395. *Studies in the Light Absorption of Organic Compounds. Part VIII. Azo-compounds.*

By A. Burawoy.

It has been shown in previous communications of this series that there appear between 2000 and 8000 A. two different types of absorption band due to two different types of chromophore: (i) bands of very low intensity ($\varepsilon < 2000$) due to multiple linkages (*R*-bands, *R*-chromophores); (ii) bands of high intensity ($\varepsilon > 5000$) due to conjugated systems (*K*-bands, *K*-chromophores). These two types of absorption band also obey very different optical laws. In the present paper the absorption spectra of numerous azo-compounds are reported, with a view to testing the validity of the classification previously given. The previous results are confirmed.

The chemical problem of the light absorption (colour) of organic compounds consists primarily in establishing what groups or atoms (chromophores) are necessary for the presence of the electron (or electron system) responsible for the appearance of an absorption band between 2000 and 8000 A. Previous investigations (Burawoy, *Ber.*, 1930, **63**, 3155; 1931, **64**, 462, 1676; 1932, **65**, 941, 947; 1933, **66**, 228; *J. pr. Chem.*, 1932, **135**, 145) have shown that such bands are always due to two different types of chromophore, producing two different types of absorption band: (i) Unsaturated atoms of free radicals such as the methyl carbon atom of triarylmethyls, and all multiple linkages (being in a radical-like state) (*R*-chromophores, *R*-bands); (ii) conjugated systems, *i.e.*, all those represented by the general formula (I) (*K*-chromophores, *K*-bands)

$$\text{(I.)}\quad \mathrm{A{\cdot}[CH{:}CH]_{\mathit{n}}{\cdot}CH{:}B}$$

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

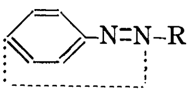
The changes of the position and intensity of these absorption bands due to changes of the chromophoric groups or their substituents, etc., have also been discussed. It has been shown that these two types of absorption band are not only distinguished by their

Compound.	*R*-Band, A.		*K*-Band, A.	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
Benzeneazomethane	4035	87	2595	7,800
* ,,	(none)		3340	9,900
Benzeneazotriphenylmethane	4205	180	2660	13,500
Azobenzene	4480	425	3130	20,000
* ,,	(none)		4225	28,800
Benzeneazodiphenyl	4505	900	3345	30,000
Benzeneazo-α-naphthalene	4630	1170	3700	14,000 ‡
p-Methoxyazobenzene	4400	750	3380	24,700
† ,,	4305	1050	3415	24,000
o- ,,	4550	676	3145	13,600
† ,,	4480	893	3165	14,000
m- ,,	4445	560	3125	22,000
p-Aminoazobenzene	(infl.)		3620	27,500
N-Benzeneazopiperidine	(none)		2895	16,000
Benzeneazo-α-naphthyl methyl ether	(infl.)		3920	17,800 §
Benzeneazo-β-naphthyl methyl ether	4690	1420	3720	8,100 ‖
Benzophenone	3380	110	—	—
Benzpinacolin	3330	220	—	—

* Solvent, sulphuric acid.
† Solvent, alcohol.
‡ Another band at 2690 A., $\epsilon = 12,000$.
§ Another band at 2700 A., $\epsilon = 14,800$.
‖ An inflexion at 2700 A., $\epsilon = 13,500$.

very different intensities, but also follow different absorption laws. The results obtained represent a classification of the chromophoric groups and their laws which considers all known facts and can be systematically tested by the investigation of new examples. In the present paper the absorption spectra of numerous azo-compounds are reported, and serve as a further test of the validity of this classification. In the table are enumerated the absorption maxima and molecular extinction coefficients of the compounds in hexane solution (unless otherwise stated). The determinations were 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.

According to Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3011), azomethane, NMe:NMe, in alcohol possesses a band at 3470 A. ($\varepsilon < 10$) distinguished by the very low intensity characteristic of all *R*-bands (cf. *Ber.*, 1930, **63**, 3155). There is no doubt that it is due to the azo-group. Replacement of a methyl by a phenyl group, as in benzeneazomethane, NPh:NMe, displaces this *R*-band to longer wave-lengths (4035 A., $\varepsilon = 87$), as is the case for the *R*-bands of all multiple linkages (*ibid.*, p. 3158). In addition, since benzeneazomethane contains a conjugated system indicated by the broken line in (II; R = Me), a new band appears at 2595 A. ($\varepsilon = 7800$) with the high intensity characteristic of all *K*-bands (*loc. cit.*) (Fig. 1).

