

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

## The Viscosity of *cis* and *trans* Decahydronaphthalene

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Considerable work has been done in these Laboratories during the last few years on the properties of the cyclic and dicyclic naphthene hydrocarbons. The present paper deals with viscosity measurements on the *cis*- and *trans*-forms of decahydronaphthalene over a range of temperature from  $-30$  to  $180^\circ$ .

### Experimental Procedure

The materials used for this work had been specially purified. The *cis*-isomer after eight recrystallizations had a freezing point of  $-43.25^\circ$ . In the case of the *trans*-compound the freezing point,  $-31.16^\circ$ , obtained after twenty recrystallizations, was slightly higher than had previously been recorded, *viz.*,  $-31.47^\circ$ .

The viscometers available were modifications of the Ostwald type. They were made in accordance with British Standards Specification No. 188-1937, and were specially designed to reduce deviations from Poiseuille's law to a minimum. For a given viscometer and constant volume of liquid where no external pressure is used the equation

$$\eta = \frac{\pi g H r^4 t}{8V(l + \lambda)} - \frac{mV\rho}{8\pi(l + \lambda)t}$$

is recommended by various authorities.<sup>2</sup> Here the symbols have the following meaning

- $\eta$  = viscosity in absolute units
- $r$  = radius of tube
- $l$  = length of tube
- $H$  = average acting hydrostatic head
- $V$  = volume of fluid
- $\lambda$  = a fictitious amount added to length of tube to correct for the extremities
- $m$  = a constant which is here taken as 1.12
- $\rho$  = density of fluid
- $t$  = time of efflux

Where the tube is to be calibrated with liquids of known viscosity the above equation can be expressed in the simple form  $\eta = Cpt - c\rho/t$ . The constants  $C$  and  $c$  can then be determined by experiment. It can be shown from the above equation that the second term is less than 2.5% of the first provided the efflux time is greater than one-hundred seconds. Hence it is clear that the

kinetic energy correction can be kept small by selecting a viscometer which will give a sufficiently long efflux time.

Loading errors did not arise in this work since the same liquid was used throughout each series of measurements. Furthermore the liquid levels were kept constant at all temperatures, thus ensuring that the mean liquid head remained constant over the entire range. Again, the dimensions of the viscometer were such as to make errors due to drainage and surface tension differences negligible. Another possible source of error lies in the fact that the viscometer may not always be vertical. The error is proportional to  $(1 - \cos \theta)$ , where  $\theta$  is the angular deviation from the vertical, and hence is about 0.1% for  $\theta = 2.5^\circ$ . Such a deviation was easily detected by means of a small plum-bob.

A very important question is whether or not the constants of the instrument remain truly constant throughout the series of experiments. One possible effect is that of temperature. Although, as stated above, special pains were taken to ensure that the same apparent efflux volume,  $V$ , was used at all temperatures, there might still have been an error caused by expansion of the glass. Taking the mean coefficient of expansion of glass as  $0.1 \times 10^{-4}$ , and considering a range of  $200^\circ$ , we can show readily that  $C$  will increase by 0.2%, and  $c$  by 0.4%. The latter error will obviously have a negligible effect on the final results. Since the calibration covered the range from  $20$  to  $100^\circ$  the constants are probably correct near  $60^\circ$ , and hence the maximum error due to a variation in  $C$  would not likely exceed 0.1%. Some workers think that the constants may also vary because of continuous changes in the capillary bore owing to solvent action of the liquids and cleaning solutions used. In the present work it was considered very unlikely that the decalin would act on the glass, and care was taken not to leave strong cleaning solutions in the viscometer over long periods of time.

The viscometer was cleaned with concentrated dichromate solution, water, alcohol and ether in turn. Before each series of measurements the instrument was rinsed and left in contact with the test liquid for several hours.

The constant temperature bath consisted of a cylindrical Pyrex jar of about 11-liters capacity (45 cm. deep and 20

(1) Standard Oil Company of British Columbia Research Fellow, 1940-1941.

