

388. *Topochemistry. Part VI.* Experiments on Photochromy and Thermochemistry of Crystalline Anils of Salicylaldehydes.*

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Some crystalline salicylideneanilines (anils) undergo reversible colour change when irradiated with ultraviolet light (photochromy). This phenomenon is largely topochemically dominated since: (i) no correlation exists between photosensitivity and the chemical nature of the ring-substituents, and (ii) polymorphic forms of a given anil differ markedly in light-sensitivity.

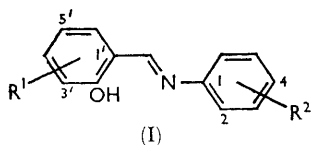
Absorption spectra measured in solid films of several (monomorphic and dimorphic) anils in temperature ranges from -180° to near the melting points suggest the following classification: α -type; photochromic, pale yellow at all temperatures, not thermochromic: β -type; not photochromic, colour varies with temperature, thermochromic.

Further experimental data include the crystallographic constants of 15 anils in their various polymorphic forms, the fluorescence spectra of thermochromic and photochromic crystals, and the thermal fading rates of several photo-coloured materials, including *O*-deuterated anils.

HAVING discussed in previous communications of this series the geometry of irreversible reactions in the solid state (dimerisation, isomerisation) we proceed to analyse in this and subsequent Papers the mechanism of reversible reactions. As example of the latter type of system we have chosen the photochemistry of anils of *o*-hydroxybenzaldehydes, partly because of the large amount of information available on the polymorphism and photo-behaviour of these compounds (see early summaries^{1,2}), and partly because of the ease with which they can be prepared. Preliminary accounts of our work on this system have been presented.³⁻⁵

Photochromy.—Salicylideneanilines (I) (referred to as “anils” in this Paper; and for convenience of discussion locants in the aniline ring are unprimed, those in the salicylidene ring are primed, when the term “anil” is used) are pale yellow to dark orange when freshly prepared. Some of the pale yellow anils are sensitive to ultraviolet light (*e.g.*, 3655 Å) in which their colour deepens to red or brown; certain anils exist in more than one crystal modification, not all of which are necessarily photochromic. Previous work^{6,7} has shown, and we have confirmed, that the colour change in photochromic crystals is not accompanied by any observable changes in the *X*-ray diffraction pattern and infrared (i.r.) spectrum of the crystal. Many previous attempts have been made to correlate photochemical activity with other properties of the members of this family of compounds; no definite correlation has as yet been established.

The photo-colour can be “eradicating” by heat or irradiation with visible light (*e.g.*, 4358 Å). Fading rates are characteristic for each compound and, wherever polymorphism occurs, for each (photochromic) crystal modification. Stobbe¹ had found that certain systems (fulgides, hydrazones, and stilbene derivatives) were photochromic



* Part V, preceding paper.

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

² Chalkley, *Chem. Rev.*, 1929, **6**, 217.

³ Cohen, Hirschberg, and Schmidt, in “Hydrogen Bonding,” ed. Hadzi, Pergamon, London, 1959, p. 293.

⁴ Cohen and Schmidt, in “Reactivity of Solids,” ed. de Boer, Elsevier, Amsterdam, 1961, p. 556.

⁵ Cohen and Schmidt, *J. Phys. Chem.*, 1962, **66**, 2442.

⁶ de Gaouch and Le Fèvre, *J.*, 1939, 1457.

⁷ Tien and Hunsberger, *Chem. and Ind.*, 1955, 119.

only within certain temperature limits. Senier's work⁸ suggested that this was probably also true of the anils and that this temperature range varied from compound to compound.

Thermochromy.—Senier⁹ observed that many of the more deeply coloured crystalline anils were thermochromic, *i.e.*, reversibly changed to lighter colours on being cooled to solid carbon dioxide-acetone temperature. It has more recently been reported¹⁰ that all anils are thermochromic in solution; since the long-wavelength absorption band of many of these compounds lies in the near-ultraviolet region and tapers off into the visible, normal high-temperature broadening of this band can cause a visually observable deepening of the colour. It had not previously been established whether or not solid-state thermochromy was due to similar band-broadening.

Senier⁸ further described several anils which could be obtained in two crystal forms differing markedly in colour (pale yellow/orange red; chromoisomerism). These polymorphic anils were also studied by Anselmino¹¹ and Manchot.¹² The last author claimed to have shown that chromoisomerism was associated with the hydroxyl group of the aldehyde moiety. While Manchot's evidence is weak the fact remains that chromoisomerism, photochromy, and thermochromy have not been observed in the anils of *o*-methoxybenzaldehyde and of benzaldehyde.