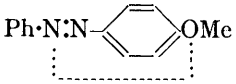


(II.)*

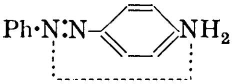
A comparison of the spectra of benzeneazomethane (II; R = Me), benzeneazotriphenylmethane (II; R = CPh_3), azobenzene (II; R = Ph), benzeneazodiphenyl (II; R = C_6H_4Ph), and benzeneazo-α-naphthalene (II; R = α-$C_{10}H_7$) (Fig. 1) shows that the *R*-band is displaced to longer wave-lengths in this order (cf. *Ber.*, 1930, **63**, 3155, for the effect of different hydrocarbon substituents on the *R*-bands of other multiple linkages).

The interpretation of the effect of the different hydrocarbons on the *K*-band of benzeneazomethane is rather difficult. Although the intensive bands appearing in the spectra of these substances are, undoubtedly, due to conjugated systems, yet in such substances as benzeneazo-α-naphthalene or -diphenyl no exact attribution of this band to one of the several conjugated systems present is possible. If we make the simplifying assumption that the absorbing conjugated system is in all cases the same as in benzeneazomethane (indicated in II), we see that the various groups R are substituents not only of the azo-*R*-chromophore but also of this chromophoric (conjugated) system. Consequently, they also displace the *K*-band in the same series to longer wave-lengths. However, it is possible that in the case of benzeneazo-α-naphthalene the chromophoric group will be represented by the system indicated in (V). Furthermore, this substance possesses a second intensive band at 2690 A. ($\varepsilon = 12{,}000$), probably identical with a band characteristic of naphthalene itself (fine structure with most intense bands at 2720 and 2750 A.).

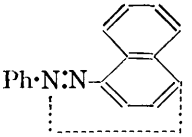
The effect of the amino- and the hydroxy-group is very remarkable. It has been shown (*loc. cit.*) that these groups displace a *K*-band considerably to longer wave-lengths



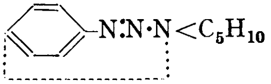
(III.)



(IV.)



(V.)



(VI.)

if they are on the end of the absorbing conjugated system (cf. I; A = OR,NR_2). In agreement with this, the *K*-band is displaced to longer wave-lengths in the series: azobenzene, *p*-methoxyazobenzene (III), *p*-aminoazobenzene (IV) (Fig. 2), benzeneazo-α-naphthalene (V), benzeneazo-α-naphthyl methyl ether (as III) (Fig. 3), and benzeneazomethane (II; R = Me), *N*-benzeneazopiperidine (VI) (Fig. 4).

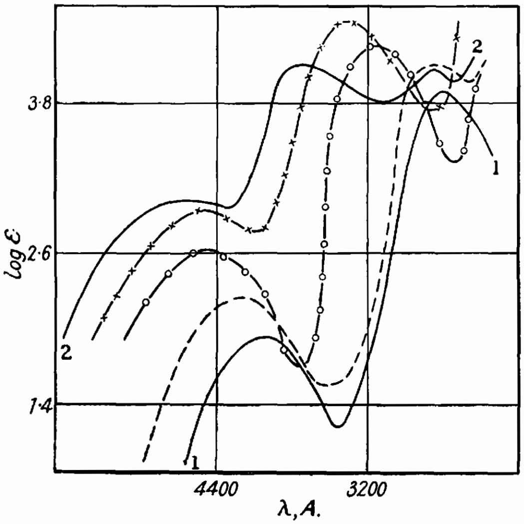
On the other hand, in a branch of a conjugated system or as substituents of an

---

* The broken line only formally indicates the conjugated system.

