194. *Chromophoric Groups. Part I. Ultra-violet Absorption Spectra of Indene and Certain of its Derivatives.*

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The theory of band spectra postulates three types of bands correlated severally with (*a*) changes in rotational energy, (*b*) simultaneous changes in rotational and vibrational energy, and (*c*) simultaneous changes in the rotational, vibrational, and electronic energy of the molecule. The selective absorption of polyatomic organic vapours in the visible and the ultra-violet region is of type (*c*), and the number of degrees of freedom is so great as to make a satisfactory analysis very difficult. In solution, the degree of resolution achieved under high dispersion is much inferior to that obtained with vapours, and even with indifferent solvents such as hexane and heptane the effects of quantised rotational changes are no longer recognisable. For a large number of absorbing substances dissolved in alcohol or hexane, broad regions of selective absorption are shown in the visible and ultra-violet, with no indications of resolution into narrower bands, whilst with other substances a number of sub-maxima are shown, the frequency differences between which are approximately constant. These correspond with interatomic vibration frequencies.

Certain groupings, notably C:C, C:O, N:N, are regarded as chromophores in the sense that they give rise to selective absorption in the region 180—800 mμ. There is no difficulty in conceiving a valency electron in such groupings being raised to a higher energy level as a result of the act of absorption; but when the phenyl group or an entity containing several conjugated double bonds gives rise to a special absorption band, difficulties at once arise. It is difficult to localise the act of absorption in a chromophore containing three double bonds, and it is necessary to draw a distinction between simple and complex chromophores. In a *simple chromophore* the electron, which, by the act of absorption, is raised to a higher level, is simultaneously under the control of two atoms, *e.g.*, in the three groups specified above, whereas in a *complex chromophore* such as C_6H_5 and CH:CH·C:O, the groupings responsible for the band may contain more than two atoms, although the act of absorption occurs in a simple chromophore within the complex chromophore, the possible transitions of the electron concerned being determined by the properties of neighbouring atoms or groups. A complex chromophore may thus be a very large unit; it is a chromophore if the existence in a molecule of the definite large grouping is a condition for the appearance of a particular band. Thus a certain minimum of conjugated double bonds is necessary for the appearance of the absorption band associated with the visible colour of, *e.g.*, carotene.

If the absorption spectra of hydrocarbons are considered, the evidence indicates that *all* saturated hydrocarbons, aliphatic or hydroaromatic, are transparent, or practically so, in the region 200—800 mμ. Selective absorption in hydrocarbons is therefore due to unsaturation, but whilst ethylene and the butadienes only exhibit selective absorption beyond 225 mμ in the direction of the Schumann region, yet selective absorption occurs at longer and longer wave-lengths as unsaturation is increased in the order benzene, naphthalene, anthracene, carotene, perylene, for instance. The chromophore, or the group determining the spectral location of absorption, includes what Radulescu (*Ber.*, 1931, **64**, 2223) has termed the "shared resonator" or the entire "electron constellation." This can only mean that the individual electron, which by the act of absorption is raised to a higher energy level, has its energy diagram modified as the result of the presence of other centres of unsaturation. A longer or shorter succession of conjugated double bonds determines the possible transitions of a valency electron in a double bond, and although a very large number of transitions may be theoretically possible, it may plausibly be argued that regularities in the spectra indicate that the important ones may not be too numerous for useful classification.

Let us imagine that a series of absorption bands can be identified with the chromophores CH:CH, CH:CH·CH:CH, . . . $(\mathrm{CH{:}CH})_n$; each band should correspond with a particular energy level to which a valency electron in the C:C group is raised, and the notation $\mathrm{C{:}C}_\alpha$, $\mathrm{C{:}C}_\beta$, $\mathrm{C{:}C}_\gamma$ should facilitate description. In the same way, the statement that a particular absorption band arises only from unsaturation in a molecule containing *n* conjugated double bonds may be expressed by $\mathrm{C{:}C}_{(\mathrm{C{:}C})_n}$ as a description of the chromophore.

Again, acetone has two bands, one at 187 mμ (Ley and Arends, *Z. physikal. Chem.*, 1931, **12**, *B*, 32) and another near 275 mμ. Both are due to the carbonyl group and can be written $\mathrm{C{:}O}_\alpha$ and $\mathrm{C{:}O}_\beta$, respectively. In mesityl oxide, the latter band is displaced and may be described as $\mathrm{C{:}O}_\gamma$ or $\mathrm{C{:}O}_{\mathrm{C{:}C}}$, intimating that the chromophore contains both the carbonyl and the ethenoid group, and that the act of absorption occurs for an electron under the joint control of carbon and oxygen, but that its transition probability is different from that of the corresponding electron in acetone, in virtue of an induced effect from the double bond. Mesityl oxide also shows a band near 234 mμ due to the ethenoid linkage. The chromophore may be written $\mathrm{C{:}C}_{\mathrm{CO}}$, indicating that the act of absorption occurs at the ethenoid linkage, the transition of the electron concerned being different from that of the corresponding electron in ethylene in virtue of an induced effect from the carbonyl group.

