

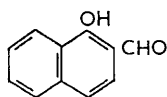
390. Topochemistry. Part VIII.* The Effect of Solvent, Temperature, and Light on the Structure of Anils of Hydroxynaphthaldehydes.

By M. D. COHEN, (the late) Y. HIRSHBERG, and G. M. J. SCHMIDT.

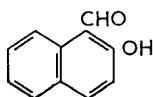
The spectra of anils of 1-hydroxy-2-naphthaldehyde and of 2-hydroxy-1-naphthaldehyde vary markedly with polarity of solvent and with temperature. These anils are photo-colourable in rigid glasses at suitable temperatures. The coloured species has spectral characteristics similar to those of the species dominant in polar solutions, at low temperatures in non-polar solutions, or in the crystal at room temperature.

No such sensitivity of spectrum to solvent, temperature, or irradiation has been found with anils of 2-hydroxy-3-naphthaldehyde and 2-methoxy-1-naphthaldehyde.

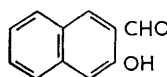
As an extension of the studies described in Part VII* the photo-properties of anils of the *o*-hydroxynaphthaldehydes have now been investigated. While several anils of 2-hydroxy-1-naphthaldehyde had been found to be non-photochromic in the crystal¹ we wished to test the activity of the anils of the isomeric aldehydes in the solid state, and of the anils of all the hydroxy-aldehydes in rigid solution. Anils of the three isomeric



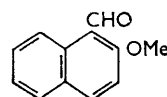
(I)



(II)



(III)



(IV)

o-hydroxynaphthaldehydes (I)—(III), and of 2-methoxy-1-naphthaldehyde (IV) were prepared and tested for photochromy and thermochemy in the crystal and for photoactivity in rigid solutions. The effect of solvent on their spectra at room temperature and the influence of variation in temperature on their solutions in non-polar solvents were also investigated.

TABLE I.
New anils of hydroxynaphthaldehydes.

Anil from		M. p. (°C)	Formula	Analysis					
aldehyde	aniline			Found (%)			Requires (%)		
				C	H	O	C	H	O
I	<i>p</i> -CO ₂ Et	145	C ₂₀ H ₁₇ NO ₃	74.85	5.45	15.2	75.2	5.4	15.0
				75.0	5.65	15.2			
I	<i>p</i> -OMe	95	C ₁₈ H ₁₅ NO ₂	77.5	5.5	11.15	77.95	5.45	11.5
				77.6	5.5	11.2			
I	<i>p</i> -Br	138	C ₁₇ H ₁₂ NOBr	61.9	3.9	5.45	62.6	3.7	5.0
				61.9	3.9	5.5			
III	<i>p</i> -CO ₂ Et	166	C ₂₀ H ₁₇ NO ₃	75.0	5.6	15.2	75.2	5.4	15.0
				75.0	5.5	15.2			
III	<i>p</i> -OMe	199	C ₁₈ H ₁₅ NO ₂	77.6	5.8	11.1	77.95	5.45	11.5
				77.7	5.8	11.1			
III	<i>p</i> -Br	229	C ₁₇ H ₁₂ NOBr	61.9	3.8	5.8	62.6	3.7	4.9
				61.6	3.9				
IV	<i>p</i> -Br	109	C ₁₈ H ₁₄ NOBr	63.4		Br, 23.6	63.55	4.15	Br, 23.5

EXPERIMENTAL

Preparation of Materials.—The aldehydes were synthesised by known methods;²⁻⁵ of the anils prepared those listed in Table I have not been described previously.

* Part VII, preceding paper.

¹ Senier and Clarke, *J.*, 1911, **99**, 2081.

² Russel and Lockhart, *Org. Synth.*, 1942, **22**, 63.

³ Weil and Ostermeyer, *Ber.*, 1921, **54**, 3217.

⁴ Calvin and Melchior, *J. Amer. Chem. Soc.*, 1948, **70**, 3273.

