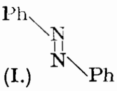
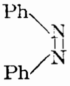
395. *The Dipole Moments of Benzocinnoline and Benzocinnoline Oxide in Relation to those of* cis-*Azo- and -Azoxy-benzene.*

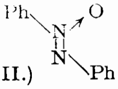
By K. E. CALDERBANK and R. J. W. LE FÈVRE.

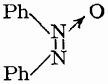
The identifications of the azo- and azoxy-benzenes of m. p.s 71° and 84° as the *cis*-isomers, made previously on dipole-moment evidence, receive further support from an examination of benzocinnoline and its *N*-oxide.

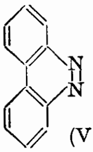
HARTLEY and LE FÈVRE (*J.*, 1939, **531**) discussed the dipole moments found for the two isomeric azobenzenes (I, II) in reference to *inter alia* those previously recorded (Gehrckens and Müller, *Annalen*, 1933, **500**, 296) for the (apparently) corresponding azoxybenzenes (III, IV). Circumstances then prevented the intended extension of the argument by analogy to benzocinnoline (V) and its *N*-oxide (VI).

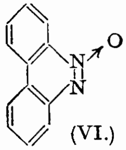

(I.)
M. p. = 68°, μ = *ca.* 0 D.


(II.)
M. p. = 71°, μ = 3·0 D.


(III.)
M. p. = 36°, μ = 1·7 D.


(IV.)
M. p. = 84°, μ = 4·7 D.


(V.)
μ = 3·9 D.


(VI.)
μ = 5·2 D.

These two compounds are now found to have the moments shown above. In both cases the values are higher than those of the related diaryl *cis*-substances (II) and (IV), but not more so than might be expected from other pairs, such as :

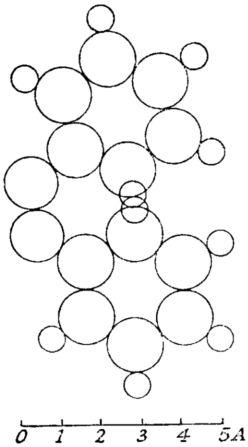
	μ, D.			μ, D.	
Diphenylamine [1]	1·0	(A)	Diphenyl ether	0·9	(B)
Carbazole [2]	2·09		Diphenylene oxide	1·2	
Benzoic anhydride [3]	4·15	(C)	Diphenylmethane	0·23	(D)
Diphenic anhydride [4]	5·3		Fluorene [5, 6]	0·5—0·8	
Benzophenone	3·0	(E)	*cis*-Stilbene	0	(F)
Fluorenone [5]	3·35		Phenanthrene	0·6	
			Benzil [7]	3·7	(G)
			Phenanthraquinone [7]	5·6	

[1] Smythe, unpublished determination. [2] Cowley and Partington, *J.*, 1936, **47**. [3] Oesper and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 768. [4] Le Fèvre and Vine, *J.*, 1938, 972. [5] Hughes, Le Fèvre, and Le Fèvre, *J.*, 1937, 202. [6] Sirkin and Schott-Lvova, *Acta Physicochim. U.R.S.S.*, 1944, **19**, 379. [7] Caldwell and Le Fèvre, *J.*, 1939, 1614.

Other figures (unmarked) from *Trans. Faraday Soc.*, 1934, **30**, Appendix.

It is clear that several causes may operate to produce the increases of moment noted, *e.g.*, geometrical distortion due to ring closure, prevention of rotation of the phenyl groups in all cases, and of the benzoyl groups in (C) and (G), with consequent alteration of the anisotropy of molecular polarisability, and hence the degree of internal induction of polarisation by the stronger dipolar links present, change of bond moments by *oo′*-covalent union [*e.g.*, μ_{CO} or μ_{HC} in (C) and (E)], or what amounts to the same thing—modification of mesomeric forms following the increased possibilities of conjugation, etc.

FIG. 1.



These phenomena, in general, are difficult to diagnose separately. However, for certain instances—such as (II) and (V), (IV) and (VI), (A) and (B)—where the resultant is largely the vector sum of two Ar $\rightarrow$ X components, rough estimation of the part played by the geometrical explanation seems straightforward. As an illustration we consider the molecules (II) and (V).

