amounts of 2,3- and 2,1- isomers by substitution into a 2-substituted anthracene. A rigorous chemical proof of structure of III and IV is in progress and will be reported later, along with details of the above reactions and evidence (derived from infrared and proton magnetic resonance spectra) concerning the bond structure of anthracene.

DEPARTMENT OF CHEMISTRY
FORDHAM UNIVERSITY
NEW YORK 58, N. Y.

JOHN L. FERRARI
I. MOYER HUNSBERGER

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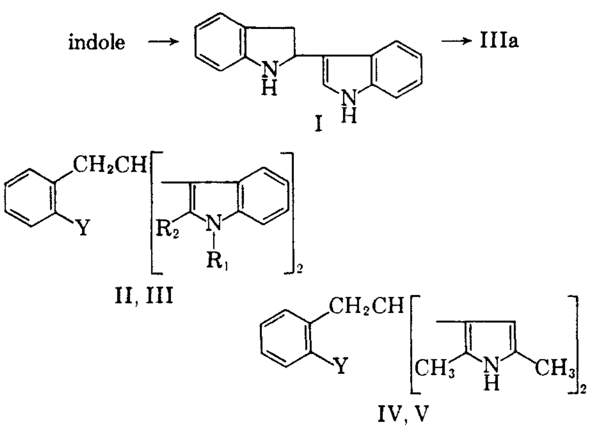
The Synthesis of Triindole, and Mixed Indole and Indole:Pyrrole Trimers

Sir:

The structure of triindole, the stable terminal product from the acid-catalyzed polymerization of indole, remained an enigma from the time of its discovery in 1913[1] until 1954, when a structure was proposed which could be derived through a plausible electronic mechanism.[2] Based on the discovery that it forms a Schiff base with benzaldehyde, and, therefore, must contain a primary amino group, Smith proposed the bisindole structure IIIa for triindole. The mechanism proposed for the formation of triindole[3] involves diindole as an intermediate. The correct structure for diindole (I), first proposed in 1954,[2] was confirmed by degradation in 1957.[4] We have now confirmed structure IIIa for triindole by an independent synthesis.

In the manner common for formation of bisindoles, by condensation of indoles with aldehydes,[5] an excess of indole condensed with *o*- nitrophenylacetaldehyde[6] in warm acetic acid solution (100°, 2 hr.) to give 3,3′-[2-(2-nitrophenyl)ethylidene]-bisindole (IIa) in 85% yield, light yellow crystals from ethanol water, m.p. (softens above 205°) 208–209°; *Anal.* Calcd. for $C_{24}H_{19}N_3O_2$ (381.42): C, 75.57; H, 5.02: N, 11.02. Found: C, 75.64; H, 5.20; N, 11.10; ν_{NH} 3450, ν_{NO_2} 1522, 1347 cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 223 mμ (log ϵ 4.84), 275 (4.12), 282 (4.13), 291 (4.08). Hydrogenation of IIa at 2 atm. in methanol over Raney nickel catalyst gave triindole (IIIa) in 77% yield, m.p. and mixed m.p. with an authentic sample,[7] 169–170.5°. The infrared spectra of the two samples in Nujol were identical in every respect.



II, IV. Y = NO_2
III, V. Y = NH_2
IIa, IIIa. R_1 = R_2 = H
IIb, IIIb. R_1 = H, R_2 = CH_3
IIc, IIIc R_1 = R_2 = CH_3

In a similar manner (except at 50°, 17 hr.) were prepared 2,2′-dimethyl-3,3′-[2-(2-nitrophenyl)-ethylidene]bisindole (IIb) in 87% yield, pale yellow crystals from 95% ethanol, m.p. 231–232.5°; *Anal.* Calcd. for $C_{26}H_{23}N_3O_2$ (409.47): C, 76.26; H, 5.66; N, 10.26; Found: C, 75.98; H, 5.89; N, 10.49; ν_{NH} 3380, ν_{NO_2} 1530, 1365 cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 228 mμ (4.80), 283 (4.18), 292 (4.14); 1,1′,2,2′-tetramethyl-3,3′-[2-(2-nitrophenyl)ethylidene] bisindole (IIc) in 99% yield, yellow crystals from 95% ethanol, m.p. 180–181.5°; *Anal.* Calcd. for $C_{28}H_{27}N_3O_2$ (437.52): C, 76.86; H, 6.22; N, 9.61; Found: C, 76.94; H, 6.31; N, 9.83; ν_{NO_2} 1523, 1357 (also strong bands at 1381 and 1371) cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 230 mμ (4.81), 287 (4.16), 294 (4.16); and 2,2′,5,5′-tetramethyl-3,3 -[2-(2-nitrophenyl)ethylidene]bispyrrole (IV) in 90% yield, golden yellow crystals from 95% ethanol, m.p. (darkens above 185°) 217–218°; *Anal.* Calcd. for $C_{20}H_{23}N_3O_2$ (337.41): C, 71.19; H, 6.87; N, 12.45; Found: C, 70.89; H, 7.06; N, 12.69; ν_{NH} 3330, ν_{NO_2} 1518, 1340 cm.$^{-1}$ in Nujol; ultraviolet spectrum in 95% ethanol contains only rising end absorption.

Hydrogenation as with triindole gave the corresponding amines: IIIb in 79% yield, colorless crystals from methanol water, m.p. (softens at 175°) 245–246°; *Anal.* Calcd. for $C_{26}H_{25}N_3$ (379.48): C, 82.29; H, 6.64; N, 11.07; Found: C, 82.28; H, 6.72; N, 10.99; ν_{NH} 3420 (strongest), 3350, 3190 cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 229 mμ (4.82), 285 (4.18), 292 (4.15); IIIc in 79% yield, colorless crystals from methanol water, m.p. 182–183°; *Anal.* Calcd. for $C_{28}H_{29}N_3$ (407.54): C, 82.51; H, 7.17; N, 10.31; Found: C, 82.57; H, 7.24; N, 10.06; ν_{NH} 3480, 3390 cm.$^{-1}$ in Nujol;

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[1] K. Keller, *Ber.*, **46**, 726 (1913).

[2] G. F. Smith, *Chem. and Ind.* (*London*), 1451 (1954).

[3] For a further discussion of the mechanism of formation of triindole and mixed indole and indole:pyrrole trimers, see W. E. Noland and C. F. Hammer, *J. Org. Chem.*, **25**, forthcoming (1960).

[4] H. F. Hodson and G. F. Smith, *J. Chem. Soc.*, 3544 (1957).

[5] E. Fischer, *Ann.*, **242**, 372 (1887).

[6] R. A. Weerman, *Ann.*, **401**, 1 (1913).

[7] O. Schmitz-Dumont, B. Nicolojannis, E. Schnorrenberg, and H. H. Saenger, *J. prakt. Chem.*, **131**, 146 (1931).

λ_{max} in 95% C_2H_5OH: 231 mμ (4.83), 289 (4.16), 294 (4.15); V in 65% yield, colorless crystals (which darken rapidly) from methanol, m.p. (softens and darkens at 183°) 197–199°; *Anal.* Calcd. for $C_{20}H_{25}N_3$ (307.42): C, 78.13; H, 8.20; N, 13.67; Found: C, 77.98; H, 8.29; N, 13.70 ν_{NH} 3380 (strongest), 3320, 3240 cm.$^{-1}$ in Nujol. The melting point and infrared spectrum of the latter showed it to be identical with indole:di-2,5-dimethylpyrrole trimer,[3] thus confirming structure V for the mixed trimer by an independent synthesis.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINN.

WAYLAND E. NOLAND
WILLIAM C. KURYLA[8]

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