389. *Topochemistry. Part VII.* The Photoactivity of Anils of Salicylaldehydes in Rigid Solutions.*

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All anils of salicylaldehydes investigated undergo colour changes when their solutions in rigid glasses are irradiated with ultraviolet light. The effect is reversed when the solutions soften. In some solvents the change can be reversed photochemically even while rigidity is maintained.

Anils of aldehydes lacking an *o*-hydroxyl group show no photoactivity.

PART VI * has discussed experimental work on the photoactivity of solid salicylidene-anilines. It was concluded that the photo-behaviour of these compounds is topochemically controlled since photochromy and thermochromy, shown to be mutually exclusive properties in the solid state, may be found in different polymorphic forms of the same anil. It was further shown that the " coloured " species obtained by the photochemical or thermal mechanisms resemble each other in their spectral properties: however, little information on their molecular structures could be derived from the spectra in solid films.

The present and succeeding (Part VIII) Papers deal with the properties of salicylidene- and hydroxynaphthylidene-anilines in solution and in rigid organic glasses. (Stobbe's experiments[1] on anils incorporated in films of resins had suggested to him that photochromic properties are not maintained in the amorphous state; however, we felt that those experiments had been too crude in their choice of " solvent " to be significant.) Our experiments were designed to test the photo-properties of the isolated anil molecules in an environment of lesser rigidity than that imposed by the crystalline lattice, and to obtain better spectral data than was possible with crystalline materials.

The initial rigid-state experiments were conducted with solutions of salicylidene-*m*-toluidine in methyl cyclohexane–ligroin at liquid-air temperature. They showed that irradiation causes, in such solutions, a colour-change similar to that occurring in the crystal (yellow to red). Later experiments proved this to be a general effect occurring with most anils in a variety of rigid solvents. The photo-colour is stable as long as rigidity

* Part VI, preceding paper.

[1] Stobbe, *Ber. Verhandl. Sächs. Akad. Wiss. Leipzig*, 1922, **74**, 161.

is maintained, but begins to fade immediately the glass is allowed to soften. In some instances the colour can be photo-eradicated even while rigidity is maintained.

EXPERIMENTAL

Details of the apparatus have been published elsewhere. The early experiments utilised a quartz Dewar flask and housing in which the irradiating beam was at right angles to the measuring beam of the spectrophotometer.[2] In later experiments a modified Dewar flask and housing were used which allowed irradiation parallel to the measuring beam.[3]

With methylcyclohexane–ligroin an appreciable turbidity was observed at low temperatures; the resulting " background absorption " was a function of the history of the sample. Even with these solutions, however, the qualitative implications of the experiments are clear. Particular care was necessary with ethanol–methanol–ether because of strong cracking tendencies.

Boric acid and glycerol as well as other polyhydric alcohols such as propylene glycol, react with the C=N bond of the anils, for absorption in the 3400 Å conjugation band in the last two solvents decreases with time and finally vanishes completely. The absence of photo-colourability in boric acid points in the same direction.

Solution of the anils in paraffin oil generally required gentle heating. Even then, the weighed quantities did not always dissolve, and the saturated solutions were employed. Heating was also necessary to dissolve the anils of p-hydroxybenzaldehyde and of 3-hydroxy-2-naphthaldehyde (next paper) in non-polar solvents. Comparison of the spectra of such solutions with the spectra of the same compounds in methanol (generally prepared without heating) gave no indication that heating had caused decomposition.

In some rigid media, notably paraffin oil, spontaneous fading of the photo-colour takes place after removal of the irradiating arc. Whilst this fading was not appreciable during the measurement of a few spectral points it became considerable during the period of measurement of the whole spectrum. The absolute absorbance values and the wavelengths of the absorption maxima are therefore not precisely determined; however, the overall picture remains undistorted.

The problem of fading was more troublesome in investigations of photo-eradication of the ultraviolet-induced colour. In order to differentiate between the photo-eradication and " thermal " bleaching, when the latter was appreciable, we measured, as rapidly as possible, absorption at a few key wavelengths.

Cells were carefully dried before use; no attempt was made to exclude air from the quartz cell before stoppering. No correction was applied to the measured spectra for the contraction of the solution on cooling. This contraction, between room temperature and the temperature of rigidity, is less than 10% for paraffin oil and of the order of 25% for methylcyclohexane–ligroin.