Thus, the literature suggests that the photo-properties of solid anils are not entirely controlled by molecular structure; rather, the evidence points to the conclusion that the molecular packing arrangement in the crystal is the operative factor in the phenomena under discussion. The problems before us may therefore be described as the relation between photochromy and thermochromy on the one hand and crystal structure on the other. In order to be able to tackle this problem we need additional information on photochromy, *e.g.*, the nature of the photo-coloured species, the mechanism of photo-coloration and -eradication and of thermal fading, the significance of the lower temperature limit, and consideration of the possibility that absence of photochromy is due to too narrow a temperature range between the lower limit and an upper limit where the rate of fading is as fast as the rate of photo-coloration. As to thermochromy, information is required on the mechanism of colour formation, whether by thermal broadening as in solution or by some other process; in the latter event the nature of the coloured species needs to be determined.

Topochemical studies require the use of properly defined, crystallographically homogeneous materials; our first task was therefore the study of polymorphism in a series of anils. The choice of derivatives was based on the needs of the parallel X-ray structure investigations; we therefore worked mainly with mono-chloro-, -bromo-, and -methyl-derivatives, a choice supported by the additional reason that these non-polar substituents are not likely to dominate the molecular packing arrangement in the crystal lattice.

EXPERIMENTAL

Crystals of the anils were grown from solutions and from the melt, and tested for polymorphism by X-ray methods. Cell dimensions and space groups were determined from zero- and *n*-level Weissenberg photographs taken about at least two principal axes; the cell dimensions are generally accurate to 1% or better.

For spectroscopic (absorption) measurements we used thin crystalline films prepared from the melt between the outer face of a quartz absorption cell and a quartz plate. The cell contained "blank" solvent which served to receive the thermocouple tip. Films of most polymorphic forms could be obtained by crystallisation at appropriate temperatures or by direct solid-solid conversion. (A film of the 3-methylanil consisting of a supercooled melt proved to be photochromic at low temperature.)

⁸ Senier, Shepheard, and Clarke, *J.*, 1912, **101**, 1952.

⁹ Senier and Shepheard, *J.*, 1909, **95**, 1943.

¹⁰ Chaudé and Rumpf, *Bull. Soc. chim. France*, 1951, (5), **18**, 342.

¹¹ Anselmino, *Ber.*, 1910, **43**, 462.

¹² Manchot, *Annalen*, 1922, **388**, 103.

Crystal modifications which could not be obtained as films were prepared by recrystallisation: their reflectances (R) were measured and thence the reflectance functions $f(R) = (1 - R)^2/2R$ calculated; $f(R)$ is proportional to the apparent molecular extinction coefficient provided that particle size is uniform and re-absorption can be ignored;¹³ since in these experiments particle size was not controlled our results are qualitative only.

Rate-of-fading measurements were conducted on thin anil films prepared as described above. Temperature control of the film was achieved by water circulating from a thermostat through the spectrophotometer cell mounted within a quartz Dewar flask. Since measurement was thus made through the circulating water a bubble trap was introduced into the line from the thermostat. The anil was photo-coloured with 3655 Å light irradiating simultaneously both sides of the film, *i.e.*, through the quartz plate and the spectrophotometer cell; the Dewar flask was then transferred to the measuring compartment of the spectrophotometer where it was exposed to the measuring beam (usually 4800 Å) only during actual measurement so that photochemical "bleaching" was minimised.

For fluorescence measurements the powdered anil was held in a quartz cell within a quartz Dewar flask which replaced the hydrogen lamp in the lamp-housing of a Unicam S.P. 500 spectrophotometer. The anil was irradiated with 3655 Å light from a high-pressure mercury arc placed outside the lamp-housing. The fluorescent light was collected by the concave mirror and dispersed in the monochromator. Measurements were made at constant slit-width with a 1P21 photomultiplier. The results have not been corrected for variation of sensitivity with wavelength.

O-Deutero-derivatives were prepared from 1 part of the anil suspended in 20 parts of heavy water (D_2O). Sufficient anhydrous dioxan was added to dissolve the anil at reflux temperature. Reflux in a dry atmosphere was continued for an appropriate period of time. (The rate of hydrogen exchange varies markedly from compound to compound: for *N*-2-cyanopropyl-salicylideneamine several hours' reflux was required in order to effect >90% exchange, whereas for *N*-2-chlorosalicylideneaniline 1 hr. on the steam-bath sufficed.) Replacement of the hydroxyl hydrogen by deuterium was followed by n.m.r. measurements, and the total uptake determined by mass-spectrometric analysis. The solution was cooled and the anil precipitated by addition of heavy water; where necessary crystallisation was assisted by seeding. The precipitate was filtered off, recrystallised from anhydrous dioxan, and dried in a vacuum. The corresponding "light" anils were recrystallised from dioxan before use.

