THE VARIATION OF THE

REFRACTIVE INDEX AND DISPERSION

WITH TEMPERATURE OF THE

CIS AND TRANS ISOMERS

OF DECAHYDRONAPHTHALENE

by

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CONTENTS

I INTRODUCTION

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

cis   trans
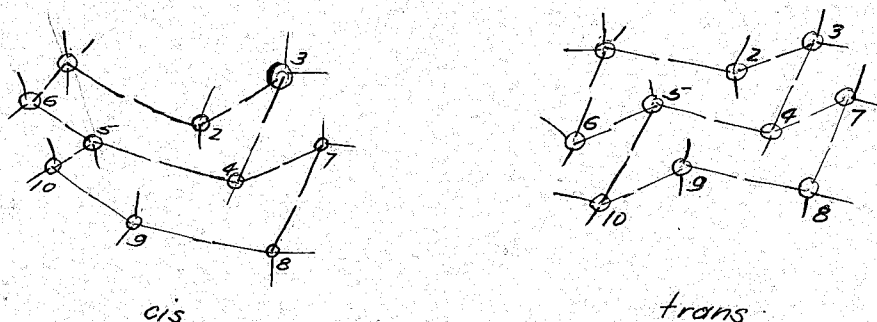
In previous investigations of the temperature effect on the physical properties such as specific heats[2] and surface tension[3], the trans form has shown no abnormalities, but the cis form has revealed definite discontinuities. These discontinuities are probably due to transformations of isomeric forms. 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.

1. Seyer, W. F. Assoc. Prof. of Chem. Eng. University of B.C.
2. Davies, G. F. M.A. Sc. Thesis 1939
3. Davenport, C. H. B.A. Sc. Thesis 1938

II PREPARATION

the first successful separation of the two isomers was accomplished in 1936-37 by Dr. W. F. Seyer and R. D. Walker.[4] 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.
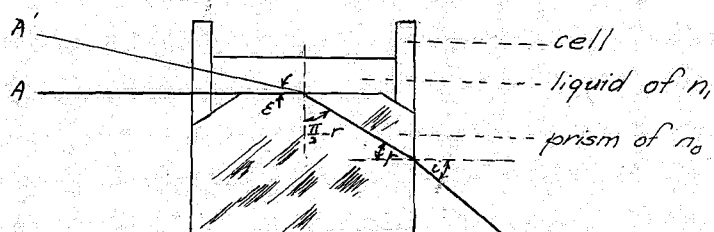
4. Walker, R. D. M.A. Sc. Thesis 1937

	Cis		Trans.	
	f. p.	n_D^{20}	f. p.	n_D^{20}
Int. Crit tables 5	-----	1.4828	-----	1.4701
Huckel 6	$-51.\ °$ C	1.47950	$-36°$ C	1.46958
Walker 7	$-42.60°$ C	1.48084	$-30.30°$ C	1.46948
Sample used for This research 8	$-43.22°$ C	1.48098	$-30.84°$ C	1.46934

III APPARATUS

(a) Refractometer

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

Equations for the light refraction from A'

$n_1 \sin \varepsilon = n_0 \sin (\frac{\pi}{2} - r)$

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

$\sin \varepsilon \to 1$

$\therefore n_1 = n_0 \sin (\frac{\pi}{2} - r)$ ------------------------(1)

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.

8. Morel, Watson, & Yip. B.A. Sc. Thesis 1940

$$n_o \sin r = n_a \sin i = \sin i \text{---------------}(2)$$

$$n_a = 1 \text{ (for air)}$$

square & combine (1) & (2)

$$n_{,} = \sqrt{n_o^2 - \sin^2 i} \text{-----------------------}(3)$$

Since n_o is given for the prism and angle i is observed, $n_{,}$ 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 $\pm.00005$ for n, 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_o to be constant (the value of n_o 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

$\triangle n_o =$ 		"		" 	correction per degree rise

n_t = corrected refractive index.

then $n_t = n_o + K$

where K = correction value

$$n_{,}^2 = n_o^2 - \sin^2 i$$

$$n_t^2 = \left[n_o + (t-15)\triangle n_o\right]^2 - \sin^2 i$$

$$K = \frac{n_o}{n_{,}} \triangle n_o (t-15)$$

Values given for the prism used:-

	C	D	F
$\triangle n_6$	.000024	.000028	.000039
n_o^{15}	1.61839	1.62333	1.63573

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 $\pm 0.01^{\circ}$ C, but the thermometer reading can be read only to $\pm 0.02^{\circ}$ C accuracy.