Transmission measurements of anils adsorbed on silicic acid were made by the method described by Robin.[4]

RESULTS

Room-temperature Spectra.—The spectral characteristics of a few anils of salicylaldehyde are indicated in Table 1. The molar extinction coefficients (ϵ) are given in parentheses alongside the wavelengths of the corresponding absorption maxima. Multiple values, in braces, indicate the splitting of the main band into a number of maxima, or shoulders (sh).

A few of the spectra are presented in Figs. 1 and 2. The longest wavelength, high absorption, band must be ascribed to the complete, conjugated, π-electron system.[5] Its maximum lies, for most compounds, at 3300—3500 Å and has an ϵ of *ca.* 12,000—14,000; $\lambda_{max.}$ and ϵ are considerably higher in the nitro- and dimethylamino-derivatives.

[2] Hirshberg and Fischer, *J.*, (a) 1953, 629; (b) 1954, 297.
[3] Hirshberg and Fischer, *Rev. Sci. Instr.*, 1959, **30**, 197.
[4] Robin, *J. Chem. Educ.*, 1956, **33**, 526.
[5] Brocklehurst, *Tetrahedron*, 1962, **18**, 299.

It has been noted [6,7] that polarity of the solvent has a bathochromic effect on these solutions. This colour difference is most likely due to the low-intensity band found in the visible region (*ca.* 4400 Å) in the polar solvents. The intensity of the absorption in this

TABLE 1.

The absorption characteristics of some anils of salicylaldehyde
$[2'-HO·C_6H_4·CH=N·C_6H_5R-4]$.

	Wavelength (Å) for soln. in			Wavelength (Å) for soln. in	
R	MeOH	$C_6H_{11}Me$	R	MeOH	$C_6H_{11}Me$
NO_2	3680(22,900), 3650sh, 3400sh	*3600sh, 3220—3260(21,970)	OMe	4300(310)	3580sh, 3560(17,300), 3510(17,000), 3460(16,700), 3280sh, 2900(8,000)
CO_2Et	4400(13), 3420(14,160), 3280sh	3480(12,940), 3440sh, 3230(11,880), 3060(12,220)		3480(16,800), 3250sh	2690(11,120), 2320(20,700)
	2900—3000sh, 2790(16,610), 2750sh, 2380(15,170)	3000sh, 2730(15,810), 2380(17,200)		2700(10,060), 2280(18,980)	
			Me	4400(280), 3380(12,850), 3200sh, 3000sh	3420—3460(14,300), 3200sh, 3050sh
Br	3700sh, 3380—3460(13,800), 3190(13,650), 3000sh	3460(12,400), 3210(11,250), 3000sh		2690(11,500), 2260(19,000)	2900sh, 2690(13,600), 2320(22,600)
	2720(14,480), 2300(21,400)	2700(13,340), 2320(18,900)	NMe_2	4800sh, 3800—3880(20,600), 3400sh	3820(24,000), 3300sh
H	4400(220), 3360(11,970), 3100sh	3420(10,500), 3100sh, 3020(8,450)		2700sh, 2440(14,750)	2680sh, 2450(17,430)
	2690(13,600), 2230(21,560)	2680(12,420), 2270(19,700)			

* In decalin, because of the low solubility in methyl cyclohexane.

long wavelength band or tail appears to parallel the " electron-repelling " power of the *para*-substituent. Thus $\varepsilon_{max.}$ for this band falls off in the following order (methanol at room temperature):

$$p\text{-}Me_2N·C_6H_4 > PhCH_2 > p\text{-}MeO·C_6H_4 > p\text{-}MeC_6H_4 > Ph$$
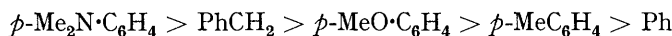
whilst for the chloro-, bromo-, iodo-, ethoxycarbonyl-, and nitro-substituted compounds absorption in this region is negligible.

A similar subsidiary band has been found in all salicylideneanilines adsorbed on silicic acid (*e.g.*, Fig. 3). No such band occurs in the spectra of anils of *o*-methoxy- (Fig. 4) and *p*-hydroxy-benzaldehydes.