On this basis, the absorption bands of organic compounds show in the first instance the occurrence of a finite number of electronic energy levels for a few simple diatomic groupings like C:O, C:C, and N:N, etc. The recognition of these different levels is, however, complicated by the existence of vibrational levels, and there are many instances where the actual wave-length of maximum absorption in a band resolved into sub-groups represents apparently an electronic frequency plus or minus a vibrational frequency or a simple multiple thereof. In order, therefore, to deduce the electronic levels, it is desirable where possible to make allowance for this effect, and in many cases of broad unresolved bands, it is important to realise that the observed frequency of maximum absorption may only be an approximation to the true and theoretically significant electronic frequency, quite apart from the difficulty of accurately determining the maxima by experiment.

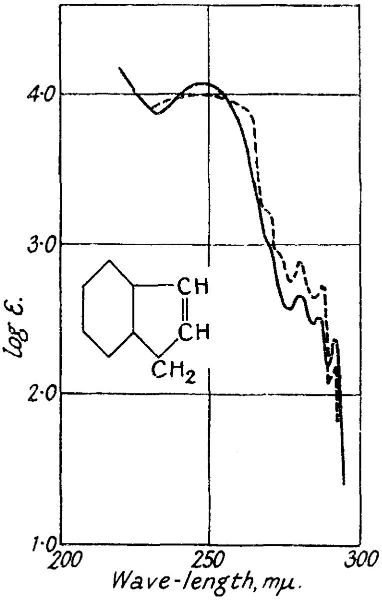
From the chemical point of view, it would be attractive to assume that the molecules of a substance showing two bands due to the same complex chromophore (*e.g.*, mesityl oxide, C:C·C:O) exist as an equilibrium mixture of " isomeric " forms differing only in energy content. Such an idea, however, involves the physically repugnant notion of a plurality of ground states, and all that can safely be said concerning strong and weak bands in the same chromophore is that the extinction coefficients at the maxima represent the probabilities of the occurrence of the transitions concerned, rather than the proportions of these very hypothetical " isomerides."

If the absorbing molecule contains several simple chromophores, together constituting one or more complex chromophores, a whole series of electronic transitions is possible. Thus the chromophore $(\mathrm{C{:}C})_{10}$ may be necessary for one absorption band due to an electronic transition of a valency electron in a C:C group influenced by nine other conjugated double bands, but within that chromophore a second chromophore, say $(\mathrm{C{:}C})_6$, may give rise to another band, and a third, say $(\mathrm{C{:}C})_4$, to yet another. The substance may give rise to several absorption bands each representing the difference between two terms in the C:C spectrum. Carotene, $C_{40}H_{56}$, for instance, with 13 conjugated double bonds, exhibits maxima at 280, 348, and 462 mμ, each of which must be due finally to a valency electron in a double bond. The obvious possibilities of complexity in electronic levels are not necessarily realised in the spectra of such polyatomic molecules, although the selection principles operating are unknown.

In order to examine the above ideas and elucidate the effects of double bonds we have studied a number of hydrocarbons containing conjugated double bonds, *viz.*, indene and its derivatives.

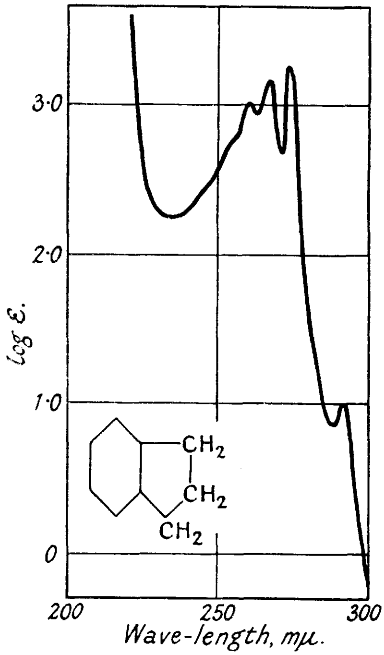
Indene.—The results obtained by different workers on the absorption spectrum of indene are discordant; for instance, Stobbe and Farber (*Ber.*, 1924, **57**, 1838) and Stobbe and Zschoch (*ibid.*, 1927, **60**, 457) record a weak maximum at 281 mμ together with much higher absorption towards shorter wave-lengths, whereas Charlampowiczowna and Marchlewski (*Bull. Acad. Polonaise, A*, 1930, 376) find a broad unresolved band in alcoholic solutions with $\lambda_{max.}$ 249·4 mμ and $\varepsilon_{max.}$ 10,900, but instead of a maximum at 281 mμ their curve merely flattens out in the region 270—280 mμ. On the other hand, Schwartz (*Arch. Phys. biol.*, 1931, **9**, 131; *Centr.*, 1932, i, 643) examined indene in hexane and observed a maximum at 250 mμ with a high extinction coefficient; maxima were also found at 280, 270, 262·5, 256, 250 (intense), 242, 234 (?), and 220 mμ.

