280. cis-*Azo-compounds. Part III. Absorption Spectra.*

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The absorption spectra, usually in chloroform, of numerous substituted *cis*-azobenzenes have been determined from *ca.* 280 to 480 mμ. All exhibit the two-banded structure of the spectra of the *trans*-isomerides which have also been determined or redetermined, the intensity of absorption rather than the trivial changes in wave-length providing the chief distinguishing feature. Absorption spectra of stereoisomeric forms of bisbenzeneazobenzene and 4 : 4′-bisbenzeneazodiphenyl are also described.

THIS paper describes the absorption spectra of numerous *cis*-azo-compounds prepared by an irradiation–chromatographic adsorption technique (J., 1938, 876, and preceding paper) and their relation to the spectra of their *trans*-isomerides.

The determinations were made with a Hilger " Barfit " quartz spectrograph (E 498), an iron-tungsten spark being used as the source of light. The solvent, except where otherwise stated, was chloroform. Experiment had shown that the reversion *cis* → *trans* takes place less readily in non-ionising solvents, the sharper separation of the absorption bands in such solvents being a secondary advantage. We determined a number of spectra in petroleum which had been freed from aromatic hydrocarbons, but the very low solubility of many azo-compounds in petroleum induced us to make most of our determinations in chloroform. The absorption curves are of similar form in these solvents, but although the band heads are only very slightly different in the several compounds we examined in both solvents, yet the intensities are markedly higher in petroleum.

As the *cis*-isomerides were all prepared by irradiating a solution of the *trans*-compound and the effect of short periods of irradiation is not completely known, experiments were necessary to ensure that the spectra determined are in reality those of the *cis*-compounds and not of partly isomerised products. The identity of the spectra obtained in determinations on the same solution at intervals confirmed that the irradiation during the determination had no appreciable effect on the stereochemical composition of the material in solution. Similarly, the possibility of activation of the reversion by products of photochemical oxidation of chloroform was shown to be of no significance.

Intensities are expressed throughout as $\log_{10}\varepsilon$, where $\varepsilon = (1/cl)\log_{10}I_0/I$ (c = concentration in mols./litre, l = length of tube in cm.).

The main numerical results are summarised in the following table, where $\log_{10}\varepsilon$ is given in parentheses. Multiple values indicate a splitting of the main band into a number of maxima.

Compound $C_6H_3RR''\cdot N_2\cdot C_6H_4R'$.			*cis*-.		*trans*-.	
R.	R′.	R″.				
H	H	H	324 (4·18)	438 (3·06)	319 (4·29)	445 (2·47)
m-Me	H	H	299 (3·96)	447 (3·34)	322 (4·30)	446 (2·83)
p-Me	H	H	299 (3·78)	450 (2·25)	330 (4·17)	448 (2·78)
m-Me	*m*-Me	H	329 (3·84)	424 (3·24)	331 (4·18)	447 (2·79)
p-Me	*p*-Me	H	326 (4·02)	444 (3·06)	338 (4·36)	445 (3·05)
p-Cl	H	H	332 (4·07)	445 (2·94)	327 (4·33)	445 (2·81)
p-Br	H	H	324 (4·04)	445 (3·05)	330 (4·36)	445 (2·88)
p-I	H	H	324 (4·29)	447 (3·25)	337 (4·47)	447 (2·91)
m-NO_2	H	H *	325 (4·27)	273·5 (4·22)	328 (4·43)	273·5 (4·00)
			322 310·5 (4·32) 308	265·5 258·5 (4·16) 251·5	320 311 (4·10)	265·5 253 (3·91) 252·5
p-NO_2	H	H *	330 (4·22) 321	—	327·5 (4·20)	—
p-NO_2	*p*-NO_2	H	—	—	341·5 (4·46)	—
p-OEt	H	H	350 (3·86)	439 (3·05)	351 (4·36)	445 (3·10)
o-OMe	H	H	351 (4·23)	440 (3·07)	327 (4·21)	445 (3·16)
o-OH	*o*-OH	H	—	—	330 (4·30)	425 (4·18)
o-OMe	*o*-OH	H	—	—	320 (4·00)	381 (4·04)
o-OMe	*o*-OMe	H	—	—	324 (3·90)	376 (4·00)
p-OH	*p*-OH	H	α359 (4·31) β364 (4·29)	—	—	—
,,	,,	,, *	α364 (4·48) β368 (4·48)	—	—	—
p-OMe	*p*-OMe	H	360 (3·61)	435 (2·85)	366 (4·38)	450 (2·75)
o-OMe	H	*p*-OMe	373 (4·28)	—	371 (4·31)	—
o-OMe	H	*o*′-OMe	368 (3·65)	455 (3·00)	368 (4·26)	—
p-PhN_2	H	H	(*cis–cis*)	366 (4·20)	440 (3·14)	
			(*cis–trans*)	356 (4·27)		
			(*trans–trans*)	368 (4·57)		
p-$PhN_2C_6H_4$	H	H	(*cis–cis*)	360 (4·47)	442 (3·79)	
			(*cis–trans*)	363 (4·52)	442 (4·06)	
			(*trans–trans*)	369 (4·66)		
1-Benzeneazo-4-methoxynaphthalene *			262·5 (4·13) 270	278·5 (4·07)	268 (4·30)	392 (4·32)
				389·5 (4·17)		

