

**RESTRICTED**

**ENCLOSURE (A)**

ENCLOSURE (A)

ON THE PHYSICAL PROPERTIES  
OF SOME PURE HYDROCARBONS  
(In Five Parts)

by  
DR. S. KOMATSU

Prepared for and Reviewed with Author by  
the U. S. Naval Technical Mission to Japan

December 1945

## ENCLOSURE (A)

## TABLE OF CONTENTS

Part I	Relation between Molecular Structure and Physical Properties	
I.	Introduction .....	Page 13
II.	Boiling Point .....	Page 14
III.	Density or Molecular Volume .....	Page 15
IV.	Cracking Temperature .....	Page 18
V.	Absorption Spectra of the Ultra Violet Rays .....	Page 18
Part II	The Identification of Hydrocarbons by the Use of Raman Spectra .....	Page 43
Part III	Some Tabulated Physical Properties of Important Hydrocarbons	Page 56
Part IV	Data on the Ultra Violet Absorptive Properties of Some Hydrocarbons .....	Page 63
Part V	Data on the Raman Spectra of Hydrocarbons .....	Page 75

## ENCLOSURE (A)

## LIST OF ILLUSTRATIONS

Figure 1(A)	Absorption Spectra of o-Xylene and Cyclopentane and Their Thermal Decomposition Products .....	Page 28
Figure 2(A)	Absorption Spectra of the Oxidation Products of o-Xylene and Cyclopentane .....	Page 30
Figure 3(A)	Absorption Spectra of Benzene and Its Derivatives .....	Page 32
Figure 4(A)	Absorption Spectra of Naphthalene in 1/1000 Molar Alcohol Solution .....	Page 34
Figure 5(A)	Absorption Spectra of Dihydronaphthalene in 1/1000 Molar Alcohol Solution .....	Page 35
Figure 6(A)	Absorption Spectra of Tetrahydronaphthalene in 1/1000 Molar Alcohol Solution .....	Page 36
Figure 7(A)	Anthracene Reduced at 175°C .....	Page 37
Figure 8(A)	Anthracene Reduced at 200°C .....	Page 38
Figure 9(A)	Anthracene Reduced at 225°C .....	Page 39
Figure 10(A)	Anthracene Reduced at 250°C .....	Page 40
Figure 11(A)	Anthracene Reduced at 300°C Solid Product .....	Page 41
Figure 12(A)	Anthracene Reduced at 300°C Liquid Product .....	Page 42
Figure 13(A)	Absorption Spectra .....	Page 69
Figure 14(A)	Absorption Spectra .....	Page 70
Figure 15(A)	Absorption Spectra .....	Page 71
Figure 16(A)	Absorption Spectra .....	Page 72
Figure 17(A)	Absorption Spectra .....	Page 73

## ENCLOSURE (A)

## LIST OF TABLES

Table	I(A)	Examples Illustrating the Relation between Molecular Volume and Molecular Structure .....	Page 22
Table	II(A)	Relative Forces and Dimensions of Certain Hydrocarbon Linkages .....	Page 23
Table	III(A)	Heats of Formation of Hydrocarbon Linkages .....	Page 23
Table	IV(A)	Thermal Decomposition Products .....	Page 24
Table	V(A)	Some Physical Properties .....	Page 25
Table	VI(A)	Thermal Reaction Products .....	Page 26
Table	VII(A)	Excitation Energies of Compounds Containing the Benzene Nucleus .....	Page 27
Table	VIII(A)	X-ray Comparison of Ethylenic and Carbonyl Linkages ..	Page 27
Table	IX(A)	Raman Spectra of the Isomerized Product of n-Butene ..	Page 45
Table	X(A)	Raman Spectra of the Dehydrated Product of n-Butanol .	Page 46
Table	XI(A)	Raman Spectra of Each Fraction .....	Page 47
Table	XII(A)	Raman Spectra of Cyclohexane, Cyclohexene and Methylcyclopentane .....	Page 48
Table	XIII(A)	Raman Spectra of Dihydronaphthalene and Indene .....	Page 49
Table	XIV(A)	Raman Spectra of Each Fraction of Sanga Sanga Gasoline (No. 1) .....	Page 50
Table	XV(A)	Raman Spectra of Each Fraction of Sanga Sanga Gasoline (No. 2) .....	Page 51
Table	XVI(A)	Raman Spectra of Each Fraction of Sanga Sanga Gasoline (No. 3) .....	Page 52
Table	XVII(A)	Raman Spectra of Each Fraction of Sanga Sanga Gasoline (No. 4) .....	Page 53
Table	XVIII(A)	The Component of Sanga Sanga Gasolines .....	Page 54

## ENCLOSURE (A)

Part I  
RELATION BETWEEN MOLECULAR STRUCTURE  
AND PHYSICAL PROPERTIES

## I. INTRODUCTION

The relation between the chemical constitution of organic compounds and their physical properties has been studied by many investigators. Important results of the investigations are discussed in the following books:

- S. Smiles: *The Relation Between Chemical Constitution and Some Physical Properties* (1910).
- H. Kaufmann: *Beziehungen zur physikalische Eigenschaften u. Chemische Konstitution.*
- S. KOMATSU: *General Organic Chemistry* (1931)
- W. A. Waters: *Physical Aspects of Organic Chemistry* (1935)
- R. Kremann: *Physikalische Eigenschaften u. Chem. Konstitution.* (1937).
- V. Henri: *Structure des Molecules* (1925)
- N. V. Sidgwick: *The Covalent-Link in Chemistry* (1938)

The conclusion of these researches mentioned in these books is that the boiling point, density, or molecular volume and refractive index of the organic substances are, as a rule, partly additive and partly constitutive. The author maintains that the chemical reactions of organic compounds can be anticipated from their physical properties. For many years the author has been endeavoring to verify this belief at the Biochemical Laboratory, Kyoto Imperial University.

\* \* \* \* \*

- S. KOMATSU & R. NODZU: *J. Chem. Soc. Japan* 45 (1923) 153
- S. KOMATSU & R. AMATATSU: *Mem. Coll. Sci. Kyoto Imp. Uni. A.* 13, (1930) 329
- S. KIMURA: *Ibid.*, A, 14, (1931) 173
- S. TANAKA: *Ibid.*, A, 22, (1939) 97
- S. KOMATSU & MAKAYAMA: *J. Chem. Soc. Japan* 54 (1933), 558.
- S. ARAKI: *J. Chem. Soc. Japan* 51 (1930), 560, 52 (1931) 818
- S. KOMATSU & HAOIWARA: *Ibid.*, 51 (1930) 552.
- M. HAOIWARA: *Ibid.*, 56 (1935) 269.
- T. OGAWA & T. YOKOTA: *Bull. Chem. Soc. Japan* 5 (1930) 266
- R. WAKAI: *Ibid.*, 5 (1930) 136.
- Y. KAGEHIRA: *Ibid.*, 6 (1931) 241.
- S. FUJITA: *J. Chem. Soc. Japan* 60 (1941) 296.

\* \* \* \* \*

The present volume is a short summary of the data of the physical properties such as the boiling point, density or molecular volume, refractive index, cracking temperature, absorption spectra of ultra violet rays and the Raman spectra. These data are taken from the researches on pure hydrocarbons, carried out in the chemical laboratories of the Imperial Universities and the Institutes in Japan, and also deal with the significance of physical properties to organic chemistry.

## ENCLOSURE (A)

II. BOILING POINT

The boiling point of hydrocarbons of paraffin series  $C_nH_{2n+2}$ , increases with the number of carbon atoms in the molecule.  $CH_2$  in the homologous series shows constancy in some intervals of carbon number, but this mean value decreases in ascending the series. (S. KOMATSU; General Organic Chemistry, P. 27)

No. of intervals of carbon	Mean value for $CH_2$ (°C)
$C_1 - C_5$	40
$C_6 - C_{10}$	25
$C_{11} - C_{15}$	20
$C_{16} - C_{20}$	15

That is, the boiling point of the hydrocarbons depends both on the mass and structure of the molecule.

