195. *Chromophoric Groups. Part II. Absorption Spectra of Naphthalene, Hydronaphthalenes, and Related Compounds.*

By R. A. MORTON and A. J. A. DE GOUVEIA.

Naphthalene.—Early work on naphthalene (cf. Baly and Tuck, J., 1908, **93**, 1902) was hampered by the lack of a source of light showing a continuous spectrum and by the semiquantitative methods then in use for determining intensities of absorption. It is therefore not surprising that only three maxima were observed, *viz.*, at 320, 311, and 270 mμ. Henri and Steiner (*Compt. rend.*, 1922, **175**, 421) obtained a very much better resolution with a solution in hexane, and found a large number of narrow bands resembling those observed in naphthalene vapour; de Laszlo (*Z. physikal. Chem.*, 1925, **118**, 369) confirmed and extended this work. Kimura (*Mem. Coll. Sci. Kyoto*, 1931, **14**, 303) examined alcoholic solutions of naphthalene, but his results are not in agreement with earlier work, particularly with respect to extinction coefficients. It is difficult to determine these with high accuracy at the actual maximum of the narrow bands, but we found no difficulty (see Table II) in obtaining substantially the same results as Henri and Steiner and de Laszlo. Kimura obtained good resolution and the wave-lengths of maxima agree fairly closely with other data, but his extinction coefficients appear throughout to be at least 10 times too high and the persistence of individual bands is greatly exaggerated. His data on the hydronaphthalenes, which are the only quantitative results we have been able to trace, exhibit similar defects.

Δ^1-*Dihydronaphthalene.*—Kimura examined this compound, prepared from *ac*-tetrahydro-β-naphthol by dehydration with potassium hydroxide and purified by distillation (b. p. 206—207°) over sodium. Five maxima were obtained :

$\lambda_{\text{max.}}$, mμ …………	322·0	317·0	312·5	297·3	277·5
log ε ………………	0·27	0·65	1·33	3·9	4·9

In the present work three specimens have been examined : (1) a redistilled purchased product (m. p. − 12°, b. p. 209—210°) which was shown to be free from Δ^2-dihydronaphthalene by the fact that its mercuric acetate derivative was entirely insoluble in benzene; (2) a second purchased product which was repeatedly fractionated under reduced pressure (b. p. 81—83°/6—7 mm., m. p. − 12°); (3) a product obtained by heating Δ^2-dihydronaphthalene (m. p. 25·5°) with 5% sodium ethoxide in a sealed tube at 140—150° for 8 hours (cf. Strauss and Lemmel, *Ber.*, 1913, **46**, 236) (b. p. 83—84°/5 mm., m. p. − 4°).

The absorption exhibits a well-defined maximum at 262 mμ (log ε 4·01) which in hexane solution represents the peak of a broad unresolved band. The curve (Fig. 1) shows a feeble inflexion near 273 mμ and there is also a narrow band between 290 and 300 mμ ($\lambda_{\text{max.}}$ 296 mμ, log ε 2·68). A *very* weak band, at 311·5 mμ, may have been due to the presence of a trace of impurity, since its intensity varied in the three samples and was almost negligible in the best. Kimura's intensities of absorption are again too high, but by applying a correction similar to that required for naphthalene, log ε at 277·5 mμ is reduced to about 4, which, however, is still higher than our own data. Examination of his extinction coefficients at the two maxima 322·0 and 317·0 shows that his material was probably contaminated with 0·5% of naphthalene. In fact, had his preparation consisted of 99·5% of Δ^1-dihydronaphthalene, he should have been able to record the 262 mμ band. The appearance of an unresolved band with its maximum at 277·5 mμ indicates that superimposed on the absorption of Δ^1-dihydronaphthalene is that of naphthalene present in appreciable amount and displacing the observed maximum.

Δ^2-*Dihydronaphthalene.*—There appears in the earlier literature to have been some confusion between Δ^1- and Δ^2-dihydronaphthalene. Baly and Tuck (*loc. cit.*) examined a dihydro-derivative and found qualitatively the same bands as in naphthalene, the intensities being about one-tenth of those recorded for the parent substance except at 270 mμ. It is evident, from our present knowledge, that appreciable quantities of naphthalene must have been present.

We prepared Δ^2-dihydronaphthalene as follows : Naphthalene was reduced by means of sodium and ethyl alcohol (Bamberger and Lodter, *Annalen*, 1895, **288**, 75), and the resulting dihydronaphthalene was steam distilled (m. p. 15°, b. p. 212°) and treated with mercuric acetate (Strauss and Lemmel, *loc. cit.*) ; the addition compound was recrystallised and freed from Δ^1-dihydronaphthalene by extraction with benzene (Soxhlet), the Δ^2-dihydro-addition compound alone being soluble. The purified material (m. p. 120°) was treated with 30% hydrochloric acid, and the regenerated Δ^2-dihydronaphthalene (m. p. 25—26°) was redistilled, forming perfectly colourless crystals, m. p. 25·5° (Strauss and Lemmel give m. p. 24·5—25°).

The absorption curve (Table I; Fig. 2) of this material in hexane consisted of a series of narrow bands of very low extinction coefficient (1·5—10) between 331 and 297 mμ, with ill-defined bands near 293, 287, and 262 mμ and well-defined bands at 274 and 267 mμ ($\varepsilon_{\text{max.}}$ = 850 and 800 respectively). The complete absence of naphthalene from this material is difficult to guarantee, although it satisfies the usual criteria of purity.

TABLE I.

Δ^2-Dihydronaphthalene.

	$\lambda_{max.}$, mμ.		$\epsilon_{max.}$.	log $\epsilon_{max.}$.	cm.$^{-1}$.	$\lambda_{min.}$, mμ.	$\epsilon_{min.}$.	log ε.
a	331	inflexion	1·5	0·176	30,210	325	1·5	0·176
b	328·5	persistent	2·65	0·423	30,440	323	1·5	0·176
c	324·5	very small	1·65	0·217	30,810	318	1·9	0·279
d	320·7	small	2·1	0·322	31,180	309	2·7	0·431
e	315	inflexion	2·85	0·455	31,750	305	4·0	0·602
f	311	persistent	5·7	0·756	32,150	302·5	4·0	0·602
g	306·5	very small	4·2	0·623	32,630	299·5	5·0	0·699
h	303·7	very small	4·2	0·623	32,930	295·5	5·4	0·732
i	301	small	5·7	0·756	33,220	282·5	85	1·93
j	297	sharp	7·65	0·883	33,670	271·4	320	2·5
k	293	inflexion	*ca.* 30	1·48	34,130	239	110	2·04
l	287	not sharp	100	2·0	34,840			
m	274	very persistent	850	2·93	36,500 } Δ = 950			
n	267	persistent	800	2·90	37,450			
o	262	inflexion	500	2·7	38,170 } Δ = 720			
					1670			

Δ-cm.$^{-1}$ Values.

$o \longrightarrow m$	1670	$e \longrightarrow a$	1540	$d \longrightarrow a$	970
$m \longrightarrow l$	1660	$i \longrightarrow e$	1470	$c \longrightarrow c$	940
$l \longrightarrow i$	1620	$g \longrightarrow d$	1450	$f \longrightarrow d$	970
$f \longrightarrow b$	1710	$k \longrightarrow g$	1500	$g \longrightarrow e$	880
$h \longrightarrow d$	1750	$j \longrightarrow f$	1520	$k \longrightarrow i$	910
				$n \longrightarrow m$	950
Means	1690		1500		950

Raman frequencies (Bonino).