Fig. 1 is a scale drawing, flattened into the plane of the paper, of *cis*-azobenzene, based on the *X*-ray analyses by Robertson (*J.*, 1939, 232; Hampson and Robertson, *J.*, 1941, **63**, 2533). Inspection suggests that this, and many similar diaryl compounds, in assuming such a configuration would need to adopt an *oo′*-carbon-to-carbon separation of 1·78 A.; *i.e.*, less than the C . . . C total " Wirkungs-radien " (about 3—3·5 A.; Stuart, *Z. physikal. Chem.*, 1935, *B*, **27**, 353). For the stable state of these molecules, a degree of rotation (Robertson finds 50°) of the Ar-nuclei around their 1 : 4-axes is therefore understandable. Covalent union between the appropriate *ortho*-carbon atoms will, however, require an interatomic distance less than 1·78 A., namely, about 1·49 A. (the 1 : 1′-C–C distance in diphenyl). Now, the observed moment of *cis*-azobenzene is very largely a resultant of the two C $\rightarrow$ N moments, interacting at approximately 70°. A reduction of the 2 : 2′-C–C distance by 0·29 A. will tend to reduce this angle, and provided the magnitudes of the principle vectors and inter-atomic distances other than the 2 : 2′- are unaltered, to *raise* the molecular resultant moment. However, calculation shows that, from this cause, the moment of (V) should only be 103·3% of that of (II). In *fact* it is 130%, and we conclude therefore that polarisability and mesomeric, rather than geometric, factors are predominantly responsible for the point under discussion.

EXPERIMENTAL.

Apparatus.—The earlier measurements (*loc. cit.*) on *cis*- and *trans*-azobenzene were made on the resonance apparatus described by Le Fèvre and Russell (*Trans. Faraday Soc.*, 1947, **43**, 374). In Sydney, however, we have adopted, with satisfactory results, a further slight simplification (Fig. 2) of the elementary circuit arrangement mentioned in " Dipole Moments " (2nd Edition, Methuen, London, 1948, pp. 33 and 34). The chief modifications are that the valve, *V* (Radiotron 1F4, but others such as the Radiotron 33 or Osram KT2 or KT24 have been found to work equally well), the mounted quartz crystal section, *Q* (Frequency 1 mc.), the 0—10 milliammeter, *M*, and the coil, *I* (interchangeable plug-in type, for easy accommodation in C_x of liquids of different dielectric constants), are built on a 6″ × 5″ × 3″ ordinary radio chassis. At one end, battery connections are made by a multi-pin telephone plug, while from the other, shielded coaxial cables run in parallel to a Sayce–Briscoe cell, C_x (in an earthed thermostat), and to a standard variable Sullivan condenser, C_s (fitted with a slow-motion worm-drive which also serves as a revolution counting head). All other essential features remain as previously described (cf. *op. cit.*, Chapter II).

Materials.—*trans*-Azoxybenzene and benzocinnoline and its oxide were recrystallised from ethanol, and eventually had m. p.s 38—38·5°, 153—154°, and 139—139·5°, respectively. The literature values are 36° (Zinin, *J. pr. Chem.*, 1845, **36**, 99); 156° (Täuber, *Ber.*, 1891, **24**, 3085); 139° (Ullmann and Dieterle, *Ber.*, 1904, **37**, 24) or 152° (Täuber, *loc. cit.*), respectively. The 36° m. p. of azoxybenzene appears to have remained unquestioned for a century (see Beilstein, " Handbuch ", XVI, 621; XVI*, 376). Our specimen formed nearly colourless needles, in contrast with the " hellgelbe Nadeln " or the " farbloser Plättchen " (Knipscheer, *Rec. Trav. chim.*, 1903, **22**, 21) of the literature. We have therefore repeated the U.V. absorption spectrum and the dipole-moment determination recorded for this substance by Müller (*Annalen*, 1932, **493**, 166; Gehrckens and Müller, *loc. cit.*).

