

Stereochemical Studies on Hydronaphthalenes, II* Absorption Spectra of Hydronaphthalenes

By

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Our present knowledge concerning the chemical constitution and the arrangement of atoms in the molecule of naphthalene and its hydro compounds is mostly based on the studies of isomers, but no formula which satisfactorily explains the reactions of these compounds has yet been proposed. The problem of the stereochemistry of naphthalene, however, still remains to be studied further and may perhaps open up a new path to the end in view. The writer has therefore taken up this subject from the point of view of the ultra violet absorption spectra of naphthalene and its hydro compounds.

According to the investigations by Henri and others, benzene¹ shows seven absorption bands in the ultra violet region in its hexane solution, having a frequency interval of $\Delta\frac{1}{\lambda}=921\text{ cm}^{-1}$. This interval of the absorption bands ($\Delta\frac{1}{\lambda}=943\text{ cm}^{-1}$ and 1186 cm^{-1}) is also seen in the absorption bands of the methyl derivatives of benzene, such as toluene and p-xylene,² in which there is another group of absorption bands of a different frequency interval ($\Delta\frac{1}{\lambda}=236\text{ cm}^{-1}$ and 366 cm^{-1}). The first group of bands was attributed to the benzene nucleus and the origin of the absorption bands of the second group was regarded as connected with the methyl group in the molecule. Henri and his collaborateurs³ studying the absorption spectrum of naphthalene, in a

* Part I, These Memoirs A, **14**, 173 (1931).

1. Henri: *Etudes de Photochimie* 128 (1919); *Structure des molecules* 108 (1925).
Orndorff, Gibbs, McNulty and Shapiro: *Jour. Am. Chem. Soc.*, **50**, 831 (1928).
2. Klingstedt: *Compt. rend.*, **175**, 1065 (1922); Orndorff etc. loc. cit.
3. Henri and Laszlo: *Proc. Roy. Soc.*, **105**, 662 (1924).

vapour state, have noticed that there are two series of absorption bands, the first one found in the $3200 \text{ \AA} - 2820 \text{ \AA}$ region, consisting of more than 400 fine lines, is due to the naphthalene nucleus, and the second one composed of bands in the $2820 \text{ \AA} - 2500 \text{ \AA}$ region is due to the activated molecule. Similar absorption spectra were shown by naphthalene in hexane solutions¹; they also show two series of absorption bands and one band in the extreme ultra-violet at 2209 \AA° , the one series composed of 9 bands a—k ($\lambda = 3200 \text{ \AA} - 2930 \text{ \AA}$)^{*}, and the other of 8 bands 1—8 ($\lambda = 2881 \text{ \AA} - 2563 \text{ \AA}$)^{*}, and the first series classified into two groups, A and B, according to the frequency intervals $\Delta \frac{1}{\lambda} 1450 \text{ cm}^{-1}$ and 450 cm^{-1} . Methyl-naphthalene² in solution shows a series of absorption bands in the ultra violet region, which may be divided according to the frequency interval into three groups A ($\Delta \frac{1}{\lambda} = 1425 \text{ cm}^{-1}$), B ($\Delta \frac{1}{\lambda} = 475 \text{ cm}^{-1}$) and C ($\Delta \frac{1}{\lambda} = 328 \text{ cm}^{-1}$), and the latter may be attributed to the presence of a methyl group combined with the naphthalene nucleus. In the following table, the frequency intervals of the absorption bands of benzene, naphthalene and their derivatives in solution are shown for reference.

	$\Delta \frac{1}{\lambda} (\text{cm}^{-1})$		
	A	B	C
Benzene	921	—	—
Toluene	943	—	236
p-Xylene	1186	—	366
Naphthalene	1450	450	—
β -Methylnaphthalene	1425	475	328

The absorption spectrum of naphthalene was studied by the writer with its ethyl alcohol solution, which gives results similar to those obtained by Henri and Steiner³ with the hexane solution but different from the results obtained by Baly and Tuck⁴. Two series of absorption

1. Henri et Steiner: *Compt. rend.*, **175**, 421 (1922).

* See Table I in the experimental part.

