

397. Indications of Geometrical Isomerism with 2 : 2'-Azopyridine.

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The one known form, m. p. 87°, of 2 : 2'-azopyridine has a dipole moment which is more consistent with a *trans*- than with a *cis*-configuration. Its absorption spectrum resembles those of non-heterocyclic azo-derivatives. Illumination by sunlight of solutions of azopyridine causes changes in their dielectric constants and spectra which recall those observed for azobenzene and suggest a partial development of the *cis*-isomer.

IN connection with other investigations of molecules containing $-N=N-$ (Calderbank, Le Fèvre, and Northcott, *Chem. and Ind.*, 1948, 158; Le Fèvre, Northcott, and Wilson, *ibid.*, p. 732; Le Fèvre and Northcott, *J.*, 1949, 333, 944; Le Fèvre and Wilson, *ibid.*, p. 1106; Le Fèvre and Souter, *ibid.*, p. 1595; Brown, Le Fèvre, and Whittam, *J.*, 1950, 185; Freeman and Le Fèvre, *J.*, 1951, 415) it seemed of interest to examine 2 : 2'-azopyridine, especially since this substance had been thought (Kirpal and Bohm, *Ber.*, 1932, 65, 680) to exist in two isomeric forms, m. p. 87° and 81°, until Kirpal and Bohm (*Ber.*, 1934, 67, 70) showed that the lower-melting variety was really a mixture of the known azopyridine, m. p. 87°, with its 5-chloro-derivative. This paper accordingly records observations made when the material of m. p. 87° was submitted to the tests previously applied to azobenzene (Hartley and Le Fèvre, *J.*, 1939, 531) and various other azo- or diazo-compounds (references above).

Azopyridine may be prepared either *via* a hypochlorite oxidation of 2-aminopyridine or by the reduction (arsenious oxide and sodium hydroxide) of 2-nitropyridine (cf. Kirpal and Bohm, *loc. cit.*), but to avoid the chlorination reaction just mentioned we decided to apply the second two-stage process to the 2-aminopyridine available. After crystallisation from light petroleum (b. p. 40—70°), 2 : 2'-azopyridine was obtained in 25% overall yield, as stout, deep red needles, m. p. 87° (in agreement with the literature). It was stored in a darkened desiccator. Solutions were made up by weight in brown bottles and handled as far as possible with exclusion of daylight; thermostat bath liquids were coloured a deep red.

Dipole-moment measurements were made, in benzene as solvent, by the following routine : densities and dielectric constants of a fresh solution were first observed ; then it was transferred to a clear glass flask and exposed to sunlight for about 1.5 hours, after which the same readings were retaken. Since changes might be in part due to loss of solvent during irradiation, each solution was finally kept in the dark for *ca.* 2 days before a third set of ϵ_{12} and d_{12} values were recorded. Details of apparatus, procedures, etc., have been given before (*J.*, 1948, 1949; 1949, 333; for symbols, see *Trans. Faraday Soc.*, 1950, 46, 1). Experiments were performed at different seasons; during the summer, working temperatures of 30° were necessary. Our results are summarised in Table I.

It is seen that the more dilute the solution the more illumination causes change of dielectric constant, as shown by $(\epsilon_{12} - \epsilon_2)/w_1 = \alpha\epsilon_2$. This is compatible with a greater absorption of the active wave-lengths by the outer layers of stronger compared with weaker solutions. Evidently, equilibrium conditions were not attained during the exposures given. To check the point, the solution of $100w_1 = 0.81794$ was examined periodically during a total irradiation of 5 hours by bright sunlight :

Time (mins.)	0	40	120	180	300
$\alpha\epsilon_2$	2.24	3.00	3.44	4.00	4.60

The final $\alpha\epsilon_2$ value nevertheless fell to 2.54 after several days' storage of the solution in the dark. The apparent dipole moments deducible from these results are set out in Table II.

Using the Beckman photoelectric spectrophotometer, Model D.U., we repeatedly determined the absorptions of 2 : 2'-azopyridine in absolute alcohol, before and after exposure to sunlight. The figure shows a typical example, curve *a* being changed to curve *b* by 2 hours' illumination. A parallel set of observations in *cyclohexane* gives similar results (see p. 1817). In both solvents

TABLE I.