(c) Source of Light

The source of H_{α} and H_{β} 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.

$$H_{\alpha} = C = 6562 \text{ Å}$$

$$H_{\beta} = F = 4861 \text{ Å}$$

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 dif-
ficulty 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 tem-
perature variations

$$r_G = \frac{(n-1)}{d} \; 1$$

$$R_G = \left(\frac{n-1}{d}\right)_M$$

r=specific refractivity

R=molecular refractivity

subscripts refer to whose

equation

d=density

M=molecular weight

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

$$r_L = \left(\frac{n^2-1}{n+2}\right) \frac{1}{d}$$

$$R_L = \left(\frac{n^2-1}{n^2+2}\right) \frac{M}{d}$$

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]

$$r_E = \frac{(n^2-1)}{(n+0.4)}\frac{1}{d}$$

$$R_E = \frac{(n^2-1)}{(n+0.4)}\frac{M}{d}$$

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]

	r_C	r_D	r_F
carbon	2.413	2.418	2.438
hydrogen	1.092	1.100	1.115

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.

$$R_L^C = (2.413)(10) + (1.092)(18) = 42.79$$

$$R_L^D = (2.418)(10) + (1.100)(18) = 43.98$$

$$R_L^F = (2.438)(10) + (1.115)(18) = 44.45$$

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

10. Eisenlohr, Z. Physikal Chemie. 1911-75-585

Moreover, later workers[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

$$n_C^t = n_D^t - 0.292(n_F - n_C)$$

$$n_F^t = n_D^t - 0.708(n_F - n_C)$$

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.

$$\triangle n = 0.60 \triangle d$$

$$\text{or} \quad \triangle n = f(r,d) \triangle d$$

which on integration gives $f(n,d) =$ 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

$$R_G = \frac{n-1}{d} M$$

$$\triangle n = \frac{n-1}{d} \triangle d \text{------------------------(1)}$$

11. Ward and Kurtz. Ind. & Eng. Chem. (Anal. Ed.) 10-559-1938

For Lorentz-Lorentz equation:

$$R_L = \frac{n^2-1}{n^2+2} \frac{M}{d}$$

$$\triangle n = \frac{(n^2-1)(n^2+2)}{6nd} \triangle d \text{------------(2)}$$

For Eykman equation:

$$R_E = \frac{n^2-1}{n^2+0.4} \frac{M}{d}$$

$$\triangle n = \frac{(n^2-1)(n^2+0.4)}{2.8\ nd} \triangle d \text{----------(3)}$$

As a first approximation, which is substantiated by unpublished data on high boiling point compounds, the specific dispersion varies linearly with temperature[12]. 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.

$$\delta^t = \frac{n_F^t - n_C^t}{d_4^t} \qquad\qquad \delta = \text{specific dispersion}$$

$$\triangle_M = \frac{n_F^t - n_C^t}{d_4^t} M \qquad\qquad \triangle_M = \text{molecular dispersion}$$

The advantage of measuring mean dispersion[13] 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.