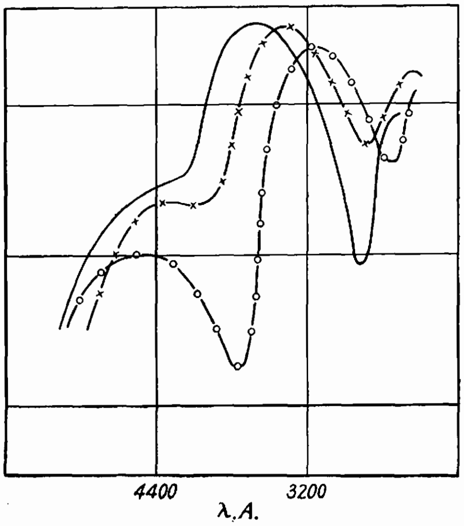
R-chromophore, these groups strongly displace the corresponding absorption band to shorter wave-lengths. This is illustrated by a comparison of the spectra of benzeneazomethane and -piperidine (Fig. 4). In the spectrum of the latter no *R*-band is detectable

FIG. 1.



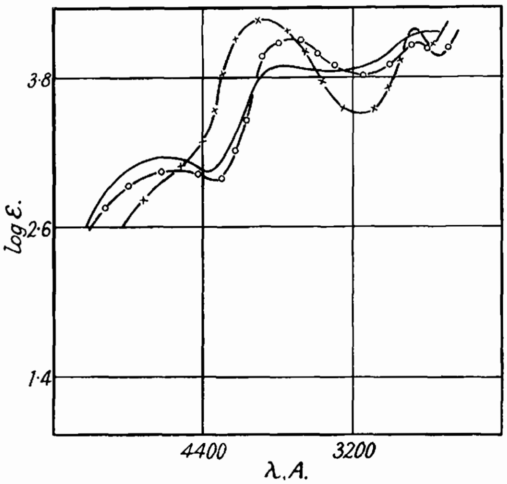
1——— *Benzeneazomethane.*
— — — *Benzeneazotriphenylmethane.*
—o—o— *Azobenzene.*
—x—x— *Azodiphenyl.*
2——— *Benzeneazo-α-naphthalene.*

FIG. 2.



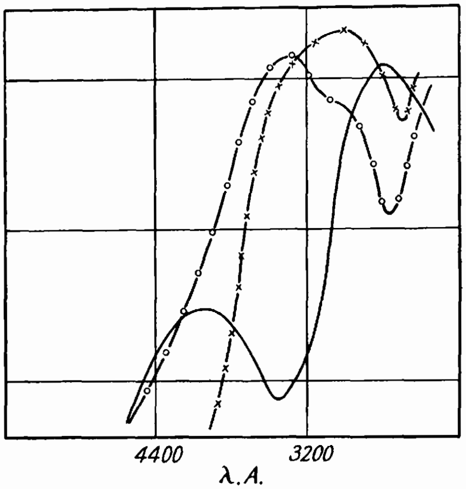
—o—o— *Azobenzene.*
—x—x— p-*Methoxyazobenzene.*
——— p-*Aminoazobenzene.*

FIG. 3.



——— *α-Benzeneazo-β-naphthyl methyl ether.*
—o—o— *Benzeneazo-α-naphthalene.*
—x—x— *Benzeneazo-α-naphthyl methyl ether.*

FIG. 4.



——— *Benzeneazomethane in hexane.*
—o—o— *Benzeneazomethane in conc.* H_2SO_4.
—x—x— N-*Benzeneazopiperidine in hexane.*

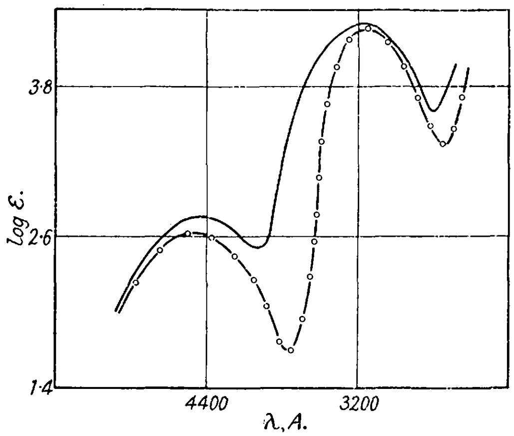
since, being strongly displaced to shorter wave-lengths, it is superposed by the intensive *K*-band present (contrast with the *K*-bands).