Δ^2-Dihydronaphthalene	3041, 2873, 2825, *1663*, 1592, 1433, 1287, 1163, 1047, *739*, 499, 468, 244.
Naphthalene	3046, *1573*, 1412, *1377*, 1245, 1142, *1023*, 936, 610, 505.
Tetralin	3049, 2922, 2862, 1602, 1583, 1456, 1433, 1374, 1283, 1204, 1160, 1038, 938, 848, 815, 815, 759, 724, 585, 567, 432.
Decalin	2922, 2856, 1448, 1360, 1260, 1165, 1046, 1017, 990, 851, 804, 753, 593, 554, 490, 402.
Benzene	3185, 3162, 3060, 2947, 2784, 1584, 1506, 1178, *991*, 849, 605. 3047, 2928, 2617, 2597, 2460.
Indene*	3053, 2913, 1607, 1546, 1453, 1355, 1288, 1204, 1057, 1015, 938, 829, 726, 591, 533, 407.

* Data by T. C. Calloway.

The group of bands at 274, 267, and 262 mμ agrees with a benzenoid substance containing an additional ethenoid linkage not conjugated to the benzene ring. Such a double bond would not be expected to affect the absorption appreciably, and Δ^2-dihydronaphthalene and 1 : 2 : 3 : 4-tetrahydronaphthalene should on this basis be practically indistinguishable as regards ultra-violet absorption. How then are the narrow bands of low intensity to be accounted for? The following possibilities must be considered : that the bands are due (*a*) to naphthalene; (*b*) to a small quantity of an addition compound between naphthalene and Δ^2-dihydronaphthalene (Bamberger and Lodter, *loc. cit.*, described a compound, m. p. 43—44°, which may be of this type); (*c*) to a hydronaphthalene of unknown structure with two double bonds in each ring.

Suggestion (*a*) suffers from the disadvantages that the 331 mμ inflexion and the 328·5 and 324·5 mμ bands are not shown by pure naphthalene, neither do the relative intensities of the different bands correspond with those of naphthalene. To test (*b*), we may temporarily ignore the first four or five bands and consider the following :

Δ^2-Dihydronaphthalene :

$\lambda_{max.}$, mμ............	311	306·5	303·7	301	297	293	287
$\epsilon_{max.}$	5·7	4·2	4·2	5·7	7·65	30	100

Naphthalene :

$\lambda_{max.}$, mμ	311	306·8	304·5	302	297·5	293	287
$\epsilon_{max.}$	345	257	257	345	400	450	6900

Proceeding on the assumption that the above good agreement in wave-lengths of maxima indicates contamination with naphthalene, the percentage of impurity may be calculated as 1·65, 1·63, 1·63, 1·65, 1·91, 1·46%. Thus the possibility of the presence of 1·6% of naphthalene cannot be ruled out in spite of the very careful purification, since the Δ^2-dihydronaphthalene may be less stable than has been hitherto assumed. Now the extinction coefficient of pure naphthalene corresponds with $\varepsilon = 110$ for 1·6%, whilst the observed ε value for our Δ^2-dihydronaphthalene at 274 mμ is 850. The intensity of absorption of the dihydro-derivative is therefore high enough largely to mask the effect of 1·6% of naphthalene. Hence, there is reasonable evidence for regarding the bands *e*—*l* as possibly due to contamination with naphthalene. This hypothesis does not, however, account for bands *a*—*d*, and the possibility of an addition compound (see p. 918) now merits further consideration.

FIG. 1.
Δ^1-*Dihydronaphthalene* (*in hexane*).

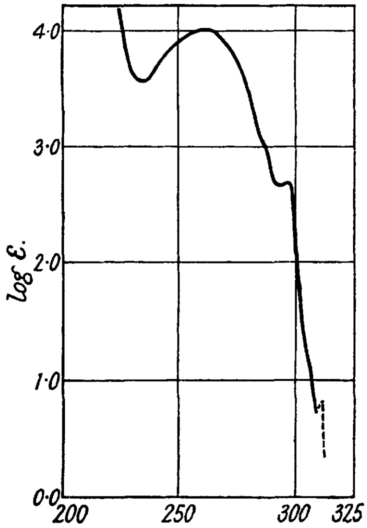


FIG. 2.
Δ^2-*Dihydronaphthalene* (*in hexane*).

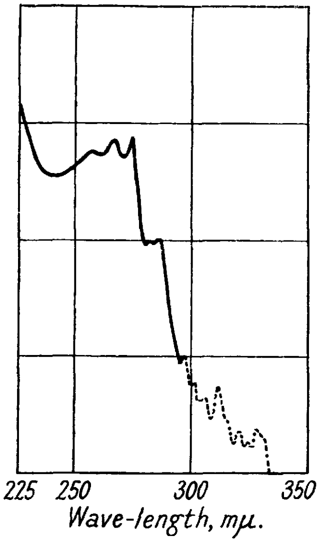
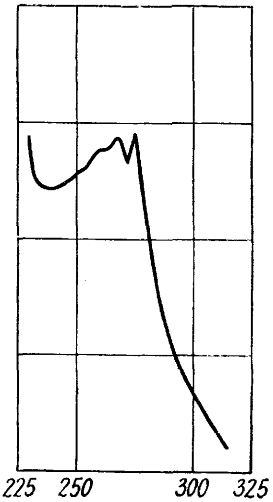
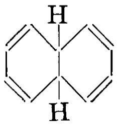


FIG. 3.
Tetralin (*in hexane*).



A sample of Δ^2-dihydronaphthalene containing unchanged naphthalene and of m. p. 40—50° was therefore prepared and examined, and the bands *a*—*d* were found to be entirely lacking. This material, from its absorption spectrum, seems to be a 1 : 1 molecular compound, and there is no trace of the 328 mμ band. It seems therefore that this band must be due to a new substance, probably an isomeric dihydronaphthalene, *e.g.*,



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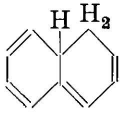

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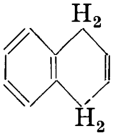
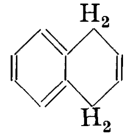


as opposed to

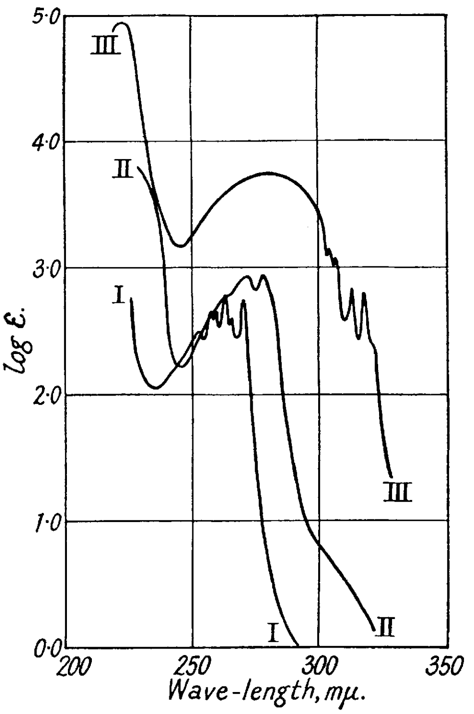


It must, however, be emphasised that the absorption spectrum of our product is entirely consistent with Δ^2-dihydronaphthalene as the principal absorbing constituent.