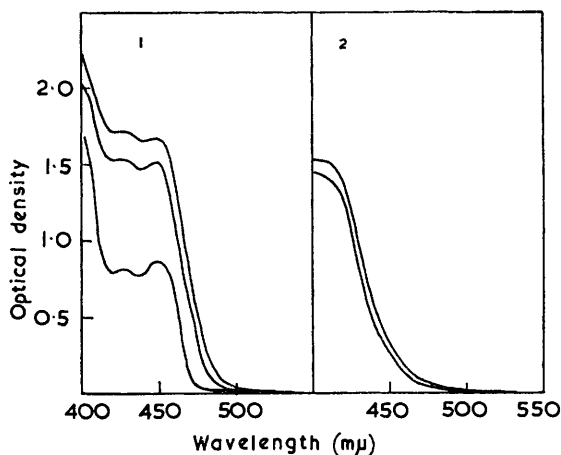
⁵ Wood and Bost, *Org. Synth.*, 1940, **20**, 11.

For studies of crystal spectra we prepared thin films from the melt by seeding just below the melting point and maintaining a temperature high enough to ensure slow crystal growth. Polymorphism was not investigated.

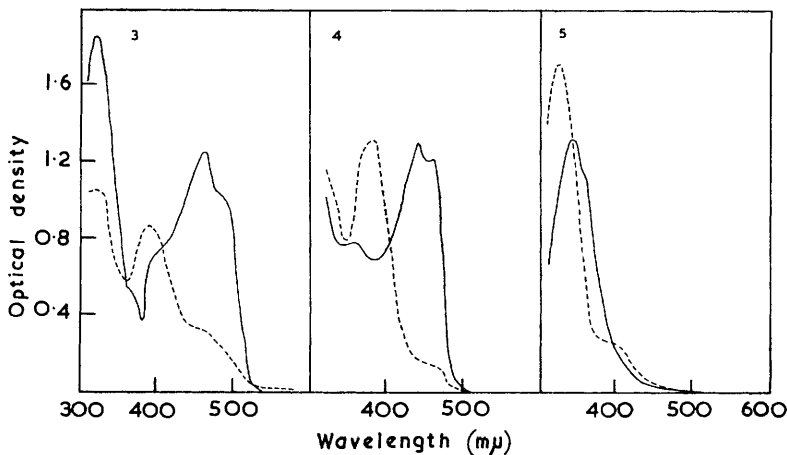
RESULTS

Spectral Behaviour of Crystalline Hydroxynaphthylideneanilines.—The crystalline anils fell into two classes:

(i) Anils of (I) and (II) absorb strongly in the range 4000—5000 Å at room temperature. Most of them are little affected by cooling; however, in a few compounds the intensity of this absorption drops on cooling [see, *e.g.*, the unsubstituted anil of (II), Fig. 1].



FIGS. 1 and 2. The absorption spectra of crystalline 2-hydroxy-1-naphthylideneaniline at (from top down) 346, 298, and 182°K (Fig. 1) and of 3-hydroxy-2-naphthylideneaniline at 360 and 296°K (Fig. 2).



FIGS. 3—5. The effect of solvent on the absorption spectra of some hydroxynaphthylideneanilines (see Table 2): non-polar solvent; —, polar solvents.

(ii) The anils of (III) and (IV) show no absorption maximum in the range 4000—5000 Å; instead there is found the tail end of a band whose maximum lies below 4000 Å (Fig. 2).

Spectral Behaviour of Hydroxynaphthylideneanilines in Solution.—The spectra of the

TABLE 2.

Solvent effects in hydroxynaphthylideneanilines.

Figure	Anil		Solv.*	Concn. (10 ⁻⁵ M)	Figure	Anil		Solv.*	Concn. (10 ⁻⁵ M)
	aldehyde	aniline				aldehyde	aniline		
3A	I	<i>p</i> -CO ₂ Et	MC/L	37.6	5A	III	unsubst.	MC/L	39.2
B	I	<i>p</i> -CO ₂ Et	E/M	45.5	B	III	<i>p</i> -CO ₂ Et	E/M	satd.
4A	II	unsubst.	MC	4.84					
B	II	unsubst.	M	4.47					

* MC, methylcyclohexane; L, ligroin; E/M, ethanol-methanol (4 : 1); M, methanol.