2. Laszlo: *Compt. rend.*, **180**, 205 (1925); *Zeit. f. Phys. Chem.*, **118**, 371 (1925).

3. *loc. cit.*

4. *Jour. Chem. Soc.*, **93**, 1902 (1908).

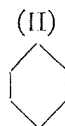
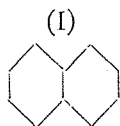
bands were found, one series composed of 9 sharp and intensive bands (A—K) in the ultra violet region ($\lambda=3400 \text{ \AA}—2900 \text{ \AA}$) which are divided into two groups according to the frequency interval (A) $\Delta \frac{1}{\lambda} = 1480 \text{ cm}^{-1}$ and (B) $\Delta \frac{1}{\lambda} = 540 \text{ cm}^{-1}$, and the other series composed of 5 broad and diffused bands in $\lambda=2900 \text{ \AA}—2500 \text{ \AA}$. The first series corresponds to the bands given by the naphthalene nucleus as mentioned by Henri, and the latter series corresponds to the bands which are said to originate from the activation of the molecule. When naphthalene is reduced to dihydro and tetrahydro compounds, the absorption spectra of their alcohol solutions, seen in the ultra violet region, are also composed of two series of absorption bands, the one series comprising two groups of the following frequency intervals, which are similar in value to those of naphthalene, but the spectra differ from that of naphthalene in the number of absorption bands.

	$\Delta \frac{1}{\lambda} (\text{cm}^{-1})$	
	A	B
Naphthalene	1480	540
Δ^1 -Dihydronaphthalene	1630	475
Tetrahydronaphthalene	1563	497

The absorption spectra shown by naphthalene solution are exhibited by solutions of the di- and tetra-hydronaphthalenes, but the absorption of light by benzene being different from that of its hydro compounds, 7 sharp absorption bands in the ultra violet region, due to the benzene nucleus, do not appear in the alcohol solutions of di- and tetra-hydro-benzenes. The relationship shown in the absorption spectra of these two series of compounds of naphthalene and benzene, leads to the idea that the chemical structure of benzene is different from that of its hydrogenated compounds, while di- and tetra-hydronaphthalene have the same chemical structure as naphthalene.

When the reduction of naphthalene was carried further to octa-hydronaphthalene and then to decahydronaphthalene, the absorption spectra of these two compounds in the ultra violet region were observed to be entirely different in nature from those of the other hydro compounds studied above, and to be composed only of broad diffused

bands in $\lambda = 2750 \text{ \AA} - 2400 \text{ \AA}$, of frequency interval $\Delta \frac{1}{\lambda} = 1500 \text{ cm}^{-1}$, which correspond to the second series of absorption bands of naphthalene, and the first series of the absorption bands due to the naphthalene nucleus was absent in these hydro compounds. These facts are in favour of the view that the chemical structure of the naphthalene molecule is partly changed in the octahydro- and decahydro-derivatives. The fact that the absorption spectra of the compounds of the naphthalene series are different from those of the benzene series may be explained by assuming a bicyclic structure for the naphthalene molecule; in the formation of dihydro- and tetrahydronaphthalene, the hydrogen atoms, may be added to one of the rings in the naphthalene molecule, but in the case of octahydro- and decahydronaphthalenes they are added to both rings. Accordingly, in the former case, the addition of hydrogen atoms to naphthalene does not effect its absorption spectra, while on further addition of hydrogen atoms only the second series of absorption bands will appear in the ultra violet region owing to the partial change in the chemical structure of naphthalene. The absorption bands of the second series, which are situated from the neighbourhood of $\frac{1}{\lambda} = 35000 \text{ cm}^{-1}$ to the more ultra violet region as may be seen in Figs. 1-5, are observed to appear throughout all the compounds of the naphthalene series. As to the origin of these bands, the writer is inclined to accept the hypothesis that there is some vibration of a bicyclic carbon linking I, but hesitates to agree with the view proposed by Henri as described above, and some properties of benzene and its hydro compounds, which are not met with in naphthalene and its hydro compounds are explained by accepting the monocyclic carbon linking II for the compounds of the benzene series.