2 : 2'-Azopyridine in benzene.

$100w_1$.	ϵ^{25} .	d_4^{25} .	$\alpha\epsilon_2$.	βd_2 .	$100w_1$.	ϵ^{25} .	d_4^{25} .	$\alpha\epsilon_2$.	βd_2 .
0	2.2725	0.87378	—	—					
Solutions before exposure.					Solutions immediately after exposure.				
0.55181	2.2852	0.87527	2.30	0.270	0.55181	2.2944	*	3.97	*
0.72095	2.2892	0.87572	2.32	0.269	0.72095	2.2989	*	3.66	*
0.81794	2.2908	0.87596	2.24	0.266	0.81794	2.2996	*	3.31	*
1.0942	2.2978	0.87680	2.31	0.276	1.0942	2.3076	*	3.21	*
Exposed solutions after 2 days' storage in dark.									
0.55181	2.2838	*	2.05	*	0.81794	2.2933	*	2.54	*
0.72095	2.2884	*	2.21	*	1.0942	2.2993	*	2.44	*
$100w_1$.	ϵ^{30} .	d_4^{30} .	$\alpha\epsilon_2$.	βd_2 .	$100w_1$.	ϵ^{30} .	d_4^{30} .	$\alpha\epsilon_2$.	βd_2 .
0	2.2628	0.86718	—	—					
Solutions before exposure.					Solutions immediately after exposure.				
1.3189	2.2922	0.87058	2.23	0.258	1.3189	2.3019	*	2.96	*
1.6537	2.3000	0.87148	2.25	0.260	1.6537	2.3075	*	2.70	*
2.0323	2.3083	0.87248	2.24	0.261	2.0323	2.3145	*	2.54	*
Exposed solutions after storage in the dark.									
1.6537	2.3031	*	2.54	*	1.20323	2.3090	*	2.27	*

* No significant changes from values for unexposed initial solutions.

TABLE II.

	Temp.	αE_2 .	βd_2 .	∞P_T , c.c.	${}_D P$, c.c.	μ , D.
Before exposure	25°	2.29	0.270	122.7	55 *	1.8
	30°	2.24	0.260	122.6	55	1.8
After exposure	25°	up to 4.6	0.27	up to 203	55	up to 2.7

* From following $[R_L]_D$ values: $C_5H_5N = 24.1$; $H = 1.1$, azo-group = 9 c.c. approx. (*cf. J.*, 1949, 2082).

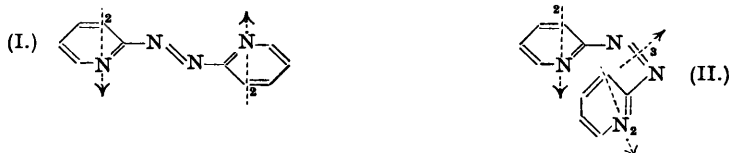
a slow reversion occurs on storage in the dark, the alcoholic solutions after 2 days at room temperatures showing a 30% return, whilst those in *cyclohexane*, when kept at 40° for the same time, appeared to have recovered by *ca.* 80%.

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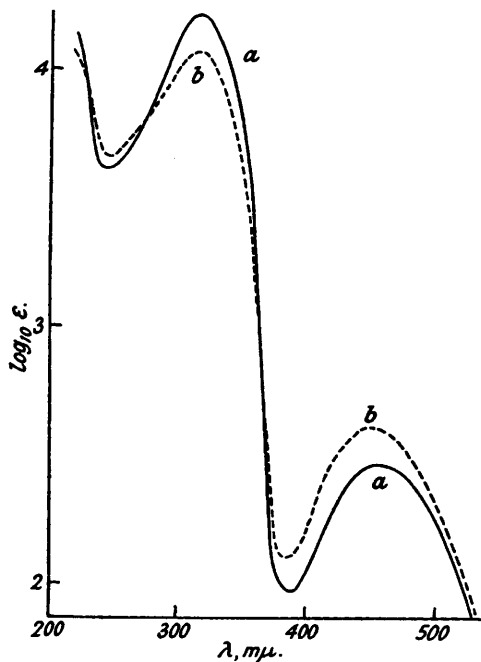
DISCUSSION.—Qualitatively the above facts are reminiscent of those known for azobenzene ; their quantitative interpretation is less straightforward because the pyridyl radicals themselves each add an extra component moment to the molecular resultants of *cis*- or *trans*-2 : 2'-azopyridine. However, we may note that Rau and Narayanaswamy (*Z. physikal. Chem.*, 1934, B, 26, 23) were able to make reasonably correct forecasts of the moments of a number of pyridine derivatives by assuming that the parent skeleton contributes a component of about 2.2 D. acting as though directed from the β -carbon to the nitrogen atom (with the negative pole towards the latter). Such a view is actually in better agreement with measurements on *o*-phenanthroline than that adopted by Fielding and Le Fèvre (preceding paper).

