641. *Tautomerism and Geometrical Isomerism of Arylazo-phenols and -naphthols. Part I. 4-Phenylazo-1-naphthol.*

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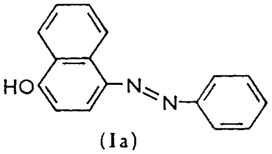
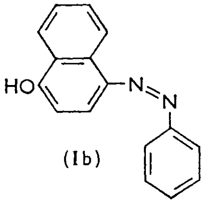
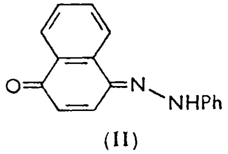
4-Phenylazo-1-naphthol (I) exists in solution as an equilibrium mixture with its tautomer, α-naphthaquinone phenylhydrazone (II). On cooling, this equilibrium shifts towards the latter (in methylcyclohexane) or towards the former (in alcohol). The alcoholic solution at −140° contains practically only the former (I), which on irradiation with light at various wavelengths is photoequilibrated with its *cis*-isomer, in analogy with other azo-compounds. Between −135° and −90° the unstable *cis*-isomer is thermally converted into the stable *trans*-isomer *via* the phenylhydrazone. Each step has an activation energy of about 11 kcal./mole, as compared with about 23 kcal./mole for the normal *cis* ⟶ *trans* conversion. No direct photoconversion involving the hydrazone seems to take place. Similar results were obtained with solutions in tetrahydrofuran–methyltetrahydrofuran.

KUHN and BAER [1] were the first to point out that 4-phenylazo-1-naphthol (I) exists in solution as a tautomeric equilibrium mixture with the phenylhydrazone (II). Their results were confirmed and extended by several authors.[2]

One would expect tautomer (I) to exist in a *cis*- and a *trans*-form (Ia and b) in analogy with azobenzene,[3] the azonaphthalenes,[4] and 4-hydroxyazobenzene,[5,6] but attempts to achieve such isomerisations have hitherto been unsuccessful.[7]


(Ia)


(Ib)


(II)

The present investigation,* by the low-temperature technique,[8,9] was undertaken in order to find evidence for any photoisomerisations and thermal isomerisations (Ia) $\rightleftarrows$ (Ib), and to show if and how such isomerisations are affected by the tautomerism (I) $\rightleftarrows$ (II). The latter point is of particular interest because one can envisage a thermal *cis* ⟶ *trans* isomerisation with the hydrazone as intermediate, *viz.*, (Ib) ⟶ (II) ⟶ (Ia). Such a route may be energetically " cheaper " than the direct route (Ib) ⟶ (Ia).

Spectra in Various Solvents, at Different Temperatures.—Results of such measurements are given in Fig. 1*A*, *B*, *D*. If, with previous authors, we assign the absorption band around 400 mμ to the *trans*-azo-isomer (Ia) and the band around 480 mμ to the hydrazone (II), these results confirm the effect of the solvent on the equilibrium (I) $\rightleftarrows$ (II) reported by Burawoy and Thompson.[10] In addition, they show that cooling has little effect on this equilibrium in toluene or tetrahydrofuran, but shifts it strongly in favour of the hydrazone in methylcyclohexane (Fig. 1*B*), and in favour of the azo-compound in ethanol–methanol

