Acid-catalysed Rearrangements in the Aryliminoindoline Series. Part II.[1] Crystal and Molecular Structure of 2-Anilino-3-(1-methyl-2-phenylindol-3-yl)-3-phenyl-3*H*-indole Monohydrate

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Acid treatment of (*N*-alkylindolyl)indolinimines and indolylindolinimines gives retrogression, hydrolysis, and phenyl or indolyl transposition (in position 2) reactions: products obtained by phenyl transposition further give rise to a double transposition with formation of 2-arylimino-3-(1-alkyl-2-phenylindol-3-yl)-3-phenyl-3*H*-indole. The structure of 2-anilino-3-(1-methyl-2-phenylindol-3-yl)-3-phenyl-3*H*-indole monohydrate (XIa) has been determined by *X*-ray analysis by use of 4 972 independent reflections measured by diffractometer and refined by least-squares to *R* 0.074. A mechanism for the rearrangements is suggested. The structure was solved by direct methods. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 12.60(1)$, $b = 15.74(1)$, $c = 16.45(1)$ Å, and $\beta = 124.9(2)$.

In a previous paper [1] we have reported the transposition reactions which (*N*-alkylindolyl)-*N*-alkyl indolinimines undergo by acidic treatment. We now report further results obtained by acid treatment of (*N*-alkylindolyl)-indolinimines (I) and of indolylindolinimines (VII). These results are quite different from those obtained with the *N*,*N'*-dialkyl-derivatives and provide further information about the mechanism of these transpositions.

RESULTS

(*a*) *Action of Trichloroacetic Acid in Chloroform at Room Temperature on Products* (I).—The (*N*-alkylindolyl)indolinimines (I; a—e), obtained by reaction of protonated aryliminoindolines (V) with indoles,[2] when treated with trichloroacetic acid in chloroform at room temperature for 15—20 h, give the phenyl transposition products (IV; a—e) together with the retrogression products (V) and (VI) (Scheme 1).† The structure of the product (IVa) was established by *X*-ray diffraction methods [3] and those of

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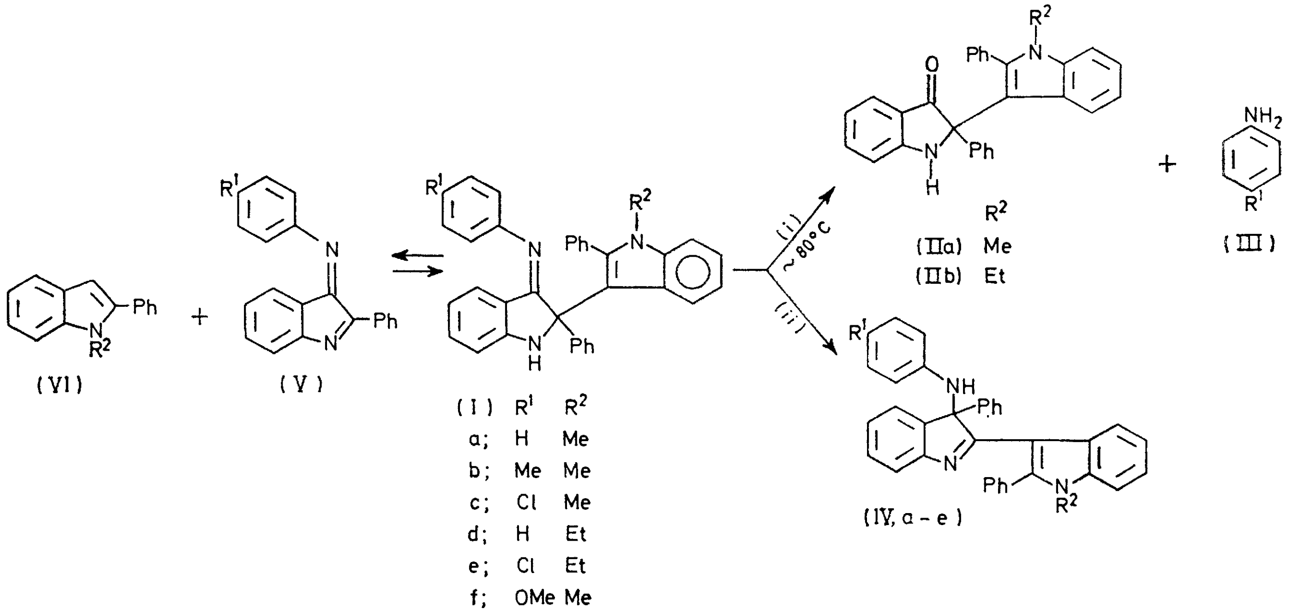
† In the case of (If) only the retrogression products are obtained.

[1] Part I, M. Colonna, L. Greci, L. Marchetti, G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *J.C.S. Perkin II*, preceding paper.

