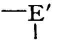
258. *The Light Absorption of Organic Compounds, and the Nature of Unsaturated Linkages.*

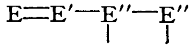
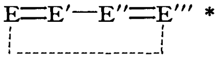
By A. BURAWOY.

The two topics mentioned in the title are related. It will first be shown that two different types of group producing two different types of absorption band are responsible for the light absorption between 2000 and 8000 A. of all organic compounds: (i) "Multiple" linkages in a radical state, indicated in (I), and unsaturated atoms of free (mono)radicals such as triphenylmethyl (*R*-chromophores; *R*-bands); (ii) conjugated systems, *i.e.*, all systems expressed by (II) (*K*-chromophores, *K*-bands). (For the conception of a conjugated system, cf. *J. pr. Chem.*, 1932, **135**, 145.)

(I.)  $\underset{|}{E}-\underset{|}{E'}$ (II). $A\cdot[CH{:}CH]_n\cdot CH{:}B$

($A{=}R, OR, SR, NR_2, O^-, S^-, NR^-$; $B{=}CR_2, NR, O, S, \overset{+}{N}R_2, \overset{+}{O}R, \overset{+}{S}R$.)

From this it will be concluded that organic compounds containing multiple linkages represent equilibria between electron-isomeric molecules, *i.e.*, molecules of the same atomic but different electronic structure. They may appear as (bi)radicals (III), as molecules with "perfected" conjugated systems (IV), and, as can be shown indirectly, as saturated molecules with real double bonds (V).

(III).  $E{=}E'-\underset{|}{E''}-\underset{|}{E'''}$ (IV.)  $E{=}E'-E''{=}E'''$ * (V.) $E{=}E'-E''{=}E'''$

The first two states contain the chromophores responsible for the absorption bands between 2000 and 8000 A., the saturated molecules not absorbing in this spectral region (for the interpretation of the states containing the *R*- or *K*-chromophores, see p. 1187).

It will also be shown that this result agrees with or is supported by the other properties of compounds with unsaturated linkages.

LIGHT absorption in the ultra-violet and in the visible spectral region is due to electrons (the fine structure of these bands due to vibrational and rotational differences of the molecules can be neglected for present purposes). Experience has shown that organic compounds containing only saturated bonds show only absorption bands with a maximum below 2000 A., whereas absorption in the longer ultra-violet and in the visible spectrum is always connected with the presence of so-called multiple linkages or such unsaturated atoms as the methyl carbon atom of the triarylmethyls. The present investigation is concerned with this empirically limited, but clearly defined, spectral region.

According to experience, not more than one electron of every molecule of an organic compound takes part in the absorption between 2000 and 8000 A., and its effect is purely constitutive. The problem is therefore to determine which atomic groups possess the electron or electronic system responsible for the appearance of the absorption bands between 2000 and 8000 A. Such groups are called chromophoric groups.

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* The dots only formally indicate a conjugated system.

With this problem is connected the investigation of the influence of changes in the chromophoric group or its substituents on the absorption bands. The laws governing these changes can only be established empirically owing to the constitutive nature of light absorption, and it is the object of these investigations to classify the absorption bands and to study the laws governing them. Obviously, it is necessary to identify these absorbing groups chemically before their electronic structure can be studied by the methods of theoretical physics.

The two different types of chromophoric groups and absorption bands will now be discussed separately, but it must be remembered that the spectra of most organic compounds show many absorption bands, often of both types. Unless stated to the contrary, the spectra of the substances given as examples are new determinations carried out with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high-tension spark being employed as the source of light. The molecular extinction coefficient ε is defined by $I/I_0 = 10^{-\varepsilon cl}$, and all values of λ are given in Ångström units.

R-*Chromophores* (*Radical Chromophores*).—The spectra of organic compounds containing only single bonds, *e.g.*, hexane and *cyclo*hexane, do not show absorption bands with a maximum between 2000 and 8000 A.; these only appear in compounds like acetone, trimethylethylene, nitromethane, azomethane, keten, tetramethylethylene nitrosochloride, etc. [Table I, (i)—(vi)], and are doubtless due to the double bonds present in these compounds. All these absorption bands (*R*-bands) belong to the same type; for they all obey the same very characteristic optical laws (see also Burawoy, *Ber.*, 1930, **63**, 3155; J., 1937, 1865).

The following statements refer to the *R*-bands.

(1) The *R*-bands have values of ε less than 2000.

(2) The effect of substitution of different hydrocarbon residues is shown in Table II.

TABLE I.

	Compound.	Solvent.	Colour.	$\lambda_{max.}$.	$\varepsilon_{max.}$.
(i)	$CMe_2{=}O$	EtOH	—	2720	15·8
(ii)	$CMe_2{=}CHMe$ *	C_6H_{14}	—	2340	0·06
(iii)	$NMeO{=}O$	EtOH	—	2710	18·6
(iv)	$NMe{=}NMe$ †	,,	—	3470	*ca.* 10·0
(v)	$CH_2{=}C{=}O$ ‡	C_6H_{14}	—	3240	14·6
(vi)	$CMe_2Cl{\cdot}CMe_2{\cdot}N{=}O$ §	C_6H_6	Blue	6900	18·0
(vii)	$SMe{\cdot}N{=}O$	—	Red	—	—
(viii)	$C_5H_{11}{\cdot}O{\cdot}N{=}O$	EtOH	Yellowish	3720 ‖	62·0
				3570	75·0
				3445	71·0
				3330	53·0
				3240	32·0
(ix)	$NMe_2{\cdot}N{=}O$	EtOH	Yellowish	3435	97·0
(x)	$CPh_2{=}S$	Et_2O	—	6050	66·0
(xi)	$C(p\text{-}OEt{\cdot}C_6H_4)_2{=}S$	,,	—	5925	360
(xii)	$C(p\text{-}NMe_2{\cdot}C_6H_4)_2{=}S$	,,	—	5730	850
(xiii)	$NPh{=}NPh$	C_6H_{14}	—	4480	425
(xiv)	$m\text{-}OMe{\cdot}C_6H_4{\cdot}N{=}NPh$	,,	—	4445	560
(xv)	$p\text{-}OMe{\cdot}C_6H_4{\cdot}N{=}NPh$	,,	—	4400	750

* Lüthy, *Z. physikal. Chem.*, 1923, **107**, 285.
† Hantzsch and Lifschitz, *Ber.*, 1912, **45**, 3011.
‡ Lardy, *J. Chim. physique*, 1924, **21**, 281.
§ Hammick and Lister, J., 1937, 491.
‖ Fine structure.