RESULTS

Crystallographic Properties.—The methods of preparation and properties of our series of anils are given in Table 1, and their crystallographic constants in Table 2. Space-group assignment, whenever ambiguous, is based on positive piezoelectric tests; on the argument, as in the 3-bromoanil, that the molecular mirror plane required by the higher-symmetry space group is ruled out by the dimensions of the unit cell and of the molecule; in the 4-bromoanil, on the successful refinement of the $(0kl)$ zone based on space group $Pbc2_1$ rather than $Pbcm$; or on the full three-dimensional refinement of *N*-5-chlorosalicylideneaniline in space group $Pca2_1$ (see Part IX).

Several points may be noted: firstly, the general similarity in cell dimensions amongst members of this series suggests that molecular shapes are approximately the same throughout; since the shortest axis (3.97 Å) in this series is incompatible with a *cis*-configuration at the $>C=N-$ group we may assume that all molecules are in the *trans*-form. Structure analyses of the 4-Cl, 4-Br, 2-Cl, and 5'-Cl compounds confirm the *trans*-configuration.^{3,14}

Secondly, the space group of the $Fd2d$ modification of salicylideneaniline calls for comment: we have carefully checked the cell dimensions, (Laue) symmetry, and systematic absences by long exposure of large crystals, and believe the space group to be as stated. However, $Fd2d$ requires 16 molecules per unit cell while the cell volume and the density [$d(\text{floatation}) = 1.21$] indicate 8 molecules per cell. This contradiction can be resolved by the assumption that the molecules crystallise with a statistical twofold axis of symmetry;

¹³ Kortüm and Schöttler, *Z. Elektrochem.*, 1955, **57**, 353.

¹⁴ Papers IX and X of this series.

TABLE 1.

Preparation and properties of some crystalline salicylideneanilines.

Anil (I) *		Form	Preparation	M. p.	Thermo- chromy	Photo- chromy
H	H	α_1	From MeOH by evaporation	51°	None	+
		α_2	From pet. (b. p. 30—60°) at low temperature		?	+
H	2-Me	β	From pet., rapidly filtered; from melt, seeded	49.5	Wk	—
		α	From MeOH; from β on long contact with pet.; from melt, seeded	52.3	None	+
H	2-Cl	α		83	None	+
H	2-Br	α		87	None	+
H	3-Me	α		39.5	None	+
H	3-Cl	β		94	Wk	—
H	3-Br	β		98	Wk	—
H	4-Me	β		90	St	—
H	4-Cl	β		104	Wk	—
H	4-Br	α		109	None	+
† H	4-CO ₂ Et	β	From EtOH, slowly cooled	83	St	—
		α	From pet., quenched; from melt	87.5	None	+
4'-Me	H	β	From solution; from α , on contact with solvent; from melt at high temp.	93.4	St	—
4'-Me	H	α	From pet., evaporated; from melt, quenched	91.4	None	+
‡ 5'-Me	H	β	From EtOH, slowly cooled; from melt, slowly cooled	74	St	—
		$\alpha(?)$	From pet., quenched; from melt, quenched	69	None	—
§ 5'-Cl	H	β_1	From pet., quenched; from melt, quenched	—	Wk	—
		β_2	From melt and solution, slowly cooled; from β_1	110	St	—
§ 5'-Br	H	β_1	From pet., quenched; from melt, quenched	—	Wk	—
		β_2	From melt and solution, slowly cooled; from β_1	122.5	St	—

* Numbering as in (I). † On heating, the β ("red") form melts and recrystallises as α ; β is not transformed into α when held below its melting point even for long periods. ‡ On slow heating α melts and recrystallises as β ; it is not clear whether or not this transformation can occur also in the solid state. § Of these two compounds, the yellow forms are metastable with respect to the red at all temperatures, and change into them monotropically; the rate of this conversion is very sensitive to seeding.

TABLE 2.

Crystallographic constants of some salicylideneanilines.