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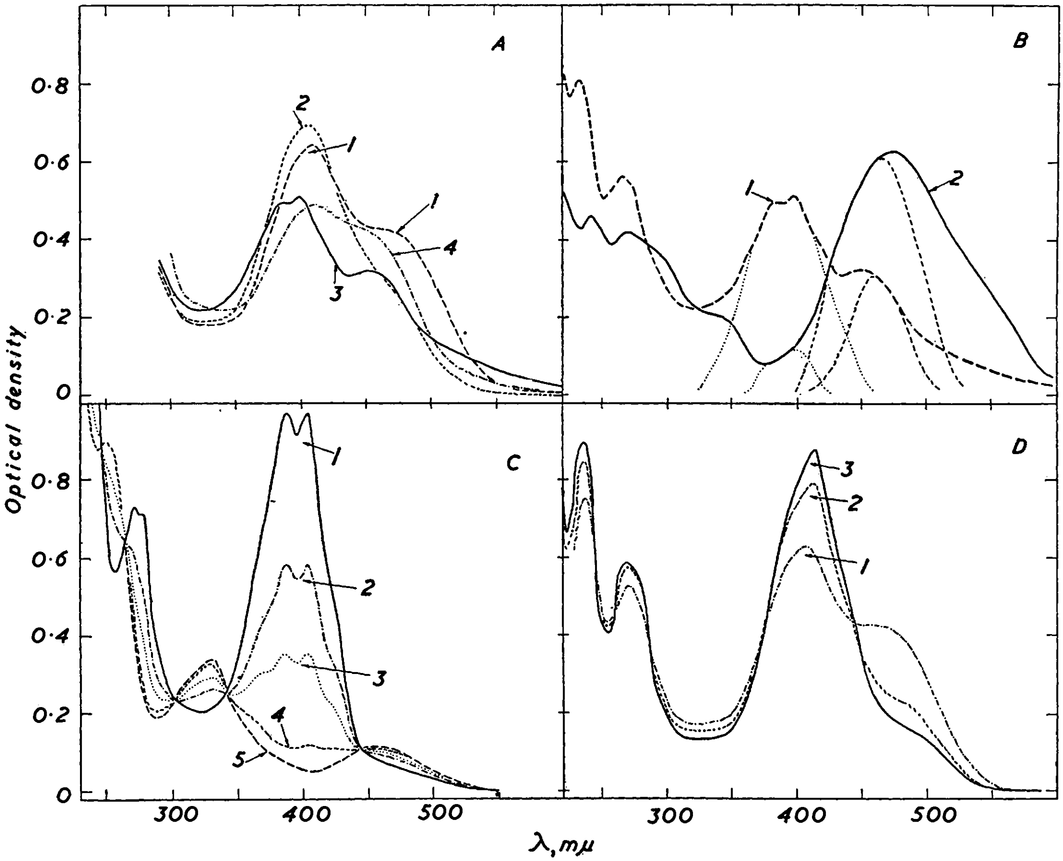
* For a preliminary account see *Bull. Res. Council Israel*, 1958, **7**, *A*, 227.

[1] Kuhn and Baer, *Annalen*, 1935, **516**, 143.
[2] Sawicki, *J. Org. Chem.*, 1957, **22**, 743, where earlier references are listed.
[3] Hartley, *J.*, 1938, 633.
[4] Fischer, Frankel, and Wolovski, *J. Chem. Phys.*, 1955, **23**, 1367.
[5] Schulte–Frohlinde, *Annalen*, 1958, **612**, 138.
[6] Unpublished work.
[7] Brode, Gould, and Wyman, *J. Amer. Chem. Soc.*, 1952, **74**, 4647.
[8] Hirshberg and Fischer, *J.*, 1954, 297.
[9] *Idem, Rev. Sci. Instr.*, 1959, **30**, 197.
[10] Burawoy and Thompson, *J.*, 1953, 1443.

(Fig. 1*D*). The results obtained with the solution in methylcyclohexane, a non-polar solvent, probably indicate a genuine temperature-dependence of the equilibrium (I) $\rightleftharpoons$ (II) and can therefore be used to compute the enthalpy difference between the two tautomers by application of the van't Hoff isochore. Such a computation, the ratio of the absorption bands at 400 and 470 mμ (indicated by thin lines in Fig. 1*B*) being assumed to be proportional to the ratio (I) : (II), gives 2 ± 0·2 kcal./mole for ΔH in (I) $\longrightarrow$ (II) + ΔH, and appears to be the first value reported for this reaction.

FIG. 1. (*A*) *Solutions of* (I) *at room temperature.* 10 *mg./l. in* (1) *ethanol,* (2) *tetrahydro-*2*-methylfuran, and* (4) *toluene,* (3) *about* 8 *mg./l. in methylcyclohexane* (*saturated solution*).