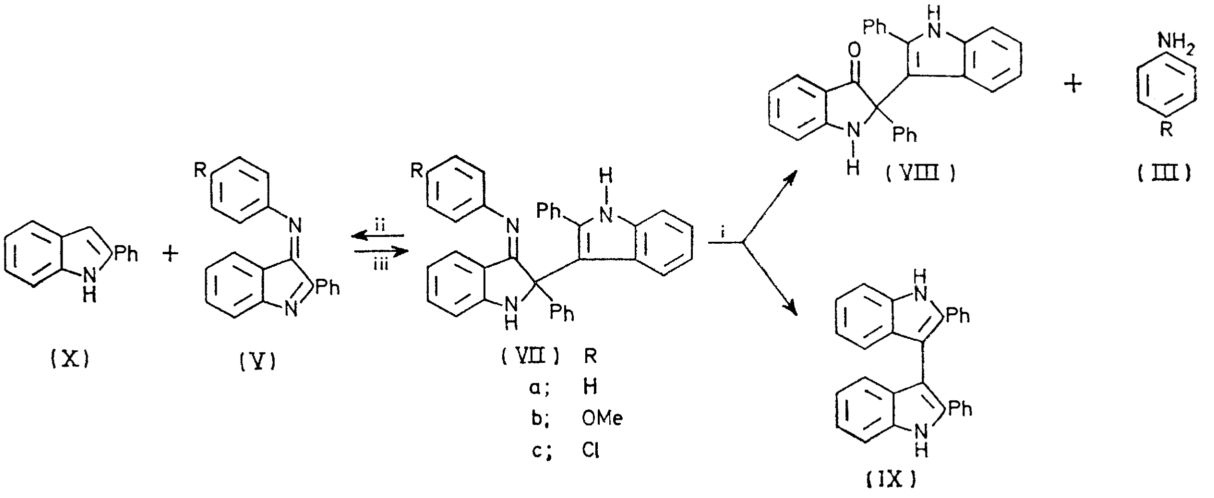
[2] M. Colonna, L. Greci, and L. Marchetti, *Gazzetta*, 1975, **105**, 665.

[3] E. Foresti Serantoni, A. Krajewski, R. Mongiorgi, and L. Riva di Sanseverino, *Cryst. Struct. Comm.*, 1975, **4**, 403.

the other compounds of the same class (IV; b—e) were related to it on the basis of the spectroscopic behaviour. Under the same experimental conditions the non-alkylated derivatives (VII; a and c) show a different behaviour (Scheme 2): the transposition products are not obtained and small amounts of the retrogression compounds (V) and (X) are formed. From the reaction with trichloroacetic acid, the trichloroacetate of (VII) is formed, from which the base can be obtained by treatment with $NaHCO_3$.



SCHEME 1 Reagents: i, EtOH, HCl, *ca.* 80 °C; ii, $CHCl_3$, CCl_3CO_2H



SCHEME 2 Reagents: i, EtOH, HCl, *ca.* 80 °C; ii, $CHCl_3$, CCl_3CO_2H; iii, room temperature

(*b*) *Action of Hydrochloric Acid in Boiling Ethanol for a Short Time on Products* (I).—The products (I; a and f), in boiling ethanol and hydrochloric acid gave the hydrolysis compounds (II; a and b) and the aromatic amines (III) (Scheme 1). In all cases, retrogression products (V) and (VI) were also obtained. Similar behaviour is shown by compounds (VII), (Scheme 2), with the difference that, as well as the retrogression [(V) and (X)] and hydrolysis products [(VIII) and (III)], the bi-indolyl (IX) was obtained. Compound (IX) is formed by transposition of the indolyl group and subsequent reduction, as observed for the (*N*-alkylindolyl)-*N*-alkylindolinimines.[1] The structures of the products (II), (VIII), and (IX) have been established by comparison with known samples, prepared by other reactions.[4,5]

(*c*) *Action of Hydrochloric Acid in Ethanol by Prolonged Boiling on Products* (IV).—Products of the phenyl transposition (IV; a and c), although stable in acidic ethanol at room temperature, undergo a second transposition of the Wagner–Meerwein type when heated under reflux for *ca.* 3 h, leading to products (XI; a and b) (Scheme 3). The structure of product (XIa) has been determined by *X*-ray methods and that of (XIb) was assigned on the basis of spectroscopic data (Table 1).

Molecular Geometry of 2-*Anilino*-3-(1-*methyl*-2-*phenylindol*-3-*yl*)-3-*phenyl*-3H-*indole* (XIa) *Monohydrate*.—A projection of the structure with the arbitrary numbering

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[4] M. Colonna, L. Greci, and L. Marchetti, *Gazzetta*, in the press.
[5] M. Colonna and A. Monti, *Gazzetta*, 1962, **92**, 1421.

