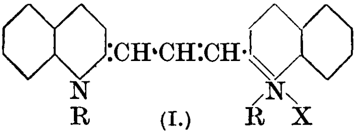
CCCCXVIII.—*Carbocyanine Dyes with Substituents attached to the Three-carbon Chain.*

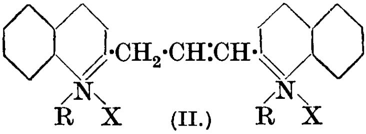
By Frances Mary Hamer.

The carbocyanine dyes are characterised by the three-carbon chain, $:CH\cdot CH:CH\cdot$, linking two heterocyclic nuclei containing nitrogen, which is tervalent in one nucleus, quinquevalent in the other. By varying the nature of these nuclei, seven types of carbocyanine have been made: 2 : 2′-carbocyanine, 2 : 4′-carbocyanine, 4 : 4′-carbocyanine, thiocarbocyanine, oxacarbocyanine, indocarbocyanine (see Hamer, J., 1927, 2796; Bloch and Hamer, *Phot. J.*, 1928, **68**, 21) and selenocarbocyanine (Clark, this vol., p. 2313), whilst, should the nuclei in a given carbocyanine differ from each other (compare Mills and Raper, J., 1925, **127**, 2466), still other possibilities would arise.

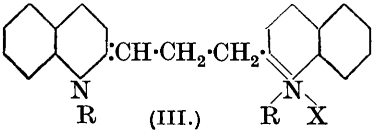
There are only three recorded instances of carbocyanines with substituents attached to the three-carbon chain. The earliest is that of the dinitro-derivative obtained by treatment of a 2 : 2′-carbocyanine with nitric acid (Mills and Hamer, J., 1920, **117**, 1550). To the reason cited in the original paper for considering this to be a substitution and not an addition product of the carbocyanine may be added another, based upon a comparison of the stability relationships of two pairs of compounds. In the case of the first pair, the 2 : 2′-carbocyanine (I) is stable, whilst its monoacid salt (II) is unstable except in the presence of excess of acid. But



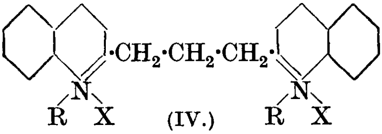
(I.)



(II.)



(III.)

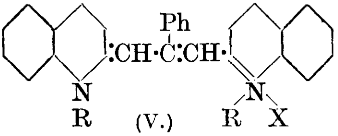


(IV.)

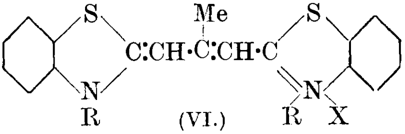
with the second pair, the stability relationship is reversed, for the dihydro-derivative (III) of the 2 : 2′-carbocyanine is unknown, whereas the corresponding salts, the methylenediquinaldine dialkylhalides (IV), are stable substances, crystallisable from water (Hamer, J., 1923, **123**, 246). Since the dinitro-compound in question is stable, it is more probably a substitution product of the stable substance (I) than of the unstable dihydro-derivative (III).

Neocyanine is the second instance of a carbocyanine with a substituent attached to the three-carbon chain, since the view has recently been advanced that this dye is a 4 : 4′-carbocyanine in which the hydrogen atom attached to the central carbon of the chain has been replaced by a lepidyl alkylhalide group (Hamer, this vol., p. 1472).

The third case is of especial interest as being a direct synthesis : the carbocyanine (V) was prepared by the action of benzotrichloride on 1-alkyl-2-methylene-1 : 2-dihydroquinoline (Fischer and Rosenhauer, *Z. angew. Chem.*, 1923, **36**, 330; Rosenhauer, with Schmidt and Unger, *Ber.*, 1926, **59**, 2356).



(V.)



(VI.)

The classic method of carbocyanine preparation, by the action of alkali and formaldehyde on an alcoholic solution of a quinaldinium salt in the presence of a quinolinium salt, gives only negative results when acetaldehyde is used instead of formaldehyde, and carbocyanines containing a methyl group as substituent in the chain have been hitherto unknown. The condensation of quaternary salts, which contain reactive methyl groups, with ethyl orthoformate in the presence of pyridine (Hamer, J., 1927, 2796) gives far better yields of carbocyanines than does any other process; it seemed possible that similarly by use of ethyl orthoacetate, which is now readily available (Sah, *J. Amer. Chem. Soc.*, 1928, **50**, 516), there might be synthesised a series of carbocyanines possessing the chain :CH·CMe:CH·.