Similar relations occur in homologous series of organic acids,  $C_nH_{2n}O_2$ , and amines,  $C_nH_{2n+3}N$ :

No. of intervals of carbons	Organic Acids	Mean value (°C)
$C_1 - C_4$		20
$C_6 - C_{10}$		15
$C_{11} - C_{15}$		10
	<u>Amines</u>	
$C_1 - C_4$		30
$C_6 - C_{10}$		25
$C_{11} - C_{15}$		15

From these facts, we have learned that in organic compounds, carbon atoms are closely packed to form a stable group of 5 or 6 atoms; the tendency for carbon atoms to form a group will appear in cyclic compounds and also in a long carbon chain molecules.

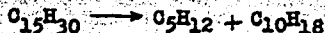
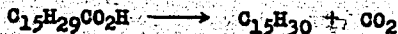
The packing force will evidently be accompanied by the diminution of space occupied by the atomic groups. The diminution of the volume occupied by the atoms themselves with 5 or 6 carbon atomic groups which they undergo by mutual compression (in other words, the energy distribution of long chain hydrocarbons for the  $CH_2$  group in the molecule) is approximately the same within some number of intervals of carbon.

These views were advanced from the occurrence of semiterpenes ( $C_{15}H_{26}$ ), terpenes ( $C_{10}H_{16}$ ), and sesquiterpenes ( $C_{15}H_{24}$ ) in nature, and benzene ( $C_6H_6$ ), naphthalene ( $C_{10}H_8$ ), and anthracene or phenanthrene ( $C_{14}H_{10}$ ) in coal tars.

When the normal paraffins of high molecular weight or long carbon chain compounds are subjected to thermal cracking it will be anticipated that fractions of  $C_5$ ,  $C_6$ ,  $C_9$ , and  $C_{10}$  atomic groups occur mostly in the distillate.

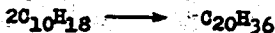
## CLOSURE (A)

As a matter of fact, the saturated paraffin hydrocarbons of the carbon atom number C<sub>8</sub>, C<sub>9</sub>, C<sub>10</sub>, C<sub>11</sub>, and also those of the carbon atom number C<sub>15</sub>, C<sub>19</sub>, C<sub>20</sub>, and C<sub>30</sub> of unsaturated character are found in tars as a main reaction product from the dry distillation of palmitic acid in a retort. The thermal reaction which occurs on the fatty acid molecule can be interpreted as follows:



The hydrocarbon residue derived from the splitting off of the CO<sub>2</sub> from palmitic acid, decomposes into C<sub>5</sub> and C<sub>10</sub> atomic groups, since the thermal stability of the atomic groups varies as proposed by G. Egloff and R. I. Moore (Met. Chem. Eng., 16 (1917) 47); that is, C<sub>12</sub>H<sub>26</sub> & C<sub>15</sub>H<sub>32</sub> are most stable and those of less and of more carbon atoms less stable.

The unsaturated groups or free radicals formed by cracking tend to polymerize.



(S. KOMATSU: Biochemical Studies on Pityrol, Mem. Coll. S, K, I, U, A, 11, (1928) 481; S. ARAKI: Thermal Cracking of Palmitic Acid, Octyl Alcohol and Hexadecane, J. Chem. Soc. Japan 52 (1931) 818.)

It is worthy of note that the abnormally high boiling points of the compounds are often associated with some of the hydrogen bonds which exist in the molecule. (L. Pauling: The Nature of the Chemical Bond, 1939, P. 270). (Refer H. INOUE; On the Relation Between Boiling Point and Chemical Constitution of Liquid Organic Compounds; J. C. S. Japan, 47 (1925) 153.)

In this connection, hydrogen peroxide and hydrazine which are used for rocket fuel, should be mentioned as one of the most interesting examples in regard to the hydrogen bonds.

### III. DENSITY OR MOLECULAR VOLUME

Density of organic liquids or the volume occupied by their molecules under corresponding states depends not only on the mass but on the nature of their chemical structures as will be illustrated with a few examples which are composed of the same number of carbon atoms—n-hexane, cyclohexane, and benzene.

It is understood from these typical examples that the ring formation is attended by a considerable contraction within the molecule, and the packing force of the molecule is greater in benzene, the aromatic compound, and smaller in n-hexane, the paraffin compound. (Based on their molecular refraction and relative density, they are classified as aliphatic monocyclic, bicyclic and tricyclic sesquiterpenes.)

These results were compatible with the distance between the centers of two singly linked carbon atoms, measured by the X-ray method, and also the heat of rupture of the links (H.R.) obtained from extrapolation of the infrared band spectra.

Hydrocarbons of higher density, therefore, should be more thermally stable than the lower density ones, and the idea is emphasized on the heats of formation of links (in Kgm-Cals) calculated from thermochemical data as shown in Table III(A).



## ENCLOSURE (A)

As a matter of fact, approximate values of the decomposition temperatures of the pure compounds obtained (1) from pressure change which was measured under constant volume by S. KOMATSU and his co-workers, (2) from the observation of ultra violet absorption spectra of the decomposed substances by S. KATO and her co-workers.

It was supposed from the heat of rupture of the links that in the thermal cracking of n-paraffins, the rupture of C-C link will take place at first, and then the rupture of C-H link, follows, while aromatic hydrocarbons behave in a different manner. The side chain and hydrogen are removed first and the disruption of the benzene nucleus follows. Cyclohexane and its alkyl derivatives when heated, must decompose entirely into the fragments of similar sizes of molecules judging from the fact that the energy contents of C-C and C-H, links have almost the same value,

The behaviour of paraffin, naphthene and aromatic hydrocarbons towards heat. is illustrated as follows:

Paraffin hydrocarbons	→	{ Hydrocarbons of small molecules and gaseous substances
Aromatic hydrocarbons	→	{ Hydrocarbons of large molecules and gaseous substances
Naphthenic hydrocarbons	→	{ Hydrocarbons of small molecules

These characteristic thermal behaviours of the hydrocarbons are due to the distribution of energy in the molecules; in paraffin and aromatic hydrocarbons, chemical energy is distributed unequally on C-C and C-H links, but the energy in the naphthenic hydrocarbons is equally distributed. (Refer. R. NAKAI, Rep. Nav. F. R. 4, No. 5, OGAWA & TAKAHASHI Ibid., No. 55, FUJIMOTO Ibid., No. 101).

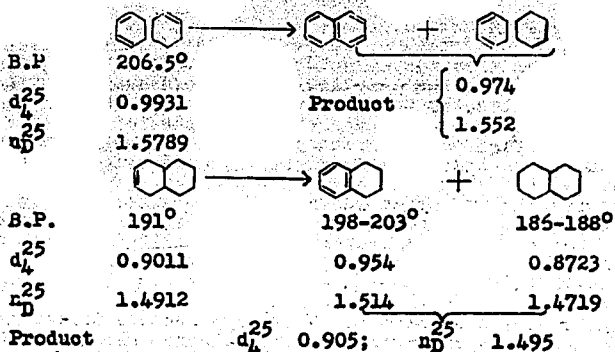
The result of the study was that hydrogenation cracking of gas oil or kerosene to obtain gasoline was a more rational treatment than thermal cracking.

When, however, pine root oil was subjected to catalytic cracking, the reaction product consisted mostly of aromatic hydrocarbons. Such a phenomenon was hardly met with in petroleum cracking, due to the chemical behaviour of terpenes, the hydro-p-cymene derivatives, which occur abundantly in the pine root oil.

A further study of force constant of links and of density is required to solve this abnormal behaviour of terpenes. Another, chemical significance of density, has been studied in the study of hydrogen transformation.

