101. *Absorption Spectra of* N-*Substituted Auramine Dyes.*

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The absorption spectra of auramine and *N*-substituted auramines, their hydrochlorides, and picrates are recorded for the range 2000—5300 A.

Substituted auramines are obtained by Fehrmann's method (*Ber.*, 1887, **20**, 2851), the hydrochloride being heated with an aromatic amine :

$$(NMe_2\cdot C_6H_4)_2C{:}NH,HCl + R\cdot NH_2 = (NMe_2\cdot C_6H_4)_2C{:}NR,HCl + NH_3 \quad \text{(I.)}$$

Fehrmann thus synthesised (I; R = Ph), but (I; R = α-naphthyl) and (I; R = β-naphthyl) were obtained by another method (D.R.P. 44077).

The salt of the unsubstituted compound is a yellow dye, and those of the phenyl and the naphthyl derivatives are orange and brownish-yellow respectively. The 2-*anthryl* derivative was prepared and, as expected, was a brown dye.

The absorption spectra of these compounds have been measured over the range 2500—5500 A.

Auramine hydrochloride and N-*substituted auramine hydrochlorides* (Fig. 1).

Substance.	*c.*	Maximum.		Minimum.		Maximum.	
		A.	log ε.	A.	log ε.	A.	log ε.
Auramine, HCl	N/10,000 N/50,000	3650	4·30	3800	4·08	4250	4·79
N-Phenylauramine, HCl	N/10,000 N/20,000	3580	4·31	3850	4·00	4220	4·45
N-α-Naphthylauramine, HCl	N/10,000 N/50,000	—	—	3450	—	4450	4·74
N-β-Naphthylauramine, HCl	N/10,000 N/50,000	—	—	3450	—	4500	4·82
N-2-Anthrylauramine, HCl	N/10,000*	—	—	3850	4·19	4150	4·28

Auramine and N-*substituted auramines* (Fig. 2).

Substance.	*c.*	Maximum.		Minimum.		Maximum.	
		A.	log ε.	A.	log ε.	A.	log ε.
Auramine	N/10,000	3600	4·38	3860	4·10	4230	4·40
N-Phenylauramine	N/10,000 N/50,000	—	—	2750	3·30	3600	4·68
N-α-Naphthylauramine	N/10,000 N/50,000	—	—	2870	3·84	3340	4·72
N-β-Naphthylauramine	N/10,000 N/50,000	—	—	2810	4·10	3450	4·76
N-2-Anthrylauramine	N/10,000*	—	—	3900	4·00	4520	4·19

Auramine picrate and N-*substituted auramine picrates* (Fig. 3).

Substance.	*c.*	Maximum.		Minimum.		Maximum.	
		A.	log ε.	A.	log ε.	A.	log ε.
Auramine picrate	N/10,000	—	—	2950	3·95	4100	4·85
N-Phenylauramine picrate	N/20,000	—	—	2750	3·95	3600	4·73
N-α-Naphthylauramine picrate	N/20,000	—	—	3000	4·05	4550	4·70
N-β-Naphthylauramine picrate	N/20,000	3450	4·51	3700	4·35	4450	4·53

* In these solutions chloroform was used as solvent.

EXPERIMENTAL.

Auramine hydrochloride was purified by crystallising " Auramine O extra conc." from alcohol; m. p. 265° (Found : C, 63·15; H, 7·2. Calc. for $C_{17}H_{21}N_3,HCl,H_2O$: C, 63·4; H, 7·5%). 5 G. of the salt were dissolved in alcohol (1500 c.c.), cooled to 0°, and aqueous ammonia (*d* 0·88; 50 c.c.) added with stirring. The base was filtered off and crystallised from alcohol (after the addition of a drop of ammonia), forming slightly yellow, small crystals, m. p. 135—136° (Graebe, *Ber.*, 1887, **20**, 3264, gives m. p. 136°). Its alcoholic solution, even if ammonia is added, is yellow (Semper, *Annalen*, 1911, **381**, 46). Its *sulphanilate*, prepared in and crystallised from alcohol, formed yellow crystals, m. p. 160° (Found : C, 62·6; H, 6·5. $C_{23}H_{28}O_3N_4S$ requires C, 62·7; H, 6·4%), and its 2-*hydroxy*-3-*naphthoate*, similarly prepared and crystallised, formed yellowish crystals, m. p. 142—143° (Found : C, 74·0; H, 6·2. $C_{28}H_{29}O_3N_3$ requires C, 73·8; H, 6·4%). Its picrate had m. p. 236° (Fehrmann, *loc. cit.*, gives 230—236°).