* Petroleum used as solvent instead of chloroform.

Spectra of trans-*Compounds.*—Our results for these isomerides confirm and amplify those of Burawoy (J., 1937, 1869). The spectra usually consist of an intense (*K*) band at *ca.* 320—370 mμ (due to the general conjugation between the N=N group and the aromatic nuclei), a second less intense (*R*) band at *ca.* 440—470 mμ, ascribed to the N=N linkage

Fig. 1.

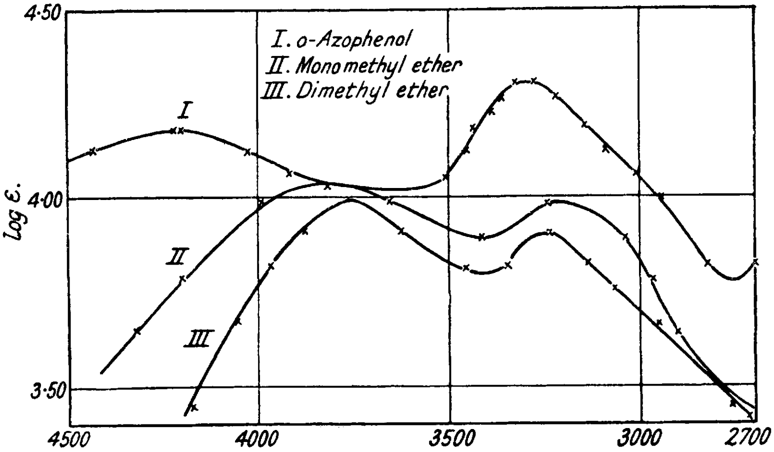
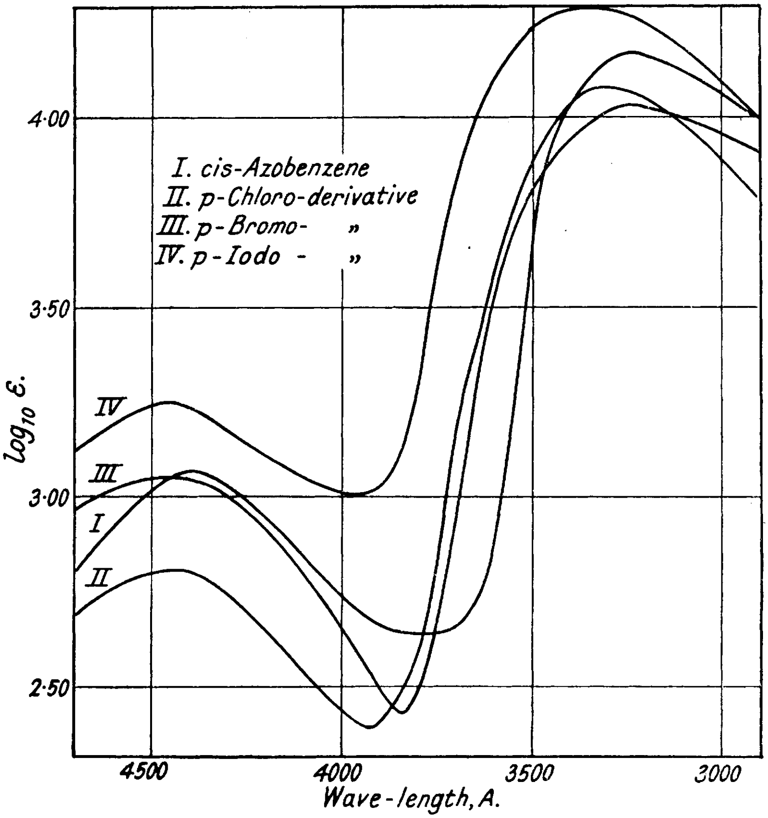
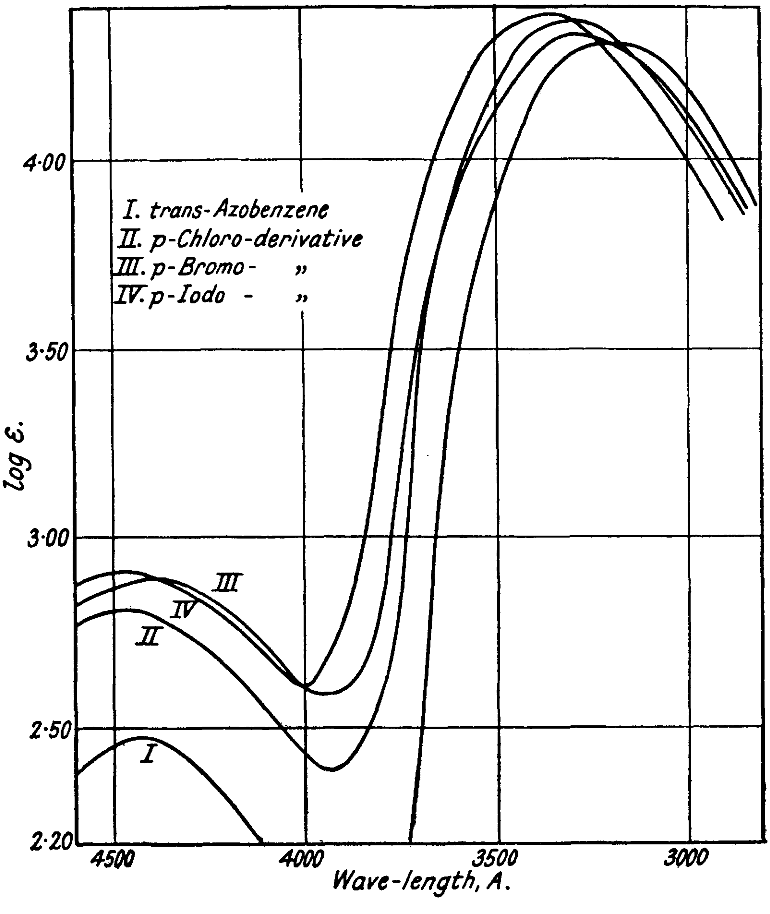