Cyclohexene when heated at 300°C in the presence of Pd-asbestos, was converted into benzene and cyclohexane. (M. Zelinsky & G. Pawlow; Ber. 57 (1924) 1066) Such a chemical reaction (so-called catalytic oxidation-reduction of the unsaturated compounds) was noticed on hydronaphthalene and its derivatives;  $\Delta$ -dihydronaphthalene was passed over Pd-asbestos heated to 250-300°C in an atmosphere of CO, and naphthalene and tetrahydronaphthalene were found to occur in the reaction product by means of the density determination, and cis-decalin under the same reaction conditions was converted into tetralin and trans-decalin:

## ENCLOSURE (A)

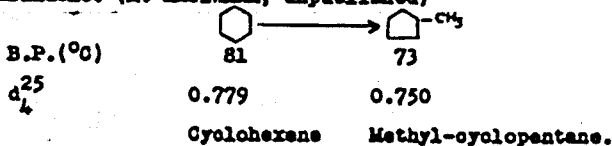


(S. KIMURA: Mem. Coll. Sci. R. I. U. A. 14 (1931) 173)

Thus unsaturated hydrocarbons by the catalytic hydrogen transformation change to stabler hydrocarbons. The catalytic hydrogen transformation was applied to cracked gasolines from petroleum or coal tars to improve the fuel quality, by which unsaturated compounds in the gasoline were removed by converting to stabler forms.

The unsaturated compounds in gasolines, tars or pine root oil, contain C=C link in the molecule, which is a chemically reactive group, but more stable toward heat than the C-C link. The C=C link, therefore, can be removed from the molecule by addition of hydrogen but not by thermocracking.

One important feature in thermochemistry is that cyclohexene by heating is converted to its stable isomer methyl cyclopentane, and tetralin in the same manner, to hydrindane. (M. HAGIWARA; unpublished)



These experimental facts harmonize with the occurrence of cyclopentane and its homologue in petroleum and indene in coal tars. The occurrence of these pentamethylene derivatives in nature is explained by assuming the thermochemical reaction occurs on hexamethylene derivatives. However, the conversion of hydrocarbons of higher density into low density isomers, seemed to contradict the hypothesis above mentioned and is hardly explained by the strain theory of Baeyer.

The investigations of the Raman spectra of these compounds gave us a more satisfactory explanation with regard to the isomerization.

## ENCLOSURE (A)

IV. CRACKING TEMPERATURE

Pure hydrocarbons which were heated externally in a quartz vessel, decomposed at a definite temperature. The cracking temperature was observed by the pressure change, and; also, by the formation of new cracked substance by means of the absorption spectra of ultra violet rays. The former experiments were carried out at the Biochemical Laboratory of Kyoto Imperial University and the latter by S. KATO at the Institute of Physical and Chemical Research, TOKYO.\*

The experimental results are shown in Table VI(A). The cracking temperature of paraffines was below 500°; that of polymethylene hydrocarbons or naphthene about 500°; and that of aromatic hydrocarbons above 700°. These results can be expected from the energy contents of various links such as C-H, C-C, C=C, as shown in Table III(A).

The energy contents of links indicate that alkyl benzene showed two or more cracking temperatures. As a matter of fact, toluene cracked at 600° and 785°, indicating that the energy of the substance was distributed unequally in the molecule. Tetralin, being a benzene-cyclohexane condensed ring compound, shows evidently two cracking temperatures 556° and 742°.

From these results, the cracking temperature of hydrocarbons seems to be the additive of those of the constituent links.

When the experimental results shown in the appendices were carefully examined, the cracking temperature of hydrocarbons was found to be partly additive and partly constitutive as in the case of other physical properties.

V. ABSORPTION SPECTRA OF THE ULTRA VIOLET RAYS

The heat of formation of the double link C=C is about 123 kg-cal, or 19 kg-cal less than that of two single links ( $2 \times 71.1 = 142.3$ ). Hence if we take the strain in a molecule to be measured by its excess energy content it would appear that the strain in cyclopentane, a 5-carbon ring, is smaller than that in amylene or the latter is more chemically reactive than the cyclopentane.

		<u>Heat of formation</u> (kg-cal)
Cyclopentane	$C_5H_{10}$	1288.7
Amylene	$C_5H_{10}$	1269.6
Calc. for	$C_5H_{10}$	1291.8

The characteristic properties of the olefinic linkage are its capacity for a direct addition of reagents such as halogens and hydrogen and its susceptibility to the attack of oxygen or oxidizing agents. It must be the C=C link in the molecule, from which electrons dissociate themselves from one of the carbon atoms and become unshared electrons, by means of absorption effect on the ultra violet rays.

\* The experimental results on o-xylene and cyclopentane by KATO are illustrated in Figures 1(A) and 2(A).

## ENCLOSURE (A)

Some organic compounds which contain the atomic groups  $C=C$ ,  $C=C$ ,  $C=O$ ,  $>CH$ ,  $>OH$ , in the molecule show, on the absorption spectra of the ultra violet rays, the characteristic feature, even in a dilution of mol/10,000. Therefore, a compound of these atomic groups was identified and confirmed even in a solution or in such a state of mixture as KATO worked in her studies on thermal cracking and oxidation. Among her experiments, the thermal cracking of benzene, toluene, ethyl benzene, isopropyl benzene and tertiary butyl benzene and their chemical reactions with oxygen are very interesting.

Table V(A) shows the experiment by which the physical properties of these hydrocarbons were measured in the Biochemical laboratory.

Table VI(A) shows the cracked products and the reaction products when equal number of molecules of hydrocarbon and oxygen are reacted at various temperatures.

The reactivity of hydrocarbons with oxygen increased in the following order:

Benzene  
Toluene  
Ethyl benzene  
Isopropyl benzene

It may be explained by the conception of the co-ordinate link that the hydrogen in the methyl group, the acceptor of electrons, which has two shared valence electrons, will carry four; the tendency of the hydrogen to act as acceptor increases gradually by replacing hydrogen atoms in the methyl group by the methyl group.

In the same way, the double links in unsaturated hydrocarbons may play a part in the coordination link.

This conception will be harmonized with the experimental results of the absorption spectra of the ultra violet rays of these compounds.

Substances forming strong intra-molecular hydrogen bonds show the absorption spectrum in the neighborhood of  $3500\text{ cm}^{-1}$ , its first overtone being at about  $7,000\text{ cm}^{-1}$  (L. Pauling: The Nature of the Chemical Bond, 1939, p. 264).

In Table VII(A) the  $\nu_0(\text{cm}^{-1})$  denotes the minimum energy for excitation of non-bonding electron, molecular vibration due to the excitation  $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ . (in wave number  $\text{cm}^{-1}$ ).

The excitation energy of the non-bonding electron of benzene nucleus is the maximum for benzene and the minimum for toluene.

Excited energy calculated in K<sub>2</sub>-Cal/mol from  $\nu_0$

	K <sub>2</sub> -Cal/mol
Benzene.....	110.0
Toluene.....	106.76
Ethyl Benzene.....	106.92
Isopropyl Benzene.....	107.14
Tert. Butyl Benzene.....	107.23

When hydrogen of the  $CH_3$  group in toluene is replaced by  $CH_2$  group, more energy is required for the excitation of the electron than that for toluene. This fact indicates that the negative character of the carbon atom in a  $CH_3$ -group decreases gradually, and in consequence the absorption spectra of isopropyl

## ENCLOSURE (A)

benzene and tertiary butyl benzene appeared in the region of long wave length and diffused while benzene and toluene showed a sharp band as can be seen in Figure 3(A).

The significance of the physical properties of organic compounds can be illustrated by the addition of oxygen to the double bonds, experimented by S. TANAKA (Mem. Coll. Sci. Kyoto Imp. Uni., A. 22 (1939) 98) on p-menthene  $\Delta^3$  and benzaldehyde.

When menthene,  $C_{10}H_{18}$  was oxidized by peracetic acid, persulphuric acid or  $H_2O_2$ , the product  $C_{10}H_{18}O$  was identified to be menthene oxide by the physical constants, in comparing with those of  $\gamma$  menthone:

The product,  $C_{10}H_{18}O$ , B.P. (74-5)<sub>14</sub>,  $d_4^{25}$  0.8946,  $n_D^{25}$  1.44369,  $n_D^{25}$  1.44595,  $n_D^{25}$  1.45148,  $n_D^{25}$  1.45502,  $(\alpha)_D$  53,17°.