(2) E. C. Bingham, "Plasticity and Fluidity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922.

cm. in diameter). It was lagged with asbestos and cotton batting, and was filled with a medium, clear petrolatum oil, which was circulated by a triple propeller. Some trouble resulted at high temperatures from the oil charring and becoming opaque; a lubricating oil, Marvelube 40, was tried but was found to be even less satisfactory. The bath was heated electrically by two Cenco immersion knives and a small nichrome coil (1 inch in diameter), the latter being hooked up to a precision thermo-regulator. A switchboard with suitable resistances enabled any temperature between 20 and 180° to be obtained. For the measurements below room temperature a double-walled, evacuated, Pyrex flask (25 cm. deep by 7 cm. in diameter) was found convenient. Acetone served as a bath liquid and the temperature was lowered and kept constant by dropping in small pieces of dry-ice. Except at the extremes, the temperature could be kept constant within  $\pm 0.02^\circ$ , and even at the highest and lowest temperatures the variation was less than  $\pm 0.05^\circ$ .

The temperature was measured with a Leeds and Northrup platinum resistance thermometer, No. 169,314, which had recently been checked by the Bureau of Standards in Washington and whose ice point had been determined several times in this Laboratory. Temperatures were calculated by means of Callendar's equations.

A Meylan stop watch, reading to 0.2 second, served as timing device. Checking against several reliable time-pieces indicated a loss of 0.02 sec. per min., and while this is well within the limit of error required by Bingham,<sup>2</sup> a suitable correction was applied to all readings. Since the viscometer was designed for an efflux time of not less than one hundred seconds, and since the final results were always averages of from five to fifteen readings, the mean error in the stop watch reading was probably less than 0.1%. Care was taken always to run the stopwatch in a horizontal position.

**Calibration.**—To cover the viscosity range of the decalin isomers and to keep the efflux times greater than one hundred seconds, it was necessary to choose an uncalibrated viscometer. The instrument was calibrated by measuring the efflux times of pure water at several temperatures and from the resulting equations the constants of the viscometer were calculated by the method of least squares. The absolute viscosities of water were taken from the data of Bingham and Jackson<sup>3</sup> and the relative densities from the Smithsonian Tables. The calibration was later checked with a sample of oil, of which the kinematic viscosity had been accurately determined at 20, 40, and 100°, from the Bureau of Standards. The constants were redetermined, using the two sets of data together, and the final equation was

$$\nu = \eta/\rho = 0.004043t - 1.52/t$$

For the measurements below 0° another viscometer of larger bore was calibrated to avoid excessively long efflux times. *cis*-Decalin was

(3) Bingham and Jackson, *Bureau Stds. Bull.*, **14**, 75 (1918).

used this time, as values for its viscosity above 0° were already known. The resulting equation for this instrument was

$$\nu = \eta/\rho = 0.05737t - 1.16/t$$

The final standard for all these measurements is the absolute viscosity of water ( $\eta = 1.005$  at 20.00°), and this, according to Cannon and Fenske,<sup>4</sup> may be in error by  $\pm 0.5\%$ . Relative to this value, however, we believe our measurements to be correct within  $\pm 0.3\%$ , except perhaps at the lower extreme of temperature where the error may be  $\pm 0.5\%$ .

**Procedure.**—The kinematic viscosities of first the *cis*- and then the *trans*-isomer were measured at 10° intervals between  $-30$  and 180°, and from these data and the densities as given by Seyer and Davenport,<sup>5</sup> the absolute viscosities were calculated as explained above. Each temperature was maintained for at least two or three hours and in some cases from twelve to twenty-four hours. In all cases the averages of numerous readings were taken. At one time it was thought that the vibration from the stirring apparatus might affect the results, and a few runs were made with the motor turned off to see if any difference could be detected. No difference was found.