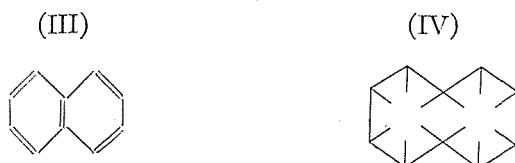


Dr. Hagiwara's¹ observation made in the course of his study of terpenes, that pinane $C_{10}H_{18}$, the saturated bicyclic compound, exhibits a selective absorption band in the ultra violet region but that a saturated monocyclic hydrocarbon such as menthane $C_{10}H_{20}$ shows no selective absorption band, supports the writer's view that there is an absorption caused by the bicyclic ring.

1. Lectured at the meeting of Chem. Soc. Japan, March (1931).

If we assume that naphthalene is represented by a bicyclic structure, some vibration between the two rings, which arises round an axis connecting the carbon atoms 9 and 10, would cause broad diffused absorption bands of the second series. This opinion as to the absorption spectra of the bicyclic compounds, however, will be settled by future studies which will appear in an article in the near future from this laboratory.

The structural formula of naphthalene reported above from the study of absorption spectra, is similar in the form of the carbon skeleton to that proposed by Erlenmeyer¹ and Graebe² III but differs from the monocyclic formula IV advocated by Bamberger³.



The writer's idea of the bicyclic nature of the naphthalene molecule is also confirmed by the study of the catalytic reduction of naphthalene and its derivatives under high temperature and high pressure⁴. When catalytic reduction of benzene under 80 atmospheric pressures of hydrogen was performed, the reaction began at 40° and proceeded very rapidly at 200°, and cyclohexane C_6H_{12} was produced as the reaction product, while naphthalene $C_{10}H_8$ absorbs hydrogen very slowly at 150° under 90 atmospheric pressures, and at 200° the yield of tetrahydronaphthalene $C_{10}H_8H_4$ was satisfactory; the latter compound was hydrogenated easily at 180° and under 90 atmospheric pressures of hydrogen to decahydronaphthalene $C_{10}H_8H_{10}$. These results lead the writer to the opinion that the distribution of energy in the naphthalene molecule differs from that of the benzene molecule in not being uniform, and this view of the distribution of energy in the naphthalene molecule was supposed from the fact that the absorption spectra of naphthalene and its hydro compounds due to the naphthalene nucleus are composed of two groups of bands of different frequency interval and this hypothesis was more clearly indicated in the experimental results obtained in the catalytic

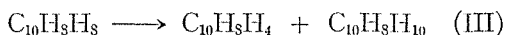
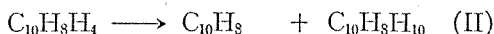
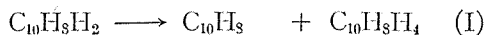
1. Ann., **137**, 346 (1886).

2. Ber., **1**, 36 (1869).

3. Ann., **257**, 1 (1890).

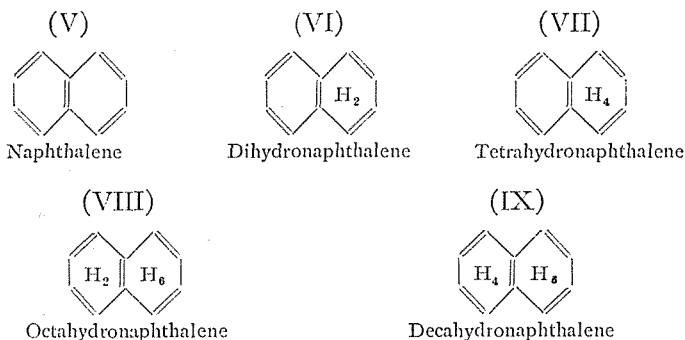
4. Kagehira: Bull. Chem. Soc. Japan, **6**, 241 (1931).

oxidation-reduction of hydronaphthalenes¹ carried out with dihydronaphthalene (I), tetrahydronaphthalene (II) and octahydronaphthalene (III). In those experiments it was proved that naphthalene and tetrahydronaphthalene, naphthalene and decahydronaphthalene, and tetrahydronaphthalene and decahydronaphthalene are formed from these compounds respectively, and the results shown in the following schemes are in favour of the view.