Anil *		Form	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β	Space group	<i>n</i>	<i>d</i> (calc.)
H	H	α_1	28.3	5.99	13.1	—	<i>Fd2d</i>	8	1.18
		α_2	14.9	6.21	12.0	—	<i>P2₁2₁2₁</i>	4	1.18
H	2-Me	β					No single crystal data		
		α	12.6	7.54	12.5	—	<i>P2₁2₁2₁</i>	4	1.18
H	2-Cl	α	12.19	6.87	13.53	—	<i>P2₁2₁2₁</i>	4	1.36
H	2-Br	α	12.3	7.19	13.6	—	<i>P2₁2₁2₁</i>	4	1.52
H	3-Me	α	12.1	7.77	12.6	—	<i>P2₁2₁2₁</i>	4	1.19
H	3-Cl	β	25.9	3.97	11.1	—	<i>Pba2</i>	4	1.35
H	3-Br	β	13.4	10.8	4.04	96° 42'	<i>P2₁</i>	2	1.55
H	4-Me	β	19.4	4.84	12.4	96° 44'	<i>P2₁/c</i>	4	1.21
H	4-Cl	β	13.6	5.85	14.9	106° 30'	<i>P2₁/c</i>	4	1.33
H	4-Br	α	7.17	6.23	26.7	—	<i>Pbc2₁</i>	4	1.53
H	4-CO ₂ Et	β	11.3	4.6	24.1	109° 5'	<i>P2₁/a</i>	4	1.50
4'-Me	H	β	12.32	4.86	19.69	101° 5'	<i>P2₁/a</i>	4	1.21
		α	24.5	7.9	6.2	—	<i>Pca2₁</i>	4	1.18
5'-Me	H	β	12.84	20.56	4.72	103° 5'	<i>P2₁/n</i>	4	1.16
		$\alpha(?)$	51.6	6.24	7.19	—	<i>Pcab</i>	8	1.21
5'-Cl	H	β_1	7.3	6.5	25.6	—	<i>Pbc2₁</i>	4	1.27
		β_2	12.32	4.53	19.48	—	(+20°) <i>Pca2₁</i>	4	1.42
			12.18	4.48	19.25	—	(-185°) <i>Pca2₁</i>	4	
5'-Br	H	β_1	26.16	7.14	6.34	~90°	<i>Cc</i>	4	1.55
		β_2	12.57	4.58	20.01	—	<i>Pca2₁</i>	4	1.59

* Numbering as in (I).

this would mean that both the hydroxyl group and the C=N bond are distributed at random in the molecular stack along the twofold axis; it would follow that the molecules are intramolecularly hydrogen bonded. In fact, in those structures for which bond lengths

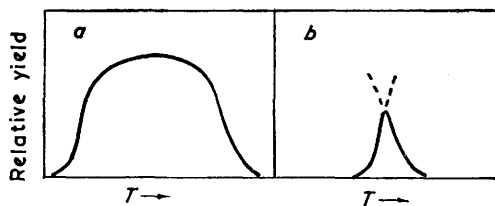
are now available, the intramolecular O...N distances are found to be short, indicating hydrogen-bonded interaction.

Photochromy.—The deep colour produced in the photochromic anils by irradiation fades in the dark. The rate of fading differs markedly from anil to anil, but in all cases increases with increasing temperature. Thus, each photochromic anil has a particular temperature above which the rate of fading is too rapid to permit measurement of the spectrum by conventional methods. In the vicinity of this temperature it is generally possible to obtain a visual impression of rapid fading.

On the other hand, in some anils the photo-induced absorption decreases as the temperatures are lowered, and finally falls to zero. In most compounds this fall-off occurs in the temperature range of negligible fading rate, and is therefore associated with a true drop in yield of the photo-product. Thus, photo-coloration of anils is observable only between lower and upper temperature limits imposed by low yield and rapid fading, respectively. A series of experiments at various temperatures, therefore, gives results such as shown diagrammatically in Fig. 1. We note in particular that a narrow "usable temperature range" implies both a low yield of photo-colour and a short life of this colour at all temperatures.

The majority of photochromic anils have a wide "usable temperature range" (e.g., in the 2-chloroanil no change in photo-yield is observed between 25 and -160°) so that measurements can be made at temperatures at which the yield is large and the colour

FIG. 1. Diagrammatic representation of yield of photo-colour as a function of temperature: (a) anil with "wide usable range"; (b) anil with "narrow usable range."



stable. On the other hand, in the 4-bromoanil and the α -form of the 4-ethoxycarbonylanil, the range is of the order of 60° so that the yield is low at temperatures where the colour is stable. Such systems represent the limit of measurement by conventional spectrophotometric techniques. With the α -form of the 2-methylanil there is no temperature at which the colour can be measured by these techniques, although at -20° a transient deep colour is visually observable.

Table 1 gives the classification into photochromic and non-photochromic anils; assignment of the α (?)-form of the 5'-methylanil is uncertain.

The spectral changes accompanying the photochromic transformation of the 3-methylanil and of the α -form of the 4'-methylanil are shown in Figs. 2 and 3, respectively. Fig. 4 provides an additional example (salicylideneaniline), and also illustrates partial eradication of the photo-colour by irradiation with light of longer wavelength (4358 \AA).

When a compound is irradiated at a temperature at which the yield is high, and is subsequently cooled to below its lower temperature limit, the photo-colour is found to persist without loss of intensity. In Fig. 3 the absorption spectrum of a compound treated in this way is compared with the absorption produced in the same sample by irradiation near the lower temperature limit. Thus, low temperature may prevent the formation of photo-colour, but does not destroy the colour once formed.

In the 2-chloroanil we have investigated the influence of temperature on the yields of both forward and reverse photo-reactions. There is little change in the yields of the forward process between 0 and -153° ; however, the efficiency of eradication decreases very markedly with decreasing temperature (Fig. 5).