FIG. 1.



Indene : ——— *in alcohol.*
- - - - - - *in hexane.*

FIG. 2.



Hydrindene (*in hexane*).

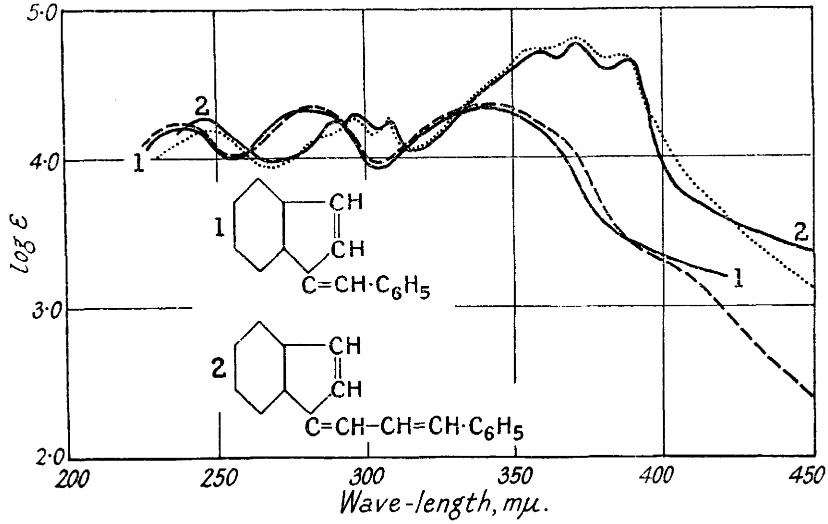
We have studied solutions of indene in alcohol and in hexane; the main absorption is on the short-wave side of 270 mμ, the extinction coefficient reaching a maximum value of about 10,000 near 250 mμ (see Fig. 1). The narrow bands are weak and somewhat ill-defined, but the spacing of the maxima shows that the wave-number separations of *ca.* 460 and 920 cm.$^{-1}$, which represent vibrational frequencies appearing regularly in the spectra of hydrocarbons, are also characteristic of indene (see table, p. 915).

Hydrindene.—Little information concerning the absorption spectrum of hydrindene can be found. The curve for a redistilled (b. p. 64°/7 mm.) Kahlbaum product dissolved in hexane is shown in Fig. 2. The absorption is very similar to that characteristic of a wide range of benzene derivatives, *e.g.*, the xylenes. The mean vibrational frequency is about 940 cm.$^{-1}$. A weak band at 291 mμ, $\varepsilon_{max.}$ 10, appears also, and although it may possibly be due to a small quantity of an impurity, it is very unlikely to be due to indene.

Indene Derivatives.—Benzylidene- and cinnamylidene-indene were prepared according to Thiele's directions (*Ber.*, 1900, **33**, 3398). The former shows three broad unresolved bands of high intensity, spaced some 6000 cm.$^{-1}$ apart (Fig. 3). The product obtained by condensing crotonaldehyde with indene shows a very similar spectrum (maxima at 335, 280, and 252 mμ), so the new absorption owes its origin to the ethenoid linkage rather than the phenyl group. The effect of an additional conjugated double bond, as in cinnamylideneindene, is to displace the 240 and 280 mμ bands of benzylideneindene some 20—30 mμ in the direction of longer wave-lengths, and in addition the bands are partially resolved. The third band, at 245 mμ, is unresolved and is more intense than in indene itself. The three bands are all of high intensity, and the separations of 6720 and 7150 cm.$^{-1}$ are of the same order. The vibrational frequency cannot be specified accurately but it appears to be of the order 1000 cm.$^{-1}$.