Fig. 2.



itself, and a third band at *ca.* 230—270 mμ. Burawoy concludes that an amino-, hydroxy-, or methoxy-group at the end of the conjugated system favours the shift of the *K*-band to longer wave-lengths and the less marked shift of the *R*-band to shorter wave-lengths, whereas *o*-groups of this nature shift only the *R*-band slightly towards shorter wave-lengths. From the table it appears that this is always the effect of a single *p*-substituent irrespective of its chemical nature, and this applies also to many compounds containing two substituents. The only exceptions noted in this work are *o*-azophenol and its mono- and di-methyl ethers which, unlike any other azo-compounds studied, possess an intense band at 380—420 mμ (Fig. 1). The appearance of a second intense band in the spectra of azo-compounds containing two positive groups is, however, probably a general phenomenon (Pongratz, Markgraf, and Mayer-Pitsch, *Ber.*, 1938, **71**, 1287). One or two methoxy-radicals in other positions in azobenzene give spectral curves of shape resembling those of methyl- and halogeno-azobenzenes (Figs. 2—5). Introduction of a further azo-group with consequent lengthening of the conjugated system results in a shift the order of which is to be compared with that effected by introducing a *p*-methoxy-group.

FIG. 3.



Spectra of cis-*Compounds.*—Our results for azobenzene itself are in good agreement with those of Le Fèvre and Vine (J., 1938, 431). The effect of isomerisation on the absorption spectrum in substituted azobenzenes is usually to cause but slight alteration in the absorption band heads, whilst the intensities may be considerably altered. The shift of the *R*-band is so slight as to be within the limits of experimental error but it is usually markedly more

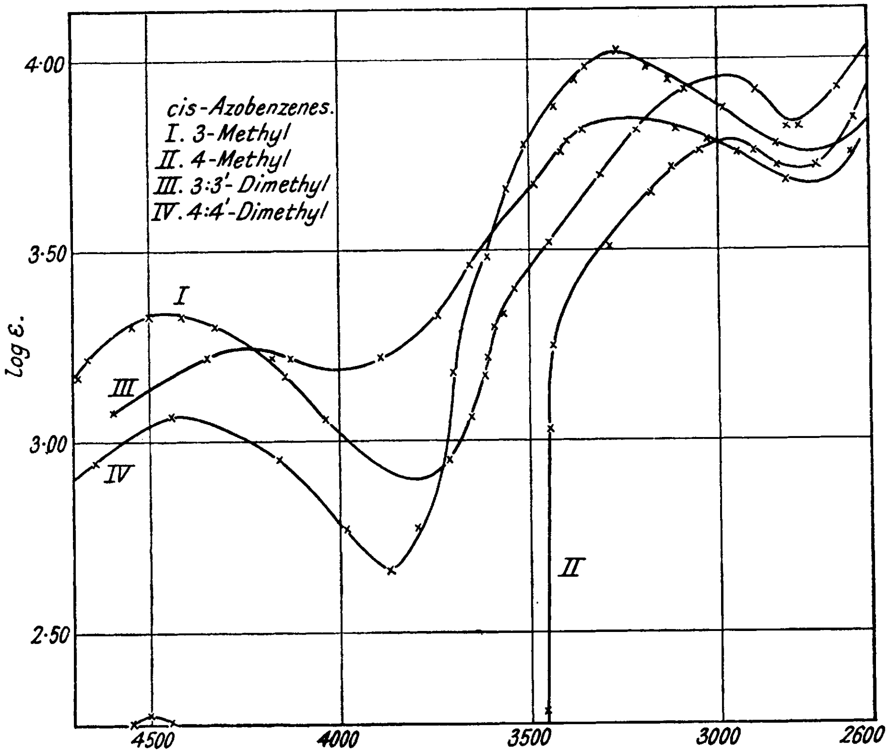

cis-Azobenzenes.
I. 3-Methyl
II. 4-Methyl
III. 3:3'-Dimethyl
IV. 4:4'-Dimethyl
I
III
IV
II
log ε.
4·00
3·50
3·00
2·50
4500
4000
3500
3000
2600

FIG. 4.