The Kinetics of Fading.—The rates of fading of crystalline films of several photo-coloured anils were determined at various temperatures. Previous kinetic studies by

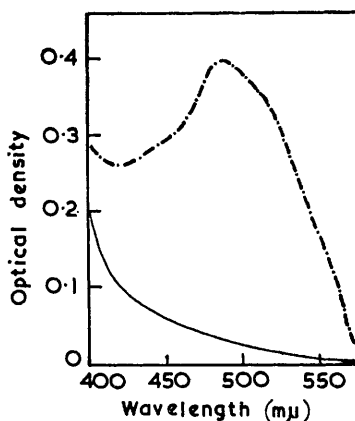


FIG. 2. The effect of irradiation on crystalline *N*-salicylidene-*m*-toluidine: —, before irradiation, at 160°K; - - - - - , after 10 min. irradiation with 365 m μ light, at 160°K.

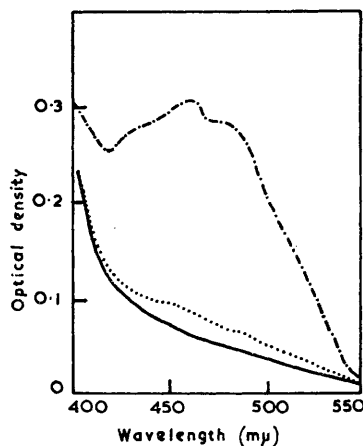


FIG. 3. The effect of irradiation at various temperatures on *N*-4'-methylsalicylideneaniline: —, 298°K; - - - - - , after 15 min. irradiation at 298°K and cooling to 200°K; ····, cooled before irradiation to 200°K, then irradiated for 20 min.

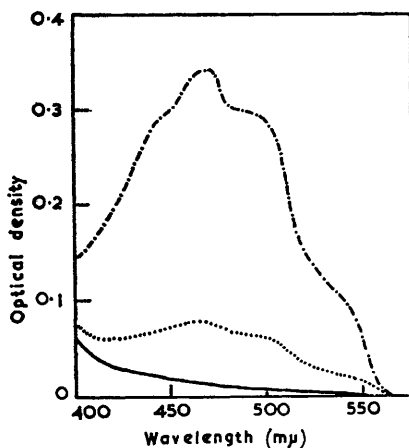


FIG. 4. Colour formation and eradication in *N*-salicylideneaniline: —, initial spectrum; - - - - - , after 20 min. irradiation with 365 m μ light; ····, after subsequent irradiation with 436 m μ light (10 min.). All at 142°K.

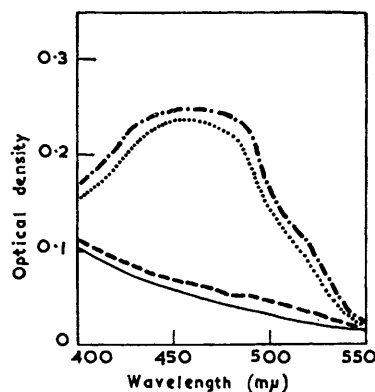


FIG. 5. The influence of temperature on the efficiency of eradication of the photo-colour in 2-chloro-*N*-salicylideneaniline: —, film at 120°K; - - - - - , after 20 min. irradiation with 365 m μ light at 120°K; ····, after subsequent 5 min. irradiation with 436 m μ light at 120°K; - · - · - , after subsequently warming to 195°K and 5 min. irradiation with 436 m μ light.

Padoa¹⁵ showed that *N*- β -naphthylsalicylideneamine faded by a second-order process; Lindemann¹⁶ on the other hand found that in *N*-salicylidene-*m*-toluidine the process was of first order.

We have confirmed the latter observation, although our measurements of rates and activation energy differ from Lindemann's values. Our methods are based on transmission

¹⁵ Padoa and Minganti, *Atti R. Accad. Lincei, Roma*, 1913, **22**, II, 500 [*Chem. Zentr.*, 1914, **85**, I, 605].

¹⁶ Lindemann, *Z. wiss. Phot.*, 1955, **50**, II, 347.

FIG. 6. First-order plots for fading of photo-coloured *N*-salicylideneaniline at: 1, 42.5°; 2, 34.7°; 3, 25.6°.