Discussion.—It is interesting to compare the absorption spectrum of indene with those of styrene and its derivatives. Ley (*Z. wiss. Phot.*, 1919, **18**, 178; *Ber.*, 1918, **51**, 1810) observed for styrene two weak maxima, 291 and 282 mμ, with an intense maximum at 246 mμ. α-Methylstyrene showed an inflexion at 280—290 mμ, and β-methylstyrene gave a band at 293 mμ, an inflexion near 277 mμ, and a strong maximum at 246 mμ. Using quantitative methods, Ramart-Lucas and Amagat (*Bull. Soc. chim.*, 1932, **51**, 965).

FIG. 3.



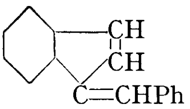
1 *Benzylideneindene:* ——— *in hexane.*
- - - - - - *in alcohol.*
2 *Cinnamylideneindene:* ——— *in hexane.*
. . . . . . *in alcohol.*

Styrene	$\lambda_{max.}$, mμ	291	281·5	243·5
	log $\epsilon_{max.}$	2·55	2·67	4·07
β-Methylstyrene	$\lambda_{max.}$, mμ	288·8	277·7	246
	log $\epsilon_{max.}$	2·6	2·7	4·0

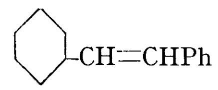
record a practically constant curve for the compounds CHPh:CH·[CH$_2$]$_n$·CH$_3$, where n = 1—7, whereas allylbenzene and compounds Ph·[CH$_2$]$_n$·CH:CH$_2$ are spectroscopically indistinguishable from ethylbenzene and, in fact, resemble hydrindene.

It is thus obvious that the resolved absorption of low intensity in the region 275—295 mμ, together with the intense unresolved band near 240—250 mμ, is common to indene and to the styrenes, so that the group CPh:C· has its own characteristic spectrum quite different from that of the phenyl group. Ring closure exerts but little influence on the absorption beyond perhaps slightly increasing the resolution into component maxima near 280—290 mμ. The double bond in the five-membered ring of indene therefore functions similarly to a true ethenoid linkage.

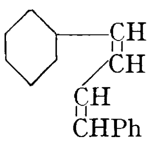
The absorption spectrum of benzylideneindene may be compared with those of stilbene and diphenylbutadiene :



$\lambda_{max.}$: 340, 280, 238 mμ. log ε : 4·3, 4·3, 4·2.



$\lambda_{max.}$: 323, 294 mμ; log ε : 4·45, 4·55 (Castille, *Bull. Acad. roy. Belge*, 1926, **12**, 498). $\lambda_{max.}$: 322, 288, 222 mμ; log ε : 4·1, 4·33, 4·1 (Ramart-Lucas and Amagat, *loc. cit.*).



$\lambda_{max.}$: 320 mμ; log ε : 3·13 Radulescu and Bărbulescu, *Ber.*, 1931, **64**, 2225). $\lambda_{max.}$: 346·5, 328·4, 312·5 mμ; log ε : 4·68, 4·68, 4·6 (Castille, *loc. cit.*).

Both stilbene and diphenylbutadiene show a very broad band of selective absorption extending from 250 to 350 mμ approx. The absence of a well-defined band with a maximum at 280 mμ in diphenylbutadiene is not evidence of the *absence* of the corresponding chromophoric group, because the absorption curve is so unusually broad as to indicate that the observed curve is really a summation curve. In benzylideneindene the separate bands which are fused together in stilbene and diphenylbutadiene are quite well shown.

Confirmation of the 280 mμ band is obtained from the data of Stobbe and Reuss (*Ber.*, 1912, **45**, 3496) on αγ-butadienylbenzene, which shows a single unresolved intense band at 282 mμ. Radulescu (*loc. cit.*) records for diphenylhexatriene high absorption in the near ultra-violet, with sub-maxima at 372, 355, and 335 mμ, whilst the corresponding values for cinnamylideneindene are 388, 371, and 358·5 mμ (see table).

In all these compounds the act of absorption concerns an electron belonging to the C:C group, either in a ring or as a true ethenoid linkage. The absorption curve will naturally be influenced by vibrational frequencies, but the fundamental chromophore is a double bond. This simple chromophore forms a part of complex chromophores in which double bonds are conjugated.