Tetrahydronaphthalene.—Kimura (*loc. cit.*) purified commercial tetralin by distillation (b. p. 204—206°) over sodium, and obtained an absorption curve very like that of naphthalene. Similar treatment of purchased tetralin gave, in our hands, a product showing almost exactly the same bands as those obtained by Kimura, except that the extinction coefficients were throughout about one-tenth of those recorded by him, but the data agree very well with a product containing 10% of naphthalene. As one of the possible impurities of tetralin is dihydronaphthalene, 50 c.c. of tetralin dissolved in ether were treated with a saturated aqueous solution of mercuric acetate and the mixture shaken during 24 hours. Only a small yellow precipitate was obtained, so the tetralin must have been practically free from dihydronaphthalene. After this treatment the absorption spectrum of the tetralin showed no improvement. Attempts to remove naphthalene as picrate fail when the tetralin contains less than 10% of naphthalene. Accordingly, the barium salt of tetralinsulphonic acid was prepared (Willstätter and Seitz, *Ber.*, 1923, **56**, 1392) and converted into the sodium salt; this was recrystallised, and the tetralin regenerated by adding 66% sulphuric acid and fractionally distilling with steam superheated to 160—180°. In the purest fraction, the most intense bands were at 274 and 267 mμ, log ε 2·91 and 2·87 respectively (see Fig. 3). The material was not, however, pure, for bands in the region 280—320 mμ were present at intensities indicating some 2% of naphthalene. Several hundred grams of barium tetralinsulphonate were then prepared and fractionally crystallised, the progress of the purification being controlled spectrographically. In order to facilitate control, the corresponding barium salts of naphthalene- and benzene-sulphonic acids were prepared and their spectra measured (see Fig. 4) :

Barium naphthalenesulphonate	$\lambda_{max.}$, mμ	317	312·5	306·7	303·2	280	
	$\epsilon_{max.}$	650	820	1,200	1,600	6,000	
Barium benzenesulphonate	$\lambda_{max.}$, mμ	269·3	265·1	262·7	258·4	256·4	252·1
	$\epsilon_{max.}$	565	340	620	430	450	310

FIG. 4.

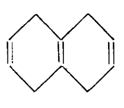


I. *Barium benzenesulphonate (water).*
II. *Barium tetralinsulphonate (water).*
III. *Barium naphthalenesulphonate (water).*

The characteristic bands of the naphthalenesulphonate were observed in the impure tetralinsulphonate, but after many recrystallisations from water, a product entirely free from them was finally obtained: $\lambda_{max.}$ 277·8, 271·1, 265 mμ; $\varepsilon_{max.}$, 840, 840, 700, respectively. This result agrees well with the data of Hantszch on tetralin-2-sulphonic acid in various solvents, bands at 277—278 and 269—271 mμ, log ε *ca.* 3, being recorded (*Ber.*, 1927, **60**, 1933). The purified barium salt was converted into the sodium salt, which was recrystallised and found to be free from selective absorption in the region 290—320 mμ. Tetralin was regenerated as before and redistilled under reduced pressure. The final product exhibited two sharp maxima at 274 and 267 mμ with an inflexion at 261 mμ, ε = *ca.* 760, 740, and 600 respectively.

In the course of the recrystallisation of the barium salt a rather elusive " impurity " was encountered. Three sharp, equally intense bands were repeatedly observed at 321·5, 313·5, and 306·7 mμ and were unmistakably different from those of barium naphthalenesulphonate. Unfortunately, the material could not be isolated, as on recrystallisation of fractions exhibiting the bands, the selective absorption disappeared from both the mother-liquor and the crystals. It is possible that isomeric tetrahydronaphthalene may exist in equilibrium. The proportion of this anomalous material is, however, small, and it is clear that the principal constituent of commercial tetralin is a substance devoid of the 290—320 mμ narrow bands present in naphthalene. Its absorption is, in fact, reasonably close to that of the xylenes.

Baly and Tuck (*loc. cit.*) found only one maximum (*ca.* 256 mμ) in the absorption spectrum of 1 : 2 : 3 : 4-tetrahydronaphthalene, the intensity being apparently just as great as that of naphthalene at 272 mμ, *viz.*, log ε *ca.* 4. It is difficult to understand this observation since the authors examined the so-called α-tetrahydronaphthalene (see inset) made by the action of phosphorus and iodine on naphthalene. Their curve for this material agrees closely with our data on 1 : 2 : 3 : 4-tetrahydronaphthalene, contaminated with a little naphthalene.



Tetrahydronaphthols.—Komatsu, Masumoto, and Kumamoto (*Mem. Coll. Sci. Kyoto*, 1924, **7**, 287) examined *ar*-tetrahydro-α- and -β-naphthols. The former shows two maxima at 281 and 269 mμ, and the latter at 286 and 267 mμ, the extinction coefficients being apparently of the order 1,000—2,000. This may be compared with the more recent data of Conrad-Billroth (*Z. physikal. Chem.*, 1933, **20**, 222) on *o*-3- and *m*-4-xylenol:

o-3-Xylenol:	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$.	*m*-4-Xylenol:	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$.
	279·0	1690		280·9	1850
	273·5	1530		274·0	1670
	270·3	1430		284·5	

We examined *ac*-tetrahydro-β-naphthol, with the following results:

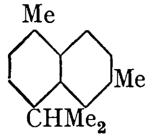
$\lambda_{max.}$, mμ.........	273·0	266·5
log ε	3·15	3·14

The material (b. p. 135°/5 mm.) also showed very feeble inflexions at 296, 315, and 325 mμ, due almost certainly to a trace of impurity (Fig. 7).

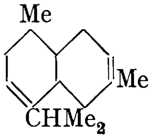
Hexahydronaphthalenes and Related Compounds.—Contrary to expectation, certain polycyclic substances containing only two double bonds within the ring system exhibit marked and characteristic selective absorption. Hence, it becomes specially important to establish the spectra of various isomeric hexahydronaphthalenes or related substances, in order to find the conditions under which two double bonds can constitute a chromophore.

The spectrographic study is difficult because the necessary degree of purity is neither easily achieved nor maintained. Hence the study of the absorption spectra of this group was commenced with two terpenes, cadinene and *iso*cadinene, both being hexahydro-derivatives of cadalene. The presence in the molecules of the methyl and *iso*propyl groups will not appreciably affect the absorption of the hexahydronaphthalene nucleus, as may be concluded from the study of the alkyl derivatives of naphthalene. These groups may in fact to a certain extent protect the hexahydro-derivatives from oxidation.

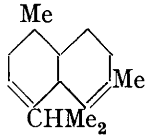
Cadinene.—The dehydrogenation of cadinene to cadalene reveals the carbon skeleton (I), and on the basis of the failure of all attempts to reduce cadinene with sodium and amyl alcohol, the ozonolysis of this compound into an acid with 15 carbon atoms, and other data (Semmler and Stenzel, *Ber.*, 1914, **47**, 2555), Ruzicka considers that cadinene is either (II) or (III) or possibly a mixture of both.



(I.)



(II.)



(III.)

Cadinene was prepared from cubeb oil (see Ruzicka and Meyer, *Helv. Chim. Acta*, 1921, **4**, 505), and also from cade oil. The oils were fractionated under reduced pressure and the fraction of b. p. 125—138°/12 mm. was dissolved in ether and saturated at 0° with dry hydrogen chloride. The cadinene dihydrochloride crystallised in needles and was recrystallised from ethyl acetate (m. p. 117—118°); it was then refluxed with alcoholic sodium hydroxide, the alcohol distilled off, and the regenerated cadinene distilled under reduced pressure (b. p. 138°/12 mm.). This material dissolved in hexane exhibits selective absorption with the following maxima:

$\lambda_{max.}$, mμ.	$\epsilon_{max.}$.	1/λ, cm.$^{-1}$.	Δcm.$^{-1}$.	Mean Δcm.$^{-1}$.
323·5	54	30,910	1610	
307·5	80	32,520	1730	1663
292·0	115	34,250	1650	
278·5	133	35,900		
246	480			