TABLE II.

$CMeR{=}O$. *

R.	$\lambda_{max.}$.	$\varepsilon_{max.}$.
CH_3	2747	17·1
C_2H_5	2770	19·4
C_3H_7	2790	21·2
Bu^{α}	2790	21·2
Bu^{β}	2810	21·2
Bu^{γ}	2850	21·2

NR:NPh in hexane (Fig. 1).

R.	$\lambda_{max.}$.	$\varepsilon_{max.}$.
CH_3	4035	87
C_6H_5	4480	425
$C_6H_4{\cdot}Ph$	4505	900
$\alpha\text{-}C_{10}H_7$	4630	1170

* Rice, *J. Amer. Chem. Soc.*, 1920, **42**, 727.

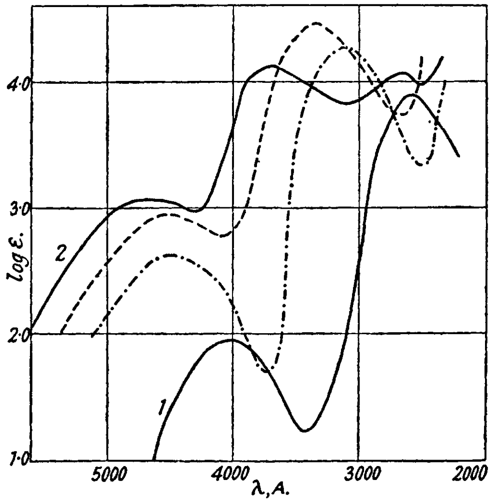
(3) Substitution by NR$_2$, OR, and SR groups displaces the band to *shorter* wave-lengths [compare Table I, (vi)—(ix)], but in aromatic compounds their effect is only slight [Table I, (x)—(xv), and Fig. 2].

(4) *R*-Bands are displaced to *shorter* wave-lengths (with increasing intensity) as the dielectric constant (dipole moment) of the solvent increases (Table VIII).

(5) Addition of an acid molecule, *i.e.*, of a hydrogen nucleus, to the chromophoric " double " bond group destroys these absorption bands in all cases; *e.g.*, the band of the thiocarbonyl group, responsible for a blue colour [see Table I (x)], disappears in the corresponding orange salts, and the band of the carbonyl group in mesityl oxide or of the azo-group in azobenzene disappears in their salts (see Table X). Hence, these low-intensity bands do not appear in the spectra of organic cations.

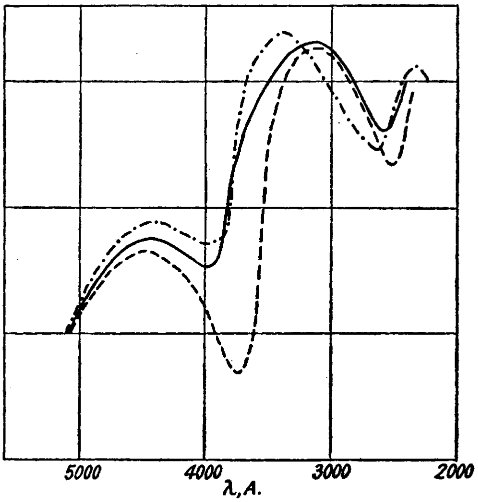
(6) These absorption bands are not due to the saturated double bonds $E{=}E'$, but to a radical state of such groups indicated by $\underset{|}{E}-\underset{|}{E}'$. This follows from the fact that the laws governing the absorption by such bonds are similar to those regulating absorption by free

FIG. 1.



1 ———— *Benzeneazomethane.*
— · — · — · — *Azobenzene.*
- - - - - - - *Benzeneazodiphenyl.*
2 ———— *Benzeneazo-α-naphthalene.*

FIG. 2.



- - - - - - - *Azobenzene.*
———— m-*Methoxyazobenzene.*
— · — · — · — p-*Methoxyazobenzene.*

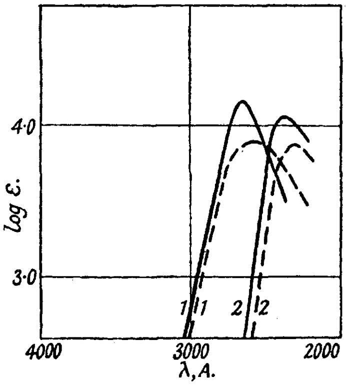
radicals, *e.g.*, the triarylmethyls. Substitution by different hydrocarbon groups and, *e.g.*, the amino- and/or the hydroxyl group has the same characteristic effect in both cases; for instance, triphenylmethyl is yellow, diphenyldiphenylylmethyl is orange, diphenyl-α-naphthylmethyl is red, *pp'p''*-triaminotriphenylmethyl is as yellow as triphenylmethyl (Wieland, Popper, and Seefried, *Ber.*, 1922, **55**, 1816), and *pp'*-dimethoxydiphenylnitrogen oxide, $(C_6H_4{\cdot}OMe)_2NO$, is only yellow, whereas diphenylnitrogen oxide is red (Wieland and Offenbacher, *Ber.*, 1914, **47**, 2111; Meyer and Gottlieb-Billroth, *Ber.*, 1919, **52**, **1476**; 1922, **55**, 823). The absorption band of triphenylmethyl (5160 A.), like all other *R*-bands, disappears in its cation, being replaced by a new band at *shorter* wave-lengths (4250 A.) produced by the conjugated system present in the ion.