Absorption Spectra.—Since the U.V. spectra of most substituted azobenzenes (Cook, Jones, and Polya, *J.*, 1939, 1315) are characterised by two bands in the regions 3000—3600 A. (" *K* " bands, $\log_{10}\epsilon$ usually *ca.* 4) and 4400—4500 A. (" R " bands, $\log_{10}\epsilon$ usually between 2 and 3), and because the former are ascribed (*idem, ibid.*) to general conjugation between the -N=N- system and the Ar nuclei, it seemed possible that information relevant to the point raised above would be revealed by ascertaining the positions of the " *K* " bands in benzocinnoline and its oxide relatively to those in *cis*-azo- and -azoxy-benzene. Absorption spectra have been accordingly determined in ethyl alcohol, a Hilger medium spectrograph being used with a rotating sector photometer and condensed tungsten-steel spark (see Fig. 3). The appropriate comparisons can be readily made from the following table (which includes certain earlier observations) :

FIG. 2.

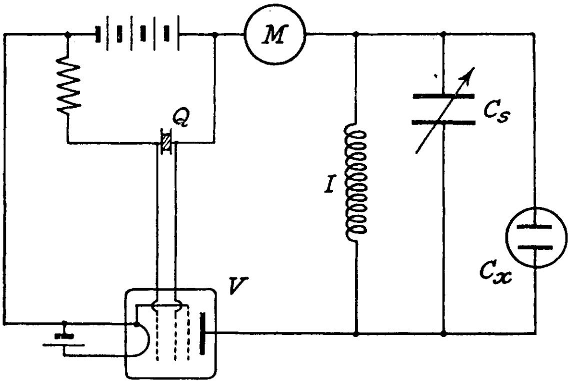
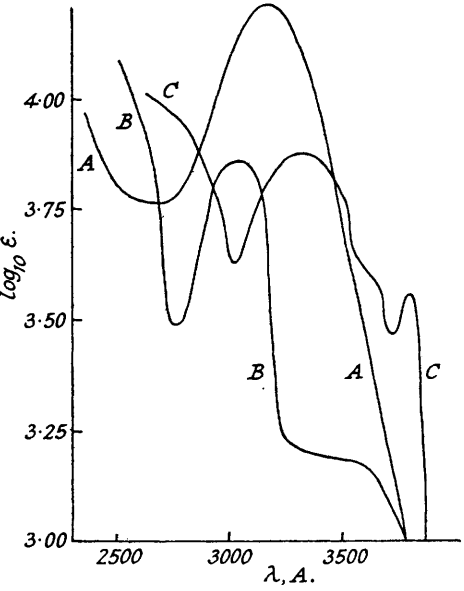


FIG. 3.



Curve A : trans-*Azoxybenzene.*
Curve B : *Benzocinnoline.*
Curve C : *Benzocinnoline oxide.*

Compound.	Solvent.	$\lambda_{max.}$.	$\log_{10}\epsilon$.	Ref.
Benzocinnoline	EtOH	3000	3·87	Present work
cis-Azobenzene	C_6H_6	*ca.* 3000	*ca.* 3·6	Le Fèvre and Vine (*J.*, 1938, 431)
,, ...	$CHCl_3$	3240	4·18	Cook, Jones, and Polya (*loc. cit.*)
,, ...	EtOH	3050	3·4—3·5	Winkel and Siebert (*Ber.*, 1941, **74**, 675)
Benzocinnoline oxide	EtOH	3320	3·86	Present work
cis-Azoxybenzene	EtOH	3350	(3·8—3·9) *	Müller (*loc. cit.*)
trans-Azobenzene	C_6H_6	3300	4·3	Le Fèvre and Vine (*loc. cit.*)
,, ...	$CHCl_3$	3190	4·29	Cook, Jones, and Polya (*loc. cit.*)
,, ...	EtOH	3200	4·2	Winkel and Siebert (*loc. cit.*)
trans-Azoxybenzene.........	EtOH	3200	4·22 *	Present work
,, ...	,,	3250	(not given)	Müller (*loc. cit.*)

* Müller does not record $\log_{10}\epsilon$ for either *cis*- or *trans*-azoxybenzene but states that the intensity of absorption of the first is approximately half that of the second. Since we find $\log_{10}\epsilon$ for the *trans*-form to be 4·22 we therefore quote 3·8—3·9 for the *cis*-isomer.