A second preparation from a larger quantity of hydrochloride which was repeatedly recrystallised showed $\lambda_{max.}$, 323·5, 307·5, 246 mμ, with ε 5·5, 8·5, and 480 respectively. The narrow bands shown in the first specimen are thus reduced to one-tenth of their original intensity, although the 246 mμ band persists unchanged. Only the last therefore relates to cadinene itself. The narrow bands must be due to a substance yielding a crystalline hydrochloride and separable only with great difficulty from cadinene dihydrochloride; alternatively, a certain amount of cadinene is oxidised during the regeneration and redistillation. Successive redistillations of cadinene have shown an increase in intensity for the narrow bands over the region 323—308·5 mμ. In order to ascertain whether the narrow bands over the region 323·5—278·5 mμ belong to the absorption spectrum of cadinene or whether they are due to a more highly unsaturated impurity, the alcoholic solution of cadinene was treated with metallic sodium. (No change in the molecule of cadinene is to be expected, for the double bonds are not conjugated.) The hydrocarbon was precipitated by dilution with water and dried in a desiccator over calcium chloride. Its spectrum then showed only a very shallow band over the region 245—250 mμ, the intensity being the same as that shown by the previous samples; all the narrow bands had disappeared and were therefore due to an impurity which probably possessed two or more conjugated double bonds. The definitive extinction curve is given in Fig. 5.

FIG. 5.

Cadinene (*in hexane*).

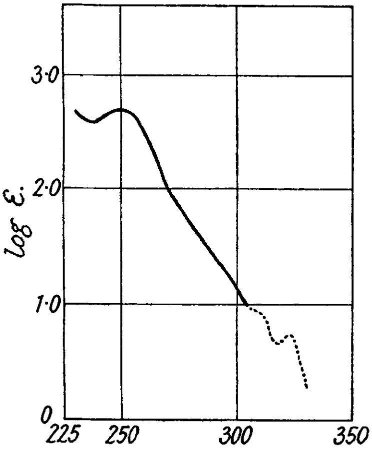


FIG. 6.

iso*Cadinene* (*in alcohol*).

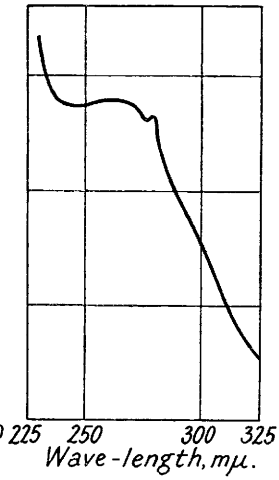
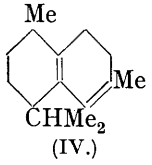


FIG. 7.

ac-*Tetrahydro-β-naphthol* (*in hexane*).

iso*Cadinene*. Cadinene is isomerised when treated with acetic acid at 230—235° under pressure or with formic acid at 100° and transformed into *iso*cadinene (Henderson and Robertson, J., 1924, **125**, 1992; Robertson, Kerr, and Henderson, J., 1925, **127**, 1946). *iso*Cadinene, although a hexahydrocadalene, differs from cadinene in that it does not yield a crystalline hydrochloride; Robertson and Henderson suggest that it is possibly represented by (IV), but no direct proof of this is available. In the present work *iso*cadinene was prepared according to the directions of Henderson and Robertson (*loc. cit.*), and purified by distillation under diminished pressure (b. p. 102—105°/4 mm.); its absorption curve showed the following maxima: $\lambda_{max.}$, 322, 315, 279·5, 262·5 mμ; $\varepsilon_{max.}$, 14, 14, 443, 569, respectively. An alcoholic solution of *iso*cadinene was subjected to mild reduction with metallic sodium, and the absorption of the isolated material exhibited maxima only at 279·5 and 262·5 mμ; $\varepsilon_{max.}$, 440 and 580 (Fig. 6). The intensities of these bands are practically unaltered, showing that only the material (impurity) responsible for the narrow bands λ 322 and 315 mμ had been hydrogenated.



(IV.)

1 : 2 : 3 : 4 : 9 : 10-*Hexahydronaphthalene*.—This was prepared by treating dibromonaphthane, from decahydro-β-naphthol *via* 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydronaphthalene, with quinoline at 200° (Leroux, *Compt. rend.*, 1910, **151**, 384). 50 G. of decahydro-β-naphthol were mixed with 100 g. of recently fused and pulverised potassium hydrogen sulphate in a 250-c.c. Pyrex Claisen flask, and heated in an oil-bath, the temperature being

increased slowly to 200—220°. Octahydronaphthalene distilled with a little water. It was dissolved in ether, shaken with aqueous potash, washed with water, dried (sodium sulphate), redistilled (b. p. 183—184°), and then fractionally redistilled under reduced pressure, the fraction distilling at 71°/7 mm., 43·5°/0·5—1 mm., being collected. A chloroform solution of octahydronaphthalene (23 g. in 150 c.c.) was cooled to − 20° and a 20% solution of bromine in chloroform was added drop by drop in slight excess. The mixture was shaken with a dilute aqueous solution of sulphurous acid, then with water, dried (sodium sulphate), and the chloroform distilled off. After cooling, a crystalline residue was obtained, and dissolved in hot alcohol. Colourless needles and an oily liquid separated. The needles were recrystallised from alcohol (m. p. 83°) and found to correspond with the material described by Leroux (*Ann. Chim. Phys.*, 1910, **21**, 473) as *cis*-2 : 3-dibromonaphthane. The oil was cooled with solid carbon dioxide–ether; colourless crystals separated and were recrystallised from alcohol (m. p. 41°). According to Leroux (*loc. cit.*), this is a mixture of *cis*- and *trans*-2 : 3-dibromonaphthane.

16 G. of the *cis*-isomeride were heated with 25 g. of quinoline in a sealed tube at 200° during 20 hours. The residue was extracted with ether, shaken with diluted sulphuric acid and water, dried (sodium sulphate), the ether removed, and the hydrocarbon redistilled, the fraction boiling at 65°/12 mm. being collected.

This material exhibits the following maxima :

$\lambda_{max.}$, mμ	319·4	314·5	311·5	309·5	305·0	296·5	288·0
log ε	0·53	0·26	0·66	0·71	0·72	1·06	1·91
$\lambda_{max.}$, mμ	284·0	274·0	267·2	261·0			
log ε	2·00	2·38	2·30	2·18			

These are undoubtedly due to naphthalene (*ca.* 1·3%, calculated from the intensity of the 311·5 mμ band) and tetralin (*ca.* 31%, from the 274 mμ band). The hexahydronaphthalene had therefore undergone considerable oxidation–reduction, yielding tetralin, naphthalene, and probably decalin. If we assume that the absorption of the hexahydronaphthalene does not appreciably obscure that of tetralin, the data show that the mixture must contain roughly 1% of naphthalene, 30% of tetralin, and perhaps 20% of decalin. The proportion of hexahydronaphthalene will therefore be unlikely to exceed 50%. By heating the dibromonaphthane at 200° in an atmosphere of nitrogen for 1½ hours with an equivalent of quinoline, a somewhat better product was obtained. This showed

$\lambda_{max.}$, mμ	319·4	311·0	296	274·0	267·0	238·0
log ε	0·30	0·44	0·48	2·69	2·64	3·42

It was by no means free from tetralin and naphthalene, but the percentage of these constituents appeared to be lower than in the first preparation because the 319·4, 311·0, 274·0, and 267·0 mμ bands were less persistent.

