CCXIV.—*Studies in Phototropy and Thermotropy.*
Part I. Arylidene- and Naphthylidene-amines.

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IN a recent paper we described a series of Schiff's bases, salicylidene-amines, one of which, salicylidene-*m*-toluidine, was found to be highly phototropic (this vol., 441). Under the influence of light waves of high refrangibility, this compound was found to change from pale yellow to orange, and when removed from that influence to return to its original colour. The phenomenon was ascribed to reversible isomeric change. We have continued this inquiry, and now submit an account of further work, in which we have studied a number of other salicylideneamines and related compounds.

Including salicylidene-*m*-toluidine, we have now found five compounds which exhibit phototropy. Looking at the constitution of these, there does not appear to be any necessary relation between the nature or the position of the substituents and the phototropic property. They are all salicylidene derivatives, but many such derivatives are not phototropic, as is the case also with the analogous *o*-hydroxynaphthylidene compounds which we have examined. It may be noted that the phototropic property is destroyed by the substitution of methoxyl for hydroxyl; further, in the case of salicylidene-*m*-toluidine, by the substitution of hydroxyl or chlorine for the methyl group, and, in salicylidene-*p*-aminobenzoic acid, either by the substitution of chlorine or methyl for the carboxyl group or by the conversion of the acid into a metallic salt.

Early in this investigation it was observed that many of the coloured bases became deeper in colour on heating, and that this change, like phototropy, was reversible. The whole of the com-

pounds in hand were then subjected to an examination to obtain further evidence, if possible, of this property. Their colour changes were noted (1) between the ordinary temperature and the temperature just below their melting points, called "the higher temperature," and (2) between the ordinary temperature and the lowest temperature we could conveniently command, that of solid carbon dioxide, called "the lower temperature." This led to the interesting fact that most of the compounds exhibit this phenomenon. Among inorganic substances this property has long been known, we need only mention that at the temperature of solid carbon dioxide, sulphur becomes almost colourless, red mercuric oxide becomes yellow, and vermilion becomes scarlet, or, on heating, zinc oxide becomes yellow, and that all these return to the original colour at the ordinary temperature. This reversible change of colour in solids depending on the temperature we propose to call *thermotropy*.

In the case of the Schiff's bases, the change of colour with rise of temperature is from yellow to orange to red, and on lowering of temperature from red to orange to yellow, but in some cases at the low temperature the colour disappears altogether. The elucidation of this question, however, must await spectroscopic measurements.

The extreme instability of the Schiff's bases, particularly those derived from hydroxyaldehydes, their characteristic tendency to form isomerides, is further illustrated by the differently coloured modifications which can be obtained at will by varying the method of their preparation or the temperature of crystallisation. (For other instances of the changeability of Schiff's bases, see Anselmino, *Ber.*, 1905, **38**, 3989; 1907, **40**, 3465; also Manchot and Furlong, *Ber.*, 1909, **42**, 3030.) In this connexion, allusion may also be made to the changes which these bases undergo under the influence of different solvents indicated by the different shades of colour that they exhibit in solution.

Evidence is accumulating of reversible isomeric reactions, like those described in this paper, which are indicated by physical differences, such as changes of colour. It is possible that these may be explained by hypotheses, similar to that of Hantzsch and Werner, assuming intramolecular rearrangement; but in the case of phototropy and thermotropy it should not be forgotten that the substances exhibiting these phenomena are solids. No one will doubt, however, that these differences of colour depend on isomeric change of some kind; but in the case of solids we know practically nothing of their molecules, not even of their relative molecular weights. The molecules of solids are probably far more

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complex than those of liquids or gases; indeed, they may be rather complex groups or aggregates of ordinary gaseous molecules, which would give rise to far more numerous possibilities of isomerism. It appears to us that phototropic and thermotropic reactions are more probably due to isomeric changes affecting the aggregation of molecules in solids than to intramolecular change of molecules derived from a study of gases.

The following compounds were obtained by the condensation of the respective aldehydes and amines, in the usual manner; generally in alcoholic solution, and without the application of heat.