In a number of spectra, *e.g.*, Fig. 7, we have observed the appearance of a new absorption band in methylcyclohexane–ligroin solutions cooled to liquid-air temperature. This new band lies in approximately the same wavelength range as the subsidiary band observed previously in solutions of anils at room temperature in polar solvents. This thermochromy is not to be confused with the colour change observed when solutions of the anils are heated. The latter has been found to be due to broadening of the initial absorption band into the visible region.[8]

[6] Senier and Shepheard, *J.*, 1909, **95**, 441.
[7] Gallagher, *Bull. Soc. chim. France*, 1921, **29**, 683.
[8] Chaude and Rumpf, *Bull. Soc. chim. France*, 1951, **18**, 342.

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Photochemical Results.—We have investigated the effect of ultraviolet radiation on about twenty anils of various salicylaldehydes in rigid solutions. Some of these anils, such as that of *p*-dimethylaminoaniline, are so insoluble in methyl cyclohexane–ligroin that they are almost completely precipitated from solution on cooling; we could not, therefore, test these solutions in the usual way. Paraffin oil has the advantage of high enough viscosity to maintain supersaturated conditions for a considerable period of time, particularly at low temperatures. By utilising this fact, and occasionally hazarding the use of polar solvents, we have been able to test the activities of a large number, and representative distribution, of anils in various rigid solvents and at several widely-spaced
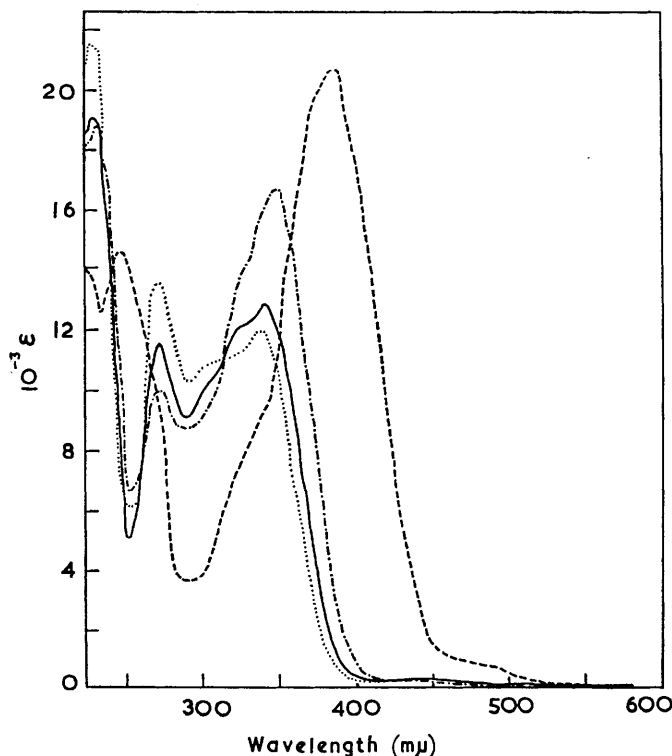

FIG. 1. The absorption spectra of some salicylidene-(4-substituted)anilines in methanol. – – – –, dimethylamino; — · — · —, methoxy; ———, methyl; · · · ·, unsubstituted.

temperatures. Some of the results are shown in Figs. 5—12; experimental details are given in Table 2. Coloration is observed in all solvents except polyhydric alcohols.

It is noted that irradiation produces similar absorption bands in all the salicylidene-anilines tested. The spectra of the photo-coloured anils of Figs. 9 and 10 were measured in order to determine the effect of the length of the conjugated system on the visible band. This effect is small, and it appears, therefore, that the complete conjugated system is not involved in the absorption process of the photo-product in the long-wavelength region.

For comparison purposes we have also studied a number of anils of other aldehydes. The results are presented in Figs. 13—19, with experimental details in Table 3. Of these anils, those of Figs. 15—18 have been described as displaying a limited photochromy in the solid state [9] (*i.e.*, weak photochromy at low temperatures, after trituration).

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[9] Senier and Forster, *J.*, 1914, **105**, 2462.

