CXXIII.—*The Colour and Constitution of the Amino-coumarins.*

By ARTHUR CLAYTON, B.Sc., A.R.C.S.

THE introduction of an amino-group into the molecule of a colourless substance does not generally cause the production of colour, but a peculiar exception is met with in the case of 6-amino-coumarin, which possesses a deep yellow colour, although coumarin itself is colourless. The cause of the yellow colour was investigated by Morgan and Micklethwait (Trans., 1904, **85**, 1230), who showed that the colour was not affected by the substitution of methyl for one or both aminic hydrogen atoms, but was destroyed by acylation or by the formation of a quaternary salt. These investigators concluded that the cause of the colour lies in some relation between the aminic nitrogen atom and the unsaturated $\cdot\text{O}\cdot\text{CO}\cdot$ group present in the lactonic ring, this conclusion being supported by the amino-group occupying a para-position with respect to the lactonic oxygen. The author of the present communication has examined a number of amino-derivatives of coumarin and its homologues with the view of obtaining further insight into the cause of the yellow colour.

Since β -naphthylamine is colourless and the only difference between the formulæ of this substance and 6-aminocoumarin is the substitution of the $\cdot\text{O}\cdot\text{CO}\cdot$ group in the latter compound for the $\cdot\text{CH}\cdot\text{CH}\cdot$ group present in the former (see formulæ), it follows that the group $\cdot\text{O}\cdot\text{CO}\cdot$ is directly involved in the production of the colour. Similarly, the amino-group is involved, because

Colourless.

Yellow.

coumarin is colourless. It has been shown by Morgan and Micklethwait (*loc. cit.*) that a mobile hydrogen atom in the amino-group does not give rise to the colour, as 6-dimethylaminocoumarin is yellow. The remaining factors possibly involved are:

1. The position in the benzenoid ring occupied by the amino-group.

2. The presence of a mobile hydrogen atom in the benzenoid ring.

3. The presence of a mobile hydrogen atom in the lactonic ring.

4. A direct connection between the $\cdot\text{O}\cdot\text{CO}\cdot$ and amino-groups, depending on or independent of their relative positions.

- (1) 5-Amino-6:7-dimethylcoumarin, 6-amino-7-methylcoumarin,

7-amino-5:6:8-trimethylcoumarin, 8-aminocoumarin, and 5:8-diamino-6:7-dimethylcoumarin were prepared by reducing the corresponding colourless nitro-compounds, and were in each case found to be yellow. As the above compounds contain the amino-group in each possible position in the benzenoid ring, the production of colour does not depend on the position occupied by the amino-group.

(2) Since 7-amino-5:6:8-trimethylcoumarin is yellow, and in this compound the benzenoid ring is completely substituted, the presence of a mobile hydrogen atom in the benzenoid ring is not involved in the colour formation.

(3) 6-Amino-4:7-dimethylcoumarin, 5-amino-4:6:7-trimethylcoumarin, 5:7-diamino-4:6:8-trimethylcoumarin, and 6-amino-3:4:7-trimethylcoumarin were prepared, and all found to be yellow, hence the presence of a mobile hydrogen atom in the lactonic ring is not necessary for the production of the colour.

(4) The formation of the yellow colour appears from the above observations to be consequent on some direct connexion between the $\cdot\text{O}\cdot\text{CO}\cdot$ and amino-groups, and the results obtained in (1) show this connexion to be independent of the relative position of these groups.

Coumarin and its derivatives exhibit additive properties due to the unsaturation of the $\cdot\text{O}\cdot\text{CO}\cdot$ group (Williamson, *Journ. Chem. Soc.*, 1875, **28**, 850; Morgan and Micklethwait, *Trans.*, 1906, **89**, 863; Clayton, *Trans.*, 1908, **93**, 524), which possesses an amphoteric nature. There is, however, a much greater tendency to combine with basic substances than with acids, so the residual affinities of the $\cdot\text{O}\cdot\text{CO}\cdot$ group may be considered to be of a weakly acid nature.

In the case of the aminocoumarins, these acid affinities would doubtless find partial satisfaction in the extra affinities available in the aminic nitrogen atom, but owing to the weakness of the union which would exist between the $\cdot\text{O}\cdot\text{CO}\cdot$ and amino-groups, it is highly probable that the bonds uniting them would be continually broken and re-formed during intermolecular motions.