A paste of auramine hydrochloride (5 g.) and aniline (5 g.) was heated for some hours at

FIG. 1.

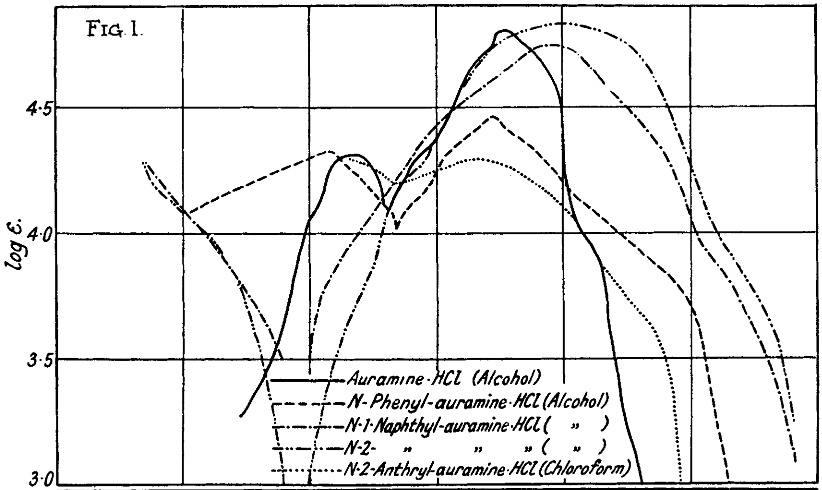


FIG. 2.

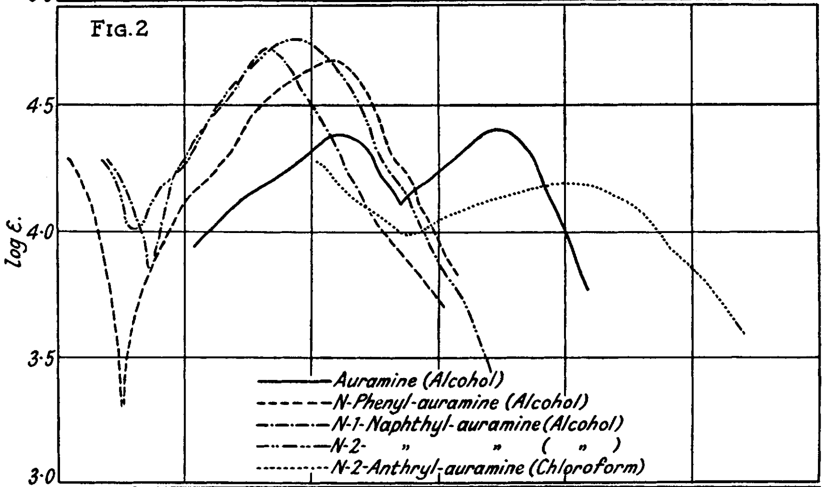
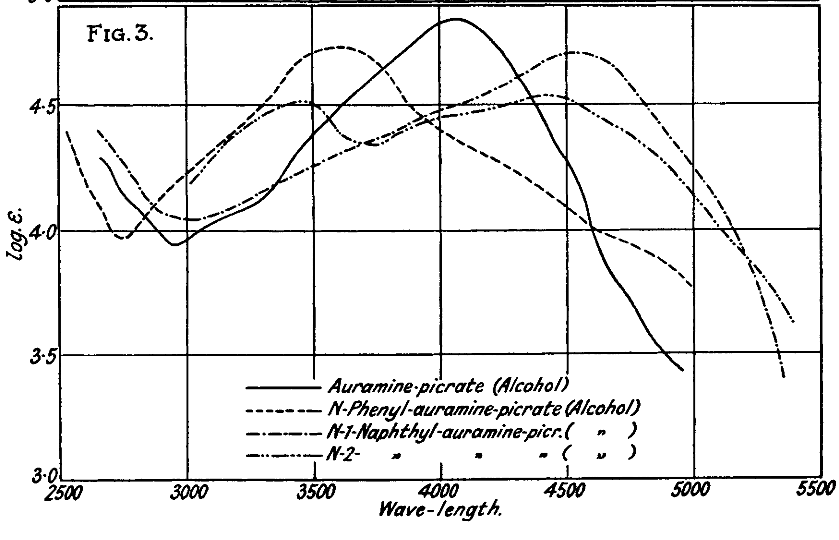


FIG. 3.