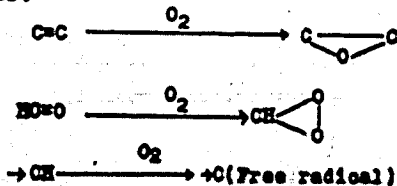
Product, $C_{10}H_{18}O$	Mol. Heat of Combustion	Parachor	
	(Kg. Cal.)	$\frac{M}{D} \gamma^{3/4}$	$\Sigma(P)$
	1302.8	396.1	381.9
$\gamma$ -menthone $C_{10}H_{18}O$	1278.7	400.9	405.1

In general, ethylene oxide compounds have been produced by the oxidation of the ethylenic compounds.

Menthene oxide when heated to 100° for 20 minutes with a drop of acetic acid was converted 25% into a brown coloured polymer.

It is well known that in physical properties, especially in the ultraviolet ray absorption, there is a close resemblance between the ethylenic and carbonyl linkages as shown in Table VIII(A), and that in chemical properties they resemble each other in the tendency to auto-oxidation, addition reactions with oxygen and halogen, and polymerization.

The tendency to gum formation in gasoline and to autooxidation of pine root oil should be attributed to the link  $C=C$ ,  $C=O$  or the more positive character of carbon atom in the molecule, and to the probable formation of ethylene oxide ring in the following manner:



In this connection, the study on styrene oxide by F. TANAKA (Bull. Chem. Soc. Japan, 16 (1941) 382.) should be noted. It has been found that the styrene oxide possessed no oxidizing action upon styrene but accelerates its polymerization.

The author has prepared the peroxides of various ketones and aldehydes by the action of hydrogen peroxide as antidetonants for diesel fuel; acetone, methyl ethyl ketone and cyclohexanone derivatives were found to give good results for

## ENCLOSURE (A)

this purpose (unpublished).

The molecular structure of naphthalene was ascertained by S. KIMURA ultra-violet absorption spectra. (Stereo chemical studies on hydronaphthalenes. Mem. Chem. Coll. Sci. Kyoto Imp. Univ., A, 14 (1931) 303).

According to his investigation, the absorption spectra of naphthalene in an alcohol solution gives two series of absorption bands, one series composed of 9 sharp and intensive bands in the region  $\lambda$  3400Å - 2900Å, which are divided into 2 groups according to the frequency interval (A)  $\Delta \frac{1}{\lambda} = 14800 \text{ cm}^{-1}$  and (B)  $\Delta \frac{1}{\lambda} = 540 \text{ cm}^{-1}$ , and the other series composed of 5 broad and diffused bands in  $\lambda = 2900\text{Å} - 2500\text{Å}$ , as can be seen in Figures 4(A), 5(A), and 6(A).

The absorption spectra of dihydro- and tetrahydro-compounds, are also composed of two series of absorption bands which are similar in frequency intervals:

	$\Delta \frac{1}{\lambda} \text{ cm}^{-1}$ (A)	(B)
Naphthalene	1480	540
$\Delta$ -Dihydro-"	1630	475
Tetrahydro-"	1563	497

The absorption of light by benzene shows 7 sharp absorption bands in the ultra violet region due to the benzene nucleus, not appearing in the alcohol solutions of di- and tetrahydrobenzenes, (see Figures 3(A), 4(A), 5(A), and 6(A)). 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 tetrahydronaphthalenes have the same chemical structure as naphthalene. However, the absorption spectra of octa- and decahydro-naphthalenes in the ultra-violet region were observed to be entirely different in nature from those of the other hydrocompounds studied above, and to be composed only of broad diffused bands in  $\lambda = 2750\text{Å} - 2400\text{Å}$  of the frequency intervals  $\Delta \frac{1}{\lambda} = 1500 \text{ cm}^{-1}$ , which correspond to the second series of the absorption bands of naphthalene and the first series of the absorption bands were absent in these hydro compounds. These facts are in favour of the view that the molecular structure of naphthalene is partly changed in the octahydro- and decahydro-compounds, such a difference in the absorption spectra between the compounds of the naphthalene series and those of the benzene series may be explained by assuming a bicyclic structure for the naphthalene molecule; in the dihydro- and tetrahydronaphthalene, the hydrogen atoms combined to one of the rings in the naphthalene molecule, but in octahydro- and decahydro-naphthalenes they are added to both rings.

Accordingly, in the former, the addition of hydrogen atoms to naphthalene did not effect its absorption spectra, while in the latter, only the second series of absorption bands would 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 were situated in the neighbourhood of from  $\lambda = 35000 \text{ cm}^{-1}$  to the more ultra violet region were observed to appear throughout all the compounds of the naphthalene series. The origin of these bands was attributed to some vibration of a bicyclic carbon linking.

Dr. HAGIWARA's observation, made in the course of his study of terpenes, that pinane, the saturated bicyclic compound, exhibited a selective absorption band in the ultra-violet region but that a saturated monocyclic hydrocarbon such as menthane showed no selective absorption band, supported the above view that there was an absorption caused by the bicyclic ring.

## ENCLOSURE (A)

This idea of the bicyclic nature of the naphthalene molecule was also confirmed by the study of the catalytic reduction of naphthalene.

By reduction, benzene yielded cyclohexane as a sole reaction product, while naphthalene absorbed hydrogen in a two or more step reaction, forming tetrahydro-, octahydro-, and decahydro-naphthalenes. These results indicated that the distribution of energy in the naphthalene molecule differed 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 were composed of two groups of bands of different frequency interval. The structure formula (1) of naphthalene, which advocated by Willstetter, was thus supported to be a reasonable one from the study of absorption spectra of ultra violet rays.



By applying T. YOKOTA and H. FUJIMOTO's research on the absorption spectra of anthracene and its hydrogenated compounds, I. WATANABE, I. KOIKE, and S. IGASAKI have investigated the chemical reaction of the catalytic reduction of anthracene in presence of nickel oxide under high temperature and high pressure of hydrogen. (Rep. the Naval Fuel Research No. 143 (1941) Figures 7(A), 8(A), 9(A), 10(A), 11(A), and 12(A).

Table I(A)  
EXAMPLES ILLUSTRATING THE RELATION BETWEEN MOLECULAR VOLUME  
AND MOLECULAR STRUCTURE

Substance Formula	M.W.	B.P.	$d_4^{25}$	$V_m^{**}$	D. Temp. *	
n-Hexane	$C_6H_{14}$	84	69	0.6558	127.7	410°
Cyclohexane	$C_6H_{12}$	82	81	0.7736	105.8	550°
Benzene	$C_6H_6$	76	80	0.8715	87.2	745°
o-Xylene	$C_8H_{10}$	104	141.9	0.8509	121.7	600°
p-Xylene	$C_8H_{10}$	104	136.3	0.8566	120.7	650°
m-Xylene	$C_8H_{10}$	104	138	0.8600	120.0	650°

\* D. Temp. Decomposition Temperature

\*\*  $V_m$ . Molecular Volume. (G. Le Bass; The mol. volumes of liquid chem. compounds (1915)).