TABLE 1

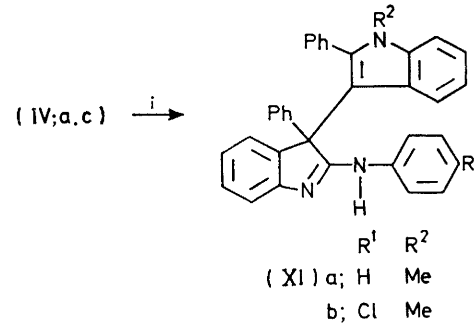
Analytical and spectral data

Compound	M.p./ °C	Formula	% Found (%) * C	H	N	I.r. $\nu_{max.}$/ cm^{-1}	^{1}H N.m.r. (δ) Me	NMe	NEt	NH	Aromatic
(IVa)	247	$C_{35}H_{27}N_3$	85.78 (85.85)	5.56 (5.55)	8.66 (8.58)	1 600 [a] 3 382 [b]		3.19 (3 H, s)		3.71 (1 H, s) [c]	6.07 (2 H, d); 6.5—7.8 (20 H, m); 9.1 (1 H, s) [c]
(IVb)	255	$C_{36}H_{29}N_3$	86.10 (85.86)	5.81 (5.80)	8.22 (8.34)	1 592 [a] 3 415 [b]	2.07 (3 H, s)	3.20 (3 H, s)		3.64 (1 H, s) [c]	6.0 (2 H, d); 6.65—7.65 (19 H, m); 9.1 (1 H, s) [c]
(IVc)	260	$C_{35}H_{26}N_3Cl$	80.38 (80.22)	5.01 (5.00)	8.21 (8.02)	1 600 [a] 3 402		3.19 (3 H, s)		3.69 (1 H, s) [c]	6.0 (2 H, d); 6.6—7.8 (19 H, m); 9.1 (1 H, s) [c]
(IVd)	255	$C_{36}H_{29}N_3$	86.01 (85.86)	5.87 (5.80)	8.32 (8.34)	1 597 [a] 3 398 [b]			1.02 (3 H, t) 3.67 (2 H, q)	3.73 (1 H, s) [c]	6.1 (2 H, d); 6.5—7.8 (20 H, m); 9.1 (1 H, s) [c]
(IVe)	240	$C_{36}H_{28}N_3Cl$	80.07 (80.35)	5.30 (5.24)	7.97 (7.81)	1 592 [a] 3 400 [b]			1.07 (3 H, t) 3.67 (2 H, q)	3.65 (1 H, s) [c]	6.0 (2 H, d); 6.6—7.8 (19 H, m); 9.1 (1 H, s) [c]
(XIa)	207	$C_{35}H_{27}N_3$	85.96 (85.85)	5.42 (5.55)	8.36 (8.58)	1 608 1 625 3 405 [b]		3.43 (3 H, s)		6.5—7.5 (24 H, m)	
(XIc)	217	$C_{35}H_{26}N_3Cl$	80.24 (80.22)	5.11 (5.00)	8.27 (8.02)	1 595 1 615 3 425 [b]		3.47 (3 H, s)		6.5—7.5 (23 H, m)	

* Required value in parentheses.

[a] $\mathrm{PhN{:}C}<$. [b] NH. [c] broad.

scheme used in the analysis is shown in the Figure, and relevant bond distances and angles are reported in Table 2.

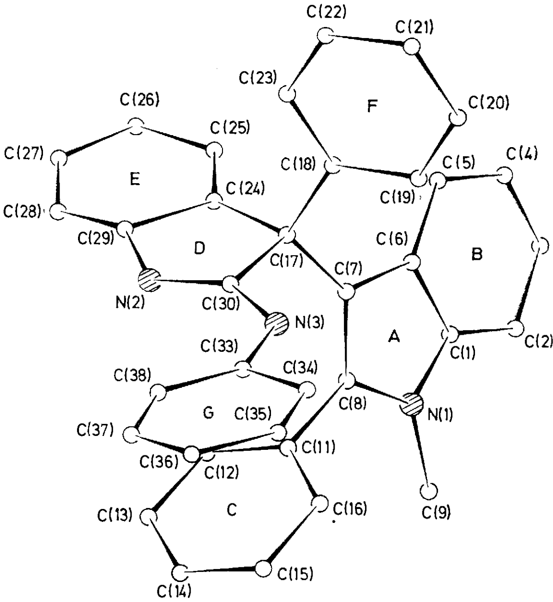


SCHEME 3 Reagents: i, EtOH, HCl

These data are practically the same as for 3-anilino-2-(1-methyl-2-phenylindol-3-yl)-3-phenyl-3*H*-indole,[3] in 1-ethyl-2-(1-ethyl-2-phenylindol-3-yl)-2-phenyl-3-phenyliminoindoline,[1] and in 1-ethyl-3-(1-ethyl-2-phenylindol-3-yl)-3-phenyl-2-phenyliminoindoline.[1]

The main point to be considered is the geometry of the 2-anilino-3*H*-indole group with particular reference to the C–N bond distances. Comparison of corresponding bond lengths in the present compound [N(2)–C(30) 1.276(5), N(3)–C(30) 1.375(5) Å] with those in 1-ethyl-3-(1-ethyl-2-phenylindol-3-yl)-3-phenyl-2-phenyliminoindoline [N(2)–C(30) 1.393(5), N(3)–C(30) 1.256(4) Å], shows that in (XIa) the double bond is virtually localized in the endocyclic C–N bond while in the second compound it is localized in the exocyclic C–N bond. On the other hand, in 3-anilino-2-(1-methyl-2-phenylindol-3-yl)-3-phenyl-3*H*-indole [3] the endocyclic C–N bond is 1.33(1) Å and the exocyclic one is 1.48(1) Å, so in the indolylindolinimines the proton is preferably attached to the exocyclic nitrogen atom.