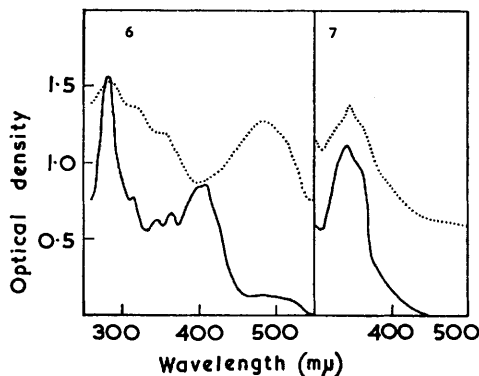
TABLE 3.

Temperature effect on hydroxynaphthylideneanilines.

Figure	Anil		Concn.* (10 ⁻⁵ M)	Figure	Anil		Concn.* (10 ⁻⁵ M)
	aldehyde	aniline			aldehyde	aniline	
8	II	unsubst.	4.93	12 †	I	<i>p</i> -CO ₂ Et	34.5
9	II	<i>p</i> -Br	3.75	13	I	<i>p</i> -Br	35.6
10	II	<i>p</i> -NMe ₂	1.38	14	II	<i>p</i> -OH	58.5
11	II	<i>p</i> -CO ₂ Et	—				

* All the solutions were in methylcyclohexane-ligroin, except that of the room temperature curve of Fig. 8, which was in methylcyclohexane (3.94×10^{-5} M) and those of Fig. 14, which were in paraffin oil. Figs. 12-14 are for 1-mm. cells. † The anil of Fig. 12 precipitates from solution on slow cooling. However, it can be held in solution by rapid "quenching"; thus, the low-temperature spectrum had to be measured through a layer of liquid air about 2-cm. thick.

anils of aldehydes (I) and (II) are sensitive to solvent: whereas in non-polar solvents a strong conjugation band is found at 3900 Å, in polar solvents this band is reduced in intensity while a very strong band appears in the visible with maxima at about 4400 and 4800 Å (Figs. 3 and 4). No such solvent effect is shown by the anils of (III) (Fig. 5) and (IV).