No definite conclusions can be drawn concerning the spectrum of the hexahydronaphthalene, but it would appear that its absorption is not selective over the region 290—245 mμ but probably has a broad band at 245—230 mμ (max. 238·0 mμ). This band is not due to tetralin or naphthalene, for the former does not show any maximum over this region and naphthalene exhibits a sharp resolved band with sub-maxima at 221·0 and 217·5 mμ. The high degree of transparency except in the extreme ultra-violet thus inferred for the hexahydronaphthalene is not surprising, for isoprene and dimethylbutadiene show bands at 219·6 mμ (log ε 4·26) and 224 mμ (log ε 4·33) respectively (Scheibe and Pummerer, *Ber.*, 1927, **60**, 2163).

Octahydronaphthalene.—Kimura studied *cis*-octahydronaphthalene, obtained by dehydration of *cis*-decahydro-β-naphthol with sulphuric acid, followed by distillation of the product over sodium. In so far as it is possible to foretell the absorption spectrum of octahydronaphthalene, it may be expected to be very transparent and free from narrow bands. As has been shown (p. 917), Kimura's treatment of the *ac*-tetrahydro-β-naphthol yielded a product containing naphthalene. The octahydronaphthalene seems likewise to have been impure. His data are :

$\lambda_{max.}$, mμ	274·7	267·3	255·0	246·3
log ε	2·6	1·6	1·8	1·9
ε	398	39·8	63·1	79·4

but, reducing his extinction coefficients to one-tenth (see p. 917), we may compare the first two bands with our own data for tetralin :

$\lambda_{\text{max.}}$ 274, 267 mμ; $\epsilon_{\text{max.}}$ 760, 740.

The presence of 5% of tetralin in Kimura's octahydronaphthalene may be inferred. The bands at 255 and 246·3 mμ in Kimura's curve are, however, very well defined and must correspond with a product not so far recognised. It is hoped to study this point further.

We prepared 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydronaphthalene by dehydration of decahydro-β-naphthol with potassium hydrogen sulphate, and fractionated it (b. p. 43·5°/0·5—1 mm.). Although difficult to obtain free from tetralin (274 and 267·3 mμ maxima), it was finally very transparent and free from selective absorption. No evidence was obtained of the 255 and 246·3 mμ maxima recorded by Kimura.

Decahydronaphthalene.—Kimura (*loc. cit.*) examined decalin (b. p. 190—192°) prepared by catalytic reduction of tetralin; it showed a band of very low intensity at $\lambda_{\text{max.}}$ 278 mμ, $\varepsilon_{\text{max.}}$ 0·5. De Laszlo (*Proc. Roy. Soc.*, 1926, **111**, *A*, 355) records that decalin is devoid of selective absorption.

In our experience the *complete* hydrogenation of naphthalene derivatives is very difficult. The purification of commercial decalin was therefore attempted by following the directions of Leroux (*Ann. Chim. Phys.*, 1910, **21**, 468), but the product contained a trace of naphthalene and much more tetralin. Reduction of this material with palladous chloride (Skita, *Ber.*, 1915, **48**, 1486) effected improvement but the product still contained tetralin. Two further reductions with platinum oxide and hydrogen (Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397) finally resulted in a liquid which in 5-mm. layers gave no detectable absorption in the region 210—800 mμ.

It is interesting to note the progress of purification as reflected in the absorption spectra. Naphthalene fairly readily disappeared and tetralin much less readily; at no stage in the purification were any bands other than those of naphthalene and tetralin recorded.

Decahydro-β-naphthol.—The purchased material showed the characteristic bands of tetrahydro-β-naphthol, but after recrystallisation from hexane, it became completely transparent down to 210 mμ.

DISCUSSION.

Substitution of alkyl groups in naphthalene effects only relatively slight changes in the absorption curve. The first band of naphthalene occurs at 320·5 mμ, log ε 1·3, and in the dialkyl products the wave-length displacement to 321·8 ± 1 mμ is slight, but the extinction coefficient increases on the average more than 10 times. In the tri-substituted products the first maximum occurs at 324·6 ± 1·4 mμ and the displacement is still small, but the intensity of absorption continues to increase rapidly. Both in naphthalene and in each of the substitution products there is a striking increase in the intensity of absorption for wave-lengths shorter than about 285—290 mμ, the average value in this second part of the spectrum being log ε 3·5—4. The parent substance and its derivatives do not differ greatly in this portion of the spectrum. The degree of resolution in the middle ultra-violet differs from derivative to derivative but there is no obvious regularity. At the same time the Δcm.$^{-1}$ values do not show a high degree of constancy. In naphthalene, two clear maxima occur at 221 and 217·5 mμ, log ε = 5. This type of selective absorption appears in all the di- and tri-substitution products, the wave-lengths being displaced by not more than some 10 mμ (Figs. 8—14).

From these results it may be concluded that the naphthalene skeleton gives rise to three separate regions of absorption :

a.	*b.*	*c.*
295—325 mμ.	250—290 mμ.	*ca.* 220 mμ.
Low ε values.	Moderately high ε values.	High ε values.
Fine resolution.	Moderate resolution.	Moderate resolution.
Δcm.$^{-1}$ 1000.	Δcm.$^{-1}$ 1000.	Δcm.$^{-1}$ *ca.* 1200.

With substitution, (*c*) persists but the demarcation between (*a*) and (*b*) is less pronounced.

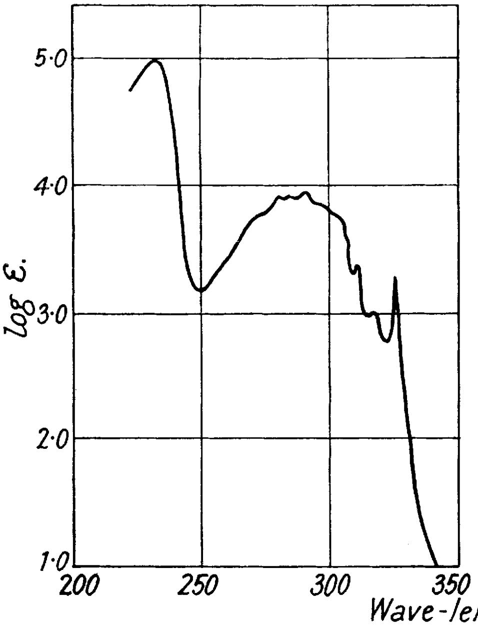


FIG. 8.
Cadalene (1 : 6-*Dimethyl*-4-iso*propylnaphthalene*) (*in hexane*).

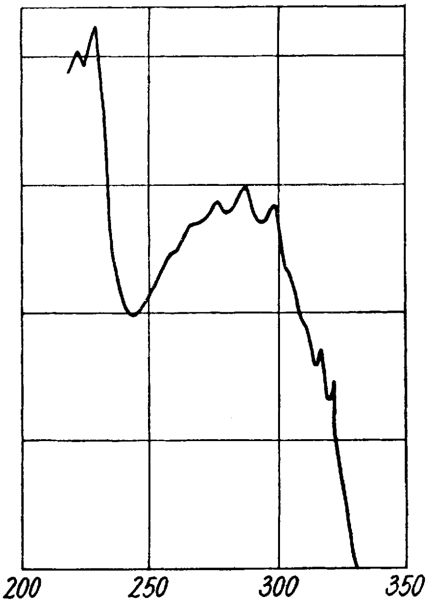


FIG. 9.
1-*Methyl*-5-*ethylnaphthalene* (*in hexane*).