Accordingly, remembering that the moment of *cis*-azobenzene is 3 D. (Hartley and Le Fèvre, *loc. cit.*), we may roughly predict the polarity ranges for the azopyridines from the figures shown on (I) and (II) as :

trans-forms, from ca. 0 to ca. 4 D. ; *cis*-forms, from ca. 1 to ca. 5 D.



However the small moment of 2 : 2'-dipyridyl (Fielding and Le Fèvre, *loc. cit.*) obviously indicates a preferred *trans*-disposition of the rotatable "pyridyl" moments in this particular molecule, and it is not unreasonable therefore to expect a similar tendency in (I) and (II), and to



2 : 2'-Azopyridine in alcohol :
(a) Before exposure. (b) After exposure.

expect that the measured resultant of *trans*-2 : 2'-azopyridine would probably be smaller than that of the corresponding *cis*-variety. The raising of the apparent moment of azopyridine by the action of daylight, and its subsequent diminution in darkness, would then be explicable, harmoniously with many other azo-compounds, as due to a partial *trans*- to *cis*-inversion and retroversion, respectively, about the $-\text{N}=\text{N}-$ group.

The spectra now recorded are also reconcilable with the process just indicated. The figure shows that the azopyridine of m. p. 87° absorbs between 2500 and 5000 Å. at two points, the

intensities of which are affected more than the wave-lengths by illumination. The same phenomena occur with *trans*-azobenzene of m. p. 68° (as well as with other azo-compounds, e.g., diazocyanides and diazosulphonates, not so directly related to azopyridine; cf. references cited on p. 1814) where the spectral changes may be recognised as a modification towards the extreme result obtained with the pure isomer of m. p. 71° (see Table III), from which we draw the conclusions set out in the summary.

TABLE III.

	Solvent.	$\lambda_{\max.}$, m μ .	$\log_{10} \epsilon_{\max.}$	$\lambda_{\max.}$, m μ .	$\log_{10} \epsilon_{\max.}$
Azopyridine (before exposure)	EtOH	317	4.22	460	2.47
Azopyridine (after exposure)	EtOH	317	4.06	450	2.62
Azopyridine (before exposure)	C ₆ H ₁₂	307	4.18	470	2.33
Azopyridine (after exposure)	C ₆ H ₁₂	307	4.09	460	2.48
Azobenzene, m. p. 68° (<i>trans</i> -) ¹	EtOH	320	4.2	450	2.5
Azobenzene, m. p. 71° (<i>cis</i> -) ¹	EtOH	305	3.4—3.5	440	3.2
4-Chlorobenzenediazocyanide (stable form) ² ...	Et ₂ O	338	4.29	438	2.48
Ditto (unstable form) ²	Et ₂ O	330	4.12	432	3.07
Potassium 2-chlorobenzenediazosulphonate (stable form) ³	H ₂ O	292	3.8	428	2.3
Ditto (after irradiation) ³	H ₂ O	ca. 290	ca. 3.7	Not recorded	
Ditto (unstable form) ³	H ₂ O	300	3.2	448	2.3

¹ Cf. *Ber.*, 1941, 74, 675. ² Cf. *J.*, 1949, 1106. ³ Cf. *J.*, 1951, 415.

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