Then, for reasons given below, the measurements on *cis*-decalin were repeated between 110 and 180°. With both the *cis*- and the *trans*-decalin the measurements were repeated at intervals coming down the scale of temperature after the upper limit had been reached. In all cases these latter gave slightly higher results. The cause of this phenomenon has not yet been determined.

### Discussion of Results

The curves obtained (Fig. 1) when  $\log \eta$  is plotted against  $1/T$  are not linear, but they are quite smooth and there appears to be no evidence to support the claims of discontinuities in various temperature ranges as suggested by Seyer and Davenport in the proceedings of the Petroleum Division of the A. C. S. (Boston Meeting, 1939). In the case of the *cis*-isomer, however, a considerable deviation begins to show itself at 110°. This deviation increased as the temperature went higher, and, furthermore, the longer the hydrocarbon was kept at any one temperature in this interval the greater its viscosity became. This is similar to the results stated by the above authors who found an increase not only in the viscosity but also in the density, and surface tension. Additional measurements on these latter properties suggested an irreversible change in the *cis*-isomer possibly due to some chemical reaction or to the formation of a structural isomer. No definite

(4) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

(5) Seyer and Davenport, *This Journal*, **63**, 2425 (1941).

Temp., °C.	VISCOSITY IN CENTIPOISES	
	<i>cis</i> -	<i>trans</i> -
-30.00	15.761	7.310
-20.00	10.677	5.394
-10.00	7.582	4.094
00.00	5.620	3.233
10.00	4.300	2.588
20.00	3.381	2.128
30.00	2.723	1.774
40.00	2.239	1.493
50.00	1.867	1.282
60.00	1.588	1.114
70.00	1.363	0.978
80.00	1.188	.865
90.00	1.045	.772
100.00	0.920	.692
110.00	.819	.626
120.00	.752	.572
180.00	.684	.521
140.00	.622	.476
150.00	.569	.438
160.00	.521	.406
170.00	.479	.375
180.00	.439	.350

evidence of oxidation or of the formation of unsaturated compounds could be found. The surface tension measurements mentioned above, and more recently measurements on the specific heats and refractive indices indicate further irregularity in the behavior of the *cis*-isomer in the region 50–52° but, as can be seen, this is not supported by the present work.

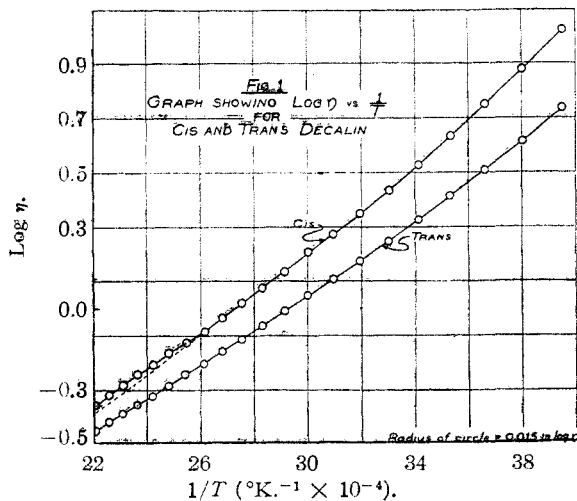


Fig. 1.

Many equations other than the simple exponential law,  $\eta = Be^{A/T}$ , have been proposed to express the temperature variation of viscosity, and several of these, including Batschinski's<sup>6</sup> relationship  $\eta = B/(v-c)$  where  $v$  is the specific

(6) A. Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

volume and  $B$  and  $c$  are constants, were tried on the present data. The results were, in general, the same, none gave linear curves and all indicated the abnormality discussed above.

