Acid-catalysed Rearrangements in the Aryliminoindoline Series. Part I. Crystal and Molecular Structures of 1-Ethyl-2-(1-ethyl-2-phenylindol-3-yl)-2-phenyl-3-phenyliminoindoline and 1-Ethyl-3-(1-ethyl-2-phenylindol-3-yl)-3-phenyl-2-phenyliminoindoline

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Heating an ethanol–hydrochloric acid solution of 1-alkyl-2-(1-alkyl-2-phenylindol-3-yl)-3-arylimino-2-phenylindolines leads to rearrangements to 1-alkyl-3-(1-alkyl-2-phenylindol-3-yl)-2-phenylimino-3-phenylindolines and to 3,3'-bi-indolyls and hydrolysis. The crystal structure of 1-ethyl-2-(1-ethyl-2-phenylindol-3-yl)-2-phenyl-3-phenyliminoindoline(Vb) and of 1-ethyl-3-(1-ethyl-2-phenylindol-3-yl)-3-phenyl-2-phenyliminoindoline(IXb) were determined by direct methods from 4 420 and 5 469 independent reflections and refined by least-squares to *R* 0.043 and 0.071. A mechanism for the rearrangements is suggested on the basis of the results of *X*-ray analysis and spectroscopic data.

As a part of our continuing interest in the chemistry and stereochemistry of indoles, we have recently[1] shown that the action of acids on bidentate 1-alkyl-2-(1-alkyl-2-phenylindol-3-yl)-3-benzoyloxyimino-2-phenylindoline systems (I) leads to the transposition products di-indolylnitrenium cations (II) when protonation involves the carbonylic oxygen, while the retrogression products (III) and (IV) are obtained when protonation occurs at the indolic nucleus. Similar behaviour is shown by the corresponding oximes. We have also found[2] that reaction of nitrosobenzenes with 1-alkyl-2-phenylindoles gives 1-alkyl-2-(1-alkyl-2-phenylindol-3-yl)-3-arylimino-2-phenylindolines (V). We now report the transpositions and hydrolysis reactions which (V) undergoes when heated in ethanolic solutions containing hydrochloric acid. Results are summarized in Scheme 1.

In the case of (Vd) we were able to separate all the products shown in Scheme 1 (following the lines α, β, and γ), in particular the bi-indolyl (VIa), the hydrolysis product (VIII), and *p*-chloroaniline (VIIc), and finally