Salicylidene-m-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$.—This phototropic compound, which was described in a previous paper (*loc. cit.*), is thermotropic, and also exhibits differences of colour in solution in different solvents. No thermotropy could be observed at "the higher temperature," just below its melting point, the latter being so near the ordinary temperature, but at "the lower temperature," that of solid carbon dioxide, the yellow phototrope became paler in colour and returned to the original colour at the ordinary temperature. The darker phototrope was not altered appreciably in colour by cooling. Solutions in ether, benzene, or light petroleum are rather lighter in colour than those in chloroform, alcohol, or glacial acetic acid.

Salicylidene-m-toluidine hydrochloride, $\text{C}_{14}\text{H}_{13}\text{ON}\cdot\text{HCl}$, was obtained as a yellow, amorphous precipitate by passing a current of dry hydrogen chloride into a solution of the base in dry ether. In presence of water, the salt hydrolyses readily. It is not phototropic, but in presence of light and moist air it decomposes. Thermotropy was detected at "the higher temperature" (150°) by a darkening in colour, the original colour returning at the ordinary temperature. There was no change of colour at "the lower temperature." It melts at 182° (corr.):

0.2214 gave 0.1274 AgCl. $\text{HCl}=14.63$.

$\text{C}_{14}\text{H}_{14}\text{ONCl}$ requires $\text{HCl}=14.72$ per cent.

Salicylidene-m-toluidine picrate, $\text{C}_{14}\text{H}_{13}\text{ON}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$.—Equimolecular proportions of salicylidene-*m*-toluidine and picric acid were dissolved in hot alcohol and mixed. Small, bright yellow needles separated immediately. This compound does not appear to be phototropic or thermotropic. It melts at 179° (corr.):

0.2130 gave 22.3 c.c. N_2 (moist) at 13° and 772 mm. $\text{N}=12.57$.

$\text{C}_{20}\text{H}_{16}\text{O}_8\text{N}_4$ requires $\text{N}=12.74$ per cent.

o-Methoxybenzylidene-m-toluidine, prepared by the interaction of *o*-methoxybenzaldehyde and *m*-toluidine, is a liquid, and was not further examined.

Salicylidene-o-4-xylidene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}_2$, is photo-

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tropic. It consists of light yellow needles, which change to an orange colour when exposed to sunlight, and resume their original colour in the dark. At "the higher temperature" (70°), the yellow phototrope exhibits thermotropy by darkening in colour and returning to the original colour at the ordinary temperature; at "the lower temperature," it becomes temporarily paler. The darker phototrope showed no thermotropy except that when kept for a short time at 70° it became paler in colour, and at the ordinary temperature appeared to be identical with the yellow phototrope. The base is soluble in the usual organic solvents, the solutions in alcohol, chloroform, or acetic acid being darker in colour than those in ether, benzene, or light petroleum. It melts at 76° (corr.):

0.2185 gave 12.2 c.c. N_2 (moist) at 14° and 746 mm. $N = 6.45$.

$C_{15}H_{15}ON$ requires $N = 6.22$ per cent.

o-Methoxybenzylidene-o-4-xylylidine, $OMe \cdot C_6H_4 \cdot CH:N \cdot C_6H_3Me_2$, was prepared by the interaction of *o*-methoxybenzaldehyde and *o*-4-xylylidine. No indication of phototropy or thermotropy could be detected. It crystallises from alcohol in pale yellow prisms, and is very soluble in the usual organic solvents; the solution in glacial acetic acid is yellow: in other solvents it is colourless, or only pale yellow. It melts, forming a yellow liquid, at 45° (corr.):

0.2751 gave 14.0 c.c. N_2 (moist) at 18° and 769 mm. $N = 5.95$.

$C_{16}H_{17}ON$ requires $N = 5.86$ per cent.

Salicylidene-m-5-xylylidine and *salicylidenemesidine* were prepared, but, proving to be liquids, were not further examined.

