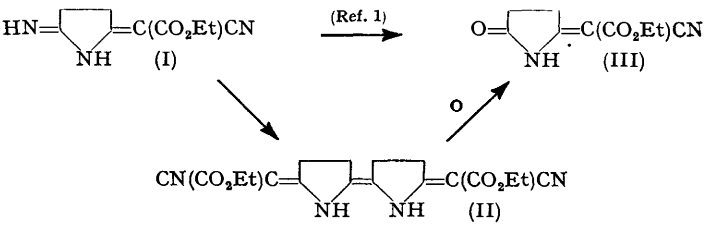
51. *Compounds containing Directly Linked Pyrrole Rings. Part I. A New Type of Pyrrole Pigment.*

By J. A. Elvidge, John S. Fitt, and R. P. Linstead.

A new magenta pigment, di-(5-cyanoethoxycarbonylmethylene-2-pyrrolidinylidene) (II), was formed in low yield when the iminopyrrolidine (I) was boiled in propionic acid and the solution kept at room temperature. On oxidation, the pigment took up *ca.* 1 mol. of oxygen and yielded 2 mols. of the pyrrolidone (III). The colour and fine structure of the compound are discussed, also its relation to indigo.

During attempts to remove, by ester exchange, the ethoxyl grouping of the pyrrolidine derivative [1] (I), the compound was treated with boiling propionic acid. A complex reaction occurred; the solution first darkened, and then during about 18 hr. at room temperature it became purple. Two strong absorption bands appeared at roughly 520 and 560 mμ. The formation of the pigment was reproducible.

The new pigment, present to the extent of only 1%, was isolated by chromatography on alumina and was crystallised extractively from benzene–light petroleum. It formed very dark red crystals with a brassy reflex. Molecular-weight estimations by the cryoscopic method in benzene, combustion analyses, and a Zeisel determination showed that the molecule was $C_{14}H_{10}O_2N_4(OEt)_2$. These figures correspond to condensation between two molecules of the original pyrrolidine with loss of two imino-groups, so that the structure (II) appeared most probable. Oxidation of the pigment in acid solution with permanganate afforded approximately 2 mols. of the known pyrrolidone (III) with the consumption of 1 molecular proportion of oxygen. The structure (II) for the pigment was thus certain.



The mode of formation of the pigment (II) from the iminopyrrolidine (I) is at present obscure. The reaction may be a bimolecular reductive coupling. Evidence on this point is being sought and the production of analogous compounds by more rational procedures is under investigation.

The pigment was soluble in organic solvents (except petroleum), in hot concentrated hydrochloric acid, and in cold aqueous sodium hydroxide. It was rapidly and irreversibly destroyed by oxidising agents and by sodium dithionite (hydrosulphite).

The pigment in solution was practically transparent in the photographic ultraviolet and in the near infrared region but it absorbed light strongly in the yellow-green part of the visible region. The positions of the two absorption maxima were markedly affected by the solvent (see Table). The Figure gives the light absorption curve for the ethanol solution; the curve for benzene solution is very similar but is shifted 16—18 mμ to the red. In mixtures of these solvents, and in chloroform and nitrobenzene, the pigment showed maxima at intermediate wavelengths. Solutions in methanol, acetone, and acetic acid resembled that in ethanol, whilst a pyridine solution resembled that in benzene. Further observations of the light absorption indicated that the pigment formed loose complexes with

Solvent	$\lambda_{max.}$ (Å)	Colour of solution	U.V. Fluorescence
Ethanol	5240, 5630	Magenta	Pale green
Benzene	5400, 5810	Violet	Pale blue

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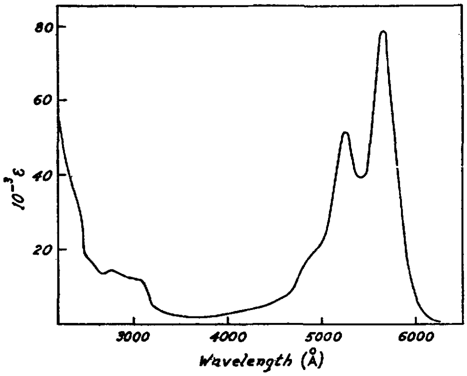
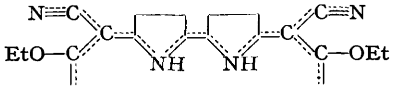
[1] Elvidge, Fitt, and Linstead, preceding paper.

metal ions; maxima were: with copper or nickel acetate in pyridine, 6270 and 6230 Å, respectively; with sodium hydroxide in water, 6050 Å. Addition of acetic acid caused immediate decomposition of these complexes and there was reversion to the twin-peak (metal-free) spectrum.

