.0°C</td>
<td>44°04'30&quot;</td>
<td>1.48054</td>
</tr>
<tr>
<td>40.0°C</td>
<td>42°36'</td>
<td>1.47011</td>
<td>40.0°C</td>
<td>43°07'30&quot;</td>
<td>1.47246</td>
<td>40.0°C</td>
<td>44°28'30&quot;</td>
<td>1.47819</td>
</tr>
<tr>
<td>45.0°C</td>
<td>43°55'30&quot;</td>
<td>1.46820</td>
<td>45.0°C</td>
<td>43°25'</td>
<td>1.47074</td>
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<td>44°47'</td>
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</tr>
<tr>
<td>50.0°C</td>
<td>43°15'</td>
<td>1.46628</td>
<td>50.0°C</td>
<td>43°48'</td>
<td>1.46848</td>
<td>50.0°C</td>
<td>45°07'</td>
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<td>50.9°C</td>
<td>45°18'30&quot;</td>
<td>1.46593</td>
<td>51.2°C</td>
<td>45°53'</td>
<td>1.46799</td>
<td>50.9°C</td>
<td>45°11'</td>
<td>1.47405</td>
</tr>
<tr>
<td>52.9°C</td>
<td>45°30'1</td>
<td>1.46479</td>
<td>55.0°C</td>
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<td>1.46727</td>
<td>52.9°C</td>
<td>45°21'</td>
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<td>54.9°C</td>
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<td>44°07'30&quot;</td>
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<td>60.0°C</td>
<td>45°58'</td>
<td>1.46205</td>
<td>60.0°C</td>
<td>44°27'30&quot;</td>
<td>1.46459</td>
<td>60.5°C</td>
<td>45°53'30&quot;</td>
<td>1.46991</td>
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<tr>
<td>65.0°C</td>
<td>44°23'30&quot;</td>
<td>1.45952</td>
<td>65.2°C</td>
<td>44°47'30&quot;</td>
<td>1.46262</td>
<td>64.5°C</td>
<td>46°09'30&quot;</td>
<td>1.46854</td>
</tr>
</tbody>
</table>
(b) continued

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Angle</th>
<th>$n_0^*$</th>
<th>Temp.</th>
<th>Angle</th>
<th>$n_0^*$</th>
<th>Temp.</th>
<th>Angle</th>
<th>$n_0^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.7°C</td>
<td>44°35'</td>
<td>1.45839</td>
<td>69.5°C</td>
<td>45°05'30&quot;</td>
<td>1.46080</td>
<td>69.3°C</td>
<td>46°30'30&quot;</td>
<td>1.46639</td>
</tr>
<tr>
<td>74.4°C</td>
<td>44°51'</td>
<td>1.45680</td>
<td>74.4°C</td>
<td>45°22'</td>
<td>1.45922</td>
<td>74.4°C</td>
<td>46°49'30&quot;</td>
<td>1.46442</td>
</tr>
<tr>
<td>80.4°C</td>
<td>45°18'30&quot;</td>
<td>1.45416</td>
<td>80.4°C</td>
<td>45°47'</td>
<td>1.45675</td>
<td>80.4°C</td>
<td>47°15'</td>
<td>1.46192</td>
</tr>
<tr>
<td>85.0°C</td>
<td>45°38'</td>
<td>1.45213</td>
<td>84.8°C</td>
<td>46°05'</td>
<td>1.45498</td>
<td>85.0°C</td>
<td>47°35'30&quot;</td>
<td>1.45990</td>
</tr>
</tbody>
</table>
Graph showing relationship between $T$ and $n^t$ of cis decalin.

Radius of circle: $10^\circ C$ and $0.005$ in $n$.
### TREATMENT OF RESULTS

(a) for trans decahydronaphthalene

<table>
<thead>
<tr>
<th>Temp.</th>
<th>( n_C^+ )</th>
<th>( n_D^+ )</th>
<th>( n_F^+ )</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 °C</td>
<td>1.47094</td>
<td>1.47340</td>
<td>1.47906</td>
<td>.8775</td>
</tr>
<tr>
<td>20 °C</td>
<td>1.46670</td>
<td>1.46939</td>
<td>1.47502</td>
<td>.8700</td>
</tr>
<tr>
<td>30 °C</td>
<td>1.46275</td>
<td>1.46540</td>
<td>1.47099</td>
<td>.8627</td>
</tr>
<tr>
<td>40 °C</td>
<td>1.45876</td>
<td>1.46139</td>
<td>1.46685</td>
<td>.8553</td>
</tr>
<tr>
<td>50 °C</td>
<td>1.45479</td>
<td>1.45732</td>
<td>1.46299</td>
<td>.8480</td>
</tr>
<tr>
<td>60 °C</td>
<td>1.45085</td>
<td>1.45349</td>
<td>1.45879</td>
<td>.8405</td>
</tr>
<tr>
<td>70 °C</td>
<td>1.44690</td>
<td>1.44945</td>
<td>1.45478</td>
<td>.8331</td>
</tr>
<tr>
<td>80 °C</td>
<td>1.44295</td>
<td>1.44549</td>
<td>1.45075</td>
<td>.8255</td>
</tr>
<tr>
<td>90 °C</td>
<td>1.43898</td>
<td>1.44149</td>
<td>1.44675</td>
<td>.8178</td>
</tr>
</tbody>
</table>