## ENCLOSURE (A)

Table II(A)  
RELATIVE FORCES AND DIMENSIONS OF CERTAIN HYDROCARBON LINKAGES

Link	H. Rup. (kg-cal)	Substance	Method	Distance (Å)
C <sub>al</sub> -C <sub>al</sub>	88	Acetone	Pre-dissociation	1.54
C <sub>ar</sub> -C <sub>ar</sub>				1.45
C = C				1.44
C <sub>al</sub> -H	97	Hexane	Infra-red	
C <sub>al</sub> -H	94	Cyclohexane	Infra-red	
C <sub>ar</sub> -H	117	Benzene	Infra-red	

(N. V. Sidgwick: The covalent link in chemistry, 110, 119)

Table III(A)  
HEATS OF FORMATION OF HYDROCARBON  
LINKAGES

Link	Heat of formation (kg-cal)
C <sub>al</sub> -C <sub>al</sub>	71
C <sub>ar</sub> -C <sub>ar</sub>	97.2
C <sub>ar</sub> -C <sub>al</sub>	79.4
C = C	123
C <sub>al</sub> -H	93.6
C <sub>ar</sub> -H	101.7

(N. V. Sidgwick: The covalent link  
in chemistry, 110, 119)





## ENCLOSURE (A)




Table V(A)  
SOME PHYSICAL PROPERTIES

I	II	III	IV	V	VI
Substance	Benzene	Toluene	Ethyl benzene	Isopropyl benzene	Tert. butylbenzene
	$C_6H_6$	$C_6H_5 \cdot CH_3$	$C_6H_5 \cdot CH_2CH_3$	$C_6H_5 \cdot C(CH_3)_2$	$C_6H_5 \cdot C(CH_3)_3$
M. W.	78	92	106	120	134
B. P. (°C)	80.2 80.6	109.8 109.9	134.5 135	150 ~ 152	165 ~ 166
$d_4^{25}$	0.8715	0.8611	0.8630	0.8596	0.8667
$n_D^{25}$	1.4960	1.4912	1.4913	1.4914	1.4962
Ab. sp. (I)	38450(3)	37305(5)	37460(5)	37580(8)	37650(7)
(V)	38612(8)	37425(3)	37490(7)	37620(9)	3770(5)
	39445(4)	37485(10)	37528(10)	38058(5)	37980(5)
	39543(10)	38020(7)	37558(8)	38103(7)	38180(10)
	40370(3)	38400(7)	37597(7)	38150(6)	38228(5)
	40460(7)	38422(9)	38423(4)	38540(10)	38608(7)
	41286(2)	38455(8)	38453(9)	38580(7)	38855(6)
	41378(7)	38668(8)	38485(9)	38812(6)	38930(5)
	41884(1)	38732(5)	38523(7)	39058(9)	39126(8)
	42300(5)	38765(5)	38763(6)	39490(4)	39546(3)
	43010(2)	38945(6)	38840(6)	39741(4)	
	43215(2)	39395(6)	38935(6)		
		39600(6)	38980(8)		
(II)	49100(7)	39367(4)	39012(7)		
	49980(10)	39850(3)	39045(7)		
	50900(10)	39880(3)	39414(6)		
	51790(8)	40248(2.5)	39445(5)	40682(2)	40082(4.5)
	52610(5)	41310(1.5)	41520(2)	41625(1)	40710(5)
					41648(1)

(S. EDWARDS &amp; S. KATO, unpublished)

## ENCLOSURE (A)

Table VI(A)  
THERMAL REACTION PRODUCTS

Temp(°C)	I	II	III	IV	V
600°C	--	--	$C_6H_5CH=CH_2$ , $C_6H_5CH=CHC_6H_5$ , $CH_2=CH_2$ , $C_6H_6$	$C_6H_5CH=CH_2$ , $C_6H_5CH=CHC_6H_5$ , $CH_3-CH_3$ , $CH_4$ , $C_6H_6$ , $CH_3CH=CH_2$ , $CH_2=CH-CH=CH_2$	$C_6H_5CH=CH_2$ , $C_6H_6$ , $CH_3, CH_3$ , $(CH_3)_2C=CH_2$ , $CH_2=CHCH=CH_2$
650°C	--	$C_6H_5-CH=CHC_6H_5$ $H_2$			
REACTION PRODUCTS WITH OXYGEN					
100°C		$C_6H_5-CH(OH)CH_3$	$C_6H_5-OH(CH_3)OH$	--	--
150°C		--	--	$C_6H_5C(CH_3)_2OH$	$C_6H_5C_2H_6CH_2OH$
200°C		$C_6H_5-CHO$	--	--	--
450°C		--	$C_6H_5-CH=CH_2$	--	--
500°C		--	--	$C_6H_5OH$ , $C_6H_5-C(CH_3)=CH_2$	$C_6H_5OH$ , $CH_3COCH_3$
550°C		$C_6H_5OH$	$C_6H_5CHO$ , $HCHO$	--	$C_6H_5C(CH_3)=CH_2$ , $HCHO$ , $C_6H_5COCH_3$
600°C ~ 650°C		--	$C_6H_5OH$	$C_6H_5COCH_3$ , $HCHO$ , $C_6H_5OH$ , $CO$	$C_6H_5CHO$ , $HCHO$ , $CO$

KUMATSU (pure hydrocarbon part I)

## ENCLOSURE (A)

Table VII(A)  
EXCITATION ENERGIES OF COMPOUNDS  
CONTAINING THE BENZENE NUCLEUS

Substance	$\nu$ (cm <sup>-1</sup> )	$\epsilon_1$	$\epsilon_2$	$\epsilon_3$	$\epsilon_4$
Benzene	38624	922	922	465	
Toluene	37485	937	960	535	455
Ethyl benzene	37528	925	957	522	412
Isopropyl benzene	37620	920	960	483	310
Ter. butyl benzene	37550	diffuse	977	530	330

Table VIII(A)  
X-RAY COMPARISON OF ETHYLENIC AND  
CARBONYL LINKAGES

Physical properties	Links	
	C=C	C=O
Perschor	23.2	23.0
$n_D$	1.7	2.2
Raman effect	1630 Å	1722 Å
Ultra-violet absorption band	2700 Å	2700-800 Å

## ENCLOSURE (A)

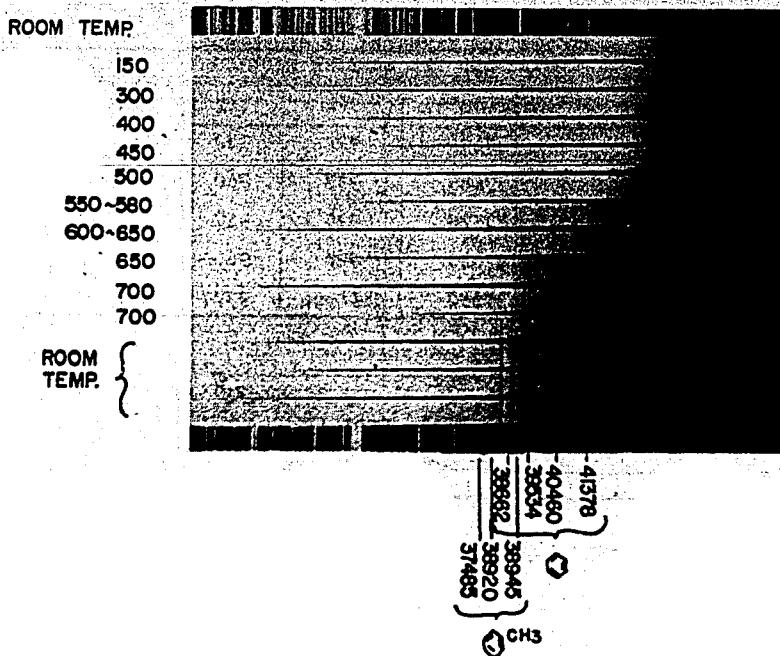


Figure 1(A)  
 ABSORPTION SPECTRA OF O-XYLENE AND CYCLOPENTANE  
 AND THEIR THERMAL DECOMPOSITION PRODUCTS

1 m. mol o-xylene was heated gradually in a 170cc quartz tube, and absorption spectra were taken at 150°, 300°, 400°, 450°, 500°, 550-580°, 600-650° and 700° respectively, the results shown in Figure 1(A) indicate that benzene and toluene were formed at about 600°C.