The fact that dihydrobenzene and tetrahydrobenzene, on being subjected separately to this reaction, yield benzene and cyclohexane in each case, shows the uniformity of the distribution of energy in the benzene molecule. The reactions occurring in hydronaphthalenes can be easily explained by assuming that the hydrogen atoms 2H and 4H in di- and tetrahydronaphthalenes, being different in behavior from the 8H atoms in the octahydronaphthalene molecule, are distributed in the same ring while in the latter compound the 8 hydrogen atoms are shared between two rings, 6H to one, and 2H to the other.

If the view as to the constitution of naphthalene advanced by Erlenmeyer and Graebe is extended to dihydro-, tetrahydro-, octahydro- and decahydronaphthalene, it is seen that these compounds are represented by formulae V—IX, of which formulae, V and IX are symmetrical in structure, while VI, VII, and VIII are unsymmetrical,



and in VIII, there occur asymmetrical carbon atoms 9 and 10, but it

1. Kimura: These Memoirs, A, 14, 186 (1931).

loses its asymmetry when the reduction progresses to decahydronaphthalene.

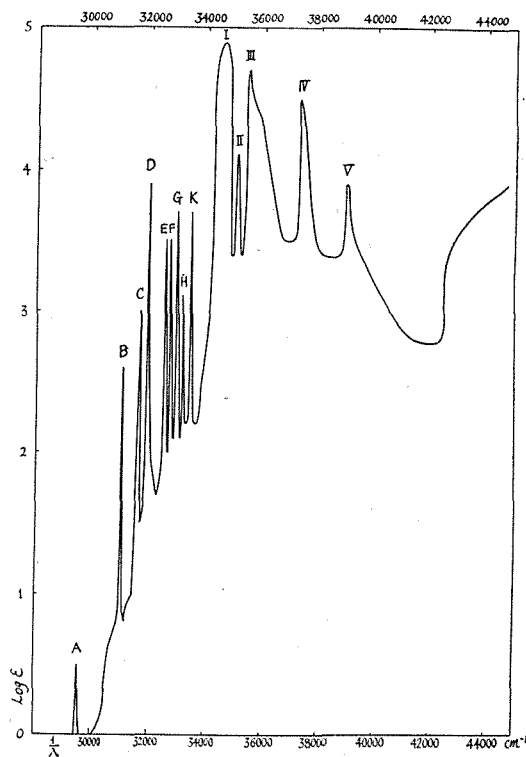
Experimental

In the experiments, the purified substances were dissolved in pure alcohol and light was passed from a Geissler hydrogen tube into the solution to get continuous ultra violet absorption spectra, which were photographed on Eastman's panchromatic film, with Hilger's spectrograph E₂. The value for $\log \epsilon$ was calculated from the equation $J = J_0 \cdot 10^{-\epsilon cd}$: $\log \frac{J}{J_0} = -\epsilon cd$, where J_0 and $J =$ the intensity of light before and after being passed into a solution of thickness d cms. and concentration c ; and the absorption curves were plotted, $\log \epsilon$ and $\frac{1}{\lambda}$ cm^{-1} being taken as ordinate and axis respectively.