If the correct formula for coumarin is that suggested by Morgan and Micklethwait (*Trans.*, 1906, **89**, 863), the amino-coumarins may be undergoing the vibratory change indicated in the subjoined formulæ for 8-aminocoumarin:

The author considers it possible that these vibrations may generate the yellow colour, and it is worthy of note that in the case of 8-aminocoumarin, where, owing to the proximity of the nitrogen and oxygen atoms concerned, the rupture of the bonds would be less easily effected, the yellow colour is much less marked than in the other amino-derivatives.

The following facts support the view expressed by the above formulæ:

(i) The above observation (p. 1350), that the colour vanishes when the supplementary valencies of the nitrogen atom are involved by the formation of a quaternary salt, and when the basicity of the amino-group is destroyed by acylation.

(ii) The fact that the hydrochlorides of all the amino-coumarins examined by the author are colourless.

(iii) The remarkable stability of the amino- and diamino-coumarins both in the solid state and in solution.

EXPERIMENTAL.

8-Aminocoumarin.—8-Nitrocoumarin (1 gram) was suspended in boiling dilute acetic acid (100 c.c.), and gradually treated with iron filings (1 gram), after which the mixture was boiled for fifteen minutes, and filtered. The filtrate yielded crystals, which, after recrystallisation from alcohol, formed pale yellow prisms, melting at 145—146°:

0.1987 gave 0.4868 CO₂ and 0.0817 H₂O. C=66.81; H=4.57.

0.1023 „ 7.5 c.c. N₂ at 20° and 756 mm. N=8.34.

C₉H₇O₂N requires C=67.08; H=4.35; N=8.70 per cent.

6-Amino-7-methylcoumarin.—A mixture of 6-nitro-7-methylcoumarin (1 gram) and 5 per cent. acetic acid (100 c.c.) was heated to boiling and gradually treated with iron filings (1 gram), after which the liquid was boiled for fifteen minutes, then cooled and filtered. The residue was extracted with alcohol and crystallised from the same solvent, when yellow needles, melting at 200—201°, were obtained:

0.1523 gave 0.3818 CO₂ and 0.0729 H₂O. C=68.37; H=5.32.

0.1216 „ 8.7 c.c. N₂ at 20° and 756 mm. N=8.14.

C₁₀H₉O₂N requires C=68.57; H=5.14; N=8.00 per cent.

6-Amino-4:7-dimethylcoumarin was prepared from 6-nitro-4:7-dimethylcoumarin in the manner described in the preceding experiment. The product, however, was extracted with glacial acetic acid, and crystallised from this solvent in yellow needles, melting at 203—205°:

0·1781 gave 0·4540 CO₂ and 0·0941 H₂O. C=69·52; H=5·87.

0·1816 „, 12·0 c.c. N₂ at 20° and 756 mm. N=7·52.

C₁₁H₁₁O₂N requires C=69·84; H=5·82; N=7·41 per cent.

5-Amino-6: 7-dimethylcoumarin.—5-Nitro-6: 7-dimethylcoumarin (1 gram) and dilute acetic acid (80 c.c.) were boiled together, and gradually treated with iron filings (0·8 gram), after which the mixture was heated for one hour. The cooled liquid was filtered and the residue extracted with alcohol, from which solvent yellow needles, melting at 189°, were obtained:

0·1630 gave 0·4148 CO₂ and 0·0871 H₂O. C=69·38; H=5·94.

0·1590 „, 10·7 c.c. N₂ at 21° and 752 mm. N=7·54.

C₁₁H₁₁O₂N requires C=69·84; H=5·82; N=7·41 per cent.

7-Amino-5: 6: 8-trimethylcoumarin. — 7-Nitro-5: 6: 8-trimethylcoumarin (5 grams) was mixed with dilute acetic acid (100 c.c.) and heated to boiling, when iron filings (5 grams) were gradually added, the mixture finally being boiled for one hour. The cooled liquid was filtered, and the residue repeatedly extracted with alcohol, in which solvent the product is somewhat sparingly soluble. Recrystallisation from glacial acetic acid yielded yellow needles, melting at 220—221°. The solution in alcohol or acetone exhibits a strong blue fluorescence, which does not appear in the solutions in benzene, toluene, or acetic acid:

0·1331 gave 0·3458 CO₂ and 0·0782 H₂O. C=70·86; H=6·60.