Furthermore, both the intensity of the *R*-bands and the dissociation of ethanes into radicals, $CR_3{\cdot}CR_3 \rightleftharpoons 2CR_3{\cdot}$, increase in the same series of substituents, *e.g.*, Me < Et < Pr < Bu; Alk < Ph < $C_6H_4{\cdot}Ph$ < α-$C_{10}H_7$; Ph < *m*-$C_6H_4{\cdot}OMe$ < *p*-$C_6H_4{\cdot}OMe$ < *p*-$C_6H_4{\cdot}NMe_2$ (compare Tables I and II). This is to be expected, since the number of the (bi)radicals, *e.g.*, $R_2C{=}O \rightleftharpoons R_2\underset{|}{C}-\underset{|}{O}$, is then becoming greater. The fact is also explained that single bonds, in contrast to " double " bonds, do not show absorption in the spectral region considered.

K-*Chromophores.*—Compounds such as acetone, ethylene, nitromethane, tetramethylethylene nitrosochloride (examined by us), azomethane, and keten have only low-intensity absorption bands between 2000 and 8000 A. Bands with high values of ε (*ca.* 10^4—10^5) appear only in the spectra of substances containing a " conjugated " system, *i.e.*, at least two adjacent double-bond groups or one double-bond group connected with an amino-, hydroxyl, or thiol group (Table III). In fact, such bands are always due to conjugated systems as indicated by formula (II).

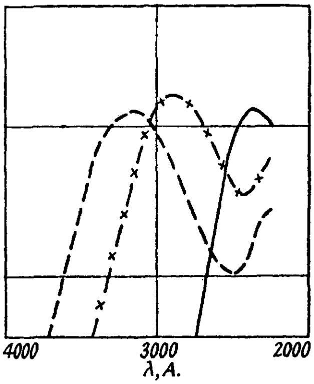
The intensive band of ethylene at 1800 A. appears to be different from the *K*-bands and should be attributed to electrons of the saturated ethenoid linkage. Whereas a *K*-band only changes its position with increasing length of the absorbing conjugated system, the ethylene band does not disappear in the spectrum of a compound with neighbouring double bonds, although a new absorption band (*K*-band) above 2000 A. appears; *e.g.*, both mesityl oxide and *cyclo*hexa-$\Delta^{1:3}$-diene show not only a band above 2000 A., but also the ethylene band below 2000 A. (for diagrams, see Ley and Wingchen, *Ber.*, 1934, **67**, 501; Allsopp, *Proc. Roy. Soc.*, 1934, *A*, **143**, 618).

FIG. 3.



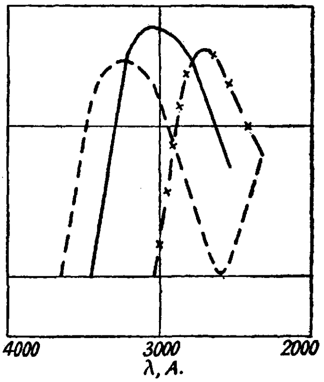
1 ——— *Thioacetamide.*
1 – · – – *Benzeneazomethane.*
2 ——— *Mesityl oxide.*
2 – – – – *Dimethylnitrosoamine.*

FIG. 4.



——— *Citral.*
–x–x– *Citrylideneacetaldehyde.*
– – – – *Citrylidenecrotonaldehyde.*

FIG. 5.



Semicarbazones of
–x–x– *Citral.*
——— *Citrylideneacetaldehyde.*
– – – – *Citrylidenecrotonaldehyde* (*m. p.* 160°).

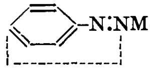
The *K*-bands have the following important features (see also *Ber.*, 1930, **63**, 3155; 1931, **64**, 462; J., 1937, 1865) :

(1) Higher intensities than the *R*-bands.

(2) Displacement towards *longer* wave-lengths with increasing length of the conjugated system (II; $n = 1, 2, 3, \ldots$) (Table IV), and in the series of terminal atoms NH $<$ O $<$ S (II; B = NH, O, S) (Table V).

(3) Displacement towards *longer* wave-lengths by introduction of an amino-, hydroxyl, or thiol group at the other end of the conjugated system, the first group having a much greater effect than the second (II; A = NH_2, OH, SH). Hence, the polarity of the conjugated system is an important factor determining the position of the band (Table VI).

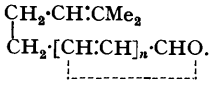
TABLE III (Fig. 3).

Compound.	Solvent.	$\lambda_{max.}$	$\epsilon_{max.}$	Compound.	Solvent.	$\lambda_{max.}$	$\epsilon_{max.}$
$CH_2{:}CMe{\cdot}CMe{:}CH_2$ *	C_6H_{14}	2260	20,000	$NMe_2{\cdot}N{:}O$	EtOH	2305	7,000
$CMe_2{:}CH{\cdot}CMe{:}O$	EtOH	2370	11,500	$NH_2{\cdot}CMe{:}S$	,,	2650	12,900
 –N:NMe	,,	2605	7,800				

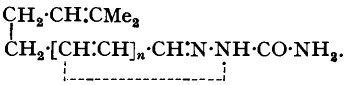
* Scheibe, *Ber.*, 1926, **59**, 1333.

(4) On the other hand, when the amino-, hydroxyl, or thiol group is in a side chain (substituent) of the absorbing conjugated system, the absorption band moves to *shorter* wave-lengths or is almost unaffected. Table VII shows these different effects for the case of benzophenone and some of its derivatives (cf. also Table IX).