All rings in the molecule are virtually planar and their reciprocal orientation can be defined by the dihedral angles reported in Table 2. Comparison of these values with corresponding ones for 1-ethyl-(1-ethyl-2-phenylindol-3-yl)-3-phenyl-2-phenyliminoindoline (AB–C 78.5, AB–DE 83.1, DE–F, 69.9, and DE–G 70.7°), shows that the main difference lies in the orientation of the phenyl ring G, which in the last-named compound is in a more crowded environment, owing to the presence of the ethyl substituent at N(2).



Projection of the structure on (001)

The water molecule is involved in a hydrogen bond with the nitrogen atom of the 3*H*-indole group $[\mathrm{O}\cdots\mathrm{N}(2^{\mathrm{I}})$

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bond distances

N(1)–C(1)	1.374(5)	C(15)–C(16)	1.405(7)
N(1)–C(8)	1.388(5)	C(17)–C(18)	1.547(6)
N(1)–C(9)	1.446(8)	C(17)–C(24)	1.510(5)
N(2)–C(29)	1.451(6)	C(17)–C(30)	1.546(5)
N(2)–C(30)	1.276(5)	C(18)–C(19)	1.396(5)
N(3)–C(30)	1.375(5)	C(18)–C(23)	1.393(7)
N(3)–C(33)	1.434(5)	C(19)–C(20)	1.402(7)
C(1)–C(2)	1.395(5)	C(20)–C(21)	1.364(8)
C(1)–C(6)	1.403(6)	C(21)–C(22)	1.390(7)
C(2)–C(3)	1.386(7)	C(22)–C(23)	1.395(8)
C(3)–C(4)	1.376(8)	C(24)–C(25)	1.398(6)
C(4)–C(5)	1.386(6)	C(24)–C(29)	1.388(5)
C(5)–C(6)	1.410(6)	C(25)–C(26)	1.364(6)
C(6)–C(7)	1.437(5)	C(26)–C(27)	1.397(7)
C(7)–C(8)	1.385(6)	C(27)–C(28)	1.393(7)
C(7)–C(17)	1.510(6)	C(28)–C(29)	1.366(6)
C(8)–C(11)	1.490(5)	C(33)–C(34)	1.401(6)
C(11)–C(12)	1.359(6)	C(33)–C(38)	1.348(5)
C(11)–C(16)	1.383(6)	C(34)–C(35)	1.393(6)
C(12)–C(13)	1.409(7)	C(35)–C(36)	1.360(7)
C(13)–C(14)	1.361(7)	C(36)–C(37)	1.391(6)
C(14)–C(15)	1.361(7)	C(37)–C(38)	1.402(6)