0·1341 „, 7·9 c.c. N₂ at 20° and 756 mm. N=6·70.

C₁₂H₁₃O₂N requires C=70·94; H=6·40; N=6·90 per cent.

6-Amino-4: 6: 7-trimethylcoumarin. — 6-Nitro-4: 6: 7-trimethylcoumarin (2 grams) and dilute acetic acid (40 c.c.) were boiled together and treated with iron filings (2 grams), after which the mixture was boiled for one hour. The cooled liquid was filtered and the residue extracted with alcohol, from which solvent 75 per cent. of the theoretical quantity of yellow needles, melting at 232—233°, was obtained. The substance is rather sparingly soluble in alcohol:

0·1812 gave 0·4699 CO₂ and 0·1047 H₂O. C=70·71; H=6·42.

0·1851 „, 11·3 c.c. N₂ at 20° and 750 mm. N=6·89.

C₁₂H₁₃O₂N requires C=70·94; H=6·40; N=6·90 per cent.

6-Nitro-3: 4: 7-trimethylcoumarin.—A solution of 3: 4: 7-trimethylcoumarin (2·3 grams) in concentrated sulphuric acid (12 c.c.) was slowly treated at 0° with a mixture of nitric acid (D 1·4) (1 c.c.) and concentrated sulphuric acid (3 c.c.), after which the liquid was kept at the ordinary temperature for thirty minutes, and then poured on crushed ice. The product crystallised from glacial acetic acid in colourless needles, melting at 169—170°:

1354 COLOUR AND CONSTITUTION OF THE AMINO-COUMARINS.

0.1994 gave 0.4515 CO_2 and 0.0832 H_2O . $\text{C}=61.76$; $\text{H}=4.64$.

0.1514 „ 7.9 c.c. N_2 at 20° and 756 mm. $\text{N}=5.93$.

$\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{C}=61.80$; $\text{H}=4.72$; $\text{N}=6.01$ per cent.

6-Amino-3: 4: 7-trimethylcoumarin. — 6-Nitro-3: 4: 7-trimethylcoumarin was reduced with iron filings and dilute acetic acid in the usual way, the liquid being boiled for twenty minutes after the addition of the iron. The cooled mixture was filtered, and the residue extracted with alcohol, from which solvent the product crystallised in yellow needles, melting at $200\text{--}201^\circ$. The alcoholic solution exhibits a brilliant green fluorescence:

0.1450 gave 0.3759 CO_2 and 0.0820 H_2O . $\text{C}=70.70$; $\text{H}=6.28$.

0.1047 „ 6.7 c.c. N_2 at 20° and 756 mm. $\text{N}=7.32$.

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C}=70.94$; $\text{H}=6.40$; $\text{N}=6.90$ per cent.

5: 8-Diamino-6: 7-dimethylcoumarin. — 5: 8-Dinitro-6: 7-dimethylcoumarin (2 grams) was heated to 100° with dilute acetic acid and gradually treated with iron filings (5 grams), the mixture being subsequently boiled for twenty minutes, then cooled and filtered. The residue was extracted with alcohol, from which solvent yellow needles, melting at $209\text{--}212^\circ$, were obtained:

0.1330 gave 16.0 c.c. N_2 at 20° and 762 mm. $\text{N}=13.79$.

$\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{N}=13.73$ per cent.

5: 7-Diamino-4: 6: 8-trimethylcoumarin. — 5: 7-Dinitro-4: 6: 8-trimethylcoumarin was reduced with iron filings and acetic acid as in the preceding experiment. The product separated from alcohol in fine, yellow needles, melting at $218\text{--}220^\circ$. There was no tendency in this or the preceding experiment to form the nitroamine:

0.1403 gave 0.3381 CO_2 and 0.0781 H_2O . $\text{C}=65.72$; $\text{H}=6.18$.

0.1093 „ 12.3 c.c. N_2 at 18° and 734 mm. $\text{N}=12.55$.

$\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C}=66.05$; $\text{H}=6.42$; $\text{N}=12.84$ per cent.

The author desires to express his thanks to the Chemical Society for a grant which has in part defrayed the expense incurred during this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.