1. Naphthalene

Naphthalene was purified by distillation on Japanese acid clay and

Fig. 1



absorption spectra of its alcoholic solution were studied. The wave numbers of the absorption bands as shown in Fig. 1 and Table I, agree with the results obtained by Henri and Steiner¹ with hexane solutions. The absorption spectra of naphthalene solutions may be divided into two series. The first consists of sharp and distinct bands from A to K shown in Fig. 1, which are divided into groups A and B with the frequency intervals $\Delta \frac{1}{\lambda} = 1450 \text{ cm}^{-1}$ and 450 cm^{-1} respectively; band C is the most intense, the other bands being arranged A, B, F and H in ascending order of intensity. The second series is composed of 5 bands from I to V, broad and diffused. The bands of both series, as may be seen from following table, correspond to absorption bands a—k and 1—9 respectively of naphthalene hexane solution observed by Henri and Steiner.

Table I

Kimura			Henri and Steiner		
Band	$\lambda(\text{Å})$	$\frac{1}{\lambda}(\text{cm}^{-1})$	Band	$\lambda(\text{Å})$	$\frac{1}{\lambda}(\text{cm}^{-1})$
A	3384	29550	a	3207	31182
B	3219	31060	b	3148	31766
C	3160	31650	c	3110	32154
D	3126	31990	d	3067	32605
E	3071	32560	e	3040	32895
F	3059	32690	f	3010	33223
G	3031	32990	g	2994	33400
H	3019	33120	h	2975	33613
K	2992	33420	k	2930	34130
I	2888	34620	1	2881	34710
II	2856	35080	2	2852	35063
III	2825	35400	3	2835	35273
IV	2684	37250	4	2755	36297
V	2567	38950	5	2724	36711
			6	2650	37736
			7	2620	38168
			8	2563	39017
			9	2209	45269

1. Compt. rend., **175**, 421 (1922).

$$\left. \begin{aligned}
 \Delta \frac{1}{\lambda}(\text{B}-\text{A}) &= 1510 \text{ cm}^{-1} \\
 \Delta \frac{1}{\lambda}(\text{E}-\text{B}) &= 1500 \text{ ,,} \\
 \Delta \frac{1}{\lambda}(\text{H}-\text{C}) &= 1470 \text{ ,,} \\
 \Delta \frac{1}{\lambda}(\text{K}-\text{D}) &= 1430 \text{ ,,} \\
 \Delta \frac{1}{\lambda}(\text{I}-\text{H}) &= 1500 \text{ ,,}
 \end{aligned} \right\} \text{Mean. } \Delta \frac{1}{\lambda} = 1480 \text{ cm}^{-1}$$

$$\left. \begin{aligned}
 \Delta \frac{1}{\lambda}(\text{C}-\text{B}) &= 590 \text{ cm}^{-1} \\
 \Delta \frac{1}{\lambda}(\text{E}-\text{D}) &= 570 \text{ ,,} \\
 \Delta \frac{1}{\lambda}(\text{II}-\text{I}) &= 460 \text{ ,,}
 \end{aligned} \right\} \text{Mean. } \Delta \frac{1}{\lambda} = 540 \text{ cm}^{-1}$$

The long and short intervals ($\Delta \frac{1}{\lambda} = 1480 \text{ cm}^{-1}$ and 540 cm^{-1}) between the absorption bands of the first series, calculated by the writer, as shown in the table, agree quite well with the results obtained by Henri and Steiner.

2. Δ^1 -Dihydronaphthalene

The Δ^1 -dihydronaphthalene used in this experiment was prepared from ac-tetrahydro- β -naphthol by dehydration with potassium hydroxide¹ and purified by distillation with metallic sodium. It shows the following properties; B. p. = (206–207); $d_4^{25} = 0.9926$; $n_D^{25} = 1.5782$.

The ultra violet absorption spectra of this substance and the wave length and wave number of the absorption bands are shown in Fig. 2 and Table II.