TABLE IV (Figs. 4 and 5).



$$\begin{array}{l}CH_2{\cdot}CH{:}CMe_2\\ \vert\\ CH_2{\cdot}[CH{:}CH]_n{\cdot}CHO.\end{array}$$



$$\begin{array}{l}CH_2{\cdot}CH{:}CMe_2\\ \vert\\ CH_2{\cdot}[CH{:}CH]_n{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2.\end{array}$$

n.	$\lambda_{max.}$.	$\epsilon_{max.}$.	$\lambda_{max.}$.	$\epsilon_{max.}$.
1	2380	13,500	2720	31,400
2	2900	16,500	3050	47,200
3	3145	12,500	3260	27,100
		(in EtOH)		

TABLE V (Figs. 6 and 7).

Substance $NMe_2{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}NMe_2){:}X$ (in EtOH).	$\lambda_{max.}$.	$\epsilon_{max.}$.
X = NH	3210	48,000
X = O	3595	33,500
X = S	4335	43,800

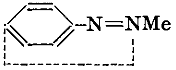
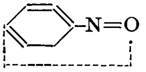
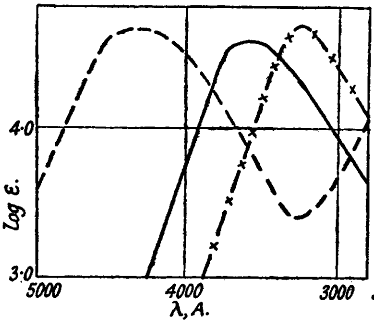
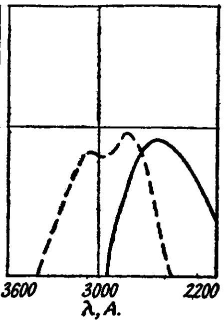
Substance. (in EtOH).	$\lambda_{max.}$.	$\epsilon_{max.}$.
	2605	7800
	2800	9000

FIG. 6.



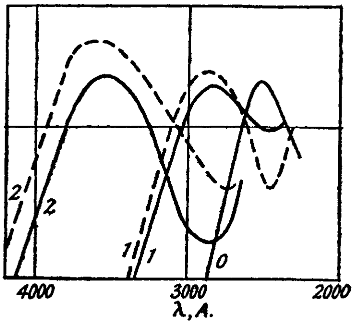
–×–×– pp′-*Tetramethyldiaminobenzophenoneimide.*
——— pp′-*Tetramethyldiaminobenzophenone.*
– – – – pp′-*Tetramethyldiaminothiobenzophenone.*

FIG. 7.



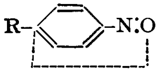
——— *Benzeneazomethane.*
– – – – *Nitrosobenzene.*

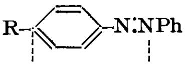
FIG. 8.



0 ——— *Benzophenone.*
1 ——— p-*Methoxybenzophenone.*
1 – – – – pp′-*Dimethoxybenzophenone.*
2 ——— p-*Dimethylaminobenzophenone.*
2 – – – – pp′-*Tetramethyldiaminobenzophenone.*

TABLE VI.

Substance  (in EtOH) (Fig. 9).	$\lambda_{max.}$.	$\epsilon_{max.}$.
R = H	2800	9,000
R = OMe	3200	20,000
R = NMe_2	4205	23,800

Substance  in C_6H_{14}.*	$\lambda_{max.}$.	$\epsilon_{max.}$.
R = H	3130	20,000
R = OMe	3385	24,800
R = NH_2	3620	27,000

* Compare J., 1937, 1865, Fig. 2.

(5) *K*-Bands, in contrast to *R*-bands, are displaced towards *longer* wave-lengths with increasing dielectric constant of the solvent (Table VIII). The contradictory behaviour of the carboxylic acids (Ley and Wingchen, *loc. cit.*) can be attributed to a superposition

on the normal solvent effect of the effect of a different degree of association or hydroxonium salt formation, the corresponding ethers showing a normal behaviour (Ley and Hünecke, *Ber.*, 1926, **59**, 510).

TABLE VII (Fig. 8).

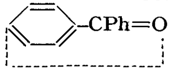
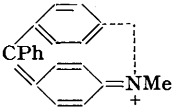
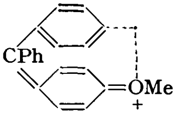
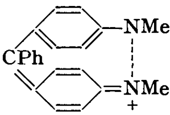
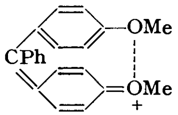
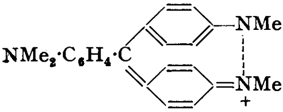
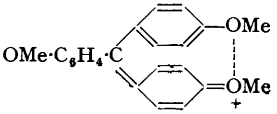
Compound (in EtOH).	$\lambda_{max.}$.	$\epsilon_{max.}$.
	2520	20,000
(*p*)-OMe·C_6H_4·CPh:O	2830	17,200
(*p*)-OMe·C_6H_4·C(C_6H_4·OMe):O	2890	23,300
(*p*)-NMe_2·C_6H_4·CPh:O	3530	24,000
(*p*)-NMe_2·C_6H_4·C(C_6H_4·NMe_2):O	3590	33,500

TABLE VIII.