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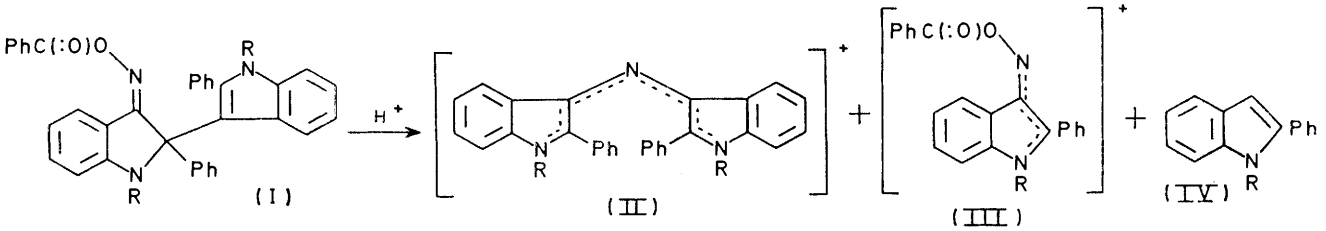
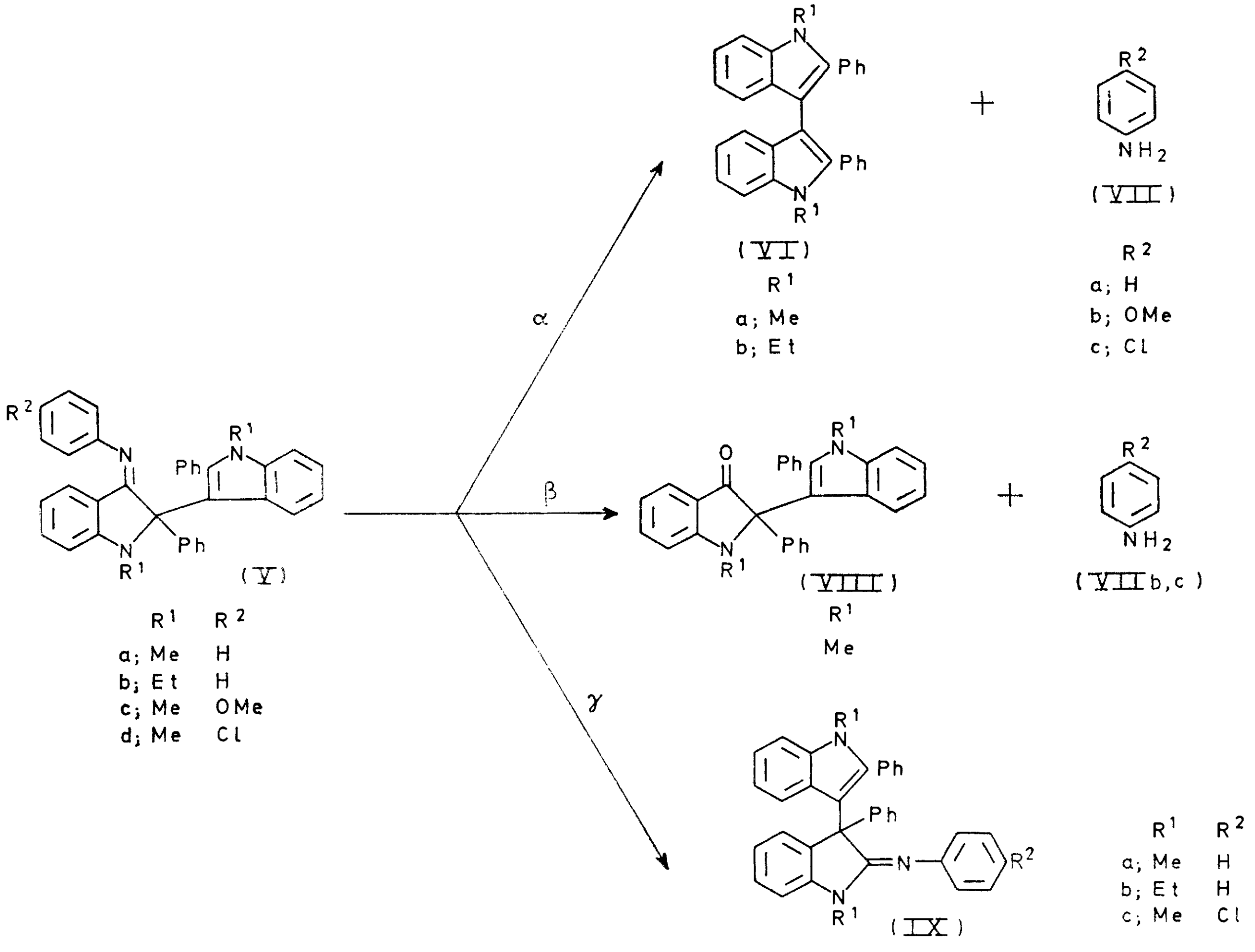
[1] M. Colonna, L. Greci, and L. Marchetti, *Gazzetta*, 1974, **104**, 395.

[2] M. Colonna, L. Greci, and L. Marchetti, *Ann. Chim.* (*Italy*), 1974, **64**, 7.

the transposition product (IXc). On the other hand, in the case of products (Va) and (Vb) the dimers (VIa) and (VIb) are isolated with transposition products (IXa), (IXb), and aniline; the product (Vc) gave the dimer (VIa), the ketone (VIII), and *p*-anisidine. It seems that the *para*-substituent at the phenylimino-group plays a role in determining the pathway of these reactions along the lines α, β, and γ of Scheme 1, but there is not enough evidence to give a full explanation of these effects. In all cases small amounts of 1-alkyl-2-phenylindoles are found in the reaction mixtures.





Scheme 1

The structure of the bi-indolyls (VIa) and (VIb) has been established on the basis of elemental analysis and by comparison of their u.v. spectra with those of the corresponding indoles (see Figure 1). Moreover the ^{1}H n.m.r. spectra show the equivalence of the two methyl groups in (VIa) and of the two ethyl groups in (VIb) and their chemical shifts are the same as in the correspondent indoles (Table 1). The linking position of the two indole rings is confirmed by the absence in the ^{1}H n.m.r. spectra of (VIa) and (VIb) of the signal due to the hydrogen at position-3 which falls at 6.4—6.5 δ (Table 1) for indoles.

The structure of the hydrolysis product (VIII) is in agreement with the presence of two bands in the i.r. spectrum at 1 705 and 1 618 cm^{-1} which are characteristic of the carbonyl group and of the $Ph{-}N{-}C{-}$ group[3] respectively, confirming the presence of an indoline system. The ^1H n.m.r. spectrum shows the non-equivalence of the two methyl groups (Table 1), as their chemical shifts are equal to those of the starting materials.

