

### 443. Aromatic Azo-compounds. Part IV.\* Absorption Spectra of Azo- and Azoxy-compounds.

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The absorption spectra of the azonaphthalenes and phenylazonaphthalenes have been examined, and it has been found that the position of the *K*-absorption band can be correlated with the degree of conjugation.

Several azoxy-compounds have also been examined. In most cases, there is a bathochromic shift in passing from the azo- to the azoxy-compound; but with 1:1'-azoxynaphthalene and *oo'*-azoxytoluene there is a pronounced hypsochromic shift. This is probably due to steric hindrance to coplanarity.

THE spectra of aromatic azo-compounds usually show several regions of absorption. There is generally a band or bands in the region 2100—2900 Å, probably due to absorption by the aromatic rings, and azobenzene and some substituted azobenzenes also show a weak absorption band at about 4400—4700 Å, evidently due to the N:N linkage itself. However, the intense band at about 3200—3700 Å has been ascribed to conjugation between the N:N group and the aromatic nuclei, and it can be shown that substituents (*e.g.*, in the *p*-positions) which increase this conjugation shift this absorption band to longer wavelengths (Burawoy, *J.*, 1937, 1865; Cook, Jones, and Polya, *J.*, 1939, 1315). It was therefore decided to determine the absorption spectra of the azonaphthalenes, the phenylazonaphthalenes, and their azoxy-derivatives.

All the compounds examined have been found to have three main regions of absorption, and these have been called regions I, IA, and II. Region I contains a single peak of high intensity at about 2200 Å, and this evidently corresponds to a similar peak at 2210 Å in the spectrum of naphthalene (*cf.* Mayneord and Roe, *Proc. Roy. Soc.*, 1935, *A*, 152, 299). Region IA contains 1—3 peaks at about 2650, 2750, and 2900 Å, and these apparently correspond to the three peaks in the spectrum of naphthalene at 2660, 2750, and 2850 Å. Region II is usually a broad band of high intensity around 3200—3800 Å. This is the band which Burawoy (*loc. cit.*) ascribed to conjugation between the azo-linkage and the

*Positions of the maxima (in Å) and corresponding log ε values in the absorption spectra of azo- and azoxy-compounds (solvent, ethanol).*

Compound	Region I	Region IA			Region II, <i>K</i> -band
Azobenzene .....	—	2290 (4.11)	—	—	3180 (4.32)
2-Phenylazonaphthalene ...	2190 (4.48)	2650 (4.13)	2770 (4.13)	2870 (4.13)	3280 (4.28)
2:2'-Azonaphthalene .....	2140 (4.57)	2620 (4.39)	2780 (4.23)	2900 (4.18)	3350 (4.37)
1-Phenylazonaphthalene ...	2190 (4.58)	2660 (4.03)	2730 (4.03)	2900 (3.94)	3720 (4.10)
1:2'-Azonaphthalene .....	2160 (4.76)	2640 (4.35)	—	3100 (4.02)	3810 (4.24)
1:1'-Azonaphthalene .....	2140 (4.87)	2660 (4.26)	—	—	4000 (4.21)
Azoxybenzene .....	2310 (3.93)	2610 (3.87)	—	—	3230 (4.16)
"α"-2-Phenylazoxynaphthalene (m. p. 125°) .....	2160 (4.51)	—	2760 (4.28)	2850 (4.23)	3400 (4.30)
"β"-2-Phenylazoxynaphthalene (m. p. 117°) .....	2140 (4.59)	2410 (4.15)	2590 (4.24)	2910 (4.08)	3310 (4.30)
2:2'-Azoxynaphthalene .....	2160 (4.71)	2630 (4.41)	2770 (4.37)	(2890) (4.24)	3460 (4.41)
"β"-1-Phenylazoxynaphthalene .....	2200 (4.54)	2690 (4.12)	—	—	3780 (4.06)
"β"-1:2'-Azoxynaphthalene .....	2160 (4.76)	(2540) (4.25)	2620 (4.29)	2910 (4.04)	3860 (4.17)
1:1'-Azoxynaphthalene .....	2180 (4.93)	2620 (4.11)	—	(2880) (3.91)	3640 (4.06)
<i>oo'</i> -Azotoluene .....	—	2350 (3.98)	—	—	3320 (4.24)
<i>oo'</i> -Azoxytoluene .....	—	2350 (3.96)	—	—	3110 (3.94)