The covalent union of the *oo'*-atoms of *cis*-azobenzene is not therefore accompanied by the increases in wave-length and intensity of absorption to be expected if benzocinnoline is the more "conjugated" of the two molecules. *cis*-Azoxybenzene and benzocinnoline oxide similarly show practically no differences.

Incidentally, the above results do not confirm the statement that the absorption of azobenzene is nearly the same as liquid or vapour or solute in polar and non-polar solvents (Horio and Yamashita, *J. Soc. Chem. Ind. Japan*, 1934, **37**, 491; Uëmura and Inamura, *Bull. Chem. Soc. Japan*, 1935, **10**, 169).

Dielectric-polarisation Measurements.—These are set out under the customary headings (explained in *J.*, 1937, 1805). The solvent was " A.R." grade benzene purified by partial freezing, decantation, and drying over sodium wire, etc. (cf. *op. cit.*, p. 31).

100 w_1.	$\epsilon_{27°}$.	$d_{4°}^{27°}$.	$\alpha\epsilon_2$.	βd_2.	100 w_1.	$\epsilon_{27°}$.	$d_{4°}^{27°}$.	$\alpha\epsilon_2$.	βd_2.
0	2·2685	0·86934	—	—	0	2·2685	0·86934	—	—
				trans-*Azoxybenzene.*					
0·5036	2·2774	0·87041	1·75	0·212	2·0211	2·3032	0·87369	1·72	0·215
0·8678	2·2835	0·87129	1·72	0·225	2·6607	2·3212	0·87543	1·98	0·229
1·0830	2·2863	0·87177	1·64	0·224					
				Benzocinnoline.					
0·1656	2·2841	0·86976	9·34	0·278	0·7596	2·3493	0·87139	10·63	0·275
0·3645	2·3078	0·87033	10·77	0·283	1·1048	2·3831	0·87225	10·38	0·267
				Benzocinnoline oxide.					
0·2350	2·3034	0·87007	14·9	0·328	0·5608	2·3576	0·87113	15·9	0·326
0·3508	2·3255	0·87045	16·3	0·328	0·6526	2·3715	0·87137	15·8	0·317
0·4315	2·3356	0·87067	15·6	0·318	0·7348	2·3866	0·87163	16·1	0·317

Refractivities.—These have been measured (Abbé refractometer) in chlorobenzene :—

100 w_1.	$n_D^{25°}$.	$d_{4°}^{25°}$.	r_{12}, c.c.	r_1, c.c.	$[R_L]_D$, c.c.
0	1·5251	1·1015	0·2783	—	—
		trans-*Azoxybenzene.*			
4·6460	1·5331	1·1052	0·2809	0·3343	66·2
		Benzocinnoline.			
6·6640	1·5371	1·1081	0·2819	0·3323	65·1
		Benzocinnoline oxide.			
4·0946	1·5336	1·1063	0·2808	0·3394	66·2

Von Auwers (*Annalen*, 1932, **499**, 131), from observations on quinoline solutions, reported $[R_L]_D = 63·6$ and 61·2 c.c., respectively, for azoxybenzene and its " iso- "form.

Dipole Moments.—The requisite mean values from the above data are used in conjunction with the appropriate constants, namely, $p_2 = 0·34184$; $C = 0·18941$ (cf. *J.*, 1937, 1805) :

	Mean $\alpha\epsilon_2$.	Mean β.	P_T, c.c.	$[R_L]_D$.	μ, D.
trans-Azoxybenzene	1·76	0·252	116·6	66·2	1·57
Benzocinnoline	10·28	0·317	382·3	65·1	3·93
Benzocinnoline oxide..................	15·77	0·371	627·6	66·2	5·22

The moment now recorded for azoxybenzene is slightly lower than that given by Gehrckens and Müller (*loc. cit.*), who, however, were working at an unstated temperature.

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