The above table was obtained from the graph on plate 1. The values for density were obtained from Davenport's\(^{14}\) equation.

\[
d_{4}^{+} = .8849 - .000742t
\]

By graphic analysis

\[
\frac{dn_C}{dt} = -.000399/°C
\]
\[
\frac{dn_D}{dt} = -.000398/°C
\]
\[
\frac{dn_F}{dt} = -.000403/°C
\]
\[
\frac{dn_{M}}{dt} = -.000016/°C
\]

\[
\delta_{M}^{+} = .00777 + .000016 \times (t-10)
\]

\[
\Delta_{M}^{+} = .07373 + .00211(t-10)
\]

14. loc.cit.
Using the above values, the equations of Gladstone-Dale, Lorentz-Lorentz, and Eykman were tests for "constancy".

<table>
<thead>
<tr>
<th>Temp.</th>
<th>( R_G = \frac{n_l}{d} )</th>
<th>( R_L = \frac{n_l - 1}{n_l + 2} )</th>
<th>( R_E = \frac{n_l - 1}{n_l + 0.4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n_C^t )</td>
<td>( n_D^t )</td>
<td>( n_F^t )</td>
</tr>
<tr>
<td>10°C</td>
<td>74.164</td>
<td>74.551</td>
<td>75.443</td>
</tr>
<tr>
<td>20°C</td>
<td>74.113</td>
<td>74.540</td>
<td>75.451</td>
</tr>
<tr>
<td>30°C</td>
<td>74.125</td>
<td>74.549</td>
<td>75.444</td>
</tr>
<tr>
<td>40°C</td>
<td>74.121</td>
<td>74.546</td>
<td>75.428</td>
</tr>
<tr>
<td>50°C</td>
<td>74.112</td>
<td>74.524</td>
<td>75.431</td>
</tr>
<tr>
<td>60°C</td>
<td>74.126</td>
<td>74.560</td>
<td>75.431</td>
</tr>
<tr>
<td>70°C</td>
<td>74.129</td>
<td>74.552</td>
<td>75.431</td>
</tr>
<tr>
<td>80°C</td>
<td>74.150</td>
<td>74.575</td>
<td>75.456</td>
</tr>
<tr>
<td>90°C</td>
<td>74.177</td>
<td>74.602</td>
<td>75.490</td>
</tr>
</tbody>
</table>
The results of the table, may be condensed to the form
\[ \frac{dR_L}{dt} = K(t); \quad \frac{dR_E}{dt} = K'(t); \quad \text{and} \quad \frac{dR_G}{dt} = 0 \]

Therefore, to find density-refractive index equation, we must use the Gladstone form.

\[ \Delta n = \frac{n-1}{d} \angle d = r_G \angle d. \]

which gives:-

for the C line. \( \Delta n = 0.529 \angle d. \)

for the D line. \( \Delta n = 0.539 \angle d. \)

for the F line. \( \Delta n = 0.545 \angle d. \)

(b) for cis decahydronapthalene.

Davenport's equation for density is given by:-

\[ d_T^L = 0.9120 - 0.000752t \]

which is linear to a first approximation over the temperature range that the refractive indices were measured; and since the refractive indices curves are discontinuous, there can be no general density-refractive index equation set up for the whole temperature range. (5° to 90°)

If we assume that at each discontinuity, there is an isomer, then by graphic analysis, it is seen that the mean dispersion for each isomer may be assumed constant (less than 0.1% error); but each isomer has a different mean dispersion.

below 35° \( \delta_n = 0.0085 \)

35° - 50° \( \delta_n = 0.0082 \)

above 50° \( \delta_n = 0.0080 \)
VII CONCLUSIONS

(a) for trans.

Although the temperature coefficient of mean dispersion is very small, a correction should be applied in using the Cauchy equations.

\[(n_T^n - n_C^n) = 0.00777 + 0.000016 (t - 10)\]

The linear variation of refractive indices with temperature shows that the trans isomer has no changes detectable by this method over the temperature range of 10°C to 90°C.

(b) for cis

The curve for cis shows 2 breaks between 5° and 85°. The following equation is derived from the wave theory of light, which means that refractive index varies inversely as the frequency of oscillation of the atoms and directly proportional to the number of electrons.

\[n^2 = 1 + \frac{\epsilon^2}{\omega_m} \sum \frac{N}{\omega^2 - \omega^2}\]

\[N = \text{no of electrons of natural frequency } \omega, \quad \omega = \text{frequency of light used.}\]

The change of number of electrons per c.c. is the density variation and since this variation is linear over the temperature range that is used, it follows that the frequency of oscillation of the atoms must be the cause of the discontinuities. Now for the oscillation frequency to vary suddenly, it means that there must be a shift in atomic structure. Therefore, a shift in position of atoms equivalent to a structural change, I conclude that cis has three isomers, the transition temperatures being 38° ± 0.5 and 51° ± 0.2.
Furthermore, in the study of the Raman effect, the cis isomer has shown a difference in oscillation energy of the atoms above and below 50°6. This has been interpreted as a structural change by the workers.

In measurements of the refractive index near 51°C there is a region where the light rays are indistinct, i.e. the rays are sharp, then they become indistinct, then sharp again when equilibrium is reached. Apparently, this is due to transition of forms taking place.

15 Zotov, G. M.A. Thesis 1940
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