The results may be summarised as follows: *photo-coloration in rigid solutions is confined to the anils of* o-*hydroxybenzaldehydes*; in the absence of a hydroxyl group (Fig. 14), when
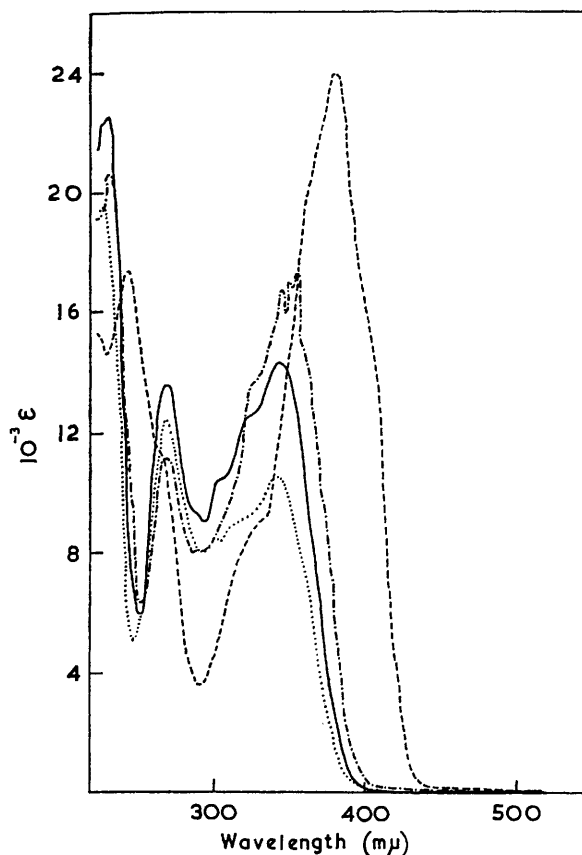

FIG. 2. The absorption spectra of some salicylidene-(4-substituted)anilines in methylcyclohexane. — — — —, dimethylamino; — · — · — · —, methoxy; ———, methyl; · · · ·, unsubstituted.

TABLE 2.

Irradiation of anils of salicylaldehydes in rigid glasses.

Fig.	Compound	Solv.[a]	Temp. (°c)	Concn. (10⁻⁵M)	Cell (mm.)	Irradn.[b] (min.)
5	4-Methylsalicylideneaniline	MC/L	−175	64·0	1	10P
6	Salicylidene-*p*-anisidine	,,	,,	6·43	10	20L
7	Salicylidene-*m*-toluidine[c]	,,	,,	85·4	1	5P
8	2-Chloro-*N*-salicylideneaniline[c]	PO	−75	85·0	1	5P
9	*NN'*-Disalicylidene-*m*-phenylenediamine[c]	,,	,,	55·0	1	6P
10	*NN'*-Disalicylidene-*p*-phenylenediamine	,,	,,	44·0	1	6P
11	4-Bromo-*N*-salicylideneaniline[c]	E/M/E	−150	17·2	20	15L
12	4-Chloro-*N*-salicylideneaniline	,,	,,	16·2	20	25L

[a] MC/L, methylcyclohexane–ligroin; PO, paraffin oil; E/M/E, ethanol–methanol–ether. [b] P, parallel; L, lateral. [c] Photochromic in the crystal.

the hydroxyl is in the *para*-position (Figs. 15—19), or when the *ortho*-hydroxyl is methylated (Fig. 13), no photo-colour is observed.

*All salicylideneanilines are photoactive in rigid solutions.* This activity appears to be

independent of the nature of the solvent, except for polyhydric alcohols. As long as rigidity is maintained variations in temperature have no effect on the stability of the photo-colour. Slow fading occurs in rigid solutions in paraffin oil which may be due to a lower micro-density and to the higher glass temperature of this as compared to other glasses used in this study.

These two results are highly relevant to the problem of solid-state photochromy: the limited incidence of photochromy in the *solid* anils of salicylaldehyde (see Part VI) had left

TABLE 3.

Irradiation of anils of benzaldehydes in rigid glasses.

| Fig.	Compound	Solv.	Concn.* $(10^{-5}M)$	Irradn. (min.)
13	4-Chloro-*N*-2-methoxybenzylideneaniline	MC/L	2·63	20L
14	4-Bromo-*N*-benzylideneaniline	PO	8·08	5P
15	*N*-4-Hydroxybenzylideneaniline	,,	Satd.	5P
16	*N*-4-Hydroxybenzylidene-*o*-anisidine	,,	,,	15P
17	4-Bromo-*N*-4-hydroxybenzylideneaniline	,,	,,	5P
18	*N*-4-Hydroxybenzylidene-α-naphthylamine	,,	,,	10P
19	*N*-4-Hydroxybenzylidene-β-naphthylamine	,,	,,	10P