(b) Bond angles

C(1)–N(1)–C(8)	108.5(6)	C(18)–C(17)–C(24)	113.1(6)
C(1)–N(1)–C(9)	124.0(10)	C(18)–C(17)–C(30)	105.2(5)
C(8)–N(1)–C(9)	126.8(10)	C(24)–C(17)–C(30)	97.4(6)
C(29)–N(2)–C(30)	105.6(6)	C(17)–C(18)–C(19)	121.0(7)
C(30)–N(3)–C(33)	126.9(10)	C(17)–C(18)–C(23)	119.9(9)
N(1)–C(1)–C(2)	129.4(9)	C(19)–C(18)–C(23)	118.7(7)
N(1)–C(1)–C(6)	108.7(7)	C(18)–C(19)–C(20)	120.6(8)
C(2)–C(1)–C(6)	121.9(8)	C(19)–C(20)–C(21)	120.4(11)
C(1)–C(2)–C(3)	116.9(8)	C(20)–C(21)–C(22)	119.6(10)
C(2)–C(3)–C(4)	122.2(11)	C(21)–C(22)–C(23)	120.9(10)
C(3)–C(4)–C(5)	121.4(9)	C(18)–C(23)–C(22)	119.9(10)
C(4)–C(5)–C(6)	117.9(8)	C(17)–C(24)–C(25)	131.9(10)
C(1)–C(6)–C(5)	119.6(8)	C(17)–C(24)–C(29)	109.2(5)
C(1)–C(6)–C(7)	106.9(5)	C(25)–C(24)–C(29)	118.9(8)
C(5)–C(6)–C(7)	133.4(10)	C(24)–C(25)–C(26)	119.3(8)
C(6)–C(7)–C(8)	106.6(6)	C(25)–C(26)–C(27)	121.3(8)
C(6)–C(7)–C(17)	124.2(7)	C(26)–C(27)–C(28)	119.7(9)
C(8)–C(7)–C(17)	129.1(9)	C(27)–C(28)–C(29)	118.5(9)
N(1)–C(8)–C(7)	109.3(6)	N(2)–C(29)–C(24)	111.1(7)
N(1)–C(8)–C(11)	118.3(6)	N(2)–C(29)–C(28)	126.6(9)
C(7)–C(8)–C(11)	132.3(10)	C(24)–C(29)–C(28)	122.2(7)
C(8)–C(11)–C(12)	119.6(7)	N(2)–C(30)–N(3)	128.5(8)
C(8)–C(11)–C(16)	121.1(8)	N(2)–C(30)–C(17)	116.8(6)
C(12)–C(11)–C(16)	119.2(8)	N(3)–C(30)–C(17)	114.7(8)
C(11)–C(12)–C(13)	121.4(8)	N(3)–C(33)–C(34)	113.4(8)
C(12)–C(13)–C(14)	118.5(9)	N(3)–C(33)–C(38)	125.2(8)
C(13)–C(14)–C(15)	121.5(9)	C(34)–C(33)–C(38)	121.4(7)
C(14)–C(15)–C(16)	119.6(9)	C(33)–C(34)–C(35)	118.5(9)
C(11)–C(16)–C(15)	119.8(9)	C(34)–C(35)–C(36)	120.5(9)
C(7)–C(17)–C(18)	114.4(7)	C(35)–C(36)–C(37)	120.4(9)
C(7)–C(17)–C(24)	111.9(5)	C(36)–C(37)–C(38)	119.5(9)
C(7)–C(17)–C(30)	113.5(6)	C(33)–C(38)–C(37)	119.5(8)

(c) Carbon–hydrogen bonds

N(3)–H(1)	1.10(3)	C(20)–H(15)	1.09(3)
C(2)–H(2)	1.02(4)	C(21)–H(16)	1.05(4)
C(3)–H(3)	1.08(3)	C(22)–H(17)	1.01(4)
C(4)–H(4)	1.02(4)	C(23)–H(18)	1.14(3)
C(5)–H(5)	1.16(4)	C(25)–H(19)	1.12(3)
C(9)–H(6)	0.95(3)	C(26)–H(20)	1.01(3)
C(9)–H(7)	0.97(3)	C(27)–H(21)	1.06(3)
C(9)–H(8)	0.88(3)	C(28)–H(22)	1.12(3)
C(12)–H(9)	1.02(3)	C(34)–H(23)	1.12(3)
C(13)–H(10)	1.20(3)	C(35)–H(24)	1.13(3)
C(14)–H(11)	1.04(4)	C(36)–H(25)	1.02(3)
C(15)–H(12)	0.99(3)	C(37)–H(26)	1.18(3)
C(16)–H(13)	1.08(3)	C(38)–H(27)	1.09(3)
C(19)–H(14)	0.93(4)		

(d) Dihedral angles between planes

AB—C	72.5	DE—F	87.0
AB—DE	68.0	DE—G	10.8

2.98(1) Å, I is at $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$]. Other contacts are of the order of van der Waals radii.

DISCUSSION

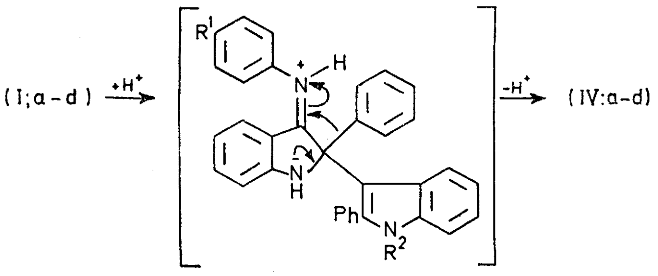
It appears from previously reported results, that acid treatment of (I) and (VII), gives rise to four possible reaction pathways, depending on experimental conditions: these are (i) retrogression, leading to products (V) and (VI) or (X); (ii) hydrolysis, giving ketones (II) and (VIII); (iii) transposition of the indolyl group at position 2, leading to (IX); and (iv) transposition of the phenyl at position 2, leading to (IV). Three of these reaction pathways have already been reported for the acid treatment of (*N*-alkylindolyl)-*N*-alkylindolinimines,[1] while the fourth is characteristic of the products (I) studied in the present work.

(i) The retrogression of products (I) to imines (V) and indoles (VI) or (X) is the inverse of the formation reaction and occurs by protonation at C-3 of the indole nucleus of (I), as previously shown in similar compounds.[1,6] The equilibrium reported in Scheme 1 has been demonstrated by acidic treatment of (Ia) in presence of 1-ethyl-2-phenylindole. After 20 h, at room temperature, product (IVd) together with the expected (IVa) is obtained: the first is derived by transposition from (Id), formed through the equilibrium, and the second by transposition from (Ia). The molar ratio of (IVa) and (IVd), as determined by ^{1}H n.m.r. spectroscopy, is equal to the ratio of the reagents (Ia) and 1-ethyl-2-phenylindole.