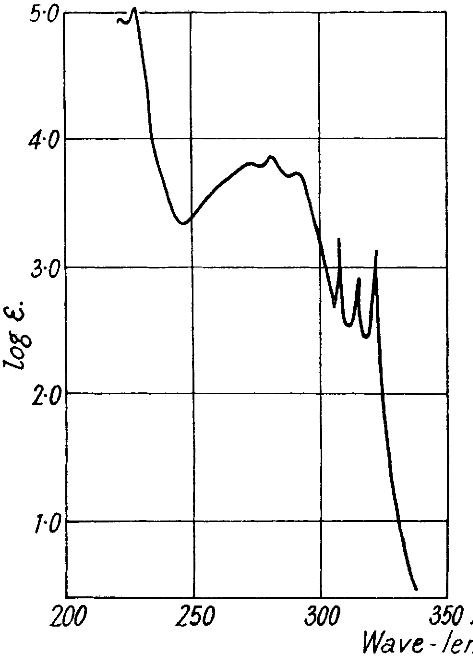


FIG. 10.
1-*Methyl*-6-*ethylnaphthalene* (*in hexane*).

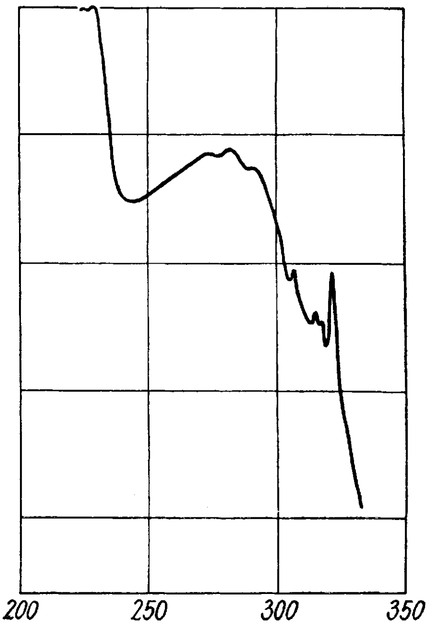


FIG. 11.
1-*Methyl*-7-*ethylnaphthalene* (*in hexane*).

The naphthalene skeleton must therefore be regarded as an absorbing entity quite distinct from benzene, but in view of the three separate regions of absorption which are *capable of some degree of independent variation*, there is no justification for regarding the skeleton as representing one single complex chromophore. Indeed, it is plausible to postulate that the observed curve is a summation of three separate curves each corresponding with a complex chromophore. Thus, the (*c*) region is closely analogous to the bands of ethylene slightly displaced, as in butadiene, and the site of the act of absorption is an electron in the ethylenic linkage, so that the chromophore may be written as $C = C–C \overset{*}{=} C$.

FIG. 12.

1 : 3 : 5-*Trimethylnaphthalene* (*in hexane*).

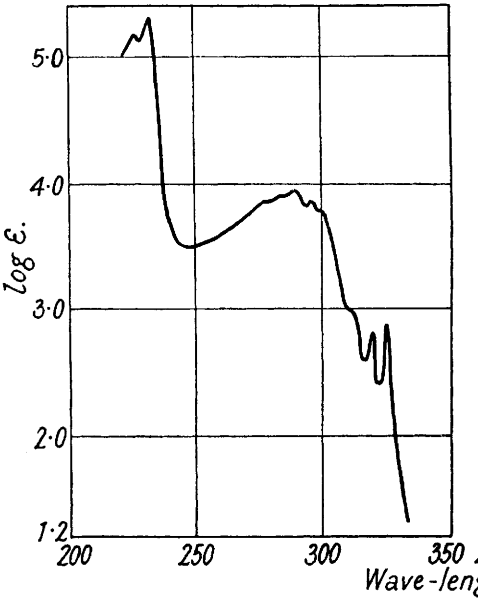


FIG. 13.

1 : 3 : 8-*Trimethylnaphthalene* (*in hexane*).

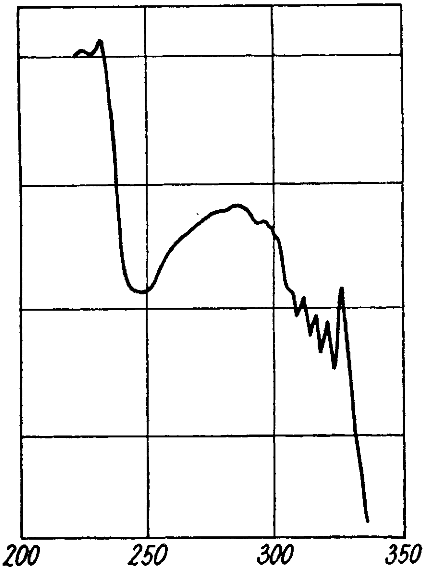
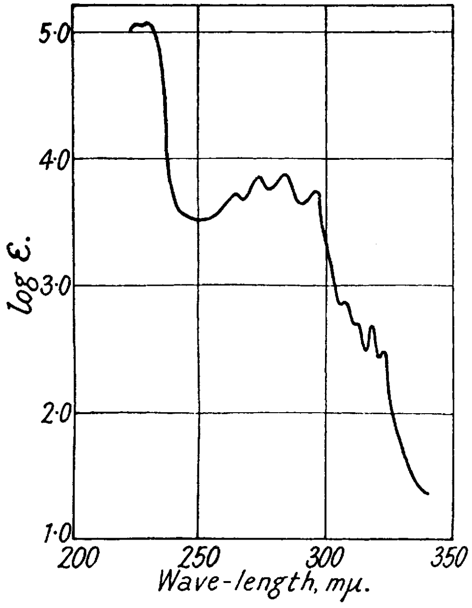


FIG. 14.

2 : 3 : 5-*Trimethylnaphthalene* (*in hexane*).



Region (*b*) is distinctly analogous to the narrow bands at 280—290 mμ, log ε 2·6—2·8, shown in indene and the styrenes, and due probably to the chromophore $C_6\overset{*}{H}_5–C = C$.

The data for quinoline and *iso*quinoline are interesting in this connexion. From Table II it will be seen that absorption begins at 310—320 mμ as in naphthalene, and that the locations of maxima agree strikingly except that the log ε values are 3·5—3·8 for quinoline and *iso*quinoline as against 1·3—3·6 for naphthalene. Regions (*a*), (*b*), and (*c*) are all shown, but the redistribution of relative intensities lends strong support to the idea of three separate mechanisms. In respect of complex chromophores containing conjugated double bonds, the analogy between the quinolines and naphthalene is obvious, and the underlying resemblance in absorption is not surprising.

Δ^1-Dihydronaphthalene may be compared with the styrenes and with indene. It is evident that region (*a*) in the naphthalene spectrum has been eliminated, but that region (*b*) is represented in an incipient form by the bands at 293 and 273 mμ. Apart from the as yet unexplained displacement of the

TABLE II.

Absorption maxima of naphthalene derivatives in hexane solution.

Unsubstituted.		1-Methyl.		2-Methyl.		2 : 6-Dimethyl.		2 : 7-Dimethyl.		1-Methyl-5-ethyl.		1-Methyl-6-ethyl.	
λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.
3205	1·3	3222	1·62	*3258*	1·65	3228	3·16	3215	2·32	3212	2·46	3220	3·15
		3187	2·13	3190	2·54	3162	2·73	3175	2·43	3170	2·70		
3148	1·95	3140	2·39	3140	2·31							3149	2·93
3110	2·54			3108	2·43	3100	2·93	3124	2·41	*3120*	*2·86*		
3068	2·4	3070	2·4					3072	2·63	*3050*	*3·3*	3070	3·24
3045	2·4			3040	2·56	3031	2·64	3031	2·65				
3020	2·54	3028	2·6										
2998		2990	2·7							2988	3·83		
2975	2·6			2978	2·56	2963	2·94						
		2932	3·54	2940	2·68							2910	3·73
2865	3·74	2890	3·56	2870	3·48					2870	3·98		
2835	3·74	2810	3·71					Broad				2808	3·86
2755	3·90			2751	3·73	Broad		2750	3·60	2760	3·86		
2722	3·90					2725	3·68	Un-				2735	3·81
		2705	3·69			Un-		resolved					
2655	3·78			2660	3·68	resolved				*2675*	*3·70*		
2565	3·70									*2585*	*3·47*		
2210	5·18	2205	4·98	2208	4·98					2284	5·25	2280	5·04
2175	5·18									2220	5·04	2230	4·94

