CXXVIII.—*Studies in Phototropy and Thermotropy.*
Part VII. Polymorphic Anisylidenearylamines
Produced by Trituration and by the Influence of
Actinic Light.

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THIS paper is a continuation of previous communications (T., 1914, **105**, 2462; this vol., p. 452) in which the *p*-hydroxy- and the *p*-hydroxy-*m*-methoxybenzylidenearylamines were studied with special reference to polymorphic varieties produced by trituration.

The following is a description of a similar study of the *p*-methoxy-analogues.

No instance of phototropy was detected, but most of the compounds gave polymorphic forms by the prolonged influence of actinic light, and most of them were found to be thermotropic. Only one gave a polymorphic variety by trituration. Triboluminescence was entirely absent.

The method of preparation was similar to that previously described, and the terms "the lower temperature" and "the higher temperature" are employed with the same meaning as before (*loc. cit.*). The compounds dissolve in the ordinary organic solvents, with the exception of dianisylidenebenzidine, which is sparingly soluble in all except nitrobenzene.

Anisylideneaniline, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_5$, was first prepared by Schiff (*Annalen*, 1869, **150**, 195), who describes it as consisting of golden-yellow plates. Freund and Becker by crystallisation from alcohol obtained colourless needles, which melted at 63° . Our specimen crystallised from light petroleum in colourless needles, which melt at $58\text{--}59^\circ$ (corr.). This compound is neither thermotropic, nor is it affected by actinic light.

Anisylidenetoluidines, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$.

Anisylidene-*m*-toluidine was prepared by Senior and Shephard (T., 1909, **95**, 1952). It is not thermotropic, nor does it polymerise under the influence of actinic light.

Anisylidene-*p*-toluidine (Steinhart, *Annalen*, 1887, **241**, 340) crystallises from light petroleum in colourless needles, which melt at $92\text{--}93^\circ$ (corr.) (Steinhart gives 92°). It is not thermotropic or affected by actinic light.

Anisylidenexylidines, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}_2$.

Anisylidene-*o*-4-xylidine crystallises from light petroleum in colourless needles melting at $74\text{--}75^\circ$ (corr.):

0.1570 gave 7.8 c.c. N_2 at 9° and 764 mm. $\text{N}=6.04$.

$\text{C}_{16}\text{H}_{17}\text{ON}$ requires $\text{N}=5.90$ per cent.

Anisylidene-*o*-4-xylidine assumes a pale yellow colour on keeping. It is thermotropic between "the lower temperature" and the ordinary temperature.

Anisylidene-*m*-4-xylidine separates from alcohol in pale yellow plates, which melt at $65\text{--}66^\circ$ (corr.):

0.1770 gave 8.8 c.c. N_2 at 12° and 763 mm. $\text{N}=5.98$.

$\text{C}_{16}\text{H}_{17}\text{ON}$ requires $\text{N}=5.90$ per cent.

Anisylidene-*m*-4-xylylidine is thermotropic between "the lower temperature" and 65°. It is not affected by actinic light.

Anisylidene-*p*-xylylidine crystallises in biscuit-coloured prisms from light petroleum, which melt at 68—69° (corr.):

0.2552 gave 12.8 c.c. N₂ at 15° and 761 mm. N=5.95.

C₁₆H₁₇ON requires N=5.90 per cent.

Anisylidene-*p*-xylylidine is thermotropic between "the lower temperature" and the ordinary temperature. On prolonged exposure to light it is converted into a slightly deeper coloured *polymorphic form*.

Anisylidene- ψ -cumidine, OMe·C₆H₄·CH:N·C₆H₂Me₃, separates from carbon tetrachloride in very pale yellow prisms, which melt at 66° (corr.):

0.2372 gave 11.4 c.c. N₂ at 13° and 754 mm. N=5.69.

C₁₇H₁₉ON requires N=5.53 per cent.

Anisylidene- ψ -cumidine is thermotropic between "the lower temperature" and about 65°. Prolonged exposure to sunlight produces no visible change.

Anisylidenechloroanilines, OMe·C₆H₄·CH:N·C₆H₄Cl.

Anisylidene-*o*-chloroaniline crystallises from alcohol in almost colourless needles, which melt at 61° (corr.):

0.2046 gave 10.0 c.c. N₂ at 17° and 762 mm. N=5.77.

C₁₄H₁₂ONCl requires N=5.71 per cent.

Anisylidene-*o*-chloroaniline is not affected by prolonged exposure to sunlight, but is thermotropic between the ordinary temperature and about 60°.

Anisylidene-*m*-chloroaniline separates from light petroleum in flat, biscuit-coloured prisms, which melt at 54° (corr.):

0.2034 gave 9.9 c.c. N₂ at 14° and 764 mm. N=5.82.

C₁₄H₁₂ONCl requires N=5.71 per cent.

Anisylidene-*m*-chloroaniline is thermotropic between "the lower temperature" and the ordinary temperature. Prolonged exposure to sunlight converts it into a slightly deeper-coloured polymorphic form.

Anisylidene-*p*-chloroaniline crystallises from light petroleum in colourless plates melting at 93—94° (corr.):

0.2063 gave 10.4 c.c. N₂ at 19° and 761 mm. N=5.90.

C₁₄H₁₂ONCl requires N=5.71 per cent.

Anisylidene-*p*-chloroaniline is neither thermotropic nor is it affected by prolonged exposure to sunlight.

Anisylidenebromoanilines, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$.