	R-Band.		*K*-Band.	
	$\lambda_{max.}$.	$\epsilon_{max.}$.	$\lambda_{max.}$.	$\epsilon_{max.}$.
CMe_2:CH·CH_2·CH_2·CMe:CH·CHO (Fig. 11).				
In hexane	3365	47·5	2325	14,700
,, alcohol	3240	65·0	2380	13,500
p-OEt·C_6H_4·C(C_6H_4·OEt):S (Fig. 12).				
In hexane	5960	366	3440	34,300
,, alcohol	5790	382	3535	30,900
p-OMe·C_6H_4·N:NPh (J., 1937, 1865, Fig. 7).				
In hexane	4400	750	3385	24,750
,, alcohol	4305	1050	3420	24,000

(6) In principle the origin and the laws of absorption of organic homopolar compounds and organic ions are similar. In the conjugated systems of cations there are only the terminal positively charged atoms $\overset{+}{N}H_2$, $\overset{+}{O}H$, $\overset{+}{S}H$ instead of N, O, S (II, B). The C=$\overset{+}{N}H_2$ group has a smaller effect than the C=$\overset{+}{O}H$ group in displacing the absorption band to longer wave-lengths, which may be compared with the smaller effect of the C=NH group than of the C=O group in homopolar compounds. For instance, the *p*-dimethylaminotriphenylmethyl ion absorbs at shorter wave-lengths than the *p*-methoxy-analogue (Table IX). On the other hand, as in homopolar compounds, a further (uncharged) dimethylamino-

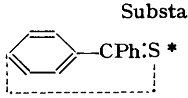
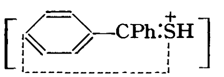
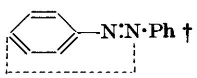
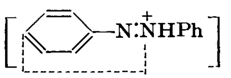
TABLE IX (cf. Brand *et al.*, *J. pr. Chem.*, 1925, **109**, 1, and Burawoy, *Ber.*, 1933, **66**, 228).

	λ.		λ.
	4580		4730
	6200		5000
	5870		4800

group, in the second benzene ring, *i.e.*, at the other end of the absorbing conjugated system, displaces the absorption band more to longer wave-lengths than a hydroxyl group, and yet a further group, in the third benzene ring, being in a branch, moves the absorption band to *shorter* wave-lengths (Table IX) (for further details, see Burawoy, *Ber.*, 1931, **64**, 1636). Incidentally, these facts prove the asymmetric structure of the absorbing ions.

(7) Unlike the *R*-bands, the *K*-bands do not disappear in the spectra of organic cations (by addition of an acid molecule to a homopolar compound). A replacement of the terminal atoms N, O, S (II, B=NH, O, S) by the same, but positively charged atom (B=$\overset{+}{N}H_2$, $\overset{+}{O}H$, $\overset{+}{S}H$) always displaces the absorption band to *longer* wave-lengths (Table X).

TABLE X.

Substance.	Solvent.	*R*-Band.		*K*-Band.	
		$\lambda_{max.}$.	$\epsilon_{max.}$.	$\lambda_{max.}$.	$\epsilon_{max.}$.
 —CPh:S *	Et_2O	6200	70	3150	17,000
 [—CPh:$\overset{+}{S}$H]	Conc. H_2SO_4	—	—	3840	25,000
 —N:N·Ph †	C_6H_4	4485	425	3130	20,000
 [—N:$\overset{+}{N}$HPh]	Conc. H_2SO_4	—	—	4225	28,800
CMe_2:CH·CMe:O ‡	EtOH	3130	57	2370	11,500
[CMe_2:CH·CMe:$\overset{+}{O}$H]	Conc. H_2SO_4	—	—	2815	17,300

* *Ber.*, 1931, **64**, 462, Fig. 9. † J., 1937, 1865, Fig. 8. ‡ This paper, Fig. 13.

(8) It is remarkable, however, that, if on the " positive " end of the conjugated system a group is present which has a greater tendency to lose an electron than the group formed by addition of the hydrogen nucleus, an interchange of the " negative " and " positive " end of the conjugated system takes place, and the *K*-band is displaced to *shorter* wave-lengths. For instance, the *K*-band of *p*-nitrosodimethylaniline (VI) is displaced to shorter wave-lengths by addition of acid, since the absorbing ion has the structure (VII) and not (VIII), which certainly would absorb at longer wave-lengths (Table XI) (see also *Ber.*, 1931, **64**, 477).

TABLE XI (Fig. 10).

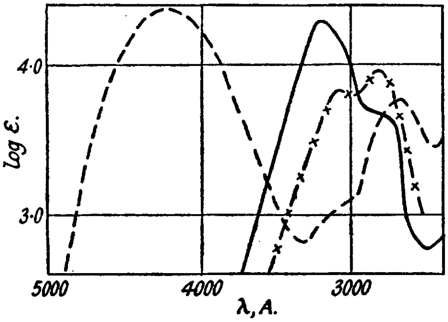
	Substance (in EtOH).	$\lambda_{max.}$.	$\epsilon_{max.}$.
(VI.)	$NMe_2 \cdot C_6H_4 \cdot N$:O	4205	23,800
(VII.)	($\overset{+}{N}Me_2$:C_6H_4:N·OH) Cl^- + HCl	3570	19,600
(VIII.)	($NMe_2 \cdot C_6H_4 \cdot N$:$\overset{+}{O}$H) Cl^-	—	—

(9) In conjugated systems of anions, instead of the amino-, hydroxyl, and thiol groups (II; A=NH_2, OH, SH) there are the negatively charged atoms (II; A = N , O^-, S^-), which have the same functions and have a stronger effect than the uncharged atoms (see, further, *Ber.*, 1931, **64**, 479).

Theory of Chromophores and Auxochromes.—The foregoing results lead to the following theory. (i) A chromophore is an atom or group which is responsible for the *appearance* of a certain absorption band, in contrast to the various substituents, which only produce a *displacement* of the band. The light absorption of homopolar organic compounds and of organic cations and anions is due either to unsaturated atoms of free radicals and multiple linkages in a radical state (*R*-chromophores) or to conjugated systems (*K*-chromophores). (ii) The so-called auxochromic groups (NR_2, OR, SR) in both homopolar compounds and ions displace the absorption band to considerably longer wave-lengths if they are on the end of the conjugated system producing the *K*-band. On the other hand, in a branch of the chromophoric groups (as substituents of both the *R*- and also the *K*-chromophores) they either displace the absorption band to shorter wave-lengths or have no appreciable effect. When they are *positively* charged, they again behave differently, having the same functions as the atoms N, O, S of the groups $C{=}NH$, $C{=}O$, $C{=}S$, etc. (II, B). Furthermore, the latter atoms, when *negatively* charged, again behave like the uncharged groups NR_2, OR, SR (II, A). Thus the conception of " auxochromic " groups is meaningless if applied to the light-absorbing properties of a substance, which have no relation to the dyeing properties.