* Satd., saturated at 100°c. Cell 10 mm. throughout.
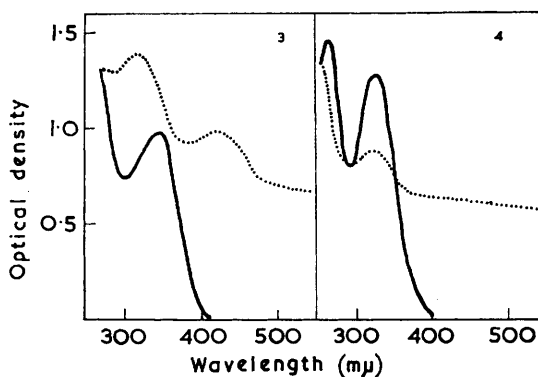
FIGS. 3 and 4. The effect of adsorption on silicic acid on the absorption spectra of 2-chloro-*N*-salicylideneaniline (Fig. 3) and 4-chloro-*N*-2-methoxybenzylidene-aniline (Fig. 4). ——, in solution in cyclohexane; · · · ·, adsorbed on silicic acid.

open the possibility of photochromy occurring in the benzylidene and *o*-methoxy-benzylidene series. Since we have now been able to show that photochromy in rigid solutions is (*a*) common to all anils of *o*-hydroxybenzaldehydes and (*b*) restricted to anils of aldehydes with an *o*-hydroxyl group, we may conclude that solid-state photochromy is (*a*) restricted to anils of *o*-hydroxyaldehydes and (*b*) topochemically controlled.

The Wavelength-dependence of the Process in Rigid Solution.* An Example of Photo-coloration and -eradication in the Rigid State.—The wavelength-dependence of the coloration process was determined in a number of anils. Throughout, maximum sensitivity corresponds to the range 3000—4000 Å; light of shorter wavelength (*ca.* 2500 Å) which produces no coloration was specifically excluded from the irradiating beam in later experiments so as to minimise concurrent irreversible decomposition. Light of 4047 Å was found to be weakly active in some compounds and inactive in others. Longer wavelengths (4358 Å and above) produce no effect.

* Light of different wavelengths in the visible and near-ultaviolet regions from a high-pressure mercury arc were isolated by means of Corning glass filters.