Salicylidene-o-chloroaniline, $OH \cdot C_6H_4 \cdot CH:N \cdot C_6H_4Cl$, separated from the alcoholic solution as an oil, which on keeping solidified to a mass of pale yellow crystals. It is phototropic; when exposed to sunlight it becomes orange, and the original colour returns in the dark. Both phototropes exhibit thermotropy; at "the higher temperature" the yellow phototrope darkens in colour, the original colour returning at the ordinary temperature; the orange phototrope at this temperature loses colour, and at the ordinary temperature appears to be identical with the yellow phototrope. At "the lower temperature," both yellow and orange isomerides become much paler in colour. *Salicylidene-o-chloroaniline* dissolves easily in the usual organic solvents; the solutions in alcohol, chloroform, or glacial acetic acid are deeper in colour than those in ether, benzene, or light petroleum. The base melts at $82-83^{\circ}$ (corr.):

0.2436 gave 12.3 c.c. N_2 (moist) at 14° and 769 mm. $N = 6.00$.

$C_{13}H_{10}ONCl$ requires $N = 6.05$ per cent.

o-Methoxybenzylidene-*o*-chloroaniline, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$, was prepared from *o*-methoxybenzaldehyde and *o*-chloroaniline in alcoholic solution, separating as a yellow oil, which soon solidified. After crystallisation from light petroleum, it was obtained as pale yellow prisms. Neither phototropy nor thermotropy was detected. It is very easily soluble in benzene, chloroform, ether, or glacial acetic acid, more sparingly so in alcohol or light petroleum. The solutions are colourless, with the exception of that in glacial acetic acid, which is yellow. The base melts at 69° (corr.):

0.2378 gave 11.8 c.c. N_2 (moist) at 15° and 767 mm. $\text{N} = 5.87$.

$\text{C}_{14}\text{H}_{12}\text{ONCl}$ requires $\text{N} = 5.71$ per cent.

Salicylidene-m-chloroaniline, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$, crystallises from alcohol or light petroleum in orange-yellow leaflets. This base is not phototropic, but exhibits thermotropy. At "the higher temperature" the solid darkens, and at "the lower temperature" becomes much paler; in either case it returns to the original shade at the ordinary temperature. It dissolves readily in the usual organic solvents, with the exception of light petroleum, in which it is less soluble; the solutions in alcohol, chloroform, or glacial acetic acid are deeper yellow than those in benzene, ether, or light petroleum. The yellow alcoholic solution becomes much paler, and the slightly yellow solution in light petroleum becomes colourless at the temperature of solid carbon dioxide. *Salicylidene-m-chloroaniline* melts at 95° (corr.):

0.2455 gave 12.6 c.c. N_2 (moist) at 14° and 773 mm. $\text{N} = 6.14$.

$\text{C}_{13}\text{H}_{10}\text{ONCl}$ requires $\text{N} = 6.05$ per cent.

Salicylidene-p-chloroaniline, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$, crystallises from alcohol or benzene in brilliant yellow needles. It is not phototropic. Thermotropy is indicated at "the higher temperature" by a distinct darkening in colour, and at "the lower temperature" by the colour becoming much paler, in both cases returning to the original shade at the ordinary temperature. It dissolves in the usual organic solvents; the solutions in benzene, light petroleum, or ether are colourless, whilst those in alcohol, chloroform, or acetic acid are yellow. At the temperature of solid carbon dioxide, the colour of an alcoholic solution becomes distinctly paler. *Salicylidene-p-chloroaniline* melts at $102\text{--}103^\circ$ (corr.):

0.2395 gave 12.3 c.c. N_2 (moist) at 14° and 769 mm. $\text{N} = 6.11$.

$\text{C}_{13}\text{H}_{10}\text{ONCl}$ requires $\text{N} = 6.05$ per cent.