The curves are sufficiently straight for their slopes to be of possible significance. If the assumed equation is  $\eta = Be^{E_{vis}/RT}$ , then the slopes,  $m$ , of our curves are given by  $m = \frac{E_{vis}}{R} = \frac{\ln(\eta_2/\eta_1)}{1/T_2 - 1/T_1}$ , where  $E_{vis}$  is the average molar activation energy for viscous flow.  $E_{vis}$  is given in the table below for the decalin isomers and also for a few other hydrocarbons of comparable size or structure. The data for these latter were taken from the work of E. B. Evans,<sup>7</sup> and from a compilation of physical data by The Texas Co.<sup>8</sup>

Hydrocarbon	$\eta_0$ (cp)	$\eta_{100}$ (cp)	$m$	$E_{vis}$ , cal./mole	
<i>n</i> -Hexane	C <sub>6</sub> H <sub>14</sub>	0.398	0.167	880	1750
<i>n</i> -Decane	C <sub>10</sub> H <sub>22</sub>	1.298	.357	1315	2615
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	1.455	.572 (50°)	1650	3285
<i>trans</i> -Decalin	C <sub>10</sub> H <sub>18</sub>	3.233	.692	1570	3125
<i>cis</i> -Decalin	C <sub>10</sub> H <sub>18</sub>	5.620	.920	1845	3670
Cyclodecane	C <sub>10</sub> H <sub>20</sub>	4.48 (20°)	1.76 (60°)	2280	4535

It is apparent that for a given number of carbon atoms, cyclization increases both the viscosity and the activation energy. It is interesting, to note that although *trans*-decalin has a higher viscosity than cyclohexane  $E_{vis}$  is about the same for both, and again that although the single ringed compound, cyclodecane, has a higher viscosity than either *cis*- or *trans*-decalin at low temperatures, its  $E_{vis}$  is also much greater, which means that at more elevated temperatures the viscosity curves will cross. The same argument applies to the two decalin isomers themselves, and a rough calculation shows that if no structural changes took place the two would have the same viscosity at about 300°.

So far we have assumed that  $dE_{vis}/dT = 0$ . The curves show that this condition definitely does not hold for the decalin isomers, and this fact suggests the possibility that from the standpoint of viscosity they may be regarded as abnormal liquids. In a general discussion on liquids held by the Faraday Society,<sup>9</sup> A. G. Ward classifies the various types of liquids and then attempts to explain departures from the simple exponential equation for viscosity in terms of structure and forces. He states that  $E_{vis}$  will vary with the tem-

(7) E. B. Evans, *J. Inst. of Pet. Technologists*, **24**, 38, 321, 537 (1938).

(8) The Texas Co., "Physical Constants of the Principal Hydrocarbons," 2nd edition, New York, N. Y., 1939.

(9) "Structure and Molecular Forces in (a) Pure Liquids and (b) Solutions," *Trans. Faraday Soc.*, **33**, 189 (1937).

TABLE I

Hydrocarbon	B. p. (760 mm.), °C.	Sp. gr. (d <sub>4</sub> <sup>20</sup> )	(cp) <sub>25</sub> <sup>o</sup>	(cp) <sub>30</sub> <sup>o</sup>	$E_{vis}$ , cal./mole	$E_{cis}/E_{trans}$	
1-Methyl-2-propyl- cyclopentane	<i>cis</i>	152.5	0.7921	0.941	0.753	2575	
	<i>trans</i>	146.3	.7774	.750	.622	2170	1.18
1,2-Diethylcyclopentane	<i>cis</i>	153.5	.7959	.815	.669	2290	
	<i>trans</i>	147.5	.7831	.723	.605	2050	1.12
1,2-Dimethylcyclohexane	<i>cis</i>	130.0	.7962	1.188	.925	2885	
	<i>trans</i>	123.7	.7760	0.863	.697	2270	1.27
1,3-Dimethylcyclohexane	<i>cis</i>	124.9	.7835	.888	.722	2390	
	<i>trans</i>	120.4	.7663	.665	.556	2050	1.17
1,4-Dimethylcyclohexane	<i>cis</i>	124.6	.7827	.933	.749	2535	
	<i>trans</i>	119.6	.7626	.749	.614	2300	1.10
Decalin	<i>cis</i>	194.6	.8967	3.792	2.723	3810	
	<i>trans</i>	185.4	.8700	2.342	1.774	3215	1.18

perature if the coördination of the molecules changes and further that a negative  $dE_{vis}/dT$ , as in the case of both *cis*- and *trans*-decalin, indicates increasing coördination, and hence directional forces. The same author goes on to say that high values of  $E_{vis}$  and of the viscosity at the freezing point characterize ionic liquids and those containing polar groups. In the latter he claims the high values indicate a possible bond rupture.

