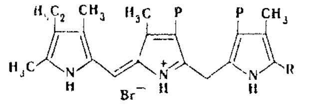
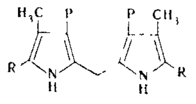
SYNTHESIS OF POLYPYRROLYL COMPOUNDS

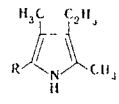
L. I. Fleiderman, A. F. Mironov,
and R. P. Evstigneeva

UDC 547.748.07

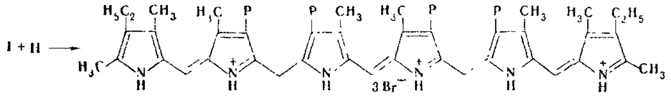
Within the framework of systematic investigations in the porphyrin series we have developed a preparative method for obtaining linear tripyrrolyl structures of types (I) and (II). From these have been synthesized polypyrrolyl compounds containing six and eight pyrrole residues. The tripyrrenes (I) and (II) were obtained by a reaction between 3,3'-di(β-methoxycarbonylethyl)-4,4'-dimethyldipyrrolylmethane (III) and formylcryptopyrrole (V) and also between the corresponding α,α'-diformyldipyrrolylmethane (IV) and the cryptopyrrole (VI). Conditions have been found which enable the side reaction of the addition of two molecules of the pyrrole to the dipyrrolylmethane with the formation of a biladiene to be reduced to a minimum. The condensation of the tripyrrenes (I) and (II) in methanol with hydrobromic acid gave the hexapyrrotriene (VII). Under similar conditions, the octapyrrotetraene was obtained from two moles of the tripyrrene (I) and the dipyrrolylmethane (IV).

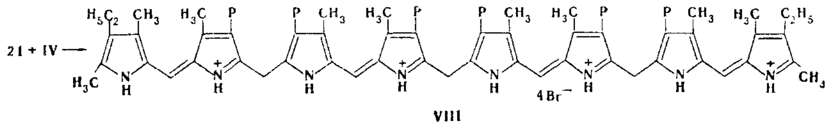

I, II


III, IV


V, VI

I R=H, II R=CHO, P=CH$_2$CH$_2$CO CH$_3$, III R=H, IV R=CHO, V R=CHO, VI R=H


VII


VIII

Compounds (VII) and (VIII) are dark-red crystalline substances possessing fluorescence in chloroform. In the visible region they have three and four absorption bands, respectively. A comparison of the absorption spectra of the dipyrrolylmethenes, the biladienes, the hexapyrrotriene, and the octapyrrotetraene shows that an increase in the length of the linear polypyrrolyl chain by one dipyrrolylmethene unit leads to the appearance of an additional maximum in the long-wave region.

2-Ethyl-8,12-di(β-methoxycarbonylethyl)-1,3,7,13-tetramethyltripyrrene hydrobromide (I), yield 94.5%, mp 146-147°C, λ_{max} CHCl$_3$ (log ε): 496 nm (4.86). Found, %: C 59.9; H 6.8; Br 14.1; N 7.9. $C_{28}H_{37}N_3O_4 \cdot HBr$. Calculated, %: C 60.0; H 6.8; Br 14.3; N 7.5.

2-Ethyl-14-formyl-8,12-di(β-methoxycarbonylethyl)-1,3,7,13-tetramethyltripyrrene hydrobromide (II), yield 70%, mp 152-154°C, λ_{max} CHCl$_3$ (log ε): 492 nm (5.04). Found, %: C 59.6; H 6.4; Br 13.3; N 7.1. $C_{29}H_{37}N_3O_5 \cdot HBr$. Calculated, %: C 59.2; H 6.5; Br 13.3; N 7.1.

2,28-Diethyl-8,12,18,22-tetra(β-methoxycarbonylethyl)-1,3,7,13,17,23,27,29-octamethylhexapyrrotriene trihydrobromide (VII), yield 92%, λ_{max} CHCl$_3$ (log ε): 451 (4.66), 492 (4.92), 551 nm (5.18). Found,%: C 56.4; H 6.2; Br 19.7; N 6.7. $C_{57}H_{72}N_6O_8 \cdot 3HBr$. Calculated,%: C 56.5; H 6.2; Br 19.8; N 6.9.

M. V. Lomonosov Moscow Institute of Fine Chemical Technology. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, p. 1146, August, 1973. Original article submitted November 2, 1972.

2,38-Diethyl-8,12,18,22,28,32-hexa(β-methoxycarbonylethyl)-1,3,7,13,17,23,27,33,37,39-decamethyl-octapyrrotetraene tetrahydrobromide (VIII), yield 94%, $\lambda_{\max}$ $CHCl_3$ (log ε): 450 (4.73), 470 (4.83), 513 (5.02), 559 nm (5.38). Found, %: C 55.8; H 6.1; Br 19.5; N 6.9. $C_{77}H_{96}N_8O_{12}\cdot 4HBr$. Calculated, %: C 56.1; H 6.1; Br 19.4; N 6.8.