Salicylidene-m-aminophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, separates in orange crystals on the addition of salicylaldehyde to a solution of *m*-aminophenol in dilute acetic acid. On dissolving in hot

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benzene, and adding an equal volume of light petroleum, reddish-orange scales of the base are obtained. This compound is not phototropic, but exhibits thermotropy, the colour of the crystals becoming darker at "the higher temperature" and much paler at "the lower temperature," returning to the original colour in both cases at the ordinary temperature. It is easily soluble in alcohol, chloroform, or glacial acetic acid, forming deep yellow solutions; in ether, forming a pale yellow solution; in benzene or light petroleum, in both of which it is less soluble, the solutions are colourless. The deep yellow alcoholic solution becomes much paler at the temperature of solid carbon dioxide. Salicylidene-*m*-aminophenol melts at 128—129° (corr.):

0.2653 gave 14.9 c.c. N_2 (moist) at 15° and 766 mm. $N=6.63$.

$C_{13}H_{11}O_2N$ requires $N=6.57$ per cent.

Salicylidene-p-aminobenzoic acid, $OH \cdot C_6H_4 \cdot CH:N \cdot C_6H_4 \cdot CO_2H$, crystallises from alcohol in bright yellow, silky needles. This compound is phototropic. When exposed to the action of sunlight, it darkens in colour, and returns to the original colour in the dark or in subdued daylight. Both the light and the dark coloured phototropes exhibit thermotropy. At "the higher temperature" both isomerides darken in colour; on cooling to the ordinary temperature, the paler phototrope resumes its original colour, and the same colour is exhibited by the deeper coloured phototrope, which apparently changes to the paler isomeride; at "the lower temperature" both phototropes become paler in colour. This base is easily soluble in alcohol, chloroform, or glacial acetic acid, less so in ether, benzene, or light petroleum. The solutions show about the same tint of yellow; the addition of water to the solution in glacial acetic acid, or of hydrogen chloride to the solution in alcohol, removes the colour, doubtless by hydrolysis. Salicylidene-*p*-aminobenzoic acid melts at 265—266° (corr.):

0.2134 gave 10.5 c.c. N_2 (moist) at 18.5° and 770 mm. $N=5.78$.

$C_{14}H_{11}O_3N$ requires $N=5.81$ per cent.

Sodium salicylidene-p-aminobenzoate,

was prepared by dissolving *p*-aminobenzoic acid in hot alcohol, exactly neutralising with sodium hydroxide solution, and adding the calculated quantity of salicylaldehyde. Yellow prisms were obtained, very much paler in colour than the free acid. This salt is thermotropic, but not phototropic. At "the higher temperature" it changes to red, and at "the lower temperature" becomes almost colourless; in each case returning to its original tint at the ordinary temperature. It dissolves in cold water or alcohol, forming a deep yellow solution, which hydrolyses on warming:

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0.7399 gave 0.1998 Na_2SO_4 . $\text{Na}=8.76$.

$\text{C}_{14}\text{H}_{10}\text{O}_3\text{NNa}$ requires $\text{Na}=8.68$ per cent.

Calcium salicylidene-p-aminobenzoate,

was obtained in pale yellow leaflets by the interaction of salicylaldehyde and an alcoholic solution of *p*-aminobenzoic acid, which was previously neutralised by calcium hydroxide solution. No phototropy could be detected, but thermotropy was observed by a darkening of colour at "the higher temperature." The salt dissolves in cold water, and the solution hydrolyses on warming:

0.6690 gave 0.1683 CaSO_4 . $\text{C}=7.41$.

$\text{C}_{28}\text{H}_{20}\text{O}_6\text{N}_2\text{Ca}$ requires $\text{C}=7.71$ per cent.

Barium salicylidene-p-aminobenzoate,

consists of small, yellow needles, and exhibits similar properties to the calcium salt. It is thermotropic, but not phototropic. At "the higher temperature" it becomes darker, and at "the lower temperature" paler in colour, the original colour returning, in each case, at the ordinary temperature.

For analysis, the salt was dried at 100° :

0.5551 gave 0.2110 BaSO_4 . $\text{Ba}=22.38$.