This hope has only been realised in the case of the thiocarbocyanines, with which the ethyl orthoformate and pyridine method is also most successful. By condensing 1-methylbenzthiazole alkylhalides with ethyl orthoacetate in the presence of pyridine, three new dyes of the general formula (VI) were prepared, the yields of pure products varying from 37—53%. Mr. O. F. Bloch has found that these new dyes, like the unsubstituted thiocarbocyanines (compare Mills, J., 1922, **121**, 455), exert a powerful photographic sensitising action in the green. Their synthesis provides an additional confirmation of the now well-established constitution of the thiocarbocyanines.

When quinaldine ethiodide, or 1-methylbenzoxazole methiodide, was used instead of 1-methylbenzthiazole alkylhalide, the colour changes indicated the formation of a 2 : 2′-carbocyanine and an oxacarbocyanine respectively, but crystalline products were not isolated; the results were still more unfavourable with lepidine ethiodide and 2 : 3 : 3-trimethylindolenine methiodide.

EXPERIMENTAL.

8-*Methyl*-2 : 2′-*diethylthiocarbocyanine Iodide*.—1-Methylbenzthiazole ethiodide (2 g.; 2 mols.), dry pyridine (20 c.c.), and ethyl orthoacetate (2·4 c.c.; 4 mols.) were boiled together for ½ hour, during which crystals separated. These were filtered off when cold (1·01 g.; 61% yield) and recrystallised from methyl alcohol (150 c.c.); the yield of dye (0·75 g.) was 45%. The yield is much lower when the condensation is carried out in acetic anhydride solution: 21% yield of crude product, 14% after recrystallisation. For analysis, the dye was dried in a vacuum at 100—120° until of constant weight, and this method of drying was also applied to the other two members of the series (Found: C, 52·3; H, 4·7; I, 25·1. $C_{22}H_{23}N_2IS_2$ requires C, 52·15; H, 4·6; I, 25·1%). The dye formed small, copper-coloured crystals, very different from the large, steely prisms of 2 : 2′-diethylthiocarbocyanine iodide. When it was heated, decomposition began at about 280° and melting occurred at about 290°. The spirit solution shows an absorption band at λ 5400 Å. with a much weaker one at λ 5100 Å., whereas for 1 : 1′-diethylthiocarbocyanine iodide the principal band has its maximum at λ 5600 Å. Like 2 : 2′-diethylthiocarbocyanine iodide, the new thiocarbocyanine behaves in a gelatinobromide emulsion as a powerful sensitiser, giving an almost uniform band, which extends to λ 6400 Å. for moderate exposures, and shows maxima at λ 5900 Å. and λ 5200 Å. The sensitising action of the following two dyes is very similar.

2 : 2′ : 8-*Trimethylthiocarbocyanine Iodide*.—The crude substance similarly prepared from 1-methylbenzthiazole methiodide (3 g.) was washed with hot water (1·42 g. obtained; 58% yield) and recrystallised from methyl alcohol (1250 c.c.), in which it was only slightly soluble; the yield after recrystallisation (0·91 g.) was 37% (Found: C, 50·4; H, 4·1; I, 26·4. $C_{20}H_{19}N_2IS_2$ requires C, 50·2; H, 4·0; I, 26·5%). The minute crystals melt at about 298° (decomp.). The principal absorption maximum in spirit solution lies at λ 5400 Å.

8-*Methyl*-2 : 2′-*diallylthiocarbocyanine Bromide*.—Similarly from

1-methylbenzthiazole allobromide (2 g.), pyridine (5 c.c.), and ethyl orthoacetate (2·7 c.c.) was prepared a dye (1·13 g.; 63% yield), which on recrystallisation from methyl alcohol (100 c.c.) was obtained in 53% yield (0·95 g.) (Found: C, 59·7; H, 5·0; Br, 16·7. $C_{24}H_{23}N_2BrS_2$ requires C, 59·6; H, 4·8; Br, 16·5%). The blue crystals melt and decompose at about 260°. The principal absorption maximum in spirit solution is at λ 5450 Å.

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