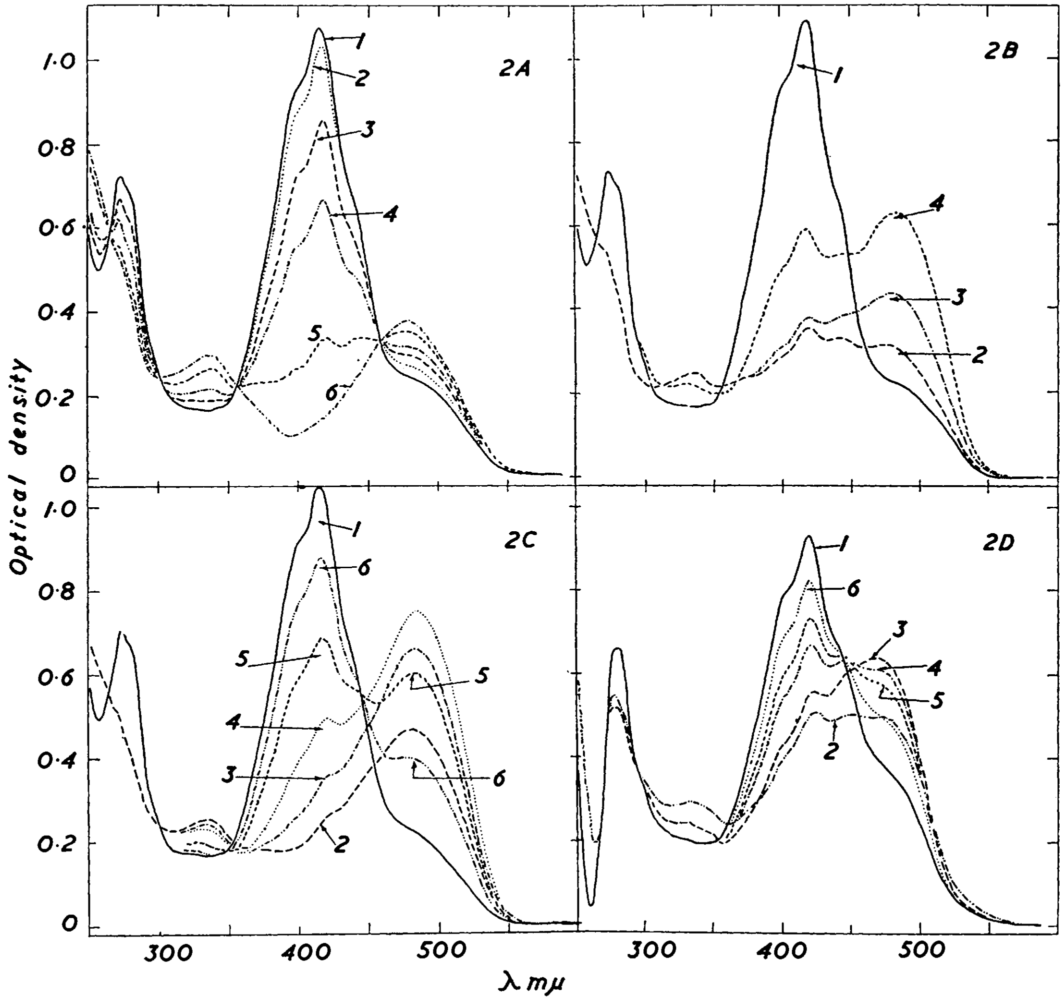
(*B*) (1) *As A*(3) *above;* (2) *cooled to* −90°. *Heavy curves depict experimental absorption spectra; thin lines indicate the absorption bands characterising the azo-compound* (*I*) *and the phenylhydrazone* (II), *submerged in the experimental curves.*

(*C*) *Solution* (11·7 *mg./l.*) *of the* O*-methyl ether in methylcyclohexane at* −18°: (1) *before irradiation;* (2), (3), (4) *after photoequilibration at* 436, 365, 405 *mμ;* (5) " cis " *computed from* (4) *and* (1), *on the assumption that the* cis*-isomer has no absorption at* 402 *mμ.*

(*D*) *Solution of* (I) (10·2 *mg./l.*) *in ethanol–methanol* (7 : 3) *at various temperatures.* (1) + 20°; (2) −67°; (3) −120°. *The spectrum at* −140° *is practically identical with* (3). *Curves* (2) *and* (3) *are corrected for the thermal contraction at the respective temperatures.*

The temperature-dependence of the spectrum in alcoholic solution (Fig. 1*D*) is probably due to a combination of effects, including the large change in dielectric constant and solute–solvent hydrogen-bonding on cooling. Cooling below −130° causes no further change in the spectrum of the alcoholic solutions, either because tautomerism is no longer possible at lower temperatures, or because it is virtually complete [in favour of (Ia)] at −130°. As will be shown below, both reasons appear to be correct. In this connection it should be mentioned that the *O*-methyl derivative of the azo-compound (I) has also a submerged absorption band at about 480 mμ (Fig. 1*C*, curve 1).

FIG. 2. (*A*) *Solution of* (I) 10·2 *mg./l.) in ethanol–methanol* (7 : 3). (1) *At* −140°; (2), (3), (4), (5) *after photoequilibration at* 546, 365, 436, 405 *mμ, respectively*; (6) "cis" *isomer, computed by assuming arbitrarily that curve* (5) *represents* 80% *of* cis-*compound.*



(*B*) (1) *As in A*(1); (2) *after photoequilibration at* 405 *mμ*; (3) *after heating to* −118°; (4) *after* 110 *min. at* −118°.

