Geometrical Isomerism of the Azonaphthalenes.

By MAX FRANKEL, REUVEN WOLOVSKY, and ERNST FISCHER.

[Reprint Order No. 6321.]

cis-2 : 2′- and *cis*-1 : 2′-Azonaphthalene have been prepared by irradiation of the solutions of the corresponding *trans*-isomers with ultraviolet light, isolated by chromatography on alumina at low temperature, and characterized by their absorption spectra; *cis*-1 : 1′-azonaphthalene has been similarly prepared and characterized in solution containing up to 60% of *cis*-isomer : it was not isolated. The dipole moments of *cis*-2 : 2′- and of *trans*-2 : 2′- and *trans*-1 : 1′-azonaphthalene were determined.

THE formation of *cis*-azobenzene during irradiation of solutions of the *trans*-isomer was first reported by Hartley (*Nature*, 1937, **140**, 281). Later (Hartley, *J.*, 1938, 633; Cook, *J.*, 1938, 876; Cook, Jones, and Polya, *J.*, 1939, 1315; Hartley and Le Fèvre, *J.*, 1939, 531), the isolation and the properties of this isomer were described in detail. (For a survey see Campbell, Henderson, and Taylor, *J.*, 1953, 1281.) Attempts to isolate the *cis*-isomers of the azonaphthalenes seem, however, to have failed hitherto (Cook and Jones, *J.*, 1939, 1311; Brode, Gould, and Wyman, *J. Amer. Chem. Soc.*, 1952, **74**, 4645).

The present paper describes the preparation and characteristic properties of *cis*-1 : 1′-, *cis*-2 : 2′-, and *cis*-1 : 2′-azonaphthalene, the isolation of the last two by adsorption on alumina at low temperature, and the separation of *cis*- and *trans*-2 : 2′-azonaphthalene by chromatography on paper.

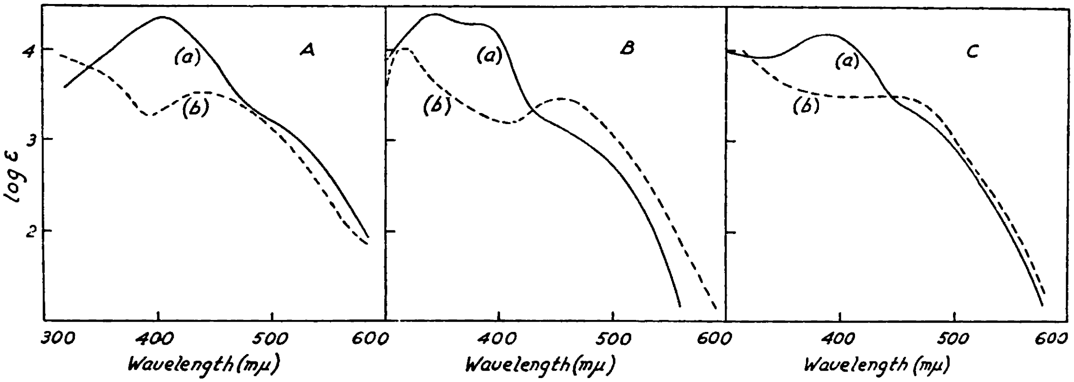
Preliminary spectrophotometric experiments showed that at room temperature the effect of ultraviolet irradiation on solutions of the three ordinary azonaphthalenes is extremely short-lived, and that a rapid thermal reversion to the original form takes place. When irradiation and spectrophotometric measurements were carried out at —25°, pronounced changes of the visible and near ultraviolet absorption spectrum were observed which were reversed at rates depending on the temperature, the solutions finally exhibiting absorption spectra identical with those observed before irradiation. The reversions proved to be first-order reactions, with the half-life times $\tau_{1/2}$, and the critical increments E_A in toluene given in the Table.

Azonaphthalene	Temp.	$\tau_{1/2}$ (min.)	Temp.	$\tau_{1/2}$ (min.)	E_A, kcal. mole^{-1}
1 : 1′-	0°	173	12·5°	29·5	22 ± 2
2 : 2′- *	29·0	150	47·0	19	22 ± 2
1 : 2′-	18·5	104	45·0	5	21 ± 2

* In chloroform at 41° $\tau_{1/2}$ = 12 min.

These figures may be compared with Hartley's results (*J.*, 1938, 638) for the thermal *cis* ⟶ *trans*-conversion of azobenzene in benzene, as follows: $\tau_{1/2}$ at 56·5° = 150 min. and at 76·6° = 21 min., E_A = 23 kcal. mole.