The influence of visible light on glasses which had previously been coloured by irradiation with ultraviolet light was also investigated. Here the effect is dependent on the solvent. Only in solutions in paraffin oil was an observable influence found. With these
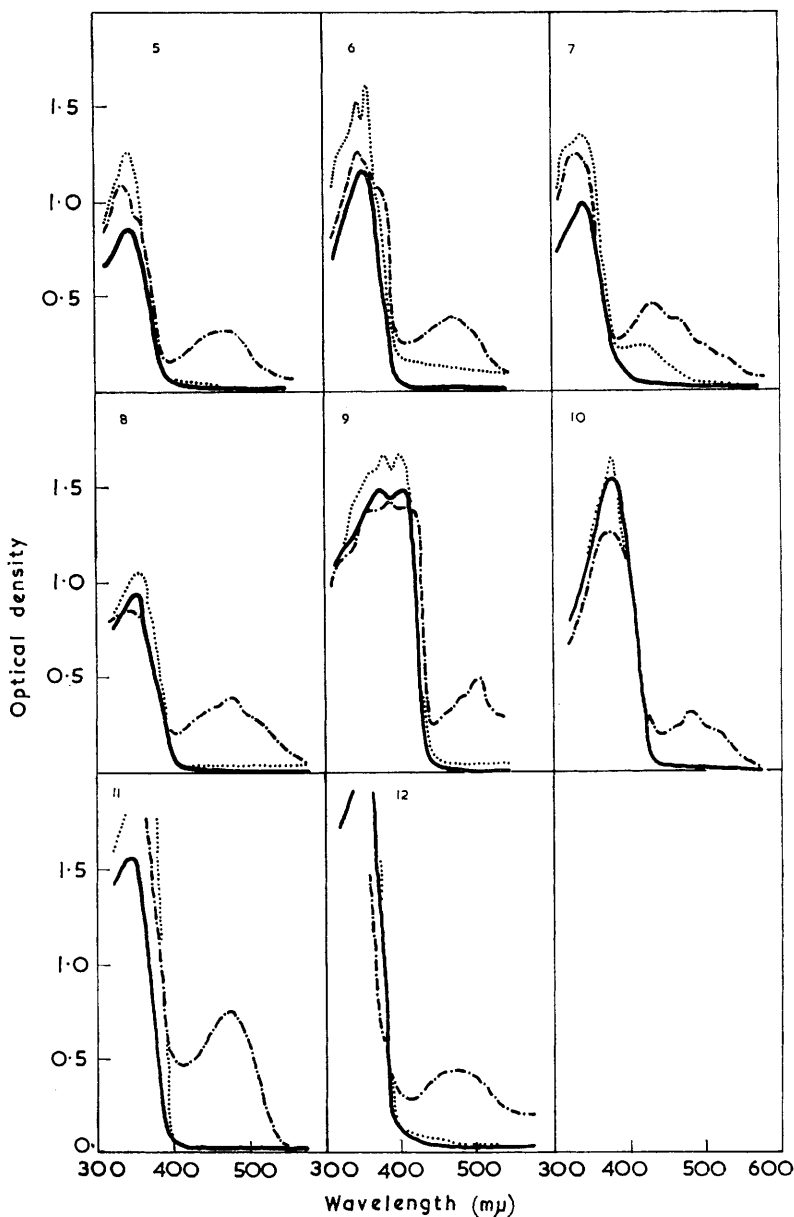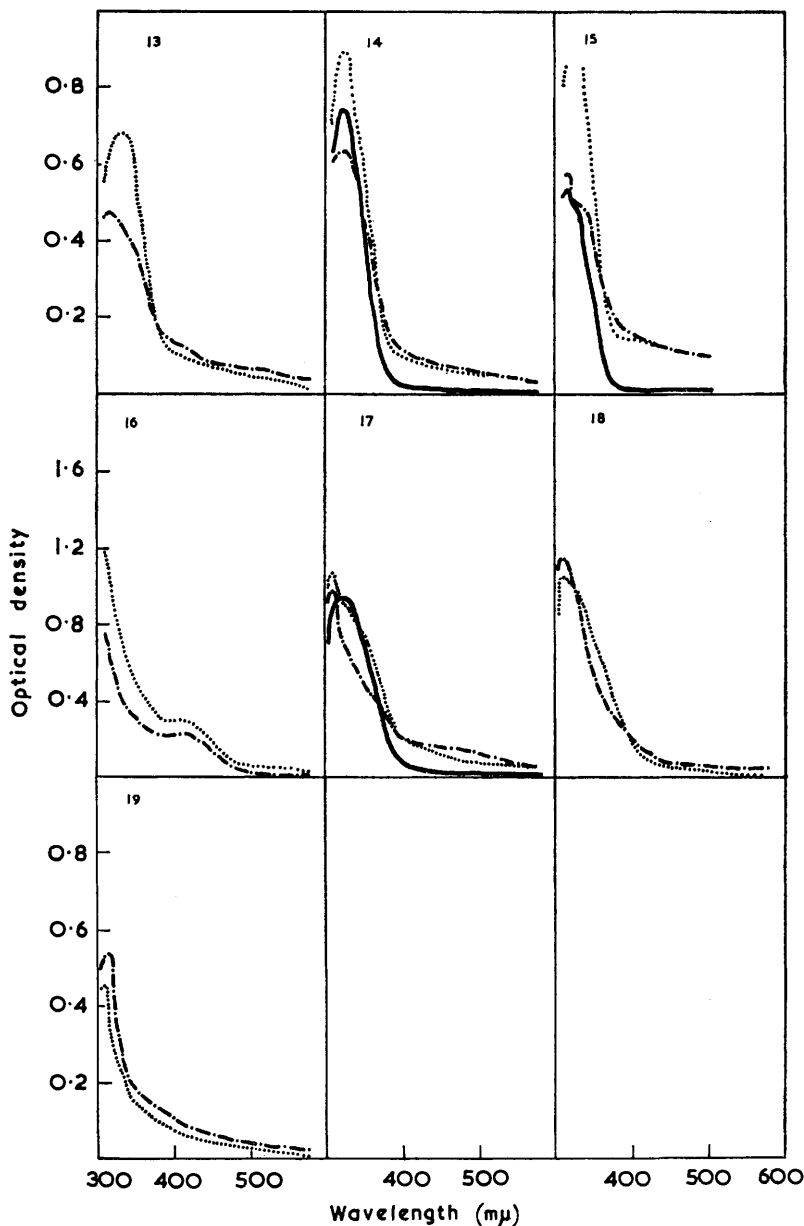
FIGS. 5—12. The effect of u.v. irradiation on salicylideneanilines in various rigid solvents (see Table 2). ——, room temperature; ····, low temperature; — · — · —, after irradiation at low temperature.

solutions it proved possible to " eradicate " the photo-colour by irradiation with light of a wavelength lying within the absorption band of the photo-form.