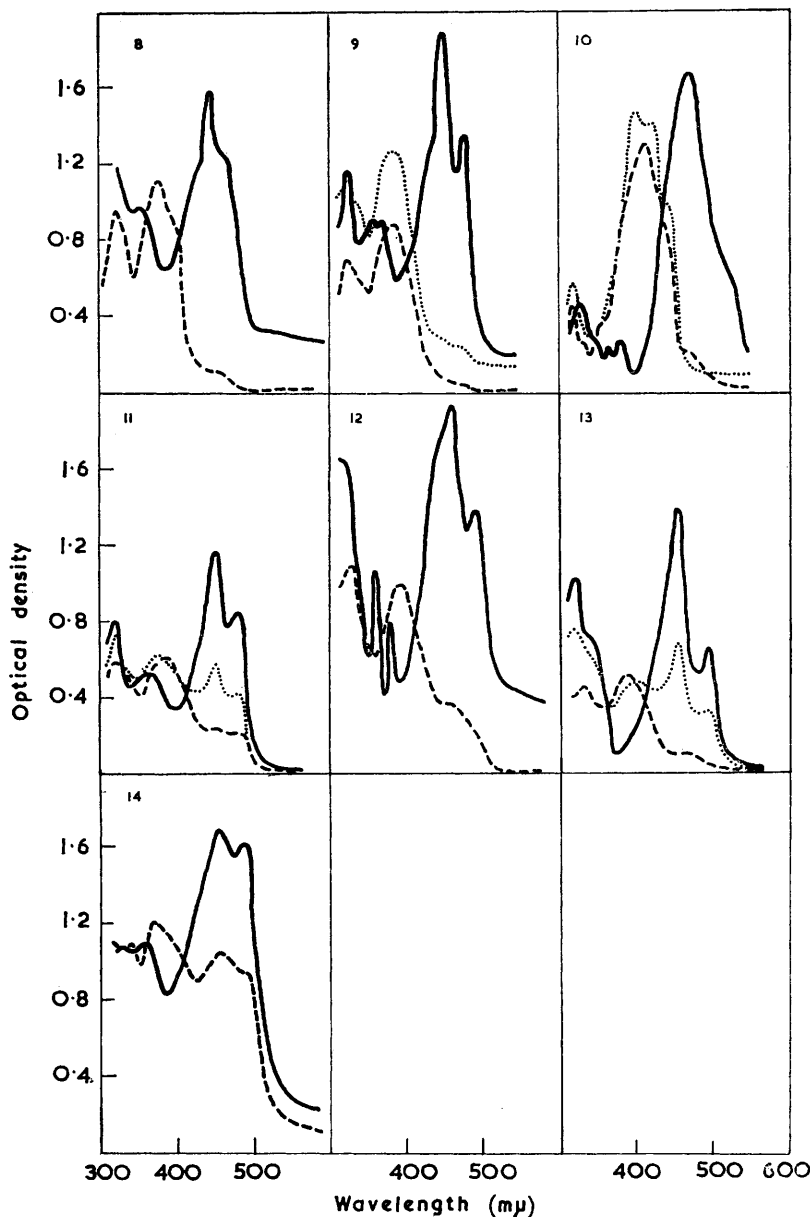


FIGS. 6 and 7. The effect of adsorption on silicic acid on the absorption spectra of 1-hydroxy-2-naphthylidene-*p*-anisidine (Fig. 6) and of 3-hydroxy-2-naphthylidene-*p*-anisidine (Fig. 7). —, in solution in cyclohexane; . . . , adsorbed on silicic acid.

TABLE 4.

Irradiation effects in anils of aldehydes (I) and (II) in rigid paraffin oil at 198°K.

Figure	Anil		Concn. (10 ⁻⁵ M)	Figure	Anil		Concn. (10 ⁻⁵ M)
	aldehyde	aniline			aldehyde	aniline	
17	II	unsubst.	—	20	I	<i>p</i> -OMe	24.9
18	II	<i>p</i> -CO ₂ Et	4.7	21	I	<i>p</i> -CO ₂ Et	37.6
19	II	<i>p</i> -OMe	54.1	22	I	<i>p</i> -Br	35.9

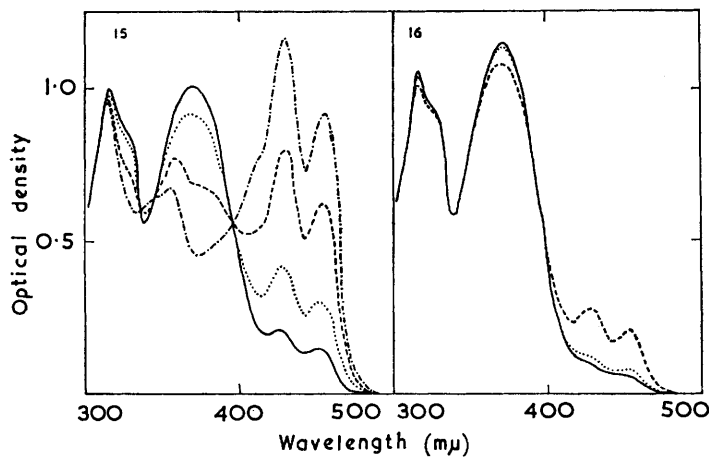


FIGS. 8—14. The effect of temperature on the absorption spectra of some anils of aldehydes (I) and (II) in non-polar solvents (see Table 3). Temperatures (full curve—lowest temperature): Fig. 8, 301, 98°K; Fig. 9, 313, 173, 123°K; Fig. 10, 299, 173, 123°K; Fig. 11, 190, 179, 160°K; Fig. 12, 301, 93°K; Fig. 13, 306, 186, 143°K; Fig. 14, 296, 214°K.