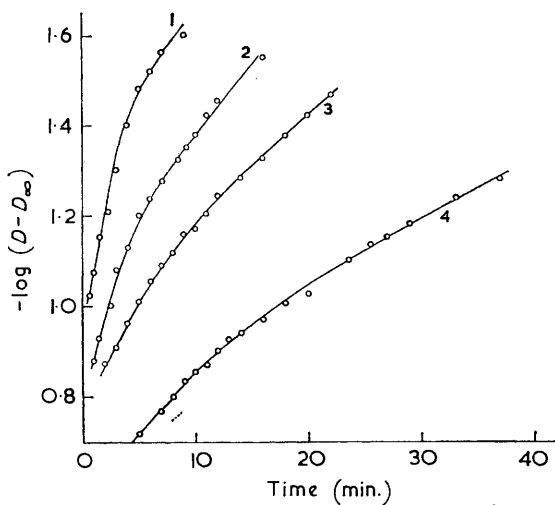
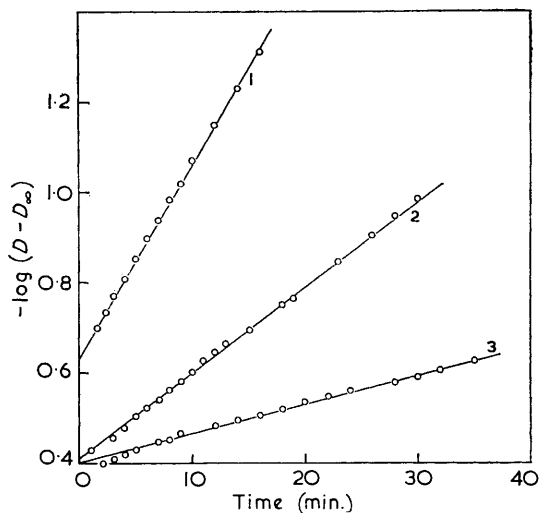
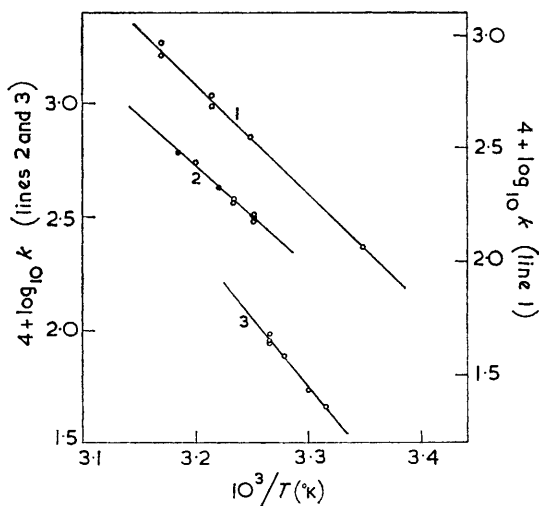


FIG. 7. First-order plots for fading of photo-coloured 2-chloro-*N*-salicylideneaniline at: 1, 54°; 2, 49°; 3, 43°; 4, 35°.

FIG. 8. Arrhenius plots for fading rates of photo-coloured: 1, *N*-salicylideneaniline; 2, *N*-2-cyanopropylsalicylideneamine; 3, salicylidene-*m*-toluidine. Open circles—"normal" anils; filled circles—deuterated anils.



rather than on reflectance measurements; both techniques involve experimental difficulties which may be considered more serious in the latter case. We find that salicylideneaniline and *N*-2-cyanopropylsalicylideneamine fade by a first-order process. The 2-chloro- and 2-bromo-anils, on the other hand, follow neither first-order nor second-order kinetics. It is possible that in the latter compounds we are dealing with two consecutive first-order processes; however, because of the large scatter of the data these results have not been analysed further.

Typical rate runs are shown in Figs. 6 and 7, and the Arrhenius plots in Fig. 8. The rate constants and activation energies are given in Table 3.

Thermochromy.—We have referred to the thermochromy of solutions of the anils, which is associated with the sharpening of the strong absorption band lying in the long-wave-length ultraviolet region. Similar band-sharpening and colour-fading are found in super-cooled melts of the anils and in some crystalline anils.

Our first intimation that this trivial effect was not the only explanation for thermochromy of anils in the solid state came from experiments with the 5'-chloroanil which occurs in two crystal modifications: the deeply orange-coloured form was found to have at room temperature a strong absorption band lying entirely in the visible ($\lambda_{\text{max.}} \sim 4800 \text{ \AA}$) region whose intensity fell rapidly on cooling and reached zero below -160° . This fading process is completely reversible; no time lag has been observed either on heating

TABLE 3.

First-order rate constants and activation energies for fading of photo-coloured anils.

<i>t</i> (°C)	10^4k (min. ⁻¹)	ΔH^\ddagger (kcal. mole ⁻¹)	<i>t</i> (°C)	10^4k (min. ⁻¹)	ΔH^\ddagger (kcal. mole ⁻¹)
Salicylideneaniline			<i>N</i> -2-Cyanopropylsalicylideneamine		
25.5	118.5	20.05	34.5	308.9	21.23
	118			324.7	
34.7	359		36.2	361.6	
	342			375.3	
38.0	485.7		39.4	541.2	
	545.5			543.5	
42.5	930		<i>N</i> -2-Cyanopropyl[hydroxy- ³ H]salicylideneamine		
	815		34.5	324.7	21.23
<i>N</i> -Salicylidene- <i>m</i> -toluidine				317.8	
28.6	46	29.84		308.6	
	46			311.0	
30.0	54		36.2	363.8	
32.0	78			375.3	
	76		37.5	423.7	
33.1	92			423.7	
	99		39.4	552.7	
	89			552.7	
			41.0	605.6	

or cooling.¹⁷ Fig. 9 shows absorption spectra of this material at various temperatures in the range from -150 to $+80^\circ$. Single-crystal Weissenberg photographs indicate no phase transition between room temperature and the temperature of liquid nitrogen: cooling is accompanied by the expected change in cell dimensions and by very small changes in molecular shape and orientation.¹⁴