(ii) Hydrolysis of (I) and (VII) to (II) and (VIII) respectively is the usual acidic hydrolysis of an imine and requires no further discussion.

(iii) Formation of the bi-indolyl (IX) from (VII) can be explained by migration of the indolyl group from position 2 to 3, followed by elimination of amine and formation of dication, which is readily reduced to bi-indolyl (IX) by the solvent ethanol, as shown previously.[1]

(iv) Products (IV; a—d) are formed from (I; a—d) by C-2 to C-3 migration of the phenyl attached to the indoline nucleus, caused by the electron-deficient carbon atom formed by protonation at the imine nitrogen (Scheme 4). The mechanism of this reaction is similar to that previously described for migration of the indolyl group.[1] The different behaviour of products (I; a—e), which give rise to transposition, with respect to products



SCHEME 4

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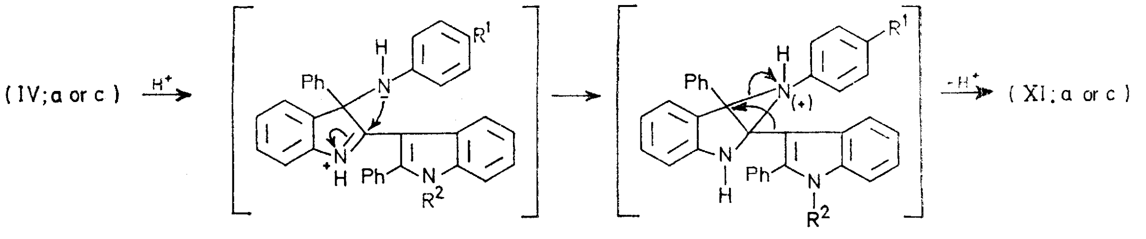
[6] M. Colonna, L. Greci, and L. Marchetti, *Gazzetta*, 1974, **104**, 395.

(VII; a—c) which do not, is probably caused by the different basicity of the indole nuclei present in the two series of compounds.

Finally, formation of compounds (XI; a and b) from (IV; a and c) can be explained by double transposition *via* a hypothetical aziridine intermediate, as shown in the Scheme 5.

We have shown for (*N*-alkylindolyl)-*N*-alkylindolinimines,[1] formation of compounds with structures similar to that of (XI; a and b). We explained this by formation of products of type (IV). In the present case we consider that isolation of products (IV) can be considered as confirmation of the previously suggested mechanism.



SCHEME 5

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls on a Perkin Elmer 257; ^1H n.m.r. spectra on a Perkin-Elmer R 12B in $CDCl_3$ by use of tetramethylsilane as internal standard; gas chromatographs were measured on a Carlo Erba Fractovap GV with silicon SE 30 columns.

(*a*) *Synthesis of Products* (IVa—e): *Action of Trichloroacetic Acid on Products* (I; a—e).—(I; a—e) (5 mmol) in $CHCl_3$ (50 ml) and trichloroacetic acid (10 mmol) in chloroform (10 ml) were mixed at room temperature and stirred for 15—20 h. The solution was then shaken with dilute $NaHCO_3$ and the chloroform layer separated, dried (Na_2SO_4), and evaporated to dryness. The residue, washed with ether, gave products (IV; a—e) (40—50%). Products were recrystallized from benzene–light petroleum. Analytical and spectroscopic data are reported in Table 1. The ethereal solution was evaporated to dryness and the residue, taken-up with benzene, was chromatographed on SiO_2. Products so obtained correspond to 1-methyl (or ethyl)-2-phenylindole (VI) and 3-arylimino-3*H*-indole (V). The same results were obtained by reaction of 3-arylimino-3*H*-indole (V) (5 mmol), trichloroacetic acid (5 mmol), and 1-alkyl-2-phenylindole (VI) (5 mmol) in chloroform (100 ml) for *ca.* 15—20 h at room temperature.

(*b*) *Retrogression: Action of Trichloroacetic Acid on Products* (I; a—f).—The foregoing reaction carried out for 2 h, gave the following products: 1-alkyl-2-phenylindole (VI), 3-arylimino-3*H*-indole (V), and the starting materials (I; a—f). Products were separated by chromatography (SiO_2) with light petroleum–ethyl acetate (9 : 1).