The following chromophores are thus possible : (1) ·C:C· ; (2) ·C:C·C:C· ; (3) C_6H_5 ; (4) ·CPh.C· ; (5) ·CPh:C·C:C· ; (6) Ph·$(C:C)_2$·Ph ; (1) and (2) give rise to absorption on the short-wave side of 230 mμ only ; (3) gives rise to absorption near 260—270 mμ of log ε = 2·6 ; (4) to two types of absorption, one of log ε *ca.* 4 at 250 mμ, and another of log ε *ca.* 2·5 at 270—290 mμ ; (5) to a band of high intensity near 280 mμ, and (6) occasions three bands.

Now this notion of complex chromophores would be much more valuable if it could be stated at which double bond the different acts of absorption occur. A notation to express such localisation may be suggested. In chromophore (4), there are obviously two alternatives at least :

(*a*) Ph·C:$\overset{*}{\mathrm{C}}$·, (*b*) $\overset{*}{\mathrm{Ph}}$·C:C·,

but further consideration of this aspect of the problem must be deferred (see this vol., p. 926) pending the accumulation of further evidence from hydroaromatic hydrocarbons, but it is plausible to suggest that the bands at 270—290 mμ of indene are due to (*b*), since log ε 2·5 (*ca.*) is shown in benzenoid compounds like toluene and tetralin. Chromophore (*a*) would correspond with the 250 mμ band, and the high extinction coefficient is consistent with this view.

		$\lambda_{max.}$, mμ.	log $\epsilon_{max.}$.	1/λ, cm.⁻¹.	Δcm.⁻¹ (vibr.).	Δcm.⁻¹ (broad bands).
Hydrindene		273·6	3·25	36,550		
		267	3·16	37,450	900	
		260	3·00	38,460	1010	
	inflexn.	254	2·75	39,370	910	
		291 ?	1·00	34,360		
Indene (in hexane)		291·5	2·21	34,300 *a*		
		287·8	2·73	34,740	440	
		280·1	2·90	35,700	960	6350 (*b*—*a*)
		273·5	2·94	36,560	860	
		270·0	3·23	37,040	480	
	inflexn.	262	3·85	38,170	1130	
		246	4·00	40,650 *b*	2480	

	$\lambda_{max.}$, mμ.	log $\epsilon_{max.}$.	1/λ, cm.$^{-1}$.	Δcm.$^{-1}$ (vibr.).	Δcm.$^{-1}$ (broad bands).
Indene (in alcohol)	290·8	2·37	34,390 *a*		
	286·5	2·50	34,910	520	5770 (*b*—*a*)
	279·5	2·65	35,770	860	
	249·0	4·06	40,160 *b*	4390	
Benzylideneindene in hexane	340·0	4·34	29,410 *a*		6300 (*b*—*a*)
	280·0	4·33	35,710 *b*		6310 (*c*—*b*)
	238·0	4·22	42,020 *c*		
Cinnamylideneindene	388·0	4·66	25,770		
	371·0	4·77	26,950	1180	
	358·5	4·72	*a* 27,890	940	
	308·5	4·26	32,420		6590 (*b*—*a*)
	297·0	4·30	33,670	1250	
	290·0	4·24	*b* 34,480	810	6340 (*c*—*b*)
	245·0	4·26	*c* 40,820	6340	

SUMMARY.

(1) The absorption spectra in alcohol and hexane of hydrindene, indene, benzylideneindene, and cinnamylideneindene were investigated.

(2) The extinction curve of hydrindene is of benzenoid type [similar to xylenes, allylbenzene and compounds $C_6H_5{\cdot}(CH_2)_n{\cdot}CH{:}CH_2$, etc.]. The chromophore is therefore located in the benzene ring and is only slightly influenced by the five-membered ring.

(3) The absorption spectrum of indene is very similar to that of styrene and alkyl derivatives, $CHPh{:}CH{\cdot}[CH_2]_n{\cdot}CH_3$. The absorption is due to the complex chromophore CPh:C, some evidence being obtained concerning the mechanism of absorption. It is assumed that the band over the region 292—262 mμ is produced by an absorbing electron of the benzene ring under the influence of the conjugated ethylenic linkage; the unresolved, intense 249 mμ band is due to an absorbing electron from the ethylenic linkage influenced by the benzene ring.

(4) The vibrational frequencies 460 cm.$^{-1}$ and 920 cm.$^{-1}$ appear in the spectrum of indene, the 940 cm.$^{-1}$ in hydrindene.

(5) Three regions of absorption are exhibited by benzylideneindene, cinnamylideneindene, and crotonylideneindene, separated by 6000—7000 cm.$^{-1}$. The separations of these regions are of the same order as those of certain highly unsaturated compounds (*e.g.*, carotene, lycopene, etc.).

(6) Correspondence between different regions of absorption and different chromophores is inferred.

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