On the strength of the above results, all the operations in the experiments undertaken to isolate the *cis*-isomers of 2 : 2′- and of 1 : 2′- azonaphthalenes were carried out at 0° in a dimly lit room. Toluene or chloroform solutions of the two compounds were irradiated and then passed through a column packed with activated alumina. Subsequent development with the same solvent produced in each of these cases two separate zones. The lower zones were washed through the column, and the upper zones eluted with the solvent containing about 1% of methanol. Evaporation of the two solutions thus obtained from each of these azonaphthalenes and subsequent drying in a high vacuum produced two compounds in each case; with 2 : 2′-azonaphthalene the orange compound (*a*) derived from the lower zone had a m. p. of 209°. The reddish compound (*b*) derived from the upper zone, upon being heated in the normal procedure in a m. p. apparatus, changed colour from reddish to orange before melting and finally melted at 209°. If (*b*) was placed in the m. p. apparatus preheated to a temperature not far below the m. p. of (*a*), besides the change of colour, liquefaction followed by immediate solidification occurred, before the m. p. of 209° was reached. On resolidification, the substance showed no m. p. depression when mixed with a sample of (*a*).



[Absorption spectra in toluene :

A, 1 : 1′-Azonaphthalene at −25°
B, 2 : 2′-Azonaphthalene at + 8° } (*a*) = *trans*-, ————
C, 1 : 2′-Azonaphthalene at −25° } (*b*) = *cis*-, – – – – –

	A (*a*)	*A* (*b*)	*B* (*a*)	*B* (*b*)	*C* (*a*)	*C* (*b*)
Max.	405 mμ (log ε 4·33)	440 mμ (log ε 3·5)	345 mμ (log ε 4·37)	315 mμ (log ε 4·0) 450 mμ (log ε 3·45)	385 mμ (log ε 4·2)	310 mμ (log ε 4·0)
Inflexion......	*ca.* 500 mμ (log ε *ca.* 3·2)	*ca.* 350 mμ (log ε *ca.* 3·7)	*ca.* 385 mμ (log ε *ca.* 4·25) *ca.* 460 mμ (log ε *ca.* 3·1)		*ca.* 460 mμ (log ε *ca.* 3·3)	*ca.* 420 mμ (log ε *ca.* 3·5)

A similar phenomenon was observed with 1 : 2′-azonaphthalene : The red compound (*a*) derived from the lower zone, when heated slowly, melted at 144—145°. The orange-red compound (*b*) derived from the upper zone, upon being heated in the m. p. apparatus, became red before melting at 144—145°. On introduction of (*b*) into the preheated m. p. apparatus, besides the change in colour, a momentary liquefaction and resolidification was observed and finally melting occurred at 144—145°. Again, no m. p. depression was observed with mixtures of resolidified samples of (*a*) and (*b*).

It appears that in both cases, on heating, a conversion of the *cis*-form (*b*) into the *trans*-form (*a*) takes place.

The Figure shows the absorption spectra of the *cis*- and *trans*-isomers of 1 : 1′-, 1 : 2′-, and 2 : 2′-azonaphthalene. In general, the type of the curves for the *cis*- and *trans*-forms agree with those found in other cases of *cis*- and *trans*-isomers of similar azo-compounds.

The dipole moments of the two isomers of 2 : 2′-azonaphthalene were zero for (*a*) in toluene at 30°, and 3·0 ± 0·1 D for (*b*) in toluene at 0°, in agreement with the *trans*- and *cis*-configuration assigned to them. Hartley and Le Fèvre (*J.*, 1939, 531) report for the *trans*- and *cis*-isomers of azobenzene in benzene zero and 3D, respectively.

The data for 1 : 1′-azonaphthalene in the Table indicate that isolation of the *cis*-isomer might be possible in this case only by working at temperatures considerably below 0°. The following procedure was adopted in order to calculate the approximate absorption spectrum of the *cis*-isomer.

The dielectric constant increment $(\delta\varepsilon)_a = \varepsilon_{\text{solution}} - \varepsilon_{\text{solvent}}$ of a toluene solution of the (assumed) *trans*-isomer leads to a molar polarisation at infinite dilution of the solute, $({}_{\infty}P_2)_{trans}$, corresponding to zero moment. Irradiation (to completion) of the solution at −25° causes a further increment $(\delta\varepsilon)_b$. From the combined increments $(\delta\varepsilon)_a + (\delta\varepsilon)_b$ the polarisation at infinite dilution of the (assumed) mixture of *cis*- and *trans*-isomers, ${}_{\infty}P_2$, is derived. The fraction of *cis*-isomer will then be given by:

$$[{}_{\infty}P_2 - ({}_{\infty}P_2)_{trans}]/[({}_{\infty}P_2)_{cis} - ({}_{\infty}P_2)_{trans}].$$

It being assumed that $({}_{\infty}P_2)_{cis}$ equals the polarisation observed for the pure *cis*-isomer of 2 : 2′-azonaphthalene, insertion of experimental figures leads to a fraction of 0·60 ± 0·05 of *cis*-isomer in the above conditions. The absorption curve (*b*) of the pure *cis*-isomer (*A* in Fig.) was reconstructed from the curves found for the pure *trans*-isomer before and after irradiation at −25°, assuming that 60% of the *trans*- is converted into *cis*-isomer.