(*C*) (1) *As in A*(1), *at* −120°; (2) *after* 30 *min. irradiation at* 405 *mμ*; (3), (4) *after* 95 *and* 260 *min., respectively*; (5) *solution heated to* −110° *and kept at this temperature for* 45 *min.*; (6) *same, after another* 50 *min.*

(*D*) *Solution of* (I) (10·3 *mg./l.) in tetrahydrofuran–tetrahydro-*2*-methylfuran* (1 : 1). (1) *At* −135°, *also at* −155°; (2) *after irradiation for* 10 *min. at* 405 *mμ*, −155°; (3) *after* 30 *minutes' irradiation with* 405 + 436 *mμ at* −135°; (4), (5), (6) *solution* (3) *after* 5, 10, *and* 20 *min., respectively.*

At room temperature ethanolic solutions were found to obey Beer's law at concentrations varying from 6×10^{-4} to $1{\cdot}5 \times 10^{-5}$ moles/l.

Irradiations.—Owing to the low solubility of the azo-compound (I) in methylcyclohexane, the solution of Fig. 1*B* is supersaturated, and irradiation results in crystallisation.

Irradiation of alcoholic solutions at temperatures down to −80° has no effect. At −140°, however, irradiation causes a typical *cis* $\rightleftarrows$ *trans* photoequilibration,[4] with a different photoequilibrium established at each wavelength (Fig. 2*A*). No thermal changes occur at this temperature. The results are closely similar to those obtained with the *O*-methyl ether of the azo-compound (I) at −18°, shown in Fig. 1*C*, and with other azo-compounds.[11] The existence of four well-defined isosbestic points corroborates the above assumption that at −140° the conversion of the hydrazone into the azo-compound is virtually complete, and the curves of Fig. 2*A* describe mixtures, in various proportions, of the *cis*- and *trans*-forms (Ia and b).

When the solution giving Fig. 2*A*, curve 5, is allowed carefully to warm to −120° (Fig. 2*B*) and kept at this temperature, the "*trans*"-band at 416 mμ at first remains almost constant, whereas the "hydrazone" band at 482 mμ is enhanced progressively (curves 3, 4 in Fig. 2*B*). Later, the 416 mμ band gradually increases in intensity too. Warming to −80° results in rapid regeneration of the original spectrum. These results indicate that the *cis*-isomer formed by irradiation at −140°, when warmed to −120°, is converted into the phenylhydrazone (II), the latter then being transformed into the *trans*-isomer. The non-existence of isosbestic points in Fig. 2*B* indicates the presence of a triple mixture of (Ia), (Ib), and (II).

Fig. 2*C* shows the results of irradiation at −120°. Curve 2, taken after cessation of irradiation, indicates that some phenylhydrazone (II) has already been formed during irradiation, as is to be expected from Fig. 2*B*. Formation of the hydrazone continues (curves 3, 4), but is soon counter-balanced by the concurrent conversion of this compound into the *trans*-azo-form (Ia) (curve 5). Curve 6 shows how the original spectrum is eventually approached. The existence of isosbestic points at 445 and 350 mμ during the later stages (curves 4, 5, 6) indicates that by then only two compounds exist in solution, namely (II) and (Ia).

Irradiation at −110° results in a mixture already rich in the hydrazone. At this temperature, conversion of the *cis*-isomer into the hydrazone is already much faster than the conversion of the latter into the *trans*-isomer.

Cooling, to −140°, of any of the mixtures depicted by the curves in Figs. 2*B* and 2*C* stops any further spontaneous reaction, indicating that both thermal steps, (Ib) ⟶ (II), and (II) ⟶ (Ia), do not take place any more at this temperature. If the solution giving Fig. 2*C*, curve 5 [constituting a mixture of (II) and (Ia)], is cooled to −140° and irradiated with light at 546 mμ, the spectrum is not affected. This proves that photoisomerisation (II) ⟶ (I) also does not take place at this temperature. Together with the results of Fig. 2*A* this makes it probable that the only photoconversion taking place at −140°, as well as at higher temperatures, is (Ia) $\rightleftarrows$ (Ib).

In order to find out whether or not the above phenomena are peculiar to solutions in a hydroxylic solvent, similar experiments were carried out in a mixture of tetrahydrofuran and its 2-methyl derivative. Fig. 2*D* shows that, qualitatively, the results in this solvent resemble those obtained with alcoholic solutions. However, in order to stop all thermal reactions, it is necessary to go down to at least −155°. At this temperature the solvent mixture tends to crystallise, whereas at −150° thermal isomerisations already set in. It was therefore experimentally impossible to do more than establish the basic similarity between the phenomena in hydroxylic and non-hydroxylic polar solvents.