It was considered possible that there might be compounds in this series with analogous absorption bands in the visible region, but of much lower intensity at room temperature than that of the 5'-chloranil. Such compounds would be visually indistinguishable from the "yellow" forms, *i.e.*, from forms having no such band at all. For this reason a survey was made of the thermochromic properties of the anils.

The results are listed in Table 1 in which the various compounds are described as having strong (st), weak (wk), or no absorption band in the visible region at temperatures

¹⁷ Aharoni and Tzalmona, unpublished observations.

just below their melting points. Fig. 9 shows the curves for a strongly absorbing substance. Spectra typical of the weakly-absorbing and non-absorbing groups are shown in Fig. 10 in which the upper curve give the spectral changes between the highest and the lowest temperatures employed. In Fig. 11 we give the reflectance functions of the "yellow" and "red" crystal modifications of two anils. Examination of the data listed in Table 1 shows that each homogeneous crystal phase of the anils is either photochromic or thermochromic, but not both. Thus, *in the crystalline anils of salicylaldehyde photochromy and thermochromy are mutually exclusive properties.* On this basis we have

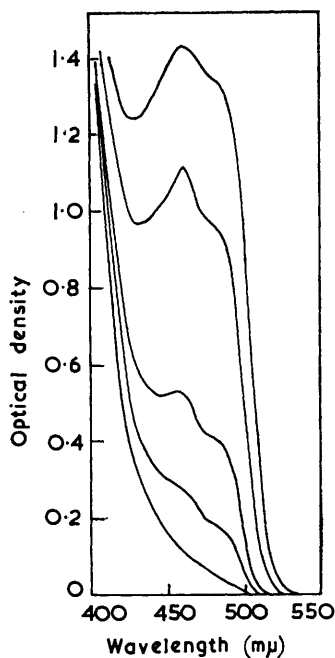


FIG. 9. The effect of temperature on the absorption spectrum of thermochromic *N*-5-chlorosalicylideneaniline. Temperatures (from top curve down): 285, 247, 193, 163, and 120°K.

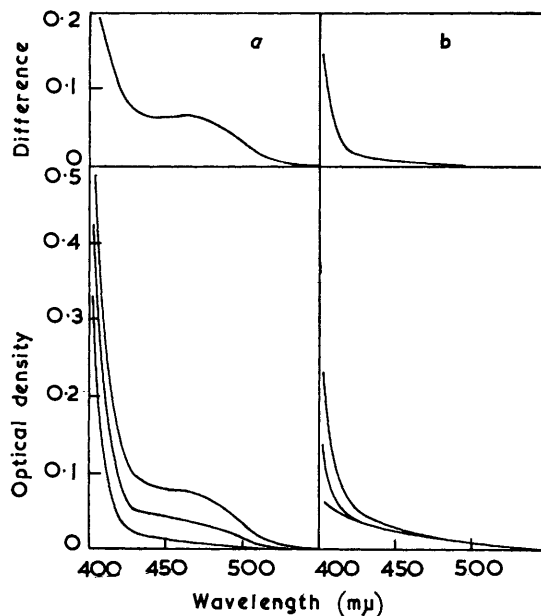


FIG. 10. The absorption spectra of 3-chloro-*N*-salicylideneaniline (*a*) at 358, 323, and 133°K, and of 2-chloro-*N*-salicylideneaniline (*b*) at 348, 304, and 129°K. Upper curves: difference between high- and low-temperature spectra.

classified these materials into groups: (α) photochromic, not thermochromic, pale yellow at all temperatures; (β) thermochromic, not photochromic, deep yellow to orange coloured at "high" temperatures.

From variations with temperature of the area under the absorption curve ($\log D$ against wave-number) one can obtain a measure of the energy difference between the red and yellow species in the thermochromic crystals.^{18,19} This has been done for the thermochromic form of the 5'-chloroanil (Fig. 12), only the low-frequency portion of the curve being used because of overlap of bands at the higher frequencies. The energy difference is found to be 1.76 kcal./mole.

Fluorescence Properties.—These properties are still under investigation but some preliminary observations can be reported now.

Thermochromic anils are strongly luminescent when irradiated with light of 3655 Å.

¹⁸ Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419.

¹⁹ Theilacker, Kortüm, and Friedheim, *Ber.*, 1950, **83**, 515.