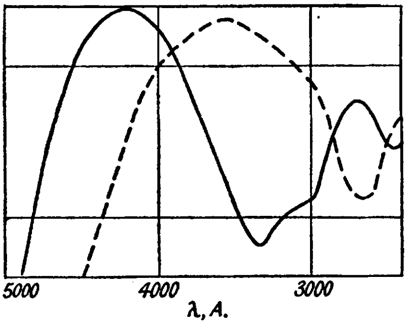
Actually, the bathochromic effect of all the groups (atoms) NR_2, OR, SR, NR^-, O^-, S^- and of the groups $C{=}CR_2$, $C{=}NR$, $C{=}O$, $C{=}S$, $C{=}\overset{+}{N}R_2$, $C{=}\overset{+}{O}R$, $C{=}\overset{+}{S}R$ is in the first case due to the increase of the length of the absorbing conjugated system. In addition, the neutral and charged atoms C, N, O, S of all these groups determine the position of the absorption band, obviously by varying the polarity of the chromophoric system (probably the electron displacement within these systems). In view of this, the author has introduced the conception of the " auxochromic " atom, defined as follows : *Auxochromic atoms are the terminal atoms of chromophoric groups (conjugated systems).* This definition also implies that their effect is not a specific property of certain atoms or groups, but is dependent on their position. A distinction may be made between " positive " and " negative " auxochromic atoms : the atoms N, O, S of the groups NR_2, OR, SR, and all negatively charged atoms in anions (II, A), are in the former category, whereas the atoms N, O, S of the groups $C{=}NR$, $C{=}O$, $C{=}S$, $N{=}NR$, $N{=}O$ and the positively charged atoms in cations (II, B) are in the latter. The uncharged carbon atom (of a $C{=}C$ group) may have both functions (for the charged carbon atom, see *J. pr. Chem.*, 1932, **135**, 145).

FIG. 9.



– x – x – *Nitrosobenzene.*
———— p-*Nitrosoanisole.*
– – – – – – p-*Nitrosodimethylaniline.*

FIG. 10.



Nitrosodimethylaniline in alcohol ————.
,, ,, *alcoholic* HCl – – – – –.

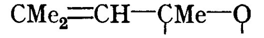
The benzene absorption band of low intensity, appearing also in its simple derivatives and complicated condensed aromatic hydrocarbons, is probably also an *R*-band, although subject to different laws (cf. Burawoy, *Ber.*, 1930, **63**, 3157; *Annalen*, 1933, **503**, 194; Pestemer *et al.*, *Monatsh.*, 1932, **59**, 113 and later; Clar *et al.*, *Ber.*, 1932, **65**, 503, 846, 1411, 1521 and later).

Nature of the So-called Multiple or Unsaturated Linkages.—Evidence for the existence of multiple linkages may be forthcoming from the stability of stereoisomers due to such bonds and, especially, from the fact that, according to the heats of combustion, the formation energy of the first bond is of the same order as that of the supposed second and third bond of multiple linkages (50—100 kg.-cals.) (see Sidgwick, Sutton, and Thomas, J., 1933, 406, and Burawoy, *Z. physikal. Chem.*, 1933, **166**, 393, for table of heats of formation).

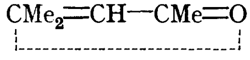
On the other hand, the classical theory of multiple linkages does not explain : (i) the greater reactivity of the second and third link than of the first; (ii) the ability of organic compounds with several neighbouring groups of unsaturated bonds to add reagents both at the atoms of a single group and at the ends of such a system; (iii) the appearance and constitutive nature of the light absorption between 2000 and 8000 A., in contrast to the behaviour of single linkages. Whereas previous attempts to modify this theory have only considered the *chemical reactivity*, the following discussion and conclusions are mainly based on the *optical properties*.

In the spectra of most organic compounds several absorption bands are present, often both *R*- and *K*-bands (compare *Ber.*, 1931, **64**, 473). In addition, some bands may be obscured owing to superposition by others. There is no possibility for different chromophoric groups, particularly of both types, to be present in the same molecule; *e.g.*, in mesityl oxide there can be present either the carbonyl group in a radical state (IX) or a "perfected" conjugated system (X),* but not both together.

(IX.)



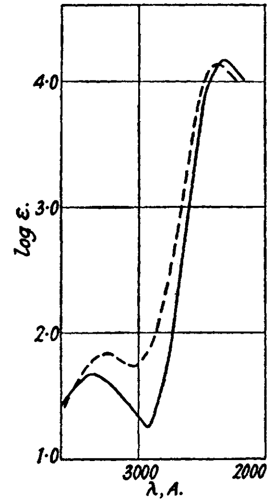
$CMe_2{=}CH{-}\underset{|}{C}Me{-}\underset{|}{O}$



$\underbrace{CMe_2{=}CH{-}CMe{=}O}$

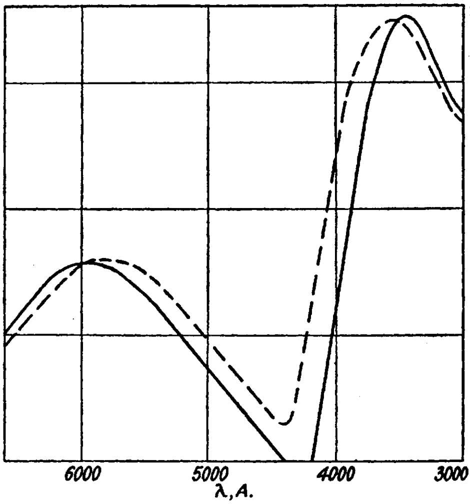
(X.)

FIG. 11.