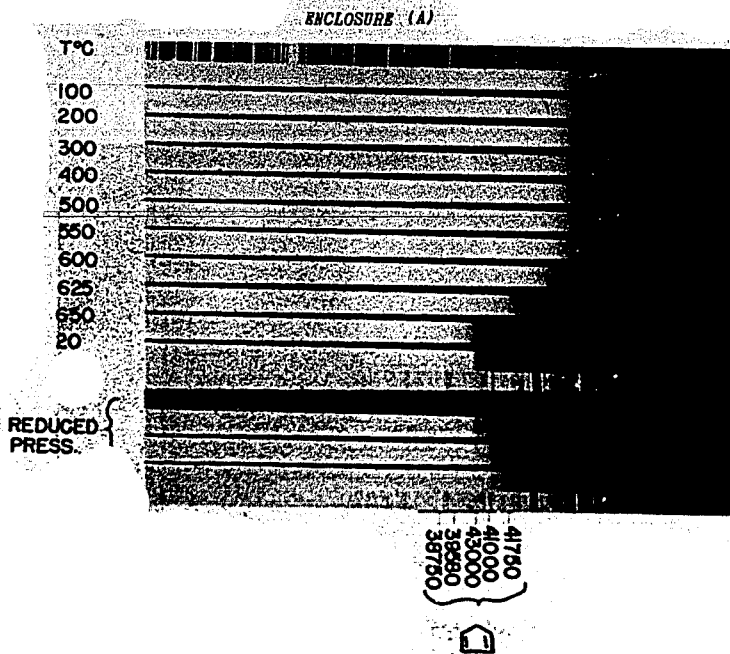


Figure 1(A)cont.

30 mg of cyclopentane were heated to 650°, the formation of ethylene and propylene at 500-550°C and of cyclopentadiene at 625°C was confirmed from the absorption spectra shown in this plate.

ENCLOSURE (A)

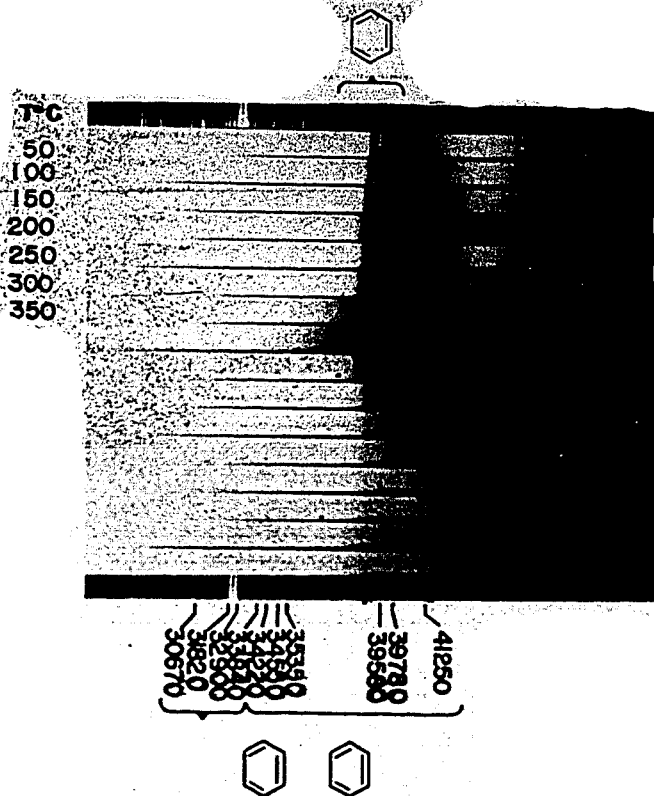


Figure 2(A)  
 ABSORPTION SPECTRA OF THE OXIDATION PRODUCTS OF  
 O-XYLENE AND CYCLOPENTANE

0.1 m. mol o-xylene was heated with 0.5 m. mol oxygen o-Tolyl carbinol at 150°C, formaline, o-toluic aldehyde and o-oxybenzaldehyde at 300°C were formed. Figure 2(A).

ENCLOSURE (A)

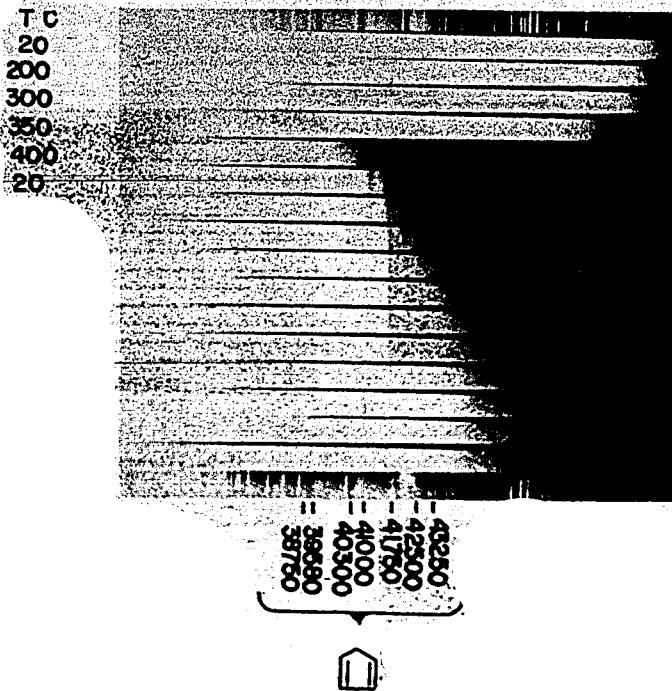


Figure 2(A) cont.

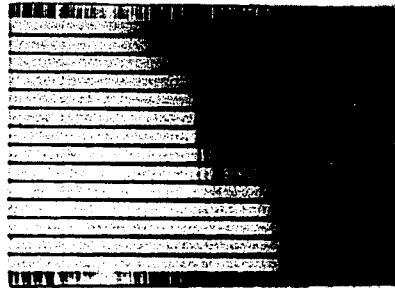
20 mg of cyclopentane was heated to 400°C with 10cc O<sub>2</sub>, and the formation of cyclopentadiene was confirmed by the absorption spectra. Figure 2(A) cont.



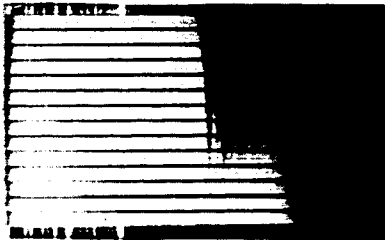
ENCLOSURE (A)



Benzene 1/100<sup>m</sup>



T-Butylbenzene 1/1000<sup>m</sup>



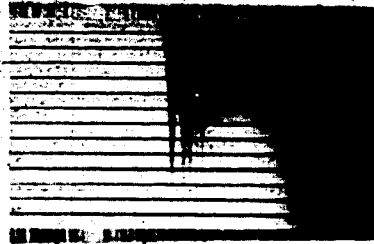
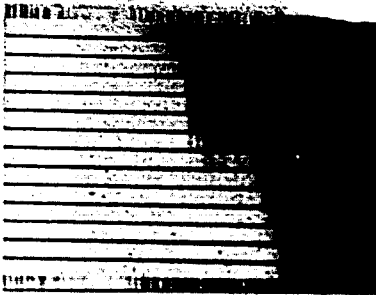
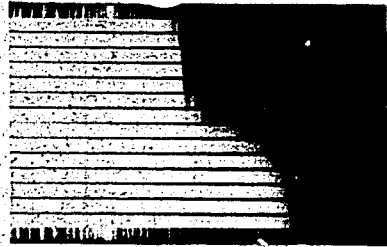
Toluene 1/500<sup>m</sup>



O-Xylene 1/1000<sup>m</sup>

Figure 3(A)  
ABSORPTION SPECTRA OF BENZENE AND ITS DERIVATIVES

ENCLOSURE (A)



Canene 1/1000<sup>x</sup>

P-Xylene 1/1000<sup>x</sup>

Figure 3(A)cont.