$\text{C}_{28}\text{H}_{20}\text{O}_6\text{N}_2\text{Ba}$ requires $\text{Ba}=22.25$ per cent.

o-Methoxybenzylidene-p-aminobenzoic acid,

was prepared in alcoholic solution, using *p*-aminobenzoic acid and *o*-methoxybenzaldehyde. It immediately separates in pale yellow needles, which, recrystallised from benzene, become much paler in colour. It is slightly thermotropic, but gives no indication of phototropy. It dissolves in alcohol, ether, or glacial acetic acid, and is sparingly soluble in benzene, chloroform, or light petroleum. The solutions are colourless, with the exception of that in acetic acid, which is yellow. The ether melts at 225.5° (corr.):

0.2469 gave 12.2 c.c. N_2 (moist) at 21° and 759 mm. $\text{N}=5.62$.

$\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{N}=5.49$ per cent.

Salicylidene- α -naphthylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$.—In a previous paper (*loc. cit.*) we described this compound as consisting of dark orange prisms which melt at 45.5° . We had overlooked an earlier description by Pope and Fleming (*Trans.*, 1908, **93**, 1916), who, however, obtained it in pale yellow needles melting at 53° . This shows the influence of slight alterations of the experimental conditions in determining the form of the product in the case of compounds containing the group $\cdot\text{CH}\cdot\text{N}\cdot$, which in so many

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instances exhibit different properties in the hands of different observers (compare Hantzsch and Schwab, *Ber.*, 1901, **34**, 828). This compound is not acted on by light, but is thermotropic; at "the lower temperature" its dark orange colour changes to canary-yellow, the former colour returning at the ordinary temperature. Solutions of this base in ether, benzene, or light petroleum are paler in colour than those in other solvents. The colour of the alcoholic solution becomes temporarily paler at "the lower temperature."

Salicylidene-β-naphthylamine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_{10}\text{H}_7$. — This compound, previously prepared by Emmerich (*Annalen*, 1887, **241**, 351), exhibits marked phototropic and thermotropic properties, its colour showing reversible variations between yellow and orange or red. We are at present submitting this compound to a more detailed investigation. Emmerich gives the melting point of this compound as 121° ; the specimens we have prepared melt at 126° (corr.).

Disalicylidene-p-phenylenediamine, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N})_2 \text{C}_6\text{H}_4$, may be obtained either in pale yellow or orange-red plates. When the aldehyde and the diamine are brought together in alcoholic solution at a temperature below 50° , the mixture remains clear for a few minutes, and then the compound quickly separates in pale yellow plates. If, however, the temperature of the experiment be above 50° , a mixture of both isomerides is formed, the proportion of the red form increasing the higher the temperature employed, but contact of solvents, in such a proportion that only a small part dissolved with the yellow plates or the mixtures obtained, changes the yellow into the more stable red isomeride. The change of the yellow into the red form by this contact with solvents, accompanied, of course, with partial solution, takes place in a few minutes when the solvent is ethyl acetate, chloroform, benzene, or acetone; in half an hour to an hour when alcohol or ether is used; whilst with light petroleum several hours are requisite. It is noteworthy that the order of solvents just given corresponds with that of the solubility of the red isomeride; it is most soluble in the first group, and least soluble in light petroleum.

No phototropy could be detected in either isomeride, but both exhibit thermotropy, and, further, at 115° the yellow isomeride changes to the red. When the yellow isomeride is heated, it gradually deepens in colour, until, at about 110° , it becomes orange. If the temperature is then lowered, the reverse changes of colour take place; if, however, the temperature is allowed to rise above 110° , the orange colour changes gradually into red and deep red until the melting point is reached. On lowering the

temperature, the reverse changes of colour are observed until a temperature of about 115° is reached; below this temperature, the orange and yellow colour does not reappear, but the red merely becomes slightly paler. This isomeric change at 115° , not being reversible, is not phototropic, although it takes place under the thermotropic conditions pertaining to that temperature. At the temperature of solid carbon dioxide, the yellow isomeride gave no indication of thermotropy, but the red isomeride became yellow, returning to red at the ordinary temperature. The red isomeride melts at $212\text{--}213^{\circ}$ (corr.):

0.2192 gave 16.7 c.c. N_2 (moist) at 17° and 769 mm. $\text{N} = 8.94$.