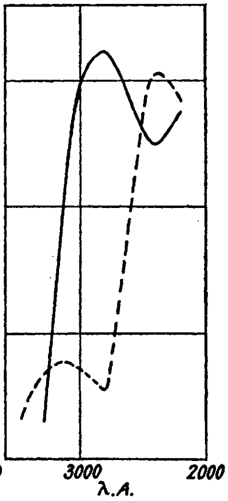
Citral in hexane ———. ,, *alcohol* – – – – –.

FIG. 12.



pp′-*Diethoxythiobenzophenone in hexane* ———. ,, ,, ,, *alcohol* – – – –.

FIG. 13.



Mesityl oxide in alcohol – – – – –. *Mesityl oxide in conc.* H_2SO_4 ———.

For this reason the chromophoric groups responsible for the different absorption bands of a compound must be present in different electron-isomeric molecules. (There is no connection between such molecules and the so-called resonance states : the former are existing states, being distinguished by different chemical and physical properties such as the light absorption, whereas the latter are non-existent, fictitious states.) This view is strongly supported by the fact that for a given series of substituents both the dissociation of the ethanes and hydrazines and the intensity of the *R*-bands increase in the same order, the latter thus showing an increase of the number of (bi)radical molecules.

Calculations based on the dispersion theory show that in all organic compounds less than one electron per molecule takes part in the total absorption between 2000 and 8000 A., and, of course, also in the absorption of every single absorption band. This is further

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* A distinction may be made between a system of neighbouring double-bond groups with alternating real single and double bonds and the same system in a different state, where no real single and double bonds are present, a " perfected " conjugated system.

independent evidence that one molecule never possesses more than *one* chromophoric group,* and that all the molecules of a compound are not identical.

It is, undoubtedly, very important that the excited states producing the *R*- and *K*-bands represent molecules in which a bond of a multiple linkage is split up (*R*-molecules) or a conjugated system is formed (*K*-molecules) (for the numbers of these molecules, see *Z. wiss. Phot.*, 1934, **32**, 289). Although the valency state of these systems is not yet clearly understood, it is certainly different from the state expressed by real single and double bonds (cf. p. 1187).

In the study of the constitution of organic compounds, the further problem arises that, in addition to the above states, an equilibrium exists with others, which do not absorb between 2000 and 8000 A. and probably correspond to the states expressed by the usual structural formulæ with real double bonds. The heats of formation derived from the heats of combustion already discussed, and possibly the comparatively great stability of geometrically stereoisomeric compounds, afford evidence for the existence of such isomers, as also does the fact that only a fraction of all the molecules takes part in the light absorption between 2000 and 8000 A.

The results obtained from absorption investigations cannot be explained by the assumption that all molecules of a compound are in the same state corresponding to the usual structural formulæ, and that the *R*- and *K*-states are only the *end* (*excited*) *states* of the electron transition connected with the light absorption.

(i) The absorption bands of the multiple linkages and of radicals such as the triarylmethyls not only appear in the same spectral region, but also follow the same optical laws. This fact represents the main evidence for the radical character of the chromophoric multiple linkages and excludes the possibility that the multiple linkages are transformed into a radical state by light absorption, since the characteristic absorption of such radicals as the triarylmethyls is certainly due to a radical-like *ground state* of the absorption.

(ii) Absorption between 2000 and 8000 A. corresponds to an energy increase of about 142—35 kg.-cals. If this corresponded to the dissociation energy of multiple linkages passing into a radical state, it could not be understood why single linkages showing similar dissociation energies (50—100 kg.-cals.) also do not absorb in this spectral region and why multiple linkages react much more easily than single linkages. Furthermore, the great chemical reactivity of multiple linkages in itself could scarcely be explained by assuming such high dissociation energies.

(iii) Conjugated systems as indicated in formula (II) are responsible, not only for the *K*-bands, but also for certain anomalies of the dipole moment, which are due to a permanent *polarisation* and not to the *polarisibility* of the molecule. For instance, the dipole moments of *p*-nitroaniline (6·4), *p*-nitrodimethylaniline (6·15), *p*-nitrosodimethylaniline (6·75), *p*-aminoacetophenone (4·29), *p*-aminoazobenzene (2·71), and *p*-dimethylaminoazobenzene (3·68) are about 1 unit higher than those calculated from the moments of the corresponding aromatic parent substances nitrobenzene (3·9), acetophenone (2·97), azobenzene (0·0), aniline (1·5), and dimethylaniline (1·58) respectively (cf. *Trans. Faraday Soc.*, 1934, Appendix; Bergmann and Weizmann, *ibid.*, 1936, **32**, 1318). In this connection it is noteworthy that the absorption bands of numerous substances, *e.g.*, nitrobenzene and dimethylaniline, are strongly displaced to shorter wave-lengths by the introduction methyl groups in the *o*-position, clearly indicating a decrease of the " conjugation " c to steric effects (unpublished work ; compare also, for spectra, Baly, Tuck, and Marsden, J., 1910, **97**, 572 ; Ley and Pfeiffer, *Ber.*, 1921, **54**, 363). Similarly, a decrease of the dipole moment anomalies was expected, and, in the meantime, has been fully confirmed by Hampson (J., 1937, 10 ; this vol., p. 981).