The light-produced absorption band usually extends from about 4000 Å to about

5800 Å, with the maximum near 4800 Å. Eradication by light of wavelength 4047, 4358, 5460, and 5770 Å was attempted in a large number of compounds; in general 5460 Å is

FIGS. 13—19. The effect of irradiation on some compounds related to the salicylidene-anilines in various rigid solvents (see Table 3). ——, room temperature; · · · ·, low temperature; — · — · —, after irradiation at low temperature.

the most effective, when there is absorption in that region, but produces no further eradication after absorption there has dropped to zero even if the absorption at the maximum (4800 Å) is still appreciable.

Light of 4047 Å can be considered to be absorbed both by the starting material and by

the photo-product. In many compounds it causes both a slight coloration (with yellow-green luminescence) of unirradiated material and a slight eradication (with red luminescence) of irradiated material. Such red luminescence on eradication was always observed with 4047 Å, occasionally with 4357 Å, but never with longer wavelengths. It appeared qualitatively to decrease the efficacy of the eradicating process.

Curves showing typical variation associated with the formation and eradication of colour are given in Fig. 20 .

Qualitative Observations on Luminescence Behaviour.—Solutions of the salicylidene-anilines, in the solvents used, do not luminesce at room temperature, but do so when the temperature has been lowered sufficiently. Their luminescence behaviour in the rigid state is affected by the nature of both solute and solvent.
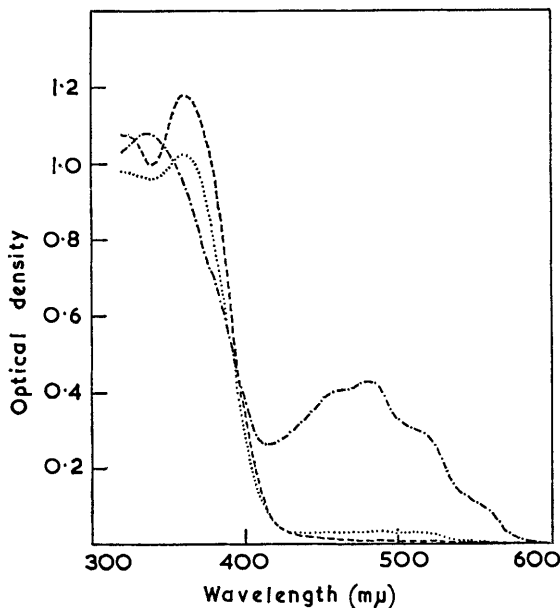

FIG. 20. Formation and eradication of colour in a rigid solution of 4-nitro-*N*-salicylideneaniline in paraffin oil. — — — —, before irradiation; — · — · —, after 5 min. irradiation with 365 mμ light; · · · ·, after 4½ min. Subsequent irradiation with 436 mμ light. All at 198°K.

Thus, those anils tested in ethanol–methanol–ether all luminesce yellow on irradiation with light of 3000—4000 Å; their luminescence changes to blue-green as irradiation proceeds. The luminescence of the anils in rigid methylcyclohexane–ligroin varies from sky-blue for *NN'*-disalicylidene-ethylenediamine, to orange for *N*-β-naphthylsalicylidene-amine, with the majority of anils tested luminescing yellow to green. With this solvent combination luminescence moves to longer wavelengths, and its intensity drops, during irradiation. Finally, the salicylidene-anilines in paraffin oil luminesce yellow to green, with little or no change observed on prolonged irradiation. The behaviour on eradication has been described in the previous section.

The anils of benzaldehyde and *p*-hydroxybenzaldehyde which were tested all display a very weak pale blue luminescence. The *p*-chloroanil of *o*-methoxybenzaldehyde does not luminesce in the visible region.

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