(*c*) *Action of Trichloroacetic Acid on* (Ia) *in the Presence of* 1-*Ethyl*-2-*phenylindole*.—(Ia) (1.2 g, 2.4 mmol) in chloroform (50 ml) were mixed, with stirring, with trichloroacetic acid (0.4 g, 2.4 mmol) and 1-ethyl-2-phenylindole (0.27 g, 1.2 mmol) at room temperature. After 20 h the solution was treated as described in (*a*). From the residue by treatment with Et_2O, a mixture of (IIa) and (IId) in molar ratio 2 : 1 was obtained. From the ethereal solution, by chromatography on SiO_2 with light petroleum–ethyl acetate (9 : 1), a mixture of the two indoles (*N*-Me and *N*-Et substituted) and the 3-arylimino-3*H*-indole (V) was obtained. The molar ratio of (IVa) and (IVd) was established by ^1H n.m.r. spectroscopy and was observed to decrease with increasing 1-ethyl-2-phenylindole.

(*d*) *Action of Trichloroacetic Acid on Products* (VII; a—c).—(VII; a—c) (5 mmol) in chloroform (70 ml) was mixed with trichloroacetic acid (5 mmol) at room temperature. A solution was slowly formed, followed by a dark-red precipitate. After 24 h this was filtered off and shown to be the trichloroacetate of (VII; a—c). Its solution in ethanol gave, when treated with aqueous $NaHCO_3$, products (VII; a—c) quantitatively. Treatment of the filtrate, with aqueous $NaHCO_3$, followed by chromatography on SiO_2, and elution with light petroleum–ethyl acetate (9 : 1), enabled isolation of small amounts of 2-phenylindole (X) and 3-arylimino-3*H*-indole (V).

(*e*) *Hydrolysis: Action of* 10% *Hydrochloric Acid on products* (I; a—f) *and* (VII; a—c).—(I; a—f) or (VII; a—c) (5 mmol) in ethanol (120 ml) and 10% hydrochloric acid (5 ml) were warmed to boiling point. The solution was then evaporated to dryness under pressure and the residue taken up with water and chloroform. The water layer was treated with $NaHCO_3$ and extracted with ether. The aromatic amine (III) was identified by gas chromatography. The chloroform layer was treated with $NaHCO_3$, dried (Na_2SO_4), and evaporated to dryness. The residue was taken up with benzene and chromatographed (SiO_2) with light petroleum–ethyl acetate, to give the hydrolysis products (II; a or b) or (VIII) with 30—40% yields; in the case of (VII; a—c) the bi-indolyl (IX) was obtained in 10—15% yields. In all cases small amounts of the retrogression compounds were also obtained.

(*f*) *Double Transposition: Action of* 10% *Hydrochloric Acid on Products* (IVa) *and* (IVc).—(IVa) and (IVc) (0.25 mmol) in ethanol (70 ml) and 10% hydrochloric acid (5 ml) were boiled for 3 h and the solution evaporated to dryness. The residue was taken up with aqueous $NaHCO_3$ and benzene. The benzene layer was dried and chromatographed (SiO_2) and products (XI; a and b) isolated (70—75%). The products were recrystallized from benzene–light petroleum. Analytical and spectroscopic data are reported in Table 1.

Crystal Structure of 2-*Anilino*-3-(1-*methyl*-2-*phenylindol*-3-yl)-3-*phenyl*-3H-*indole* (XIa) *Monohydrate*.—Crystals are colourless prisms elongated on [0 1 0]. Preliminary cell dimensions and space group were obtained from rotation and Weissenberg photographs. Lattice parameters were refined by least-squares by use of fourteen $(\theta, \chi, \phi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal Data.—$C_{35}H_{27}N_3,H_2O$, $M = 507.6$. Monoclinic,

$a = 12.60(1)$, $b = 15.74(1)$, $c = 16.45(1)$ Å, $\beta = 124.9(2)$, $Z = 4$; $D_m = 1.26$ g cm^{-3}, $U = 2\,675.7$ Å^3, Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 6.08 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Intensity data were collected up to θ 70° by use of the ω—2θ scan method and the five-points technique[7] with nickel-filtered Cu-K_α radiation on the same single-crystal diffractometer. 4 972 independent reflections were measured of which 1 135 were not used in the crystal analysis having intensities $\leqslant 2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The dimensions of the crystal specimen were *ca.* 0.24 × 0.57 × 0.33 mm in the x, y, z directions. No absorption correction was applied.

Structure Analysis and Refinement.—Structure amplitudes were put on an absolute scale by Wilson's[8] statistical method ($\bar{B} = 5.07$ Å^2) and normalised structure factor magnitudes $|E_{hkl}|$ were then derived. The structure was solved by use of 492 reflections with $|E| \geqslant 1.64$. The basis set was chosen using the programme MULTAN and the starting sets obtained by the phase permutation technique were used as input to a weighted numerical addition routine.[9] An E map computed by using the most consistent set of phases, clearly revealed the position of all the non-hydrogen atoms in the molecule. A structure-factor calculation carried out at this stage gave R 0.32. The structure was refined by block-diagonal least-squares cycles, first with isotropic and then with anisotropic thermal parameters; R was reduced to 0.085. A difference-Fourier synthesis was then computed and revealed significant residual peaks near all the positions where hydrogen atoms were expected to occur, except those of the water molecule. A few least-squares cycles were then computed, including hydrogen atoms with isotropic thermal parameters of the form $\exp(-B\sin^2\theta/\lambda^2)$, and a final R of 0.074 was obtained.