The theory of electron-isomeric molecules alone is able to explain such properties as light absorption and chemical reactivity. It is also the most probable theory, showing that there is no essential difference in the properties of the bonds of single and multiple linkages : (i) their heats of formation, derived from the heats of combustion, are of the same order ; (ii) when single bonds appear to absorb light between 2000 and 8000 A. and to show great reactivity, as in the case of hexa-arylethanes, it is recognised that the light absorption

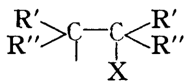
* Chromophoric groups separated by saturated groups behave, of course, independently.

is due to the free radicals present, and the great reactivity to the smallness of the dissociation energies (*e.g.*, 11·5 kg.-cals. for hexaphenylethane); (iii) in complete analogy, multiple linkages also absorb light between 2000 and 8000 A. only when opened with formation of radicals or unsaturated conjugated systems, and the chemical reactivity is also due to the small dissociation (transition) energies, which have to be concluded from the existence of electron-isomeric molecules. Small dissociation energies of single and multiple linkages are not inconsistent with the much higher bond energies as derived from the heats of combustion (50—100 kg.-cals.), since the actual dissociation energies are composed of the bond energies within the *undissociated* molecules and all other energy changes within the *dissociated* molecules (cf. Burawoy, *Z. physikal. Chem.*, 1933, **166**, 393; for attempted theoretical interpretation, see Hückel, *Z. Physik*, 1933, **83**, 632; Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362).

The possibility of addition both at the ends of a "conjugated" system and in the 1 : 2-position is also explained by the existence of electron-isomeric *R*- and *K*-molecules.

The existence of an equilibrium between electron-isomeric molecules is not inconsistent with the stability of geometrical stereoisomers such as maleic and fumaric acid. Their isomerisation will depend on the following changes: (i) Opening of the ethenoid linkage, *i.e.*, transition into the *R*- or *K*-state; (ii) rearrangement of the substituents of at least one of the carbon atoms within the *R*- or *K*-molecules, which, being dependent on the unknown structure of these molecules, might require quite considerable energy. Isomerisation cannot occur by a simple rotation round the axis of the opened carbon–carbon linkage; a rearrangement of the substituents independently of a rotation is essential (compare a model). The activation energy necessary for the thermal isomerisation, being always smaller than about 40 kg.-cals. (cf. Kistiakowsky *et al.*, *J. Amer. Chem. Soc.*, 1932, **54**, 2208; 1934, **56**, 638; 1935, **57**, 269), is in much better agreement with small dissociation energies for the second bond of an ethenoid linkage than with a dissociation energy of about 55 kg.-cals.

According to Eggert, Berthoud, Wachholtz, Kuhn *et al.* (see Freudenberg, "Stereochemie," p. 913), such isomerisations are catalysed by atoms with free valencies such as halogen or alkali, starting with the intermediate formation of radical-like molecules such as (XI). The ease of opening of the double bonds by the catalysts (in contrast to single linkages) again agrees better with the assumption of small dissociation energies.

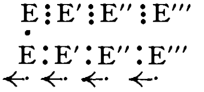


(XI.)

Structure of the Electron-isomeric Molecules.—In the present and previous papers the attribution of any special structure to the *R*- and *K*-molecules has been deliberately avoided in order to emphasise that the recognition of these states and their interpretation on the basis of the electronic theory (necessarily to a great extent speculative) are different problems. These states may be best expressed by such electronic formulæ as (XII) and (XIII), where one of the three electrons between two atoms will probably differ from the other two forming a single bond. These formulæ may, therefore, be replaced by (XII*a*) and (XIII*a*), where each atom possesses a single electron, the arrow indicating a displacement towards the next atom, possibly forming a kind of linkage.

(XII.)

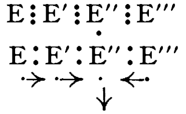
(XII*a*.)



$\underset{\bullet}{E}\vdots E'\vdots E''\vdots E'''$

$\underset{\leftarrow}{E}\,\colon \underset{\leftarrow}{E'}\colon \underset{\leftarrow}{E''}\colon \underset{\leftarrow}{E'''}$

K-State.



$E\vdots E'\vdots \underset{\bullet}{E''}\vdots E'''$

$E\colon E'\colon E''\colon E'''$

(XIII.)

(XIII*a*.)

R-State.

The presence of the free electron explains the origin of the absorption between 2000 and 8000 A., and also the fact that such states always show only one absorption band due to only one electron. The presence of three electrons between the atoms allows us to understand: (i) the comparatively great stability (small energy difference from those of the corresponding saturated molecules) of the *R*- and *K*-molecules in contrast to the instability of such simple radicals as methyl, ethyl, etc.*; (ii) the moderate stability of geometrical stereoisomers; (iii) the effect of catalysts on the isomerisation of stereoisomers and on

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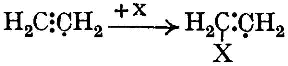
* Similar formulæ can also be devised for stable radicals such as the triarylmethyls.

the reactivity of such systems, since addition of an atom with a free valency transforms the comparatively stable *R*- or *K*-molecules, *e.g.*, of ethylene, into a much more reactive state similar to that of a simple radical (XIV).

(XIV.)



$$\mathrm{H_2C{:}\underset{\cdot}{C}H_2 \xrightarrow{+X} H_2\underset{X}{\underset{|}{C}}{:}\underset{\cdot}{C}H_2}$$

On the basis of such formulæ, the absorption between 2000 and 8000 A. is always due to free electrons, whereas electrons forming a linkage absorb at shorter wave-lengths. This agrees with the fact that the light absorption of free (mono)radicals, being due to free electrons, occurs in the same spectral region.

Such formulæ, being schematic, do not explain the laws of light absorption (dependence on different substituents and other changes of the chromophoric groups), but an understanding of these laws appears to be possible on the basis of the above structures by consideration of the so-called inductive effect of different groups. Undoubtedly, an important future aspect of the light absorption of these systems will consist in the elucidation of the electronic structures, based on the principles derived by Lapworth, Robinson, and Ingold from the chemical reactivity.

The problem of theoretical physics is different. Whereas the empirical atomic and electronic structural theories help in the elucidation of the qualitative atomic and electronic structures, theoretical physics actually can only purport to explain the stability of these structures, empirically already established, by calculating the forces and energies within the molecules. It is obvious that a treatment of such complicated structures, with which this paper deals, must be at present mainly speculative, since certain more or less arbitrary assumptions, *e.g.*, of the resonance states of substances with conjugated systems, have to be made as to these structures.

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