The results given therein, which are different from those obtained by Baly and Tuck², show four absorption bands from A to D in the region $\lambda = 3220\text{\AA} - 2973\text{\AA}$, and correspond to the first series of absorption band of naphthalene, and the absorption band E ($\lambda = 2947\text{\AA} - 2445\text{\AA}$) which is broad and diffused one, corresponds from its nature to the second series. Bands C and D are the most intense and the interval

1. Kimura: These Memoirs, A, 14, 190 (1931)

2. Jour. Chem. Soc., 93, 1907 (1908).

Fig. 2

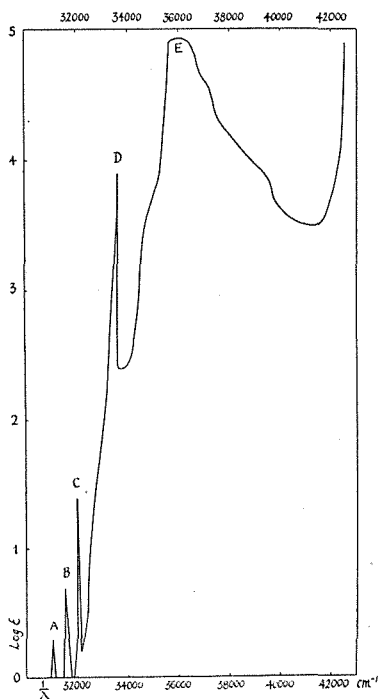


Table II

Band	$\lambda(\text{\AA})$	$\frac{1}{\lambda}(\text{cm}^{-1})$	$\Delta\frac{1}{\lambda}(\text{cm}^{-1})$
A	3220	31050	
B	3170	31550	(B-A)=500
C	3125	32000	(C-B)=450
D	2973	33630	(D-C)=1630
E	$\left\{ \begin{array}{l} 2947 \\ 2775 \\ 2445 \end{array} \right.$	36040	

of these bands, $\Delta\frac{1}{\lambda} = 1630\text{cm}^{-1}$, is the same as the long interval of the first series; another interval, which corresponds to the short one, is also noticed between bands B—A and C—B.

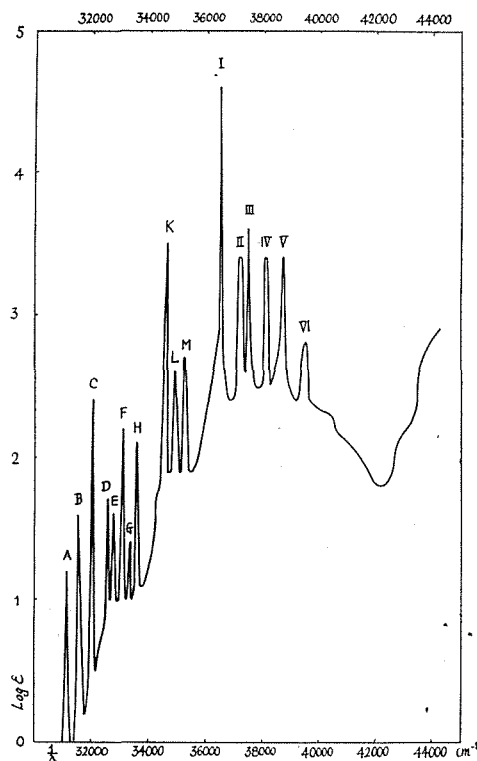
3. Tetrahydronaphthalene

Tetralin from Kahlbaum, purified by distillation with metallic sodium,

and showing the properties B.p.=(204—206); $d_4^{25}=0.9675$; $n_D^{25}=1.5408$, was used in the experiment.

In Fig. 3 and Table III, the absorption curves, the wave length and wave number of the absorption bands are shown; these results are not the same as those obtained by Baly and Tuck¹ with tetrahydronaphthalene and α -tetrahydronaphthalene.