TABLE 3

(*a*) Fractional co-ordinates (×10^4) with standard deviations in parentheses, for non-hydrogen atoms

	x	y	z
O	5 614(4)	4 380(3)	2 299(3)
N(1)	3 986(3)	3 622(2)	−324(2)
N(2)	3 969(3)	1 010(2)	1 636(2)
N(3)	5 110(2)	2 278(2)	2 487(2)
C(1)	2 800(3)	3 987(2)	−699(2)
C(2)	2 165(4)	4 629(2)	−1 405(3)
C(3)	940(4)	4 852(3)	−1 674(3)
C(4)	370(3)	4 472(3)	−1 261(3)
C(5)	992(3)	3 835(2)	−557(2)
C(6)	2 243(3)	3 594(2)	−262(2)
C(7)	3 135(3)	2 951(2)	395(2)
C(8)	4 174(3)	2 975(2)	319(2)
C(9)	4 776(4)	3 804(3)	−682(3)
C(11)	5 332(3)	2 420(2)	732(2)
C(12)	5 188(3)	1 618(3)	377(3)
C(13)	6 263(4)	1 084(3)	720(3)
C(14)	7 464(4)	1 392(3)	1 414(3)
C(15)	7 639(4)	2 192(3)	1 785(3)
C(16)	6 562(3)	2 722(3)	1 432(3)
C(17)	2 885(3)	2 351(2)	984(2)
C(18)	2 448(3)	2 792(2)	1 587(2)
C(19)	2 796(3)	3 631(2)	1 906(2)
C(20)	2 506(4)	3 998(3)	2 534(3)
C(21)	1 899(4)	3 535(3)	2 856(3)
C(22)	1 557(4)	2 697(3)	2 550(3)
C(23)	1 824(3)	2 324(3)	1 916(3)
C(24)	2 017(3)	1 623(2)	359(2)
C(25)	734(3)	1 599(2)	−471(2)
C(26)	183(4)	835(3)	−896(3)
C(27)	874(4)	77(3)	−514(3)
C(28)	2 150(4)	97(3)	317(3)
C(29)	2 681(3)	864(2)	750(2)
C(30)	4 079(3)	1 815(2)	1 747(2)
C(33)	6 315(3)	1 951(2)	3 313(2)
C(34)	7 088(3)	2 568(3)	4 027(3)
C(35)	8 264(3)	2 318(3)	4 880(3)
C(36)	8 653(3)	1 494(3)	5 010(3)
C(37)	7 890(4)	891(3)	4 285(3)
C(38)	6 708(3)	1 137(2)	3 421(2)

TABLE 3 (*Continued*)

(*b*) Fractional co-ordinates (×10^3) and isotropic thermal parameters (10^{-1} Å^2) for hydrogen atoms

	x	y	z	B
H(1)	500(3)	297(2)	240(2)	50
H(2)	257(3)	486(2)	−175(2)	56
H(3)	40(3)	537(2)	−218(2)	55
H(4)	−50(3)	470(2)	−144(2)	53
H(5)	47(3)	358(2)	−21(2)	59
H(6)	538(3)	336(2)	−50(2)	63
H(7)	533(3)	430(2)	−38(2)	66
H(8)	438(3)	382(2)	−132(2)	65
H(9)	428(3)	140(2)	−13(2)	59
H(10)	601(3)	36(2)	45(2)	71
H(11)	824(3)	100(2)	162(2)	66
H(12)	852(3)	243(2)	225(2)	56
H(13)	674(3)	338(2)	166(2)	53
H(14)	330(3)	394(2)	176(2)	60
H(15)	285(3)	464(2)	281(2)	54
H(16)	169(3)	381(2)	333(2)	51
H(17)	111(3)	238(2)	281(2)	59
H(18)	157(3)	163(2)	169(2)	55
H(19)	16(3)	220(2)	−76(2)	51
H(20)	−76(3)	70(2)	−142(2)	53
H(21)	45(3)	−51(2)	−86(2)	53
H(22)	268(3)	−52(2)	62(2)	51
H(23)	679(3)	325(2)	396(2)	57
H(24)	875(3)	286(2)	542(2)	63
H(25)	951(3)	128(2)	561(2)	62
H(26)	824(3)	19(2)	432(2)	54
H(27)	624(3)	62(2)	289(2)	51

Positional parameters together with their standard deviations are given in Table 3. Atomic scattering factors were from ref. 10 for non-hydrogen atoms and from ref. 11 for hydrogen. Observed and calculated structure factors, thermal parameters, and the basis set are listed in Supplementary Publication No. SUP 21532 (23 pp, 1 microfiche).*

[5/667 *Received*, 9*th April*, 1975]

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

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