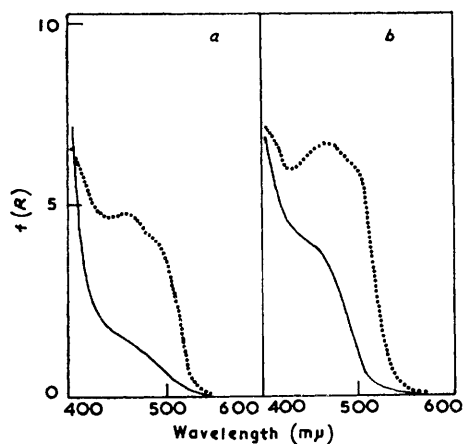


FIG. 11. The reflectance functions for 4-ethoxycarbonyl-*N*-salicylideneaniline (a) and *N*-5-bromosalicylideneaniline (b), "red" forms; —, "yellow" forms.

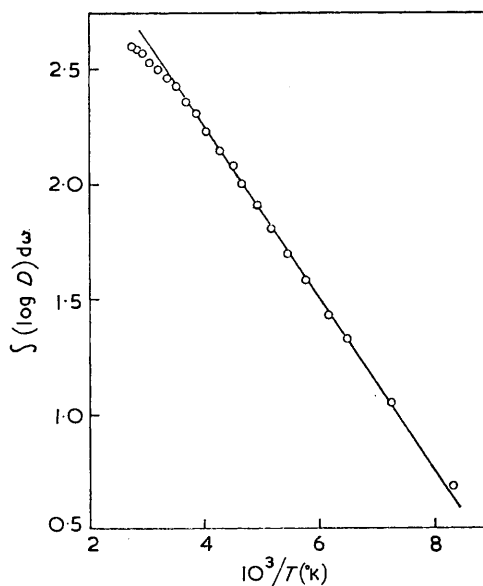


FIG. 12. Variation of area of "red" absorption curve of *N*-5-chlorosalicylideneaniline with temperature.

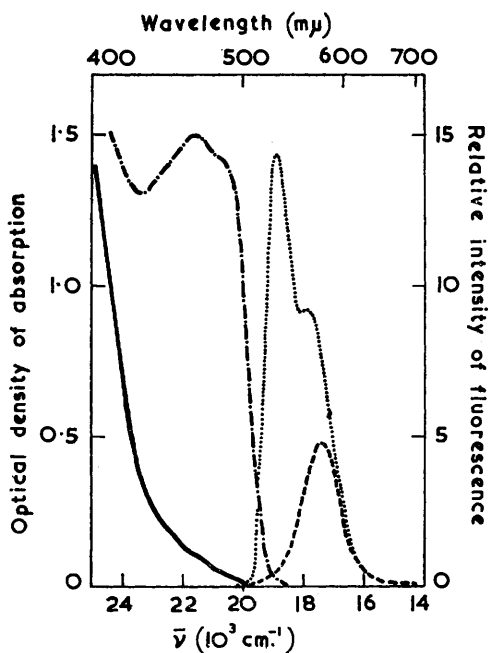


FIG. 13. Absorption and fluorescence (uncorrected) spectra of thermochromic *N*-5-chlorosalicylideneaniline: —, absorption at 120°K; - - - -, absorption at 297°K;, fluorescence at 90°K; - · - ·, fluorescence at 297°K (irradiation with 365 mμ light).

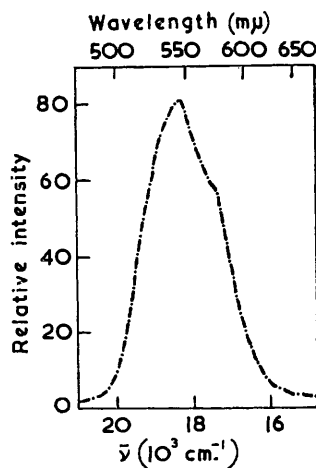


FIG. 14. Fluorescence (uncorrected) spectrum of 4-bromo-*N*-salicylideneaniline at 90°K (irradiation with 365 mμ light).

[1964]

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The light emitted is yellow at room temperature and changes to green at low temperatures. The lifetime of the emitting species is less than the time-resolving power of a conventional oscilloscope, *i.e.*, less than a few microseconds.¹⁷ The fluorescence spectra of *N*-5-chlorosalicylideneaniline at low and high temperatures, and the absorption spectra of a film of this anil at the same temperatures, are shown in Fig. 13.

By contrast, the photochromic anil crystals are not fluorescent at temperatures above their lower temperature limits; colour formation is not accompanied by fluorescence (to the eye there appears to be a dull red luminescence on irradiation with 3656 Å light; we have not been able to measure any emission of light of wavelength above 6000 Å). When these crystals are cooled the yield of photo-colour drops and fluorescence appears. The wavelength distribution of this emitted light is very similar to the fluorescence spectrum of the thermochromic crystals (Fig. 14).

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