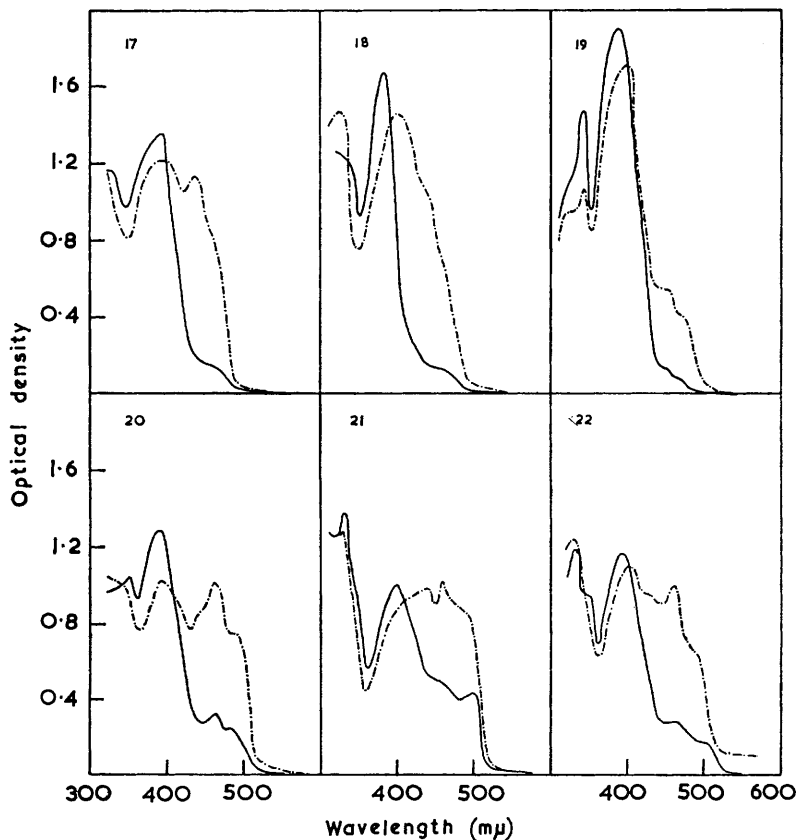
This solvent-dependence of the spectra of (I) and (II) has been described previously by the present authors⁶ and by Voss.⁷ The latter author showed that the extent of change

⁶ Cohen, Hirshberg, and Schmidt in "Hydrogen Bonding," ed. Hadzi, Pergamon Press, London, 1959, p. 293.

⁷ Voss, "Elektronen Spektren aromatischer Azomethin- und Azoverbindungen," Thesis, Technische Hochschule, Suttgart, 1960.



Figs. 15 and 16. Effect of concentration on the temperature-dependent spectral transformation of the unsubstituted anil of aldehyde (II) in solution in 2,2,5-trimethylhexane. —, 185°K; ····, 163°K; ----, 159°K; -·-·-, 146°K. Fig. 15 1 mm. cell, concn. $4.37 \times 10^{-4}M$. Fig. 16 10 mm. cell, concn. $4.37 \times 10^{-5}M$.

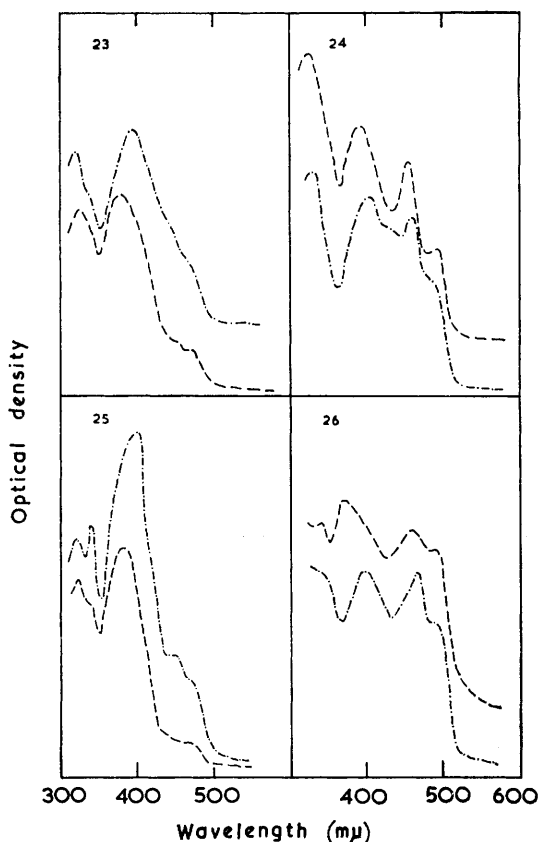


Figs. 17—22. The effect of irradiation on some anils of aldehydes (I) and (II) in rigid paraffin oil at 198°K (see Table 4). —, rigid solution before irradiation; -·-·-, after irradiation.

is determined not only by the dielectric constant of the solvent but also by its hydrogen-donating ability.

A similar distinction between the anils of (I) and (II) on the one hand, and of (III) and (IV) on the other, is found in the spectra of these compounds adsorbed on silicic acid (Figs. 6 and 7). The spectra of the anils of 4-hydroxy-1-naphthaldehyde vary with solvent but remain unchanged on adsorption on silicic acid from non-polar solution.