A paper-chromatographic technique analogous to that described for azobenzene (Frankel and Wolovsky, *Experientia*, 1954, **10**, 356) was used as an auxiliary method for the micro-separation and estimation of the two isomers of 2 : 2′-azonaphthalene.

Results of irradiation of azobenzene and the three azonaphthalenes at wavelengths other than 365 mμ will be reported separately.

EXPERIMENTAL

All work with solutions was carried out in a dimly lit room at 0°. M. p.s were determined in a Fisher–Johns apparatus.

Preparation of Azonaphthalenes.—1 : 1′-Azonaphthalene, prepared from 1-naphthylamine (Friedlaender, " Fortschritte der Theerfarbenfabrikation und verwandter Industriezweige," 1899, **4**, 1016; Nietzki and Goll, *Ber.*, 1885, **18**, 297, 3252) and recrystallised from xylene and from dioxan, had m. p. 190°. 2 : 2′-Azonaphthalene, prepared from 2-naphthylamine according to Friedlaender (*loc. cit.*) and recrystallised from toluene, had m. p. 209°. 1 : 2′-Azonaphthalene was prepared from 4-amino-1 : 2′-azonaphthalene (Nietzki and Goettig, *Ber.*, 1887, **20**, 612; Cook, Hewett, Kennaway, and Kennaway, *Amer. J. Cancer*, 1940, **40**, 62). On recrystallisation from glacial acetic acid followed by one from *n*-heptane, dark red needles were obtained (Found: C, 84·7; H, 5·0; N, 9·3. Calc. for $C_{20}H_{14}N_2$: C, 85·1; H, 5·0; N, 10·0%). We found m. p. 144—145° on slow heating, and 136° on placing the sample in the preheated m. p. apparatus. Nietzki and Goettig (*loc. cit.*) reported m. p. 136°; Cook, Hewett, *et al.* (*loc. cit.*) give 144—145°. This compound seems to exist in at least two crystalline forms.

The three azo-compounds used as starting materials throughout the present experiments were purified chromatographically at room temperature from their chloroform solutions in a column packed with activated alumina.

Adsorption Chromatography.—Columns were packed with " Fischer Scientific Co. Activated Alumina (for Absorbing), 8—14 M " ground in a mortar. Passage of the solutions through the column was accelerated by applying suction.

Irradiation.—Irradiations were carried out with a Mazda type MBW/U 125-w mercury-vapour discharge lamp, emitting 95·5% of its radiation at 365 mμ.

cis-2 : 2′-*Azonaphthalene.*—*trans*-2 : 2′-Azonaphthalene (0·2 g.) in chloroform (100 ml.) was irradiated in an evaporating dish from a distance of 5 cm. for about 3 hr. The solution, which had become red and contained about 70% of the *cis*-isomer, was passed through a column (40 cm. long, 3 cm. internal diam.) of activated alumina. All unchanged *trans*-isomer was washed through the column with 200 ml. of chloroform, while the *cis*-isomer remained adsorbed in a sharp zone 10 cm. long, beginning at 5 cm. from the top of the column. The zone containing the adsorbed material was eluted in portions with a total of 250 ml. of chloroform containing about 1% of methanol, and the resulting solutions were filtered and evaporated in the cold. The irradiation and all the following manipulations were carried out in the dark at 0°, and attempts were made to attain the solid state as quickly as possible.

cis-1 : 2'-*Azonaphthalene.*—*cis*-1 : 2'-Azonaphthalene was prepared in the same way as *cis*-2 : 2'-azonaphthalene. The isolated *cis*-compounds were kept in the dark at low temperature.

Chromatography on Paper of 2 : 2'-*Azonaphthalene.*—The ascending method was applied, strips or sheets of Whatman No. 1 filter paper being used throughout. A drop of the solution containing both isomers was placed on the paper. When working at room temperature, glacial acetic acid, or, at low temperature, glacial acetic acid–ethanol (1 : 3, v/v), was used as the mobile phase. A yellow spot containing the *cis*-isomer rapidly migrates upwards, while a yellow spot containing the *trans*-isomer remains stationary.