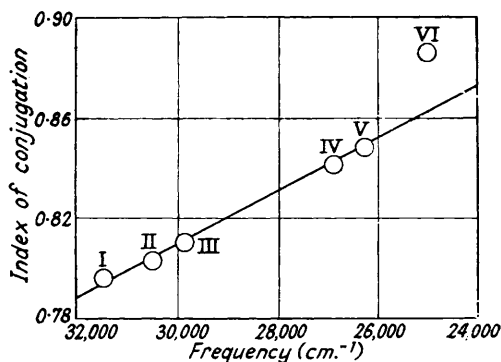
aromatic rings, and which he called the "*K*-band." Burawoy's *R*-band is difficult to identify in the spectra of the azonaphthalenes and phenylazonaphthalenes as it is usually only a point of inflexion. This band seems to be absent in the azoxy-compounds.

\* Part III, preceding paper.

The positions and intensities of the absorption maxima for these compounds are recorded in the table, and the results clearly show that the *K*-band is shifted to longer wave-lengths with increasing conjugation. The *K*-band for azobenzene is at 3180, that for 2 : 2'- at 3350, and that for 1 : 1'-azobenzene at 4000 Å. It seems that this generalisation holds quite accurately. The conjugating power of a position in an aromatic ring can be defined as  $\beta$  times the self-polarisability of that position (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, **195**, 188), and for the azo-compounds the most satisfactory index of the conjugation is probably obtained by summing the self-polarisabilities

FIG. 1. The relation between the frequency of the *K*-absorption band and the sum of the self-polarisabilities of the positions to which the N:N group is attached.

- (I) Azobenzene.
- (II) 2-Phenylazonaphthalene.
- (III) 2 : 2'-Azonaphthalene.
- (IV) 1-Phenylazonaphthalene.
- (V) 1 : 2'-Azonaphthalene.
- (VI) 1 : 1'-Azonaphthalene.



of the two positions to which the azo-group is attached. The self-polarisability of any position in a phenyl ring is 0.398, so the index of conjugation for azobenzene is 0.796; the self-polarisability of the 2-position in naphthalene is 0.405, so the index of conjugation for 2-phenylazonaphthalene is 0.803; the self-polarisability of the 1-position in naphthalene is 0.443, so the index of conjugation for 1-phenylazonaphthalene is 0.841; and so on. On using these data, there is seen to be a remarkable degree of correlation between the index of conjugation and the frequency of the *K*-absorption band (Fig. 1).

FIG. 2. Absorption spectra of 2 : 2'-azonaphthalene (—), and of 2 : 2'-azoxynaphthalene (.....), both in ethanol.

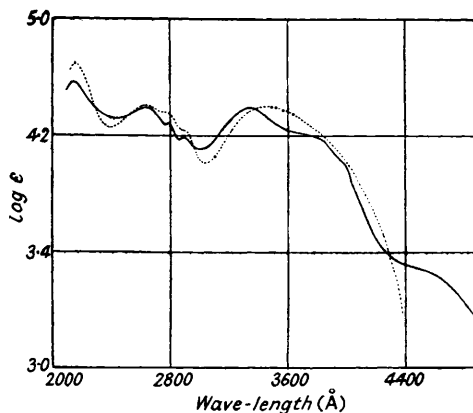
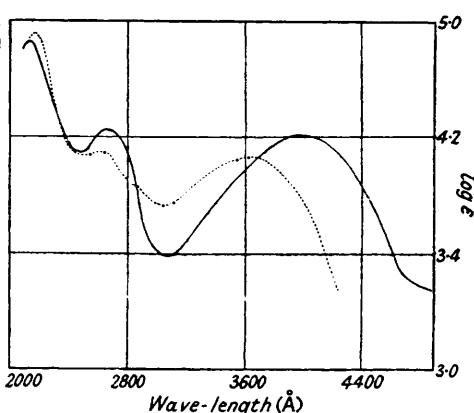


FIG. 3. Absorption spectra of 1 : 1'-azonaphthalene (—), and of 1 : 1'-azoxynaphthalene (.....), both in ethanol.