$$\delta_M^t = n_F^t - n_C^t$$

12. Grosse, A. V. & Wackher, R. C. Ind. & Eng. Chem.

Nov. 1939 pg. 614

13. Cheneveau et Vaurabourg. Bull. Soc. Chim. Memoires

1928 4^e serie 43

V RESULTS

(a) for trans decahydronapthalene

Temp.	Angle	n_C^t	Temp.	Angle	n_D^t	Temp.	Angle	n_F^t
9.2 °C	42°26'30"	1.47096	10. °C	42°56'30"	1.47345	9.2 °C	44°15'30"	1.47936
15. °C	42°49'30"	1.46872	15. °C	43°13'	1.47145	15. °C	44°39'	1.47700
20. °C	43°10'30"	1.46669	20. °C	43°38'30"	1.46934	20. °C	45°	1.47501
30. °C	43°50'30"	1.46271	25. °C	43°59'	1.46732	30. °C	45°40'30"	1.47106
35. °C	44°11'	1.46068	30. °C	49°19'	1.46536	35. °C	46°03'	1.46885
45. °C	44°51'30"	1.45676	35. °C	44°40'	1.46328	40. °C	46°23'30"	1.46685
50. °C	45°12'	1.45479	45. °C	45°19'30"	1.45938	45. °C	46°43'30"	1.46489
54.5 °C	45°29'	1.45294	50. °C	45°40'30"	1.45731	50. °C	47°03'30"	1.46293
60. °C	45°51'30"	1.45080	60. °C	46°19'	1.45349	60. °C	47°45'	1.45885
69.7 °C	46°28'30"	1.44702	69.7 °C	46°59'30"	1.44947	69.7 °C	48°24'	1.45479
79.8 °C	47°09'	1.44299	79.2 °C	47°36'30"	1.44579	79.2 °C	49°04'	1.45111
84.8 °C	47°28'30"	1.44103	84.6 °C	47°58'	1.44366	84.7 °C	49°28'	1.44879

Graph showing relationship between
T and n^t of trans decalin

n^t_c ○
n^t_D ○
n^t_F +

radius of circle
1.0°C and .0005 in N

Temperature (°C)

Refractive Index (n^t)