Anisylidene-m-bromoaniline separates from light petroleum in colourless needles, which melt at $61\text{--}62^\circ$ (corr.):

0.1978 gave 8.2 c.c. N_2 at 11° and 754 mm. $\text{N}=4.94$.

$\text{C}_{14}\text{H}_{12}\text{ONBr}$ requires $\text{N}=4.83$ per cent.

Anisylidene-m-bromoaniline is not thermotropic. On prolonged exposure to sunlight, it is converted into a very pale biscuit-coloured polymorphic variety.

Anisylidene-p-bromoaniline crystallises from carbon tetrachloride in very faint yellow needles, which melt at 120° (corr.). It becomes somewhat deeper in colour on keeping:

0.2654 gave 10.9 c.c. N_2 at 11° and 753 mm. $\text{N}=4.89$.

$\text{C}_{14}\text{H}_{12}\text{ONBr}$ requires $\text{N}=4.83$ per cent.

Anisylidene-p-bromoaniline is thermotropic between the ordinary temperature and about 118° . On exposure to sunlight, it is converted into a deep canary-yellow-coloured *polymorphic form*.

Anisylideneaminophenols, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.

Anisylidene-o-aminophenol was first prepared by Haegele (*Ber.*, 1892, **25**, 2755), who describes it as crystallising from dilute alcohol in brownish-yellow needles melting at 89° . Our specimen, crystallised from light petroleum, has the same appearance and melting point. Its solution exhibits fluorescence.

Anisylidene-o-aminophenol is thermotropic between "the lower temperature" and about 85° . Prolonged exposure to sunlight converts it into a slightly deeper-coloured *polymorphic form*.

Anisylidene-p-aminophenol was also prepared by Haegele (*loc. cit.*), who describes it as crystallising from alcohol in yellow prisms, melting at 188° . Our specimen, crystallised from xylene, consists of buff-coloured needles, which have the same melting point. It is not affected by sunlight, but exhibits thermotropy between the ordinary temperature and about 185° .

Anisylidene-p-anisidine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, was first prepared by Hantzsch and Schwab (*Ber.*, 1901, **34**, 832), who describe it as shining, white plates, melting at 142° . By crystallisation from carbon tetrachloride we obtained colourless needles melting at $146\text{--}147^\circ$ (corr.). Prolonged exposure to sunlight converts it into a very pale biscuit-coloured *polymorphic form*. It exhibits thermotropy between the ordinary temperature and about 145° ; at the latter temperature it has a pale biscuit colour.

Anisylideneaminobenzoic Acids, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$.

Anisylidene-o-aminobenzoic acid crystallises from xylene in fine, yellow needles, which melt at 145° (corr.):

0.1504 gave 7.0 c.c. N_2 at 15° and 766 mm. $\text{N}=5.56$.

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

Anisylidene-o-aminobenzoic acid is not affected by sunlight. It is thermotropic between the ordinary temperature and about 145° . Its colour is deepest at about 120° .

Anisylidene-m-aminobenzoic acid separates from xylene in biscuit-coloured needles, which melt at $151\text{--}152^\circ$ (corr.). A yellow variety which melted at the same temperature was obtained by crystallising from alcohol:

0.1472 gave 6.8 c.c. N_2 at 11° and 766 mm. $\text{N}=5.59$.

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

Anisylidene-m-aminobenzoic acid is dimorphous. Trituration converts the biscuit-coloured variety into the yellow-coloured variety. The paler-coloured variety is scarcely acted on by sunlight, but exhibits thermotropy between the ordinary temperature and about 150° . The deeper-coloured variety is converted into a brownish-yellow, polymorphic form by prolonged exposure to sunlight. It reverts to the paler-coloured variety at about 70° .

Anisylidene-p-aminobenzoic acid crystallises from alcohol in pale yellow needles, which melt at $196\text{--}197^\circ$ (corr.):

0.1168 gave 5.4 c.c. N_2 at 12° and 765 mm. $\text{N}=5.57$.

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

Anisylidene-p-aminobenzoic acid is not acted on by sunlight, but is thermotropic between the ordinary temperature and about 195° .

Dianisylidenebenzidine,

$\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$,

crystallises from nitrobenzene in yellow plates melting at $257\text{--}258^\circ$ (corr.). It is only sparingly soluble in other usual organic solvents:

0.2052 gave 12.0 c.c. N_2 at 21° and 753 mm. $\text{N}=6.73$.

$\text{C}_{28}\text{H}_{24}\text{O}_2\text{N}_2$ requires $\text{N}=6.67$ per cent.

Dianisylidenebenzidine is thermotropic between "the lower temperature" and about 250° . At higher temperatures the colour change is well marked. It is converted into a somewhat deeper-coloured polymorphic form by prolonged exposure to sunlight.

Anisylidenenaphthylamines, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$.

Anisylidene- α -naphthylamine was prepared by Pope and Fleming (T., 1908, 93, 1916), who describe it as crystallising from alcohol

in colourless plates melting at 100—101°. Our specimen, crystallised from light petroleum, consists of pale yellow plates melting at this temperature. It is thermotropic between "the lower temperature" and about 100°. Prolonged exposure to sunlight converts it into a slightly deeper-coloured *polymorphic form*.

Anisylidene- β -naphthylamine was prepared by Steinhart (*loc. cit.*). Our specimen, crystallised from light petroleum, consists of pale yellow plates, which melt at 99° (corr.) (Steinhart gives 98°). It is thermotropic between "the lower temperature" and about 95°. Prolonged exposure to sunlight converts it into a slightly deeper-coloured *polymorphic form*.

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