Spectrophotometric Technique.—All measurements and most irradiations were carried out in the special Dewar-type cells described by Hirshberg and Fischer (*J.*, 1953, 629; 1954, 297, 3129). In each experiment, the concentration was checked by re-measuring the absorption spectrum after heating the solution, in the cell, for ½ hr. at about 90° and recooling to room temperature (at 90° rapid conversion into the *trans*-isomer occurs).

Dielectric-constant Increments, and Results of Dipole-moment Measurements.—The method used at 30° has been described by Bergmann, Weizmann, and Fischer (*J. Amer. Chem. Soc.*, 1950, **72**, 5009). For measurements involving irradiations of the solutions *in situ* a modified Sayce–Briscoe cell was used, the contents of which could be mixed by alternative application of suction and pressure to one of the side-arms, in an atmosphere of dry nitrogen. The cell was placed in a large unsilvered Dewar flask filled either with water and crushed ice (for work at 0°) or with ethanol (for work below 0°). The ethanol bath was cooled below the desired temperature by liquid nitrogen introduced at a controlled rate into a copper container immersed in the bath. Thermoregulation to ±0·02° was in this case achieved by means of a mercury-in-glass thermoregulator, controlling the current in a heating element placed at the bottom of the bath. In the following summary of the results, Le Fèvre's nomenclature and method of calculation (Harris, Le Fèvre, and Sullivan, *J.*, 1953, 1622) are used. Owing to the low solubility of both *trans*-azonaphthalenes, the increments of dielectric constant, $\delta\varepsilon$, density, δd, and index of refraction, δn_D, were measured only at one concentration, in toluene at 30°, with the following results :

	10^4w	$10^4\delta\varepsilon$	$10^4\delta n_D$	$10^4\delta d$
trans-1 : 1'-Azonaphthalene	105	60	—	25
trans-2 : 2'-Azonaphthalene	82	45	22	19·5

These figures yield the following empirical constants, molar polarisations, ${}_\infty P_2$, and molar refraction, ${}_\infty R_2$, at infinite dilution :

Azonaphthalene	$C\alpha\varepsilon_1$	β	$C'\gamma n_1^2$	${}_\infty P_2$ (ml.)	${}_\infty R_2{}^D$ (ml.)
trans-1 : 1'-	0·105	0·28	—	103·5 ± 3	—
trans-2 : 2'-	0·102	0·28	0·158	102·5 ± 3	113 ± 3

The molar refraction R^D calculated for azonaphthalene from bond refractivities (Vogel *et al.*, *J.*, 1952, 514) is about 93 ml. The observed ${}_\infty R_2$ is probably somewhat increased by anomalous dispersion (Bergmann, Fischer, and Jaffe, *J. Amer. Chem. Soc.*, 1953, **75**, 3230), whereas R^D may be too low because in its calculation the resonance between the two halves of the molecule is ignored. In view of the difficulty in assessing the effect of these factors, it may be concluded that the orientation polarisation, and therefore the dipole moment, is zero for both *trans*-compounds.

For *cis*-2 : 2'-azonaphthalene the following results were obtained in toluene at 0° :

10^4w	3·1	14·9	20·6	29·7	36·7	42·1
$10^4\delta\varepsilon$	37	69	93	135	162	187

whence $\delta\varepsilon = 4{\cdot}70w - 65w^2$, and $({}_\infty P_2)_{cis} = 307$ ml. If the observed $({}_\infty P_2)_{trans} = 102{\cdot}5$ ml. is taken as equal to the distortion polarisation, we get an apparent moment in toluene of 3·02 ± 0·05D.

For 1 : 1'-azonaphthalene in toluene at −25° and a weight fraction of $w = 0{\cdot}0029$, the observed $\delta\varepsilon$ before irradiation was 0·0034, increasing to 0·0107 after irradiation. The latter value leads to an apparent molar polarisation ${}_{\infty}P_2$ of 244·5 ml. for the assumed mixture of *cis*- and *trans*-isomers.

Thanks are expressed to Dr. Y. Hirshberg in whose laboratory the spectrophotometric determinations were carried out.

DEPARTMENT OF ORGANIC CHEMISTRY, THE HEBREW UNIVERSITY,
JERUSALEM, ISRAEL (M. F. AND R. W.).
LABORATORY OF PHOTOCHEMISTRY AND SPECTROSCOPY,
THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOT, ISRAEL (E. F.).

[*Received, April 12th,* 1955.]