ENCLOSURE (A)

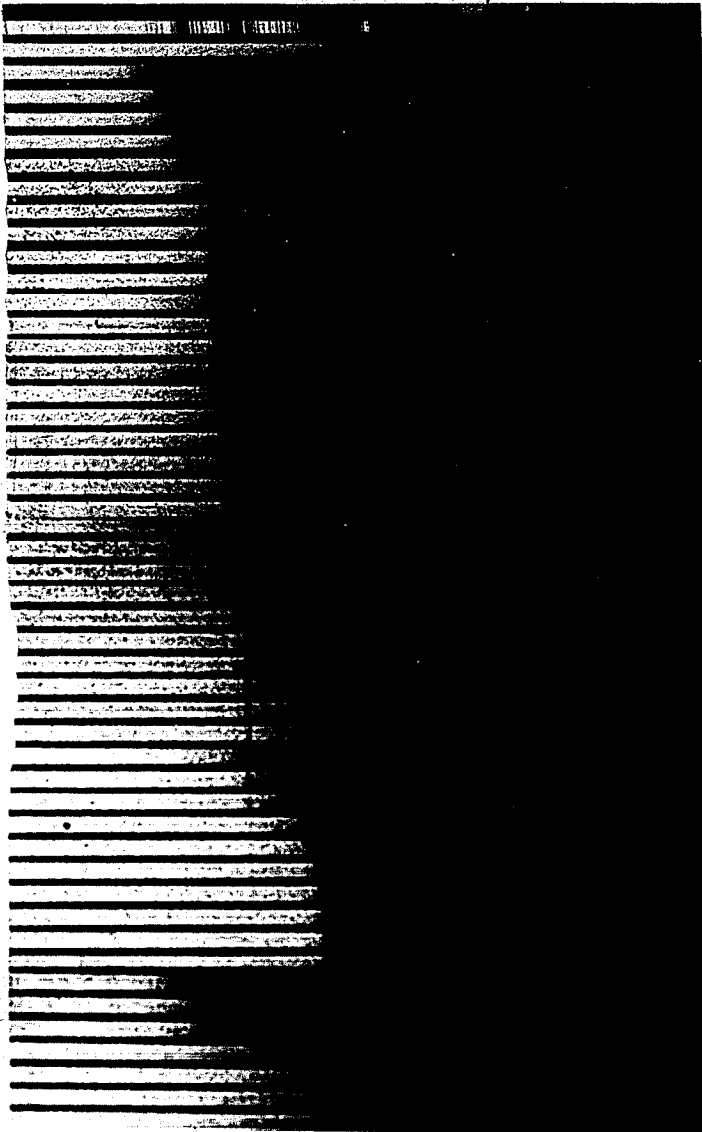


Figure 4(A)  
ABSORPTION SPECTRA OF NAPHTHALENE  
IN 1/1000 MOLAR ALCOHOL SOLUTION

ENCLOSURE (A)

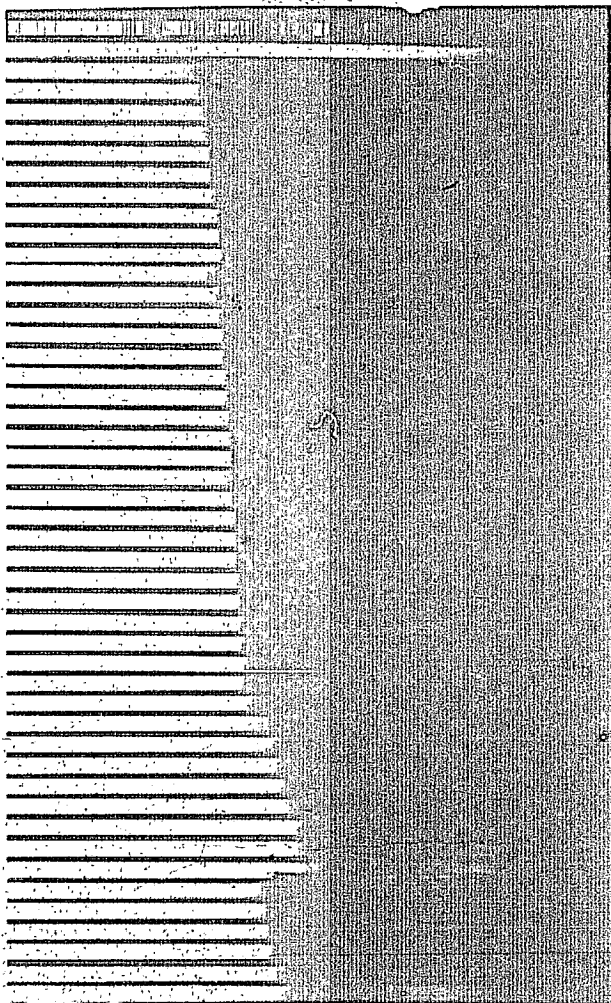


Figure 5(A)  
ABSORPTION SPECTRA OF DIHYDRONAPHTHALENE  
IN 1/1000 MOLAR ALCOHOL SOLUTION

ENCLOSURE (A)

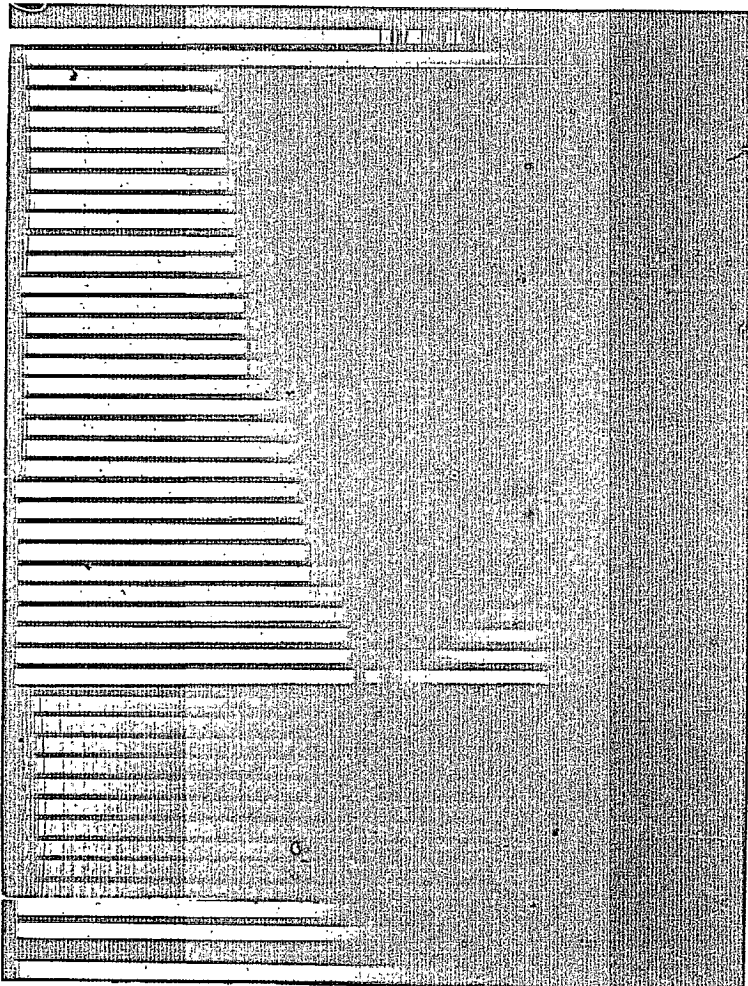


Figure 6(A)  
ABSORPTION SPECTRA OF TETRAHYDRONAPHTHALENE  
IN 1/1000 MOLAR ALCOHOL SOLUTION

## ENCLOSURE (A)

Pure anthracene (M.P. 216-216.5°C) was reduced at 175°, 200°, 225°, 250° and 300°, in the presence of 1% nickel oxide under 100 atmosphere's pressure of H<sub>2</sub>.

The product was studied by the absorption spectrum of its cyclohexane (n<sub>D</sub><sup>25</sup> 1.42330) solution.

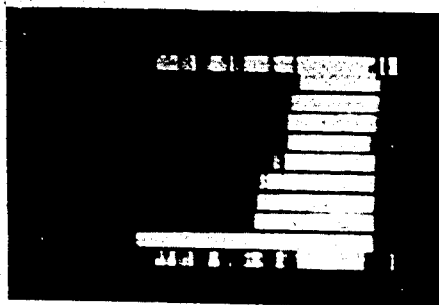
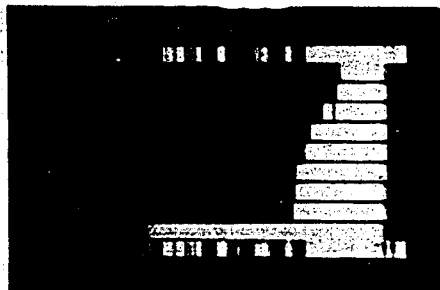
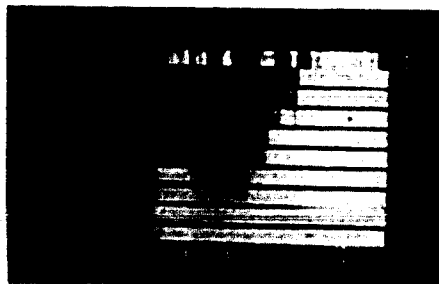


Figure 7(A)  
ANTHRACENE REDUCED AT 175°C

The reaction product at 175°C consisted of 90% tetrahydroanthracene and 10% octahydroanthracene.