The striking optical properties of the new pigment were not obviously compatible with the straightforward bond structure (II). Thus the simplest principles[2] suggested that the system would be equivalent to a linear hexaene for which the position of longest-wavelength absorption is 360 mμ (ε 70,000). The discrepancy between this prediction and observation is much greater than with the simpler pyrrolidine derivatives (I), (III), etc. (see ref. 1). Indigo, however, presents a good analogy for intense visual colour in a relatively simple structure. The light absorption at unexpectedly long wavelength by indigo is now attributed to resonance, the suggested canonical forms being the classical bond structure, four dipolar forms and one tetrapolar form.[3] For the new pigment, the number of electronic isomers of the inadequate structure (II), comprising dipolar and tetrapolar forms of the kind invoked for the simple pyrrolidines[1] and for indigo, is no less than twenty-three. It is very reasonable, therefore, to regard the molecule of the new pigment as a resonance hybrid: it is perhaps best represented as (IV). The twenty-four canonical possibilities indicate that negative charge is carried over the extremities of the molecule and to a smaller extent at the centre, and that there is electron deficiency at the heterocyclic nitrogen atoms. In two-thirds of the hypothetical canonical forms the central link has full double-bond character: the oxidative scission to the pyrrolidone (III) in good yield is thus accommodated.



Light absorption of the dipyrrolidinylidene (II) *in ethanol.*



(IV)

The changes in positions of the absorption maxima with solvent are similar to those encountered with indigo solutions.[4] Indeed, the effect is an expected characteristic of dyes which have easily polarisable molecules.[5] The suggested resonance-hybrid structure (IV) is certainly of this type.

The finding that an intensely coloured compound can result from the *direct linking* of two *partially reduced* pyrrolic rings as in (II) seems to be a new discovery in pyrrole chemistry.

EXPERIMENTAL

We are indebted to Mr. F. H. Oliver and his staff of the microanalytical laboratory of this Department for the analyses, including the direct determination of oxygen.

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[2] Braude, *Ann. Reports*, 1945, **42**, 105.

[3] van Alphen, *Chem. Weekblad*, 1938, **35**, 435.

[4] Scheibe, Dörfling, and Assmann, *Annalen*, 1940, **544**, 240.

[5] Hünig and Rosenthal, *ibid.*, 1955, **592**, 161; Hünig and Requardt, *ibid.*, p. 180; cf. Kiprianov and Timoshenko, *Ukrain. khim. Zhur.*, 1952, **18**, 347.

Di-(5-cyanoethoxycarbonylmethylene-2-pyrrolidinylidene).—5-Cyanoethoxycarbonylmethylene-2-iminopyrrolidine [1] (I) (4 g.), propionic acid (40 c.c.), and pyridine (1 c.c.) were heated together under reflux for 1 hr., and the dark solution was then kept at room temperature overnight. The purple mixture was diluted with benzene (100 c.c.) and filtered, and the solution run on to a column (90 × 6 cm.) of alumina (Spence, type H). The chromatogram was developed with benzene and when the bands ceased to move the column was kept overnight. During this time, a brown band, adjacent to the main violet-blue band of the pigment, changed to that colour. The several violet-blue bands were then eluted with 5% ethanol in benzene. The eluate was evaporated to 10 c.c., and light petroleum (b. p. 80—100°) (100 c.c.) was added. The pigment (25 mg., 0·7%) crystallised during *ca.* 3 hr. and was purified to constant light absorption by extractive crystallisation [6] with 20% benzene in light petroleum (b. p. 80—100°). *Di-(5-cyanoethoxycarbonylmethylene-2-pyrrolidinylidene)* formed small very dark red prisms with a slightly greenish, brassy reflex; it had no characteristic m. p. [Found: C, 61·0; H, 5·8; O, 18·1; N, 15·4; OEt, 24·2%; *M* (cryoscopic in benzene), 387 ± 50. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·6; O, 17·9; N, 15·7; OEt, 25·3%; *M*, 356]. The pigment gave a dull purple smear when rubbed on glazed paper. Light absorption in EtOH: $\lambda_{max.}$ 5630, 5240 Å (ε 78,600, 51,400); in benzene, $\lambda_{max.}$ 5810, 5400 Å (ε comparable).

Oxidation of the Pigment.—(i) To a solution of the pigment (30 mg.) in glacial acetic acid (20 c.c.), aqueous sulphuric acid (0·3 c.c.; 1 : 1) was added, followed by 0·1N-potassium permanganate until the colour of the pigment was discharged [uptake of O, 1·3 mols. (corrected by a control). Scission of 1 aza-link between pyrrolic rings requires 0; one double bond, 1; one methine link 2 mols. of O]. The solution was evaporated to a small volume in an evacuated desiccator (KOH), and then a little crushed ice was added. The product (5 mg.) that separated was identified as 5-cyanoethoxycarbonylmethylene-2-pyrrolidone by m. p. and mixed m. p. with an authentic specimen.[1]

(ii) Similarly, the pigment was oxidised at 10 times the above dilution with 0·01N-potassium permanganate (1 mol. of O). The solution then had $\lambda_{max.}$ at 2750 Å with $E_{max.}$ corresponding to a yield of 1·9 mols. of 5-cyanoethoxycarbonylmethylene-2-pyrrolidone, a small quantity of which was isolated and identified as previously.

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[6] Barrett, Dent, and Linstead, *J.*, 1936, 1726.