1-Methyl-7-ethyl.		1 : 3 : 5-Trimethyl.		1 : 3 : 8-Trimethyl.		2 : 3 : 5-Trimethyl.		1 : 6-Dimethyl-4-*iso*propyl (Cadalene).		Quinoline.		*iso*-Quinoline.	
λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.
3215	2·93	3244	2·88	3258	3·18	3232	2·48	3253	3·3				
3172	2·54	3192	2·83	3201	2·91	3186	2·70	3174	2·99			3175	3·55
3150	2·62			3158	2·96							3125	3·42
		3100	*2·99*	3110	3·10	3130	2·71	3102	3·36	3108	3·8	3092	3·37
3070	2·97			*3060*	*3·15*	3078	2·88	*3060*	*3·55*	3058	3·5		
								3000	*3·75*			3046	3·30
		2992	3·78							2991	3·55	2985	3·50
		2951	3·84	2980	3·65								
2918	3·77	*2905*	*3·90*	2950	3·70	2960	3·76	2954	3·84	2926	3·35	2900	3·38
		2889	3·97							2868	3·35		
2818	3·90	*2870*	*3·90*	2850	3·83	2838	3·89	2840	3·90			2843	3·38
		2772	3·86	2775	3·79			2798	3·90	2753	3·65		
2740	3·86					2736	3·86	*2750*	*3·75*				
						2648	3·73					2620	3·57
2287	5·01	2313	5·30	2315	5·12	2298	5·06	2320	4·96			*2272*	*3·9*
2250	5·00	2261	5·16	2250	5·05	2253	5·06	2280	4·92			2155	4·70

Note. Figures in italics represent inflexions.

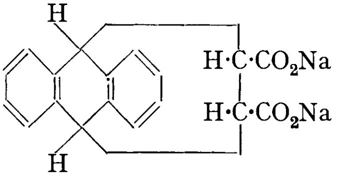
245—250 mμ band of indene and the styrenes to 260 mμ, the selective absorption of Δ^1-dihydronaphthalene is in good agreement with the ·CPh⁚C· group as the chromophore.

Δ^2-Dihydronaphthalene, on the other hand, gives an absorption spectrum almost exactly agreeing with that of 1 : 2 : 3 : 4-tetrahydronaphthalene, and provides confirmation of Ramart-Lucas and Amagat's contention (*Bull. Soc. chim.*, 1932, **51**, 965) that a double bond not conjugated to the benzene ring has no influence whatever on the benzenoid absorption; *e.g.*, Ph·CH$_2$·CH⁚CH$_2$ and Ph·[CH$_2$]$_n$·CH⁚CH$_2$ agree with ethylbenzene. The results for pure tetralin at once fall into line. The type of absorption associated with the benzenoid chromophore is thus very constant, and the statement that three maxima, *ca.* 274, 267, 260 mμ, log ε 2·5—3·2, describe its properties is fully verified.

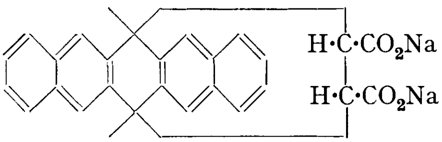
Further confirmation is provided by Clar's data (*Ber.*, 1932, **65**, *B*, 503, etc.) on the compounds formed by the interaction of maleic anhydride and various hydrocarbons. Thus (V) agrees with tetralin and Δ^2-dihydronaphthalene, whilst (VI) agrees fairly well with naphthalene.

It is curious that the group of three conjugated double bonds retains very similar chromophoric properties even if a nitrogen atom is interposed, as in pyridine, the picolines, and lutidines. Pyridine has maxima at 262·8, 256·7, 251 mμ (Δcm.$^{-1}$ = 905); α-picoline, 268·5, 262·0, 256 mμ (Δcm.$^{-1}$ = 910); β-picoline 269, 262, 255·5 mμ (Δcm.$^{-1}$ = 985), and the only lutidine which has been measured shows a maximum at about 267 mμ. These data exhibit a close analogy with benzene, toluene, and the xylenes respectively. This view is supported by the data on cadinene and *iso*cadinene. These compounds only show very ill-defined selective absorption at intensities between those of tetralin and octahydronaphthalene.

(V.)



$\lambda_{max.}$, mμ.	272	266	260
log $\epsilon_{max.}$	3·25	3·05	2·8



(VI.)

$\lambda_{max.}$, mμ	321	307	287·5	280	270	240
log $\epsilon_{max.}$	—	—	3·85	4·2	4·3	5·0

Difficulties arise when polycyclic substances with only two double bonds in the ring system are considered. Well-marked selective absorption is often shown, and a few examples may be considered. Abietic acid (VII) is clearly a derivative of 1 : 2 : 3 : 4 : 5 : 10-hexahydronaphthalene and exhibits intense, well-resolved, selective absorption (Fig. 15) :

FIG. 15.
Abietic acid (in hexane).

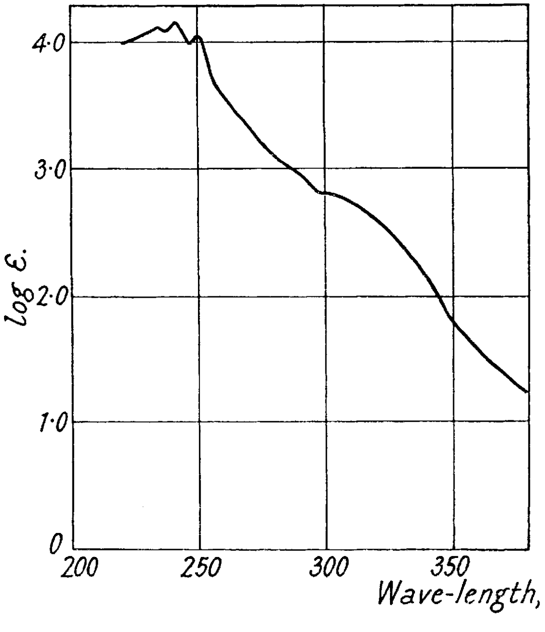
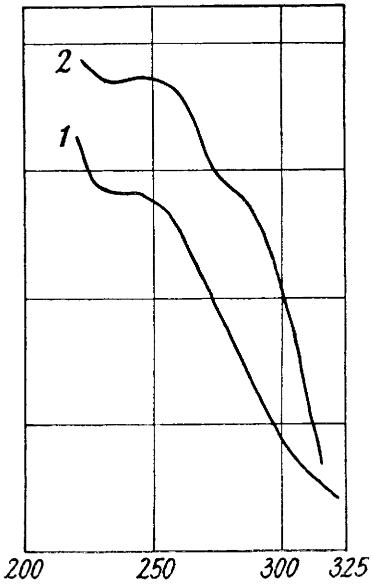


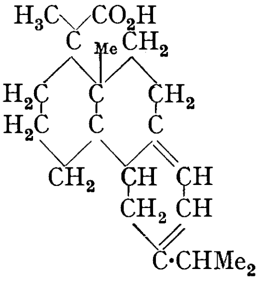
FIG. 16.
1. *α-Camphorene.*
2. iso*Tricyclo-α-camphorene.*



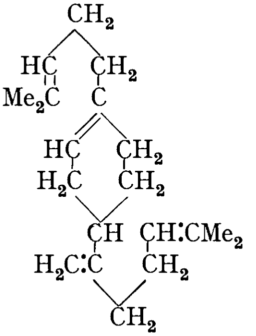
Alcoholic solution.			Hexane solution.		
$\lambda_{max.}$, mμ.	cm.$^{-1}$.	log $\epsilon_{max.}$.	$\lambda_{max.}$, mμ.	cm.$^{-1}$.	log $\epsilon_{max.}$.
250·5	39,920	4·03	249·7	40,040	4·10
241·2	41,460	4·13	242·5	41,240	4·16
234	42,740	4·10	234	42,740	4·16

Δcm.$^{-1}$ = *ca.* 1400.