ENCLOSURE (A)

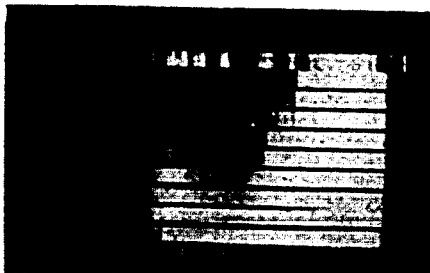
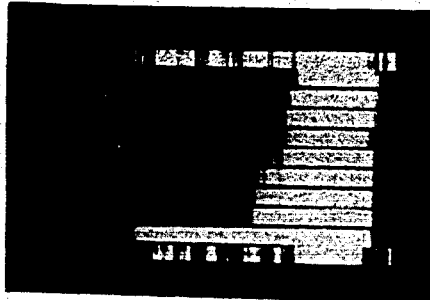
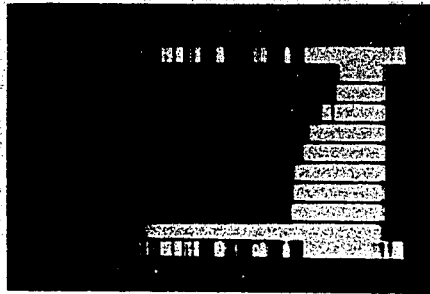


Figure 3(A)  
ANTHRACENE REDUCED AT 200°C

The reaction product at 200°C consisted of 100% tetrahydroanthracene, and trace of dihydroanthracene.

## ENCLOSURE (A)

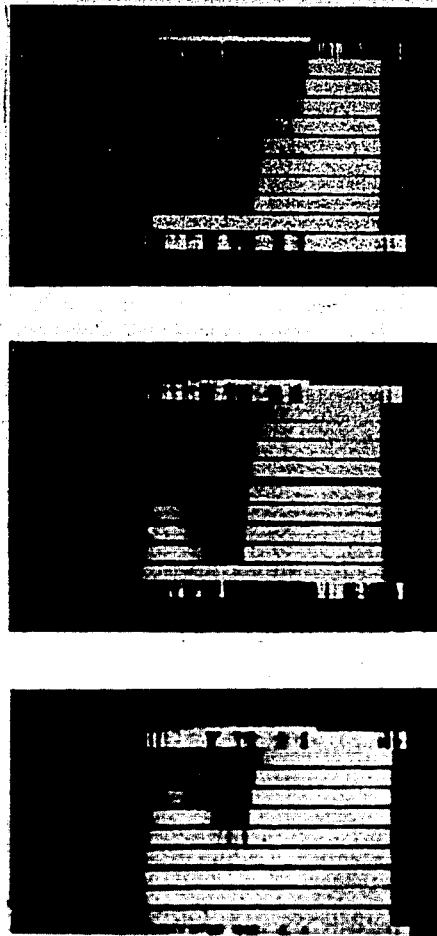


Figure 9(A)  
ANTHRACENE REDUCED AT 225°C

The reaction product at 225°C consisted of mostly octahydroanthracene and a small amount of tetra and perhydro compounds.



ENCLOSURE (A)

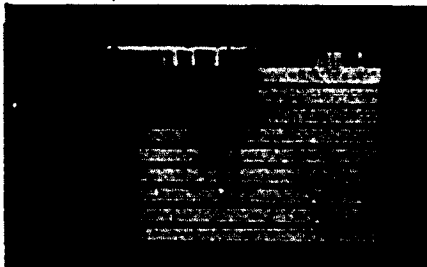
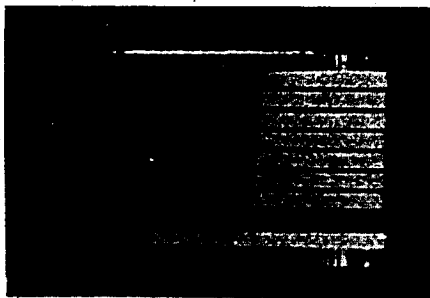


Figure 10(A)

ANTHRACENE REDUCED AT 250°C

The reaction product at 250°C consisted of octahydro, tetrahydro and perhydroanthracene.

## ENCLOSURE (A)

The reaction product at 300°C, consisted of the solid (M.P. 71-72°C) (Plate V) and the liquid ( $d_4^{25}$  0.9710,  $n_D^{25}$  1.5280). (Plate VI).

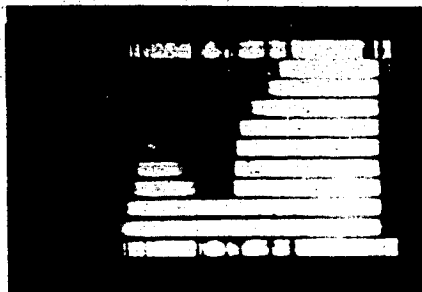
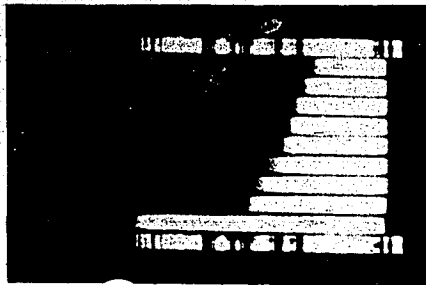
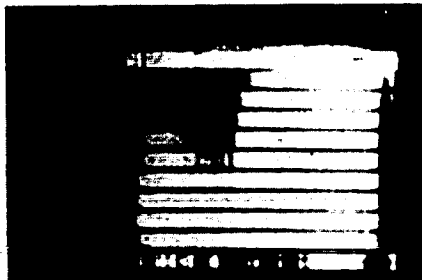


Figure 11(A)

ANTHRACENE REDUCED AT 300°C SOLID PRODUCT

The solid product consisted of mostly octahydroanthracene and with 3% tetrahydro compounds.



ENCLOSURE (A)

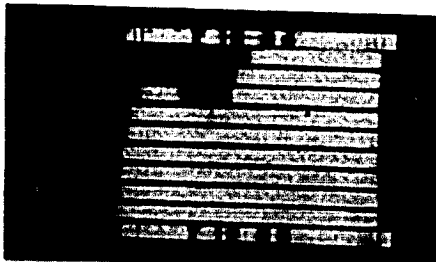
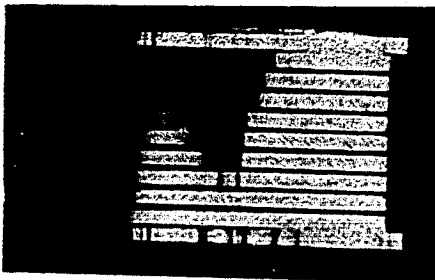
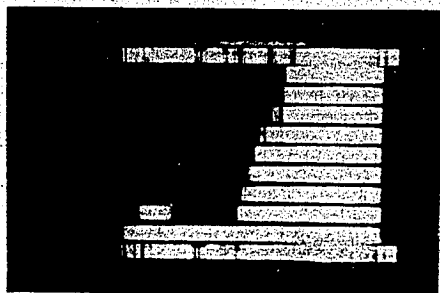


Figure 12(A)

ANTHRACENE REDUCED AT 300°C LIQUID PRODUCT

The liquid product consisted of perhydroanthracene and octahydroanthracene with a trace of tetrahydro compounds.