Eyring and his co-workers<sup>10</sup> show, also, that the above characteristics in a liquid may indicate association, by supposing that at the lower temperatures an extra "structure activation energy" is necessary to break the association bonds before the activated state for flow can be brought about. It should be pointed out<sup>11</sup> that even the simplest liquid must show a slightly decreasing activation energy with increasing temperature, if a sufficiently accurate analysis is made. This is because a liquid becomes more gas-like with increasing temperature and new equilibrium positions for the molecules to flow into become more plentiful. It can be shown, however, that this normal change in the activation energy,  $E_{vis}$ , is sufficiently small to make the simple exponential law quite accurate for most liquids. We may therefore conclude that the variations in  $E_{vis}$  for the decalin isomers indicate abnormality in structure.

Since decalin is a saturated bicyclic hydrocarbon we would not expect it to be markedly dipolar, and it certainly does not fall into the latter classes discussed by Ward. Hence, the present authors suggest that in such liquids as decalin there may be not single molecules, but molecular aggregates or macromolecules, these being naturally more plentiful at low temperatures, with a

gradually increasing degree of dissociation as the temperature rises.

The differences between the viscosities and the activation energies of the decalin isomers themselves are not easy to explain because little is definitely known about the space configurations of these two compounds. A little enlightenment is to be had, however, from an examination of the data for several other naphthenic hydrocarbons which show *cis-trans* isomerism. These data are from the Texas Co. publication mentioned above, and are given in the following table along with the corresponding data for the decalin isomers.

In each compound the *cis*-isomer has a higher boiling point, a higher specific gravity, a higher viscosity and a higher  $E_{vis}$  than the *trans*. This would suggest that the differences in these properties are characteristic of the *cis-trans* isomerism itself and do not depend upon the number, sizes or complexity of the rings. The values are much higher for the decalin isomers but the ratio of the  $E_{vis}$  for the two isomers is about the same for all the hydrocarbons shown. In view of the discussion above a possible interpretation of these results is that directional forces are more pronounced in the *cis*-isomer and hence that there is closer packing of the molecules and a greater proportion of "macromolecules."

Eyring, *et al.*,<sup>10</sup> have developed a number of relationships between  $E_{vis}$ ,  $\Delta F^\ddagger$  and  $\Delta E_{vap}$ , where  $\Delta F^\ddagger$  is the molar free energy of activation for viscous flow and  $\Delta E_{vap}$ , the molar energy of activation for evaporation. Lack of reliable vapor pressure data for decalin prevents us from making use of these relationships at the present time, but we hope to do so in a future paper.

### Summary

1. The viscosities of *cis*- and *trans*-decahydro-

(10) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 505.

(11) Private communication from H. Eyring and R. E. Powell.

naphthalene have been measured from  $-30$  to  $180^\circ$ .

2. When  $\log \eta$  is plotted against  $1/T$  straight lines are not obtained and there is evidence that the *cis*-form undergoes some change at  $110^\circ$ .

3. An attempt is made to explain the high values of  $\eta$  and  $E_{\text{vis}}$ , and also the effect of *cis-trans* isomerism on these.