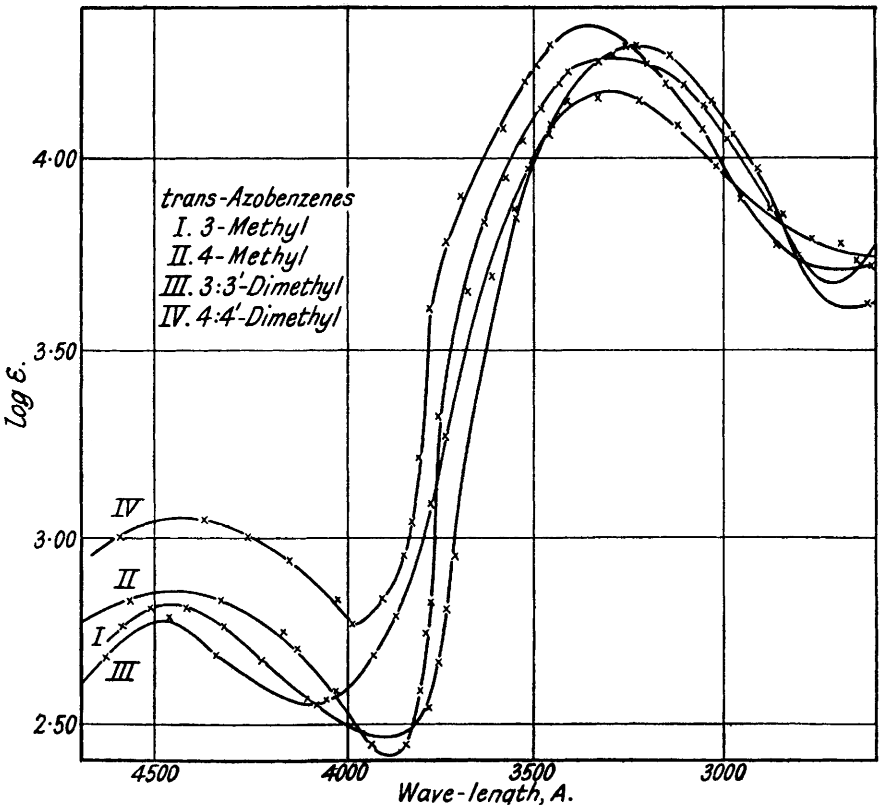
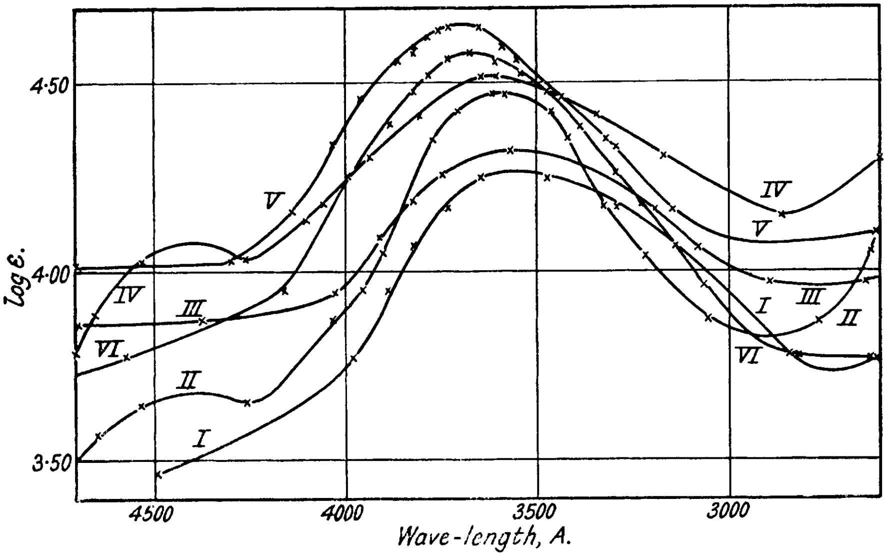

trans-Azobenzenes
I. 3-Methyl
II. 4-Methyl
III. 3:3'-Dimethyl
IV. 4:4'-Dimethyl
IV
II
I
III
log ε.
4·00
3·50
3·00
2·50
4500
4000
3500
3000
Wave-length, A.

FIG. 5.

intense in the *cis*-isomerides. On the other hand, the K-band may suffer comparatively wide shifts (although the effect is usually small) towards shorter wave-lengths; only in the cases of unsubstituted azobenzene and *o*-methoxyazobenzene is the shift in the opposite direction. Moreover, whilst remaining the most intensely absorbing part of the spectrum, the *cis*-K-band is invariably weaker than the corresponding region in the *trans*-spectrum. These effects are illustrated in the spectra of *cis*- and *trans*-azobenzene and the *p*-halogeno-derivatives (Figs. 2, 3). In the *trans*-compounds the K-band heads form a regular series with respect to their position and intensity, and this series, except for azobenzene, is maintained in the *cis*-compounds; the effect on the R-band is variable. Attention may also be directed to the surprisingly large effect of a single methyl group as in *m*- and *p*-methylazobenzene and the very slight effect observed when two symmetrical methyl groups are present (Figs. 4, 5). These general differences between spectra of the *cis*- and the *trans*-azo-series are closely parallel to the differences observed between analogous pairs of isomerides in the oxime, olefin, diazo-cyanide, and other series.

FIG. 6.



Bisbenzeneazobenzene.		Bisbenzeneazodiphenyl.	
cis-cis	I	*cis-cis*	II
cis-trans	III	*cis-trans*	IV
trans-trans	VI	*trans-trans*	V

It is surprising that stepwise isomerisation of the azo-linkage in 1 : 4-bisbenzeneazobenzene results in no regular shift of the band head, the maximum for the *cis-trans*-modification lying at a shorter wave-length than that of either of the other forms. The wave-length of the main band-head of 1 : 4-bisbenzeneazodiphenyl becomes progressively shorter and the intensities are regularly weakened as first one and then both azo-linkages are isomerised, a similar progressive weakening in intensity being observed in the case of bisbenzeneazobenzene (Fig. 6).

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