Plate 1
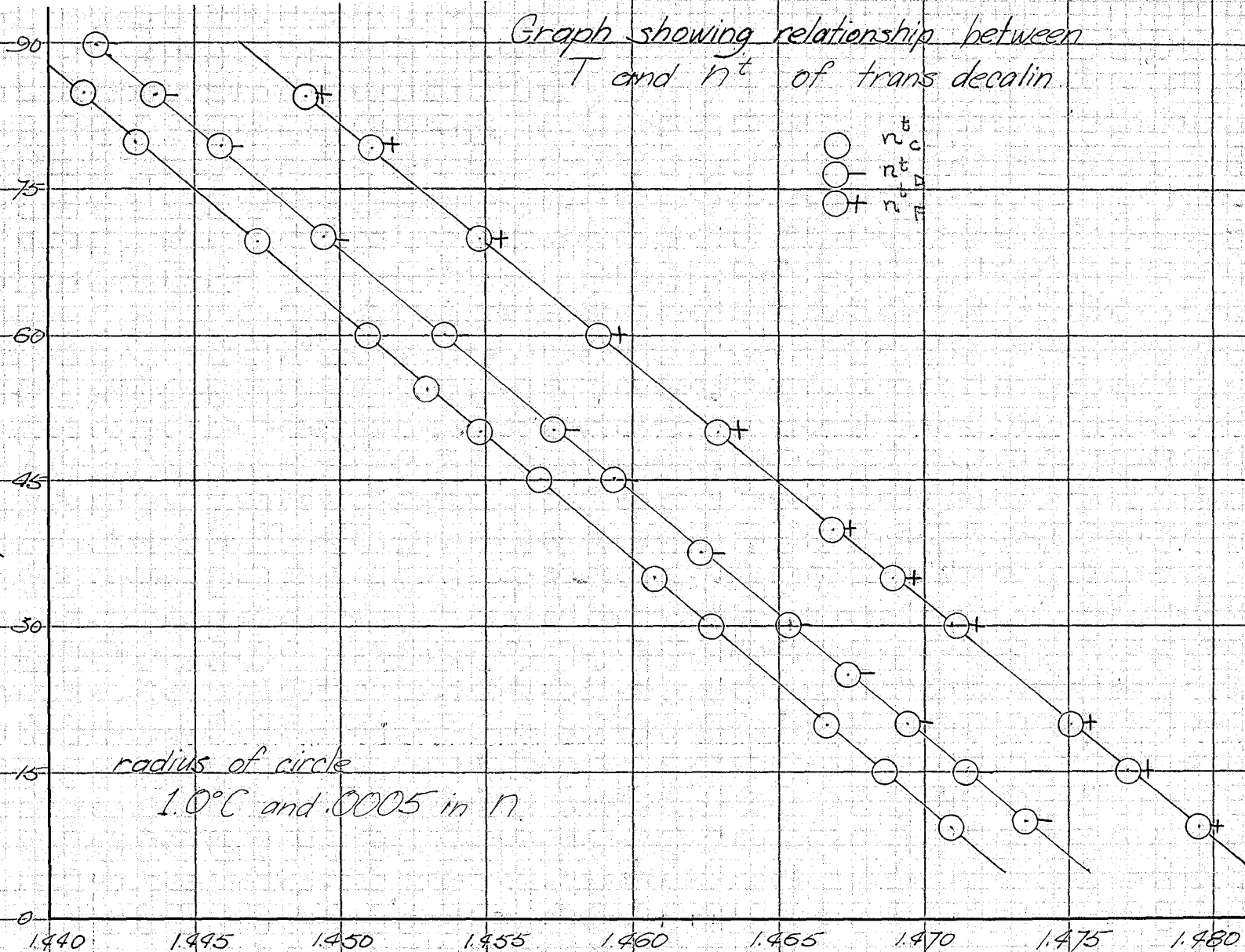
(b) for cis decahydronapthalene

temp.	angle	n_C^t	temp.	angle	n_D^t	temp.	angle	n_F^t
-----	-----	-------	6.2 °C	40°40'30"	1.48671	-----	------	-------
10.1°C	40°26'	1.48274	10. °C	40°59'30"	1.48488	10. °C	42°14'	1.49121
15. °C	40°48'30"	1.48056	15. °C	41°18'	1.48310	15. °C	42°38'	1.48892
20. °C	41°10'30"	1.47844	20. °C	41°40'	1.48098	20. °C	42°58'30"	1.48694
25. °C	41°30'30"	1.47649	25. °C	42°02'	1.47884	25. °C	43°19'30"	1.48479
30. °C	41°53'30"	1.47426	30. °C	42°23'30"	1.47675	30. °C	43°44'	1.48252
35. °C	42°15'30"	1.47211	35. °C	42°45'	1.47472	35. °C	44°04'30"	1.48054
-----	--------	-------	----	--------	-------	38.2°C	44°17'	1.47933
40. °C	42°36'	1.47011	40. °C	43°07'30"	1.47246	40. °C	44°28'30"	1.47819
45. °C	42°55'30"	1.46820	45. °C	43°25'	1.47074	45. °C	44°47'	1.47639
50. °C	43°15'	1.46628	50. °C	43°48'	1.46848	50. °C	45°07'	1.47445
50.9°C	43°18'30"	1.46593	51.2°C	43°53'	1.46799	50.9°C	45°11'	1.47405
52.9°C	43°30'	1.46479	53. °C	44°0'30"	1.46727	52.9°C	45°21'	1.47306
54.9°C	43°38'30"	1.46397	55. °C	44°07'30"	1.46662	55. °C	45°32'	1.47202
60. °C	43°58'	1.46203	60. °C	44°27'30"	1.46459	60.5°C	45°53'30"	1.46991
65. °C	44°23'30"	1.45952	65.2°C	44°47'30"	1.46262	64.5°C	46°09'30"	1.46834

(b) continued

temp.	angle	n_C^t	temp.	angle	n_D^t	temp.	angle	n_F^t
69.7 °C	44° 35'	1.45839	69.5 °C	45° 05' 30"	1.46080	69.3 °C	46° 30' 30"	1.46639
74. °C	44° 51'	1.45680	74. °C	45° 22'	1.45922	74. °C	46° 49' 30"	1.46442
80.4 °C	45° 18' 30"	1.45416	80.4 °C	45° 47'	1.45675	80.4 °C	47° 15'	1.46192
85. °C	45° 38'	1.45213	84.8 °C	46° 05'	1.45498	85. °C	47° 35' 30"	1.45990

Graph showing relationship between T and n^t of cis decalin

Plate 2.

radius of circle
1.0°C and .0005 in n.

break

Temperature

Refractive Index. (n^t)