Fig. 3



The absorption bands from A to M, appearing in the region $\lambda=3210 \text{ \AA}—2840 \text{ \AA}$, are sharp and distinct and resemble in nature the absorption bands of the first series of naphthalene. Of them, bands A, B, C, F, H and I are the most intense, and the intervals $\Delta \frac{1}{\lambda} = 1510 \text{ cm}^{-1}$ and $\Delta \frac{1}{\lambda} = 500 \text{ cm}^{-1}$, as shown in the Table III, correspond to the long and the short interval of naphthalene. The bands

1. Jour. Chem. Soc., 95, 1907 (1908).

Table III

Band	$\lambda(\text{\AA})$	$\frac{1}{\lambda}(\text{cm}^{-1})$	$\Delta\frac{1}{\lambda}(\text{cm}^{-1})$
A	3210	31150	(F-B)=1550
B	3175	31500	(H-C)=1510
C	3120	32050	(E-A)=1570
D	3073	32540	(K-F)=1570
E	3056	32720	(L-G)=1580
F	3026	33050	(B-A)= 450
G	3005	33280	(C-B)= 550
H	2980	33560	(D-C)= 490
K	2888	34620	
L	2868	34860	
M	2840	35210	
I	2745	36430	
II	2689	37180	
III	2670	37450	
IV	2625	38090	(IV-I)=1660
V	2586	38670	(V-II)=1490
VI	2532	39500	

corresponding to the second series, which appear in the region $\lambda = 2745 \text{ \AA} \sim 2532 \text{ \AA}$, 6 diffused bands from I to VI, have also the interval $\Delta\frac{1}{\lambda} = 1500 \text{ cm}^{-1}$.

4. Cis-Octahydronaphthalene

Cis-Octahydronaphthalene was obtained by dehydration of cis-decahydro- β -naphthol, M.p.=105 with $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}^1$, and was purified by distillation with metallic sodium. Its physical properties are as follows: B.p.=(191—191.5); $d_4^{25} = 0.9135$; $n_D^{25} = 1.4918$.

1. These Memoirs, A, 14, 191 (1931);

Fig. 4

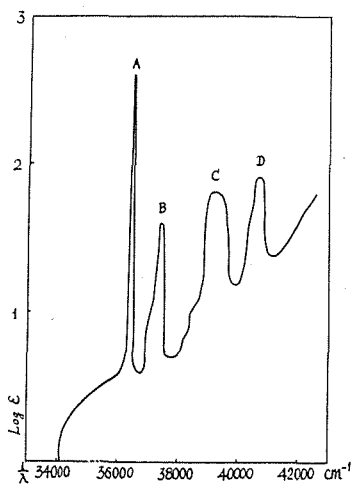


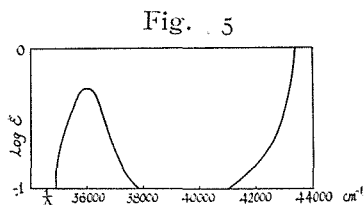
Table IV

Band	$\lambda(\text{\AA})$	$\frac{1}{\lambda}(\text{cm}^{-1})$	$\Delta\frac{1}{\lambda}(\text{cm}^{-1})$
A	2747	36430	
B	2673	37410	(B-A)= 980
C	2550	29220	(C-B)=1810
D	2463	40600	(D-C)=1380

The absorption spectrum of this compound as shown in Fig. 4 and Table IV, was composed only of four broad and diffused bands from A to D, which correspond to the second series of naphthalene and their interval is similar to that measured by the writer with the corresponding bands of tetrahydronaphthalene.

5. Decahydronaphthalene

The decahydronaphthalene used in this experiment was prepared from tetrahydronaphthalene by catalytic reduction under high pressure and high temperature, and purified by treating it with conc. H_2SO_4 , alkali and water, and then by distillation on metallic sodium. It shows B.p. = (190—192); $d_4^{25} = 0.8836$; $n_D^{25} = 1.4738$.



The absorption spectrum of this compound, as shown in Fig. 5, shows a broad, diffused band with its head situated at $\lambda=2780 \text{ \AA}$
 $\frac{1}{\lambda}=35970 \text{ cm}^{-1}$.

In conclusion, the writer wishes to express his sincere thanks to Prof. Dr. S. Komatsu for his kind guidance and valuable suggestions throughout this work and also to Dr. S. Kitashima and Dr. Mrs. S. Kato of the Institute of Physical and Chemical Research of Tokyo, for their generous gift of the Geissler tube used in these experiments.

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Laboratory of Organic- & Bio-Chemistry.