$\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N} = 8.86$ per cent.

2: 2'-Dimethoxydibenzylidene-p-phenylenediamine,

was prepared by the interaction of the diamine and *o*-methoxybenzaldehyde in alcoholic solution. After recrystallisation from alcohol, pale yellow needles of the ether were obtained. It is not phototropic, and but slightly thermotropic. It dissolves readily in most organic solvents, sparingly in ether. In glacial acetic acid, the solution is dark red. The *hydrochloride*, which was prepared by passing hydrogen chloride into an ethereal or chloroformic solution of the base, is red, in the first instance, but soon changes to orange-yellow. The base melts at 152° (corr.):

0.2492 gave 17.7 c.c. N_2 (moist) at 17° and 766 mm. $\text{N} = 8.31$.

$\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_2$ requires $\text{N} = 8.14$ per cent.

m-Hydroxybenzylidene-*m*-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\text{Me}$, was obtained in colourless crystals on the addition of the amine to the aldehyde solution. The crystals were dissolved in warm benzene, and light petroleum added, when long, colourless prisms of the base slowly separated. This compound is neither phototropic nor thermotropic. It dissolves readily in the usual organic solvents, but is sparingly soluble in light petroleum. With the exception of the solution in glacial acetic acid, which is yellow, the solutions are colourless. The *hydrochloride* is yellow. *m*-Hydroxybenzylidene-*m*-toluidine melts at $106\text{--}107^{\circ}$ (corr.):

0.2592 gave 14.6 c.c. N_2 (moist) at 16.5° and 765 mm. $\text{N} = 6.60$.

$\text{C}_{14}\text{H}_{13}\text{ON}$ requires $\text{N} = 6.64$ per cent.

p-Hydroxybenzylidene-*m*-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\text{Me}$.—*m*-Toluidine was added to a solution of *p*-hydroxybenzaldehyde in hot benzene. Small, colourless crystals separated on cooling, which, dried in the air, became slightly yellow. When recrystallised from alcohol, pale yellow plates were obtained, whilst from benzene almost colourless crystals were obtained, the latter not very well defined.

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Both the pale yellow crystals from alcohol and the almost colourless crystals from benzene, when rubbed in a mortar, became distinctly yellow. Whether these different colours represent or not distinct isomerides or isomeric mixtures was not determined.

This compound is not phototropic, but exhibits thermotropy. At "the higher temperature" the pale yellow crystals from alcohol deepen in colour, the original colour returning at the ordinary temperature; the colourless crystals from benzene do not change. At "the lower temperature" the yellow crystals become colourless, their colour returning at the ordinary temperature.

Both sets of crystals behave similarly towards solvents. The compound dissolves readily in alcohol, ether, glacial acetic acid, or ethyl acetate; less readily in chloroform or benzene; sparingly in light petroleum. The solutions are yellow except those in ether or benzene, which are almost colourless.

p-Hydroxybenzylidene-*m*-toluidine melts at 181° (corr.):

0.2663 gave 15.0 c.c. N₂ (moist) at 18° and 763 mm. N=6.53.

C₁₄H₁₃ON requires N=6.64 per cent.

Anisylidene-m-toluidine, OMe·C₆H₄·CH:N·C₆H₄Me, was prepared from anisaldehyde and *m*-toluidine. It crystallises from alcohol in small, colourless plates soluble in the usual organic solvents; in glacial acetic acid the solution is yellow; the other solvents give colourless solutions. It melts at 59° (corr.):

0.2922 gave 15.95 c.c. N₂ (moist) at 14.5° and 750 mm. N=6.32.

C₁₅H₁₅ON requires N=6.22 per cent.

Anisylidene-m-toluidine hydrochloride, C₁₅H₁₅ON·HCl.—A solution of the base in dry ether was saturated with dry hydrogen chloride, when the salt was precipitated as a pale yellow powder. It melts at 174° (corr.). When dissolved in alcohol and neutralised with a standard solution of sodium hydroxide, using phenolphthalein as indicator:

0.7553 required 27.4 c.c. (1 c.c.=0.003854 HCl). HCl=14.04.