The spectral data for the azo-compound and its *O*-methyl ether are summarised in the Table.

Kinetic Experiments.—The kinetics of the *cis* ⟶ *trans* thermal conversion of the *O*-methyl ether was investigated in methylcyclohexane in the temperature range 27·5° ($\tau_{\frac{1}{2}}$ = 25 min.) to 70° ($\tau_{\frac{1}{2}}$ = 0·25 min.). The conversion was found to be a first-order reaction, with Arrhenius constants $A = 10^{13 \cdot 3}$ sec.$^{-1}$, $E = 22{\cdot}9$ kcal./mole in $k = A\mathrm{e}^{-E/RT}$. These values closely resemble those reported for other arylazo-compounds. *E.g.*, Halpern

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[11] Fischer and Frei, *J. Chem. Phys.*, 1957, **27**, 328.

Spectral data for 4-*phenylazo*-1-*naphthol* (I) *in ethanol–methanol, and its* O-*methyl ether in methylcyclohexane.*

	Maxima		Isosbestic points	
	λ (mμ)	$10^{-3}\varepsilon$	λ (mμ)	$10^{-3}\varepsilon$
trans-(I) at −140°	470 *	4·8	*cis-trans*	
	416	21·0	457	6·5
	272	14·5	355	4·4
cis-(I) at −140°			301	4·8
	477	7·5	265	11·7
	336	5·9		
(II), calc. from Fig. 2*C* †	483	*ca.* 22	hydrazone-*trans* (I)	
	335	*ca.* 5	445	11·3
	245 *	—	*ca.* 350	*ca.* 3·9
O-Me ether of (I) at −18°	402	20·7	*cis-trans*	
	386		443	2·3
trans	276	15·0	340	5·4
	268		302	5·0
	236	25·0	263	13·7
cis	453	2·4	244	19·0
	329	7·0	232	23·6

* Inflexion. † Curve 5 in Fig. 2*C* is assumed to correspond to a mixture of (II) (40%) and *trans*-(I) (60%).

et al.[12] found for azobenzene in a large variety of solvents E between 22·8 and 24·7 kcal./mole and log A between 12·9 and 13·7.

For the azo-compound (I) in alcoholic solution it proved possible, by careful manipulation of the temperature, to differentiate to a considerable extent between the two consecutive steps (Ib) ⟶ (II) and (II) ⟶ (Ia), and to measure their kinetics separately. Both steps were found to be of the first order with regard to the compound being transformed, with estimated Arrhenius constants $A = \sim 10^{13\cdot5}$ sec.$^{-1}$, $E = 12$ kcal./mole for the first step, and $A = 10^{11}$ sec.$^{-1}$, $E = 11$ kcal./mole for the second. The following values of half-life times give an idea of the measurements involved. Step one: at −124°, 493 min.; at −110°, 15 min. Step two: at −110°, 55 min.; at −85°, 0·9 min.

With solutions of the azo-compound (I) in tetrahydrofuran–methyltetrahydrofuran, no quantitative kinetic measurements could be made, beyond those indicated in Fig. 2*D*.

Conclusions.—The above results strongly indicate that with 4-phenylazo-1-naphthol the *cis* ⟶ *trans* conversion proceeds *via* the phenylhydrazone, and that this two-step low-energy mechanism is preferred to the one-step high-energy mechanism operative in other azo-compounds. A similar mechanism may be operative in other hydroxyazo-compounds and aminoazo-compounds.

EXPERIMENTAL

Irradiations and spectrophotometric determinations were carried out in special Dewar-type cells, in a Cary Model 14 Recording Spectrophotometer.[9] The irradiation source was a 125 w Mazda type MB/U mercury lamp (with its envelope removed) housed in an elliptic reflector. The mercury lines were isolated by combinations of Corning filters (578, 546, 436, 365 mμ) or interference filters (405, 300 + 313 mμ). The concentrations given in the Figures are at room temperature, uncorrected for contraction on cooling, unless stated otherwise. Photoequilibrations required 10—100 min., depending on the wavelength of the photoactive light.

4-Phenylazo-1-naphthol was prepared according to Witt and Dedichen's directions,[13] its *O*-methyl ether according to those of Zincke and Bindewald.[14]

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[12] Halpern, Brady, and Winkler, *Canad. J. Res.*, 1950, **28**, 140.

[13] Witt and Dedichen, *Ber.*, 1897, **30**, 2655.

[14] Zincke and Bindewald, *Ber.*, 1884, **17**, 3026.