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## The Electromagnetic Mechanism of the Beta Phosphorescence of Fluorescein in Acid Solution

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### Introduction

The peculiar nature of the beta phosphorescence of fluorescein in acid solution, investigated recently by Lewis, Lipkin and Magel,<sup>2</sup> suggested to us the desirability of studying the mechanism of this emission process. The peculiarities made themselves evident in several ways. Firstly, the luminescence is of unusually long duration. Secondly, no absorption band corresponding to a transition from the normal to the phosphorescent state has been found.<sup>3</sup> Thirdly, although the fluorescein molecules in the phosphorescent state have been found to be oriented when excited to that state by polarized light, the beta phosphorescence from such molecules is but little polarized.<sup>2</sup>

It is possible to describe the radiation processes from a source which is small compared with the wave length of the emitted waves in terms of the electric and magnetic multipole moments of the source. In the case of most of the familiar sources the only significant contribution to the radiation arises from an oscillating electric dipole. Indeed, most of the selection rules used in interpreting atomic and molecular spectra are not applicable in the case of transitions other than those involving electric dipoles. Thus, many spectral lines have been observed which appear to arise from processes which are forbidden by these selection rules. Two explanations may be advanced for the occurrence of these processes. In the first place, as we have just indicated, these seeming violations may occur because a given transition involves a multipole other than an electric dipole. Secondly, they may occur because of the invalidation of the rules by external perturbations of the emitting system. The  $^2S_{1/2}$ - $^2D_{3/2, 5/2}$  doublet of potassium studied by Segrè and Bakker,<sup>4</sup> the  $^1S_0$ - $^3P_2$

and  $^1D_2$ - $^3P_0$  transitions of lead studied by Jenkins and Mrozowski,<sup>5</sup> and the  $^1S_0$ - $^1D_2$  transition of oxygen studied by Frerichs and Campbell<sup>6</sup> may be cited as examples of breakdowns of the first type. On the other hand, the  $6^3P_2$ - $7^3P_2$  transition of mercury,<sup>7</sup> which is induced by external electric fields, may be cited as an example of a breakdown of the second type.

In the case of the transitions just mentioned, the investigators were able to determine the nature of the emission mechanism (magnetic dipole, electric dipole and electric quadrupole) by a study of the Zeeman effect. Obviously, this method cannot be used to study broad spectral bands such as those of large organic molecules. In this case it becomes necessary to use the wide-angle interference method of Selényi.<sup>8</sup> This method, the interpretation of which depends on characteristic differences in directional distribution of radiation about the various elementary multipoles,<sup>9</sup> involves the study of the coherence properties of rays issuing in widely diverging directions from small sources.

### Experimental

In order to obtain interference between two beams of light issuing at a wide angle from a source, it must be of such dimensions that the interference patterns from different parts of the source do not obliterate each other. The most critical requirement as to the size of the source is that one dimension be not more than about one-twentieth of the wave length of the light. The other dimensions may be much larger and are determined by various optical characteristics of the interference apparatus. Selényi<sup>8</sup> has devised a simple experimental set-up which admirably fulfills the above requirements. We have used essentially

(5) Jenkins and Mrozowski, *Phys. Rev.*, **59**, 808 (1941).

(6) Frerichs and Campbell, *ibid.*, **36**, 151 (1930); **36**, 1460 (1930).

(7) Segrè and Bakker, *Nature*, **128**, 1076 (1931).

(8) Selényi, *Ann. Physik*, **85**, 444 (1911); *Z. Physik*, **108**, 401 (1938); *Phys. Rev.*, **56**, 477 (1939).

(9) Halpern and Doermann, *ibid.*, **52**, 937 (1937); Doermann, *ibid.*, **53**, 420 (1938); Doermann and Halpern, *ibid.*, **55**, 486 (1939).

(1) National Research Council Fellow, 1941-1942.

(2) Lewis, Lipkin and Magel, *This Journal*, **63**, 3005 (1941).

(3) These last two observations are, of course, interrelated.

(4) Segrè and Bakker, *Naturwiss.*, **19**, 738 (1931); *Z. Physik*, **72**, 724 (1931).