$\bigcirc$ ----- n_c^t
$\bigcirc$ ----- n_D^t
$\bigcirc$ ----- n_F^t

VI TREATMENT OF RESULTS

(a) for trans decahydronapthalene

Temp.	n_C^t	n_D^t	n_F^t	Density
10 °C	1.47094	1.47340	1.47906	.8775
20 °C	1.46670	1.46939	1.47502	.8700
30 °C	1.46275	1.46540	1.47099	.8627
40 °C	1.45876	1.46139	1.46685	.8553
50 °C	1.45479	1.45732	1.46289	.8480
60 °C	1.45085	1.45349	1.45879	.8405
70 °C	1.44690	1.44945	1.45478	.8331
80 °C	1.44295	1.44549	1.45075	.8255
90 °C	1.43898	1.44149	1.44675	.8178

The above table was obtained from the graph on plate 1. The values for density were obtained from Davenport's[14] equation.

$$d_4^t = .8849 - .000742t$$

By graphic analysis

$$\frac{dn_C}{dt} = -.000399/°C$$

$$\frac{dn_D}{dt} = -.000398/°C$$

$$\frac{dn_F}{dt} = -.000403/°C$$

$$\frac{d\delta_M}{dt} = -.000016/°C$$

$$\delta_M^t = .00777 + .000016 (t-10)$$

$$\triangle_M = \delta_M \frac{t+M}{M d_4^t}$$

$$\triangle_M = \frac{1.073736 + .002211(t-10)}{.8849 - .000742t}$$

14. loc.cit.

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

Temp.	$R_G = \frac{n-1}{d} M$			$R_L = \frac{n^2-1}{n^2+2} \frac{M}{d}$			$R_E = \frac{n^2-1}{n+0.4} \frac{M}{d}$		
	n_C^t	n_D^t	n_F^t	n_C^t	n_D^t	n_F^t	n_C^t	n_D^t	n_F^t
10 °C	74.164	74.551	75.443	44.014	44.212	44.661	97.948	98.436	99.532
20 °C	74.113	74.540	75.451	44.039	44.256	44.702	97.934	98.464	99.572
30 °C	74.125	74.549	75.444	44.098	44.315	44.772	98.000	98.527	99.638
40 °C	74.121	74.546	75.428	44.149	44.367	44.819	98.047	98.575	99.671
50 °C	74.112	74.524	75.431	44.196	44.408	44.874	98.086	98.625	99.727
60 °C	74.126	74.560	75.431	44.256	44.48	44.928	98.155	98.695	99.779
70 °C	74.129	74.552	75.431	44.311	44.529	44.985	98.211	98.738	99.838
80 °C	74.150	74.575	75.456	44.375	44.596	45.052	98.336	98.821	99.918
90 °C	74.177	74.602	75.490	44.546	44.664	45.126	98.379	98.908	100.017

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.

$$\Delta n = \frac{n-1}{d} \Delta d = r_G \Delta d.$$

which gives:-

for the C line. $\Delta n = .529 \Delta d.$

for the D line. $\Delta n = .539 \Delta d.$

for the F line. $\Delta n = .545 \Delta d.$

(b) for cis decahydronapthalene.

Davenport's equation for density is given by:-

$$d_4^t = .9120 - .000752t$$

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° $\delta_m = .0085$

35° -50° $\delta_m = .0082$

above 50° $\delta_m = .0080$

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.

$$(n_F^t - n_C^t) = .00777 + .000016 \ (t - 10)$$

The linear variation of refractive indices with tempera-
ture 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.

$$n^2 = 1 + \frac{e^2}{\pi m} \sum \frac{N}{N_o^2 - N^2}$$

N = no of electrons of natural frequency N_o

N = 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 freq
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, [15] the cis isomer has shown a difference in oscillation energy of the atoms above and below 50°C. 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 indistint, 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

BIBLIOGRAPHY

1 Cheneveau et Vaurabourg Bull Soc Chim

2 Davenport, C. H. M.A.Sc. Thesis 1939

3 Davies, G. F. M.A.Sc. Thesis 1939

4 Eisenlohr Z Physikal Chemie

5 Gibson & Kincaid J. A. C. S.

6 Grosse & Wackher I. E. C. (Anal. Ed.)

7 Huckel, W. Annalen der Chemie

8 International Critical Tables

9 Morel, Watson, & Yip B.A.Sc. THESIS 1940

10 Walker, R. D. M. A. Sc. Thesis 1937

11 Ward & Kurtz I. E. C. (Anal Ed.)

12 Zotov, G. M.A. Thesis 1940