C₁₅H₁₆ONCl requires HCl=13.93 per cent.

2-Hydroxy-5-methylbenzylidene-m-toluidine,

crystallises from alcohol in pale orange leaflets, very soluble in the usual organic solvents. It is not phototropic, but exhibits thermotropy; at "the higher temperature" it darkens in colour, and at "the lower temperature" it becomes paler, and returns to the original colour, in both cases, at the ordinary temperature.

In benzene, light petroleum, or ether, the solutions of this base

are faintly yellow, while those in acetic acid, alcohol, or chloroform are deep yellow; at "the lower temperature" the alcoholic solution exhibits thermotropy similar to the solid.

2-Hydroxy-5-methylbenzylidene-*m*-toluidine melts at 70° (corr.):

0.2672 gave 14.0 c.c. N₂ (moist) at 14° and 767 mm. N = 6.23.

C₁₅H₁₅ON requires N = 6.22 per cent.

2: 2'-*Dihydroxy-5: 5'-dimethyldibenzylidene-p-phenylenediamine*,
(OH·C₆H₃Me·CH:N)₂C₆H₄,

occurs apparently in two isomeric modifications; the one, crystallised from benzene, in bright yellow leaflets, which melt at 256° (corr.); the other, in yellowish-brown crystals, crystallised from glacial acetic acid, which melt about half a degree lower than the preceding isomeride. No indication of phototropy was observed, but both isomerides exhibit thermotropy at the "higher" and "lower temperatures." Both behave in the same manner towards solvents; in benzene, chloroform, or glacial acetic acid, they are sparingly soluble, and less soluble in alcohol or light petroleum:

0.2822 gave 20.1 c.c. N₂ (moist) at 18° and 760 mm. N = 8.23.

C₂₂H₂₀O₂N₂ requires N = 8.14 per cent.

5-*Bromosalicylidene-m-toluidine*, OH·C₆H₃Br·CH:N·C₆H₄Me, crystallises from alcohol in yellow plates mixed with slightly darker coloured prisms of a possible isomeride. No phototropy was detected, but thermotropy was observed at both "the higher" and "the lower temperatures." It dissolves easily in the usual organic solvents, the solutions in ether, benzene, or light petroleum being paler in colour than those in chloroform, alcohol, or glacial acetic acid. The base melts at 102—103° (corr.):

0.3262 gave 13.5 c.c. N₂ (moist) at 15° and 757 mm. N = 4.83.

C₁₄H₁₂ONBr requires N = 4.83 per cent.

5: 5'-*Dibromodisalicylidene-p-phenylenediamine*,
(OH·C₆H₃Br·CH:N)₂C₆H₄.

—This compound, after recrystallisation from nitrobenzene, was obtained in dark yellow leaflets almost insoluble in solvents of low boiling point. It is not phototropic, but exhibits thermotropy. At "the higher temperature" it is distinctly red, and at "the lower temperature" loses much of its yellow, in both cases returning to its original colour at the ordinary temperature. It melts at 306° (corr.):

0.2408 gave 12.2 c.c. N₂ (moist) at 18° and 767 mm. N = 5.91.

C₂₀H₁₄O₂N₂Br₂ requires N = 5.91 per cent.

3-*Nitrosalicylidene-m-toluidine*, OH·C₆H₃(NO₂)·CH:N·C₆H₄Me, was obtained from solution in alcohol in light red needles. It is

not phototropic, but exhibits thermotropy at both "the higher" and especially "the lower temperature." It dissolves readily in benzene, chloroform, or acetic acid, and is not so soluble in alcohol, ether, or light petroleum. The colour of the solutions is the same, but the solution in chloroform shows green fluorescence. Low temperature thermotropy was observed in the case of the alcoholic solution. It melts at 144—145° (corr.):

0.2309 gave 21.5 c.c. N₂ (moist) at 14° and 759 mm. N=10.95.