The Effect of Temperature on the Hydroxynaphthylideneanilines in Solution.—When a solution of 2-hydroxy-1-naphthylideneaniline in methyl cyclohexane–ligroin was cooled to



FIGS. 23—26. Comparison of irradiation- and thermally-produced spectra of some anils of aldehydes (I) and (II) (see Table 5). — — —, (A) thermal; — · — · —, (B) photo. The curves are displaced vertically for clarity.

liquid-air temperature a change in spectrum was noted similar to the change induced on going from a non-polar to a polar solvent at room temperature. Such spectral variations with temperature, found with all anils of (I) and (II) (Figs. 8—13), occur in most anils in the critical temperature range of -80° to -120°C . Above and below this range the changes in spectrum are ascribable to the normal influence of temperature and contraction of the solvent. In the case of the *p*-hydroxyanil of (II), the 4400—4800 Å band is of appreciable intensity at room temperature and conversion is complete on cooling to -75°C (Fig. 14).

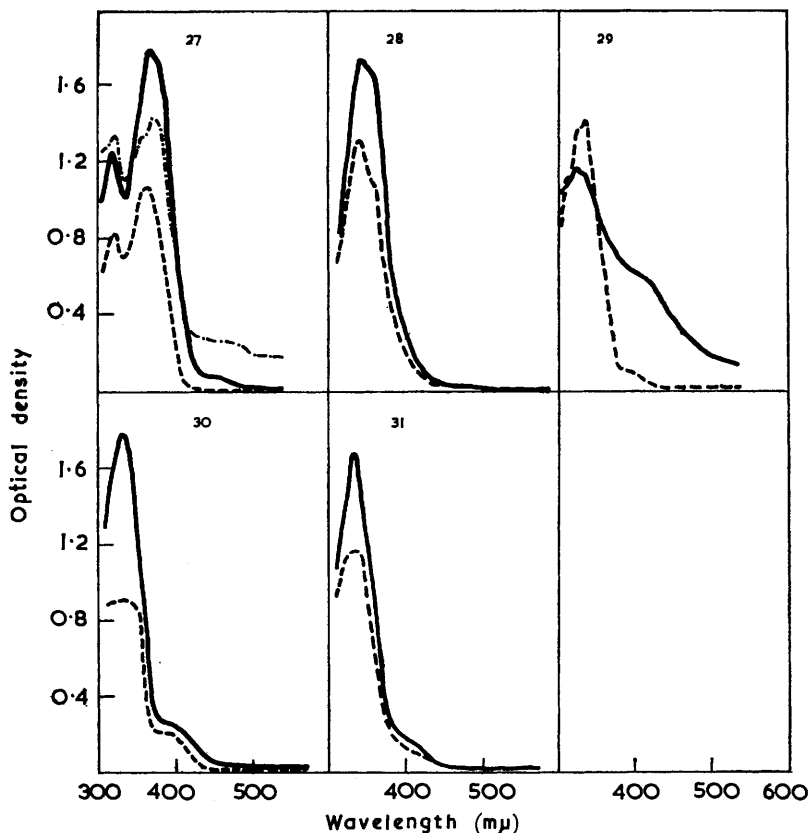
Solutions in non-polar solvents of the anils of (I) and (II), like those of the salicyl-aldehydes, are thus negatively thermochromic, with the effect much more pronounced in

TABLE 5.

Comparison of photo- and thermally-produced colours from anils of hydroxy-naphthaldehydes.

Figure *	Anil		Solv. †	Temp. (°K)	Concn. (10 ⁻⁵ M)
	aldehyde	aniline			
23A	II	<i>p</i> -CO ₂ Et	MC/L	193	—
B	II	<i>p</i> -CO ₂ Et	PO	198	satd.
24A	I	<i>p</i> -Br	MC/L	191	35.6
B	I	<i>p</i> -Br	PO	198	35.9
25A	II	<i>p</i> -Br	MC/L	173	3.75
B	II	<i>p</i> -OMe	PO	198	54.1
26A	II	<i>p</i> -OH	PO	296	58.5
B	I	<i>p</i> -OMe	PO	198	24.9

* The A curves represent thermally produced colours, while the B curves are for photo-induced ones. † MC/L, methylcyclohexane-ligroin (1 : 1); PO, paraffin oil.