The obvious suggestion that conjugation is essential for the appearance of intense selective absorption is difficult to reconcile with the data obtained on α-camphorene (VIII) and *iso*tri*cyclo*camphorene (IX) (Fig. 16), kindly furnished by Prof. Ruzicka. The second compound may be compared with 1 : 4 : 7 : 8 : 9 : 10-hexahydronaphthalene, the double bonds being well separated. On the basis of all experience in absorption spectra, such a compound should not absorb selectively. No satisfactory explanation can be offered.

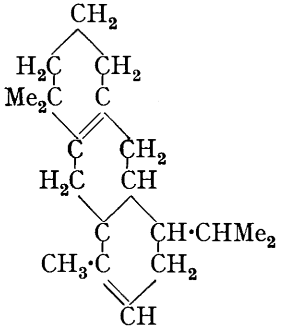


(VII.)



(VIII.)

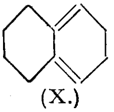
Inflexion 230—250 mμ; log ε 2·82.



(IX.)

Ill-defined band 246·5 mμ, log ε 3·72; inflexion 285 mμ.

Again, cholesterol and the sitosterols (⊨ 1) are extremely transparent and exhibit only very feeble general absorption, but numerous ergosterol derivatives exhibit very well-defined selective absorption with $\varepsilon_{max.}$ of the order 10,000. It is now accepted that in the ring system such as occurs in all the sterols and in ergosterol and its derivatives, one out of three double bonds is in the side chain at a position where its influence on selective absorption is minimal.



(X.)

On the basis of the most recent structure suggested for ergosterol, the parent substance is best considered (from the " chromophore " point of view) as a derivative of 1 : 2 : 3 : 4 : 6 : 7-hexahydronaphthalene (X), the hydroxyl group being in an *ac*-ring. As has been shown, such a position for this group (in *ac*-tetrahydro-β-naphthol) is unimportant in influencing selective absorption. A review of the literature of ergosterol derivatives discloses a considerable variety of absorption curves, mainly of a surprisingly high intensity (ε *ca.* 10,000). Calciferol exhibits no sign of resolution, but the extinction coefficient is nearly 20,000, whilst ergosterol-*D* shows absorption at 230—255 mμ of intensity ε *ca.* 11,000.

Ergosterol.			Ergosterol-*D*.			Dehydroergosterol.		
$\lambda_{max.}$, mμ.	cm.$^{-1}$.	Δcm.$^{-1}$.	$\lambda_{max.}$, mμ.	cm.$^{-1}$.	Δcm.$^{-1}$.	$\lambda_{max.}$, mμ.	cm.$^{-1}$.	Δcm.$^{-1}$.
293·5	34,070	1460	251·7	39,730	1460	342·0	29,240	1480
281·5*	35,530	1430	242·8	41,190	1360	325·5	30,720	1430
270·6	36,960	1500	235·0	42,550		311·0	32,150	1630
260	38,460	1540		Mean	1410	296	33,780	
250	40,000						Mean	1510
	Mean	1470						

* $\epsilon_{max.}$ = 11,700.

The origin of selective absorption in the sterols is too large a question to pursue further now, but the following statement seems justified. Existing data on absorption spectra make it reasonable to expect ergosterol to absorb like phenol ($\varepsilon_{max.}$ of order 2000) or tetralin ($\varepsilon_{max.}$ 800), *only if all three double bonds are in the same ring.* As they are not, and moreover the $\varepsilon_{max.}$ value is 11,700, it is plain that something entirely new in the way of a chromophore must be postulated. Allsopp (*Proc. Roy. Soc.*, 1934, **143**, *A*, 624) has shown that 1 : 3-*cyclo*hexadiene exhibits well-resolved selective absorption, in the same region as benzene but nearly 100 times as intense. This observation has wide implications especially in view of the depressing effect of the third double bond on the extinction coefficient.

There is no escape from the necessity of an explanation involving the mutual influence of two double bonds. Just so long as one benzene ring remains intact, the absorption spectra of the hydronaphthalenes and other hydroaromatic systems are capable of being reduced to order, if not " explained," but with naphthalene derivatives partly saturated in both rings, some novel effect occurs.

Frequency differences (Δcm.$^{-1}$) have been noted where possible in this work, and although the matter is not ripe for detailed discussion, the main Raman frequencies are already available. Bonino and Cella (*Atti R. Accad. Lincei*, 1931, **13**, 784) have studied the Raman spectra of decalin, tetralin, Δ^2-dihydronaphthalene, and naphthalene. The evidence shows that the frequencies 1602, 1573, and 1583 are associated with $C = C$ vibrations and 3041—3049 with $CH_{Arom.}$ in $\geqslant C{-}H$. Associated with $>C<\begin{smallmatrix}H\\H\end{smallmatrix}$ are the frequencies 2930, 2922, 2848, 2856, 2862, whilst the related frequencies 1446, 1448, 1456, 1433, are identified with $C<\begin{smallmatrix}H\uparrow\\H\downarrow\end{smallmatrix}$. The "ethylenic" linkage in the hydrogenated ring of Δ^2-dihydronaphthalene is responsible for a frequency 1663. Naphthalene itself gives rise to a characteristic frequency of 1377. Ziemecki (*Z. Physik*, 1932, **78**, 123) observed the following :

Naphthalene	511, 742, 1377, 1460, 1575, 3058.
α-Methylnaphthalene	700, 1078, 1376, 1434, 1464, 1586, 3059.
β-Methylnaphthalene	779, 1382, 1485, 1589, 3059.

whilst Bourguel (*Compt. rend.*, 1932, **195**, 311) records :

	$C = C$ frequency.		$C = C$ frequency.
1 : 3-Butadiene	1634	Styrene	1601—1636
Isoprene	1640	Phenylpropene	1599—1663
1 : 3-Pentadiene	1597—1646	Cinnamic aldehyde	1600—1629—1676

Dupont, Daure, and Allard (*Bull. Soc. chim.*, 1931, **49**, 1407) find Δcm.$^{-1}$ *ca.* 1600 in all $C_{10}H_{16}$ bicyclic terpenes, and in particular the lines 1641, 1672, 1695 are absent in saturated terpenes. The frequency 1400—1500 is ascribed to $\geqslant C{-}C\leqslant$ and in another memoir all lines below 1000 are said to be combinations of 62, 106, 670, and 953. Our own data on indene (Table I) may be compared with the above.

Two important comments are necessary concerning the correlation of Δcm.$^{-1}$ values in ultra-violet absorption spectra with Raman frequencies : (i) The Δcm.$^{-1}$ value of 1450, which recurs in the separation between sub-maxima in ultra-violet absorption spectra of unsaturated compounds (cf. ergosterol), corresponds in the Raman effect with $C<\begin{smallmatrix}H\uparrow\\H\downarrow\end{smallmatrix}$ vibrations, although the mechanism of the ultra-violet absorption is determined *in the first instance* by the existence of unsaturation. (ii) The $C{=}O$ and the $C{=}C$ vibration at 1700 and 1600 respectively are variable in different compounds, and on account of this fact alone, the application of the Raman effect to the identification of the chromophores in the absorption of unsaturated ketones is not likely to be of great assistance.

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