130° and then at 170° for some hours. The solid formed on cooling was washed with ether, dissolved in alcohol, water added, and the *N*-phenyl hydrochloride salted out and crystallised from alcohol; it formed orange micro-crystals (Found: C, 69·7; H, 6·9. Calc. for $C_{23}H_{25}N_3,HCl,H_2O$: C, 69·4; H, 7·1%), and dyed silk and wool an orange colour. The base was liberated by addition of 2N-potassium hydroxide to the hydrochloride solution, extracted with benzene, the solvent evaporated, and the residue crystallised from acetone (after the addition of a drop of aqueous ammonia). It formed small greenish-yellow crystals, m. p. 165° (Graebe, *loc. cit.*, gives m. p. 170°; Baither, *Ber.*, 1887, **20**, 3296, gives m. p. 172°); its alcoholic solution is colourless, and its picrate is red.

Auramine hydrochloride (5 g.) was thoroughly mixed with β-naphthylamine (7 g.) and heated at 150° for 16 hrs. The solid formed on cooling was powdered, washed by decantation with ether, and crystallised from chloroform. *N*-β-Naphthylauramine hydrochloride forms red micro-crystals (Found: C, 75·7; H, 6·85; N, 9·9. Calc. for $C_{27}H_{27}N_3,HCl$: C, 75·4; H, 6·6; N, 9·8%), and dyes silk and wool a brownish-yellow colour.

From the foregoing hydrochloride, the base was prepared as for its phenyl analogue. It formed small greenish-yellow crystals, m. p. 180—181°, from acetone (Found: C, 82·7; H, 7·3; N, 11·05. Calc. for $C_{27}H_{27}N_3$: C, 82·4; H, 6·9; N, 10·7%); its alcoholic solution was colourless. Its picrate formed orange-red crystals from alcohol.

The hydrochloride of the α-naphthyl analogue was prepared as for the β-naphthyl compound, and when dissolved in alcohol and basified as before it yielded the base as yellow crystals, m. p. 225° (Found: C, 82·0; H, 6·9; N, 11·1%), colourless in alcoholic solution.

The latter base (1 g.) was dissolved in acetone (50 c.c.), and 0·1N-hydrochloric acid (25 c.c.) and then water (200 c.c.) added. The solution was saturated with sodium chloride, the precipitate filtered off, and crystallised from alcohol. The brownish-yellow powder did not give the analytical results required for the *N*-α-salt (Found: C, 70·7, 74·55, 68·5; H, 6·3, 6·3, 6·1; N, 11·9, 10·9, 11·0. $C_{27}H_{27}N_3,HCl$ requires C, 75·4; H, 6·6; N, 9·8%). It dyed silk and wool a brownish-yellow colour, which changed after some days into a pale yellowish-buff. Skeins dyed with the other *N*-substituted auramine hydrochlorides kept their shade without any change.

N-α-Naphthylauramine picrate, prepared in and crystallised from alcohol, formed dark red crystals, m. p. 175—178° (Found: C, 63·3; H, 5·1. Calc. for $C_{33}H_{30}O_7N_6$: C, 63·65; H, 4·9%).

Auramine hydrochloride (5 g.) was thoroughly mixed with 2-anthrylamine (3·5 g.) and heated for 24 hours at 220°, the product being treated as in the condensation with β-naphthylamine. N-2-*Anthrylauramine hydrochloride* formed brown micro-crystals (Found: N, 8·8. $C_{31}H_{29}N_3,HCl$ requires N, 8·75%), and dyed silk and wool a brown colour. The *base*, liberated as before and crystallised from chloroform, formed brownish micro-crystals (Found: C, 84·3; H, 5·8; N, 9·0. $C_{31}H_{29}N_3$ requires C, 83·9; H, 6·6; N, 9·5%). It was nearly insoluble in alcohol; its chloroform solution was brown.

Absorption Spectra Data.—A quartz spectrograph (Adam Hilger, Ltd., London) which gave a dispersion of 25 cm. over the range in wave-length of 2000 to 10,000 A., and a tungsten-steel spectrum as a source of light were used. The spectrograph was equipped with a Spekker photometer. The solvent was alcohol except where denoted otherwise, and *c* gives the concentration.

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