C₁₄H₁₂O₃N₂ requires N=10.94 per cent.

5-Nitrosalicylidene-m-toluidine, OH·C₆H₃(NO₂)·CH:N·C₆H₄Me, crystallises from alcohol in bright yellow needles. It is not affected by light, but exhibits thermotropy at both "the higher" and "the lower temperature." The behaviour towards solvents, including the fluorescence of the chloroformic solution, and the thermotropy of the alcoholic solution, is similar to that of the isomeride just described. It melts at 139° (corr.):

0.2113 gave 19.7 c.c. N₂ (moist) at 15° and 759 mm. N=10.91.

C₁₄H₁₂O₃N₂ requires N=10.94 per cent.

Vanillidene-m-toluidine, OH·C₆H₃(OMe)·CH:N·C₆H₄Me, crystallises from light petroleum in colourless, silky needles. It is not affected by light nor by temperatures below its melting point. It dissolves in the usual organic solvents; the solution in alcohol or acetic acid is deep yellow, in chloroform it is pale yellow, and in ether, benzene, or light petroleum, colourless. If the crystals are rubbed in a mortar, they become temporarily yellow. It melts at 96° (corr.), forming a yellow liquid:

0.2574 gave 13.2 c.c. N₂ (moist) at 16.5° and 751 mm. N=5.90.

C₁₅H₁₅O₂N requires N=5.81 per cent.

Piperonylidene-m-toluidine, CH₂:O₂:C₆H₃·CH:N·C₆H₄Me, crystallises from alcohol in small, colourless prisms. It is easily soluble in the usual organic solvents, giving colourless solutions, except the solution in glacial acetic acid, which is yellow. It melts at 71° (corr.):

0.2964 gave 14.9 c.c. N₂ (moist) at 16° and 768 mm. N=5.91.

C₁₅H₁₃O₂N requires N=5.86 per cent.

2-Hydroxy-α-naphthylidene-m-toluidine, OH·C₁₀H₆·CH:N·C₆H₄Me, crystallises from alcoholic solution in orange-yellow needles. It is not affected by light, but shows thermotropy at both the "higher" and the "lower temperatures;" it dissolves in the usual organic solvents, exhibiting no differences of colour. It melts at 91.5° (corr.):

0.2376 gave 10.6 c.c. N₂ (moist) at 14° and 748 mm. N=5.17.

C₁₈H₁₅ON requires N=5.37 per cent.

2-Hydroxy-α-naphthylidene-β-naphthylamine,

which has been previously described (Bartsch, *Ber.*, 1903, **36**, 1975), crystallises from alcohol in dark orange needles. It is not phototropic, but exhibits thermotropy at both "the higher" and "the lower temperatures." Its solutions show no difference of colour. Its hydrochloride is orange. We find, in agreement with Bartsch, that the base melts at 143° (corr.):

0.2242 gave 9.2 c.c. N₂ (moist) at 17.5° and 755 mm. N=4.74.

C₂₁H₁₅ON requires N=4.72 per cent.

2: 2'-Dihydroxy-di-α-naphthylidene-p-phenylenediamine,

—This compound consists of small, glistening, crimson-red crystals. It is sparingly soluble in organic solvents. It is not affected by light, but exhibits thermotropy both at "the higher" and "the lower temperatures." It melts at 307° (corr.):

0.2226 gave 13.1 c.c. N₂ (moist) at 18° and 760 mm. N=6.80.

C₂₈H₂₀O₂N₂ requires N=6.73 per cent.

Cinnamylidene-m-toluidine, C₆H₅·CH:CH·CH:N·C₆H₄Me, crystallises from alcohol in dark yellow prisms. It is neither phototropic nor thermotropic. It dissolves in the usual organic solvents, the solutions being yellow, except that in glacial acetic acid, which is red. It forms a deep yellow *hydrochloride*. The base melts at 124° (corr.):

0.2630 gave 14.4 c.c. N₂ (moist) at 17.5° and 759 mm. N=6.33.

C₁₆H₁₅N requires N=6.33 per cent.

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