When indirectly connected with the chromophoric groups, *i.e.*, by an aromatic substituent, a hydroxyl or amino-group displaces the corresponding absorption band only slightly (in most cases to shorter wave-lengths). Thus, in contrast to the *K*-band, the

R-band of *p*-methoxyazobenzene absorbs at shorter wave-lengths than that of azobenzene (Fig. 2). Although the *R*-bands are only indicated as inflexions in the spectra of *p*-aminoazobenzene (IV) and benzeneazo-α-naphthyl methyl ether (as III), being partly superposed by the intensive *K*-bands, comparison with the spectra of azobenzene and benzeneazo-α-naphthalene, respectively, clearly indicates that this band has been displaced to shorter wave-lengths (Figs. 2 and 3).

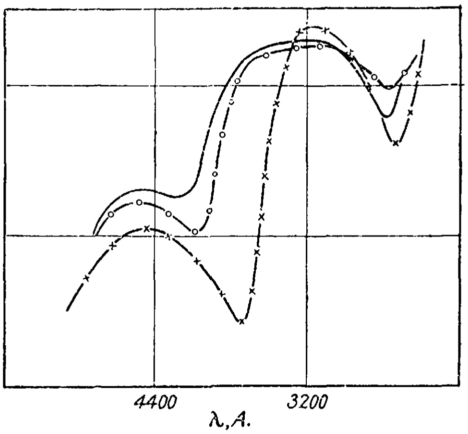
Furthermore, the methoxyl group in *m*-methoxyazobenzene, being only a substituent of both the *R*- and the *K*-chromophore, has no significant effect on the position of either the *R*- or the *K*-band of azobenzene (Fig. 5). For the same reason, the introduction of a methoxyl group in the *o*-position has only a very slight effect on the maxima of both bands. A comparison of the spectra of azobenzene and benzeneazo-α-naphthalene with those of *o*-methoxyazobenzene and benzeneazo-β-naphthyl methyl ether shows that a slight shift of both bands, this time to longer wave-lengths, has taken place (Figs. 6 and 3). This effect is, however, not comparable with the strong displacement to longer wave-lengths by a methoxyl group on the end of an absorbing conjugated system, as is already shown in *p*-methoxyazobenzene and benzeneazo-α-naphthyl methyl ether.

FIG. 5.



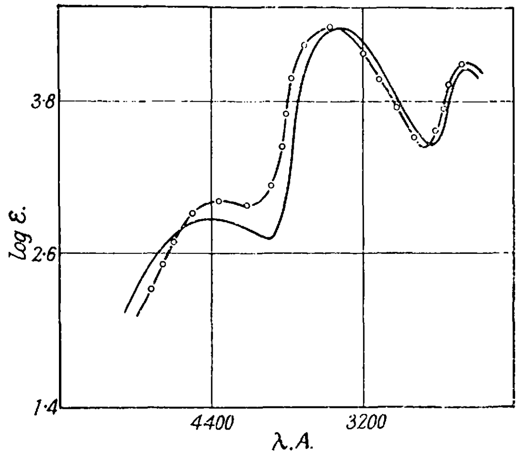
——— m-*Methoxyazobenzene.*
—o—o— *Azobenzene.*

FIG. 6.



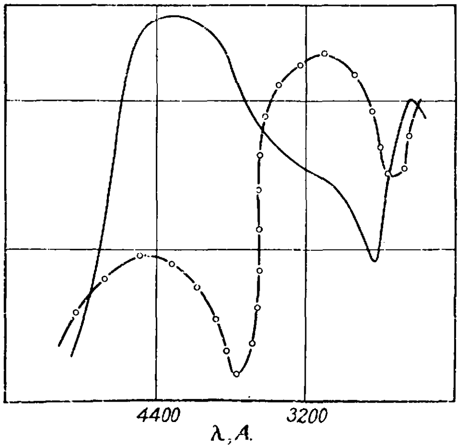
——— o-*Methoxyazobenzene in alcohol.*
—o—o— o-*Methoxyazobenzene in hexane.*
—x—x— *Azobenzene in hexane.*

FIG. 7.