The degree of conjugation is also indicated by other details in the spectra. For example, the spectrum of 2 : 2'-azonaphthalene in the IA region is very similar to that of naphthalene, three peaks being resolved. On the other hand, the increased conjugation in the case of 1 : 1'-azonaphthalene evidently disturbs the electronic configuration, and the IA region for this compound shows only one absorption maximum. The spectrum of 1 : 2'-azonaphthalene is intermediate, and two peaks have been resolved in this region.

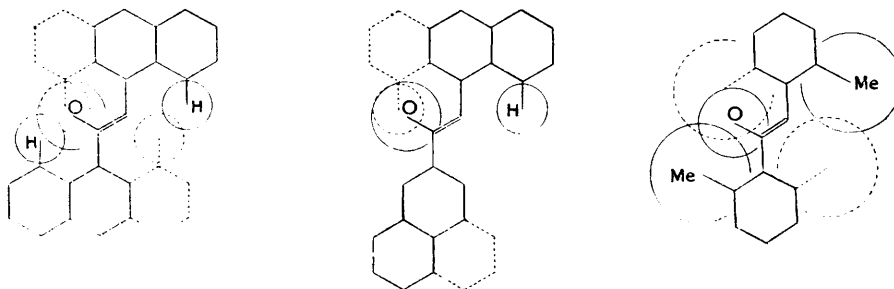
The spectra of the azoxy-compounds were found to resemble those of the corresponding

azo-compounds very closely. Three main regions of absorption (I, IA, and II) were again distinguished (see table); but no *R*-band or point of inflexion corresponding to the *R*-band (Burawoy, *loc. cit.*) could be detected.

In region II (*K*-band), with one exception, there is a *bathochromic* shift of about 70 Å in passing from an azo- to the corresponding azoxy-compound. In 1:1'-azonaphthalene, however, the introduction of the oxygen atom produced a *hypsochromic* shift of about 360 Å (Figs. 2 and 3).

The construction of scale models and of scale diagrams (Fig. 4) indicates that if the oxygen atom is attached to an azo-nitrogen atom adjacent to the 1-position in naphthalene, the molecule cannot assume a coplanar configuration. In these circumstances, conjugation would be inhibited and absorption would occur at shorter wave-lengths (cf. Beale and Roe, *J. Amer. Chem. Soc.*, 1952, **74**, 2302). On the other hand, if the oxygen is attached to an azo-nitrogen atom adjacent to a 2-position in naphthalene or to a phenyl ring, the molecule

FIG. 4. 1:1'-Azoxy-naphthalene. FIG. 5. 1:2'-Azoxy-naphthalene. FIG. 6. *oo'*-Azoxytoluene.



can assume a coplanar configuration (Fig. 5), and absorption occurs at a slightly longer wave-length than with the azo-compound itself. This indicates that the azoxy-compounds which are obtained by oxidation of 1-phenylazonaphthalene and of 1:2'-azonaphthalene cannot have the oxygen on the nitrogen atom adjacent to the 1-position of the naphthalene ring, and that these derivatives must have the alternative structures assigned to them in Part III (preceding paper).

To confirm this interpretation of the hypsochromic shift with 1:1'-azoxy-naphthalene, it was decided to examine *oo'*-azoxytoluene, for a scale diagram (Fig. 6) indicated that this molecule must also be non-coplanar. In this case a hypsochromic shift of about 200 Å was observed on passing from *oo'*-azotoluene to the azoxy-derivative, in complete agreement with expectation. Small bathochromic shifts have, however, been observed on passing from *mm'*-azotoluene to the azoxy-derivative, and from *pp'*-azotoluene to *pp'*-azoxytoluene (Cook, Jones, and Polya, *loc. cit.*; Müller and Hory, *Z. physikal. Chem.*, 1932, **162**, 281). In these *meta*- and *para*-derivatives, there is no steric hindrance to coplanarity.

*Absorption Spectra.*—The absorption spectra were all determined, in absolute ethanol, with a Hilger Uvispek Spectrophotometer.