FIGS. 27—31. Temperature, solvent, and irradiation effects on anils of aldehydes (III) and (IV) (see Table 6). - - -, room temperature; —, low temperature; — · — · —, after irradiation at low temperature.

the naphthalene series (cf. *e.g.*, Fig. 8 with Fig. 7 of Part VII). The much greater conversion in the present series of anils enabled us to measure the variation of the degree of thermal conversion with solute concentration. The results (Figs. 15 and 16) show that Beer's law does not apply to the system in the temperature range in which there is partial conversion.

From the variation of the degree of interconversion of the two absorbing species with

temperature, Voss⁷ calculates the apparent energy difference between the two species to be less than 1.5 kcal./mole. Since, however, the degree of interconversion is a function of concentration so too, presumably, is the apparent energy difference.

The Effect of Irradiation on Rigid Solutions of Hydroxynaphthylideneanilines.—None of these anils is photochromic in the crystal to ultraviolet light at room temperature. Anils of aldehydes (I) and (II) in rigid ethanol–methanol–ether or in rigid methylcyclohexane–ligroin have spectra which differ completely from their room temperature spectra in the manner indicated in the previous sections. Such rigid solutions are unaffected by irradiation with light of wavelength 3000–6000 Å.

In order to get further information about the photo-activity of these anils we required a non-polar solvent which would become rigid above -80°C , *i.e.*, above the temperature of the thermal spectral transformation; paraffin oil was investigated and found to be a suitable solvent, since it sets to a glass in the neighbourhood of -75°C .

Solutions of anils of (I) and (II) in paraffin oil at -75°C are yellow; on irradiation with 3000–4000 Å light a slight visually-perceptible deepening of colour takes place which corresponds to the modification of the spectrum indicated in Figs. 17–22.

These photo-active anils are sensitive to 3000–4000 Å light and to the 4047 Å line; in this respect they differ from the salicylideneanilines which are at most weakly affected by the 4047 Å line. Irradiation is accompanied by an intense green luminescence.

The colour formed by ultraviolet irradiation of rigid paraffin-oil solutions of anils of (I) and (II) can be photo-eradicated, the only effective line being 4358 Å. The 4047 Å line produced coloration rather than eradication, whilst in most compounds the 5460 Å line lies beyond the photo-produced absorption band. Eradication with 4358 Å light is always accompanied by weak luminescence.

TABLE 6.
Spectra of anils of aldehydes (III) and (IV).

Figure	Anil		Solv.*	Low temp. (°K)	Concn. (10 ⁻⁵ M)
	aldehyde	aniline			
27	IV	<i>p</i> -Br	MC/L	98	5.74
28	III	<i>p</i> -MeO	E/M	133	satd.
29	III	<i>o</i> -Br	MC/L	98	satd.
30	III	unsubst.	PO	194	67.6
31	III	<i>p</i> -CO ₂ Et	E/M	133	satd.

* See footnotes to Tables 2 and 5.

The *p*-hydroxyanil of (II) has the “low-temperature” spectrum already at -75°C ; its solution in rigid paraffin (Fig. 14) is thus unaffected by irradiation.

In Figs. 23–26 we give the absorption spectra of a number of photo- and thermally-produced coloured species for comparison. It is clear that the two types of coloured species obtained from anils of hydroxynaphthaldehydes have a much closer spectral correspondence than do the corresponding species from salicylideneanilines.

The Anils of the Aldehydes (III) and (IV).—The spectra of the anils of (III) and (IV) which, as reported above, are not significantly affected by polarity of the solvent or by adsorption on silicic acid, also show none of the temperature-dependence found with the anils of (I) and (II). Further, irradiation of rigid solutions of anils of (III) and (IV) produces no new absorption band in the visible region; in some compounds the absorption in the ultraviolet region decreases irreversibly. (Similar drops were observed in the anils of benzaldehyde and *o*-methoxybenzaldehyde.)

The temperature effects are indicated in Figs. 27–31. Fig. 27 shows, in addition, the effect of irradiating the rigid solution with light of 3000–4000 Å.