——— p-*Methoxyazobenzene in hexane.*
—o—o— p-*Methoxyazobenzene in alcohol.*

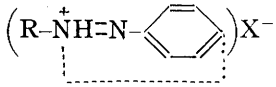
FIG. 8.



——— *Azobenzene in conc.* H_2SO_4.
—o—o— *Azobenzene in hexane.*

The dependence of the absorption bands on the solvent is again very characteristic. It has been shown (*loc. cit.*) that the *R*-bands are always displaced to shorter, and the *K*-bands to longer, wave-lengths in approximately the increasing order of dielectric constant (dipole moment) of the solvent. This is now confirmed for the azo-*R*-chromophore by a comparison of the spectra of *o*- and *p*-methoxyazobenzene in hexane and in alcohol (Figs. 6 and 7). In alcohol, the *R*-band absorbs at shorter, the *K*-band at longer, wave-lengths. Similar effects have already been observed for the azo-*R*-band of benzeneazo-β- and -α-naphthyl methyl ethers (Burawoy and Markowitsch, *Annalen*, 1933, **503**, 180). It follows that the best separation of the *R*-band and the *K*-band can be expected in hexane, for which reason the determinations have been carried out in this solvent.

The influence of the addition of an acid molecule, *i.e.*, a hydrogen nucleus, to a chromophore on the *R*- and *K*-bands emphasises their different behaviour. Whereas the addition to the *R*-chromophore destroys the corresponding band, and consequently such bands do not appear in organic cations (cf. *Ber.*, 1931, **64**, 482), yet the addition to a conjugated system, *i.e.*, the replacement of the groups $\mathrm{(N)C{:}O}$, $\mathrm{(N)C{:}NR}$, $\mathrm{(N)C{:}S}$ by the groups $\mathrm{(N)C{:}\overset{+}{O}R}$, $\mathrm{(N)C{:}\overset{+}{N}R_2}$, $\mathrm{(N)C{:}\overset{+}{S}R}$ respectively (cf. I; B), displaces the corresponding *K*-bands strongly to longer wave-lengths. As shown in Figs. 8 and 4, the *R*-bands of azobenzene and benzeneazomethane disappear and the *K*-bands are strongly displaced to longer wave-lengths in the spectra of their salts (VII; R = Ph or Me) in concentrated sulphuric acid.



(VII.)

It has been found (*Ber.*, 1931, **64**, 762) that the intensity of the *R*-bands (independently of the displacement to shorter or longer wave-lengths) for a given series of substituents increases in the same order as the dissociation of ethanes and hydrazines into their radicals. This result is of some importance for the recognition of the radical-like structure of the *R*-chromophores (multiple linkages in their absorbing state) and is again confirmed. The intensity of the azo-*R*-band increases in the series $\mathrm{Me} < \mathrm{Ph} < \mathrm{C_6H_4Ph} < \alpha\text{-}\mathrm{C_{10}H_7}$ and $\mathrm{Ph} < \mathrm{C_6H_4{\cdot}OMe}$ (*m, o, p*) (cf. table and figures).

The triphenylmethyl group shows a greater effect than a methyl group, but a smaller one than the phenyl group, although pentaphenylethyl is less associated than triphenylmethyl (Schlenk and Mark, *Ber.*, 1922, **55**, 285). However, the effect of this group on a nitrogen atom may differ from that on a carbon atom. This view is supported by the observation that the carbonyl *R*-band of benzpinacolin is, in fact, more intense ($\varepsilon = 220$) than the *R*-band of benzophenone ($\varepsilon = 110$) (cf. table; and Burawoy, *Ber.*, 1930, **63**, 3160). Incidentally, the author's previous statement that a triphenylmethyl substituent displaces an *R*-band more strongly to longer wave-lengths than a phenyl substituent is erroneous and is now corrected.

The author thanks Professor I. M. Heilbron, F.R.S., for the many facilities he has afforded him, and acknowledges with gratitude grants from the Society for the Protection of Science and Learning, London, Imperial Chemical Industries Ltd. (Dyestuffs Group), and the Research Fund Committee of the Chemical Society.

THE UNIVERSITY OF MANCHESTER.

[*Received, September 24th*, 1937.]