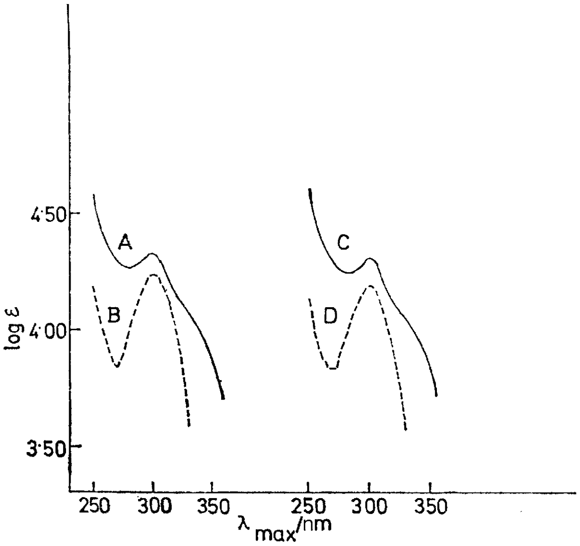


FIGURE 1 U.v. spectra ($CHCl_3$ solutions) of indoles and bi-indolyls: A, (VIa); B, (IV) R = Me; C, (VIb); D, (IV) R = Et

The structure of the transposition products has been established by *X*-ray analysis of (IXb) and by comparison of the i.r. and ^1H n.m.r. spectra of (IXb) with those of (IXa) and (IXc).

Molecular Geometry of 1-*Ethyl*-2-(1-*ethyl*-2-*phenylindol*-3-*yl*)-2-*phenyl*-3-*phenyliminoindoline* (Vb) *and of* 1-*Ethyl*-3-(1-*ethyl*-2-*phenylindol*-3-*yl*)-3-*phenyl*-2-*phenyliminoindoline* (IXb).—Figures 2 and 3 show projections of the structures of (Vb) and (IXb) respectively. Corresponding bond distances and angles are not significantly different in the two structures (Table 2). The numbering system used is shown in Figure 4. Some minor differences concern the five membered rings in the indoline nuclei as a consequence of the trigonal carbon atom being in position 3 in compound (Vb) and in position 2 in compound (IXb). In both cases the phenylimino-groups seem involved in a partial delocalisation concerning the indoline rings. In these groups the five-membered rings show significant deviations from planarity, while all the other rings in the molecule are strictly planar. The reciprocal orientation of the rings in the two molecules can be deduced from the dihedral angles (Table 2).

In both compounds packing is consistent with van der Waals interactions.

DISCUSSION

Possible hypotheses on the mechanisms of the reactions shown in Scheme 1 are summarized in Scheme 2.

TABLE 1

Analytical and spectral data

				% Found *			I.r.	^1H N.m.r. (δ)					
Compound	Recryst.[a] Solvent	M.p./ °C	Formula	C	H	N	$\nu_{max.}$/cm^{-1}	NMe[e]	NMe[f]	NEt[e]	NEt[f]	3*H*-indole	Aromatic
(Vb)	A	163	$C_{38}H_{33}N_3$	86.20 (85.54)	6.04 (6.26)	7.93 (7.90)	1 598[b] 1 660[c]			0.45 (3 H, t) 0.33 (2 H, q)	1.01 (3 H, t) 3.88 (2 H, q)		6.03—7.67 (18 H, m)
(VIa)	A	279	$C_{30}H_{24}N_2$	87.15 (87.34)	6.16 (5.86)	6.58 (6.79)			3.58 (6H, s)[g]				6.55—7.75 (18 H, m)
(VIb)	B	230	$C_{32}H_{28}N_2$	87.49 (87.23)	6.11 (6.40)	6.59 (6.35)					1.18 (6 H, t)[g] 4.06 (4 H, q)		6.58—7.2 (18 H, m)
(VIII)	A	241	$C_{30}H_{24}N_2O$	83.88 (84.08)	5.41 (5.65)	6.37 (6.54)	1 618[b] 1 705[d]	2.78 (3 H, s)	3.46 (3 H, s)				6.4—7.6 (18 H, m)
(IXa)	B	230	$C_{36}H_{29}N_3$	86.04 (85.85)	5.73 (5.80)	8.36 (8.34)	1 680[c]	2.62 (3 H, s)	3.35 (3H, s)				6.1—7.67 (23 H, m)
(IXb)	C	183	$C_{38}H_{33}N_3$	86.02 (85.84)	6.46 (6.26)	7.75 (7.90)	1 680[c]			1.10 (6 H, t)[h] 3.18—4.1 (4 H, m)			6.0—7.8 (23 H, m)
(IXc)	A	231	$C_{36}H_{28}N_3Cl$	80.36 (80.75)	5.24 (5.22)	7.81 (7.81)	1 680[c]	2.85 (3 H, s)	3.40 (3H, s)				6.07—7.67 (22 H, m)
1-Me-2-Ph-indole									3.56 (3 H, s)			6.5 (1 H, s)	6.8—7.7 (9 H, m)
1-Et-2-Ph-indole											1.20 (3 H, t) 4.04 (2 H, q)	6.2 (1 H, s)	6.8—7.7 (9 H, m)

* Calc. in parentheses.

[a] A, benzene–light petroleum; B, ethanol; C, n-heptane. [b] $Ph{-}N{-}C{-}$. [c] $>C{=}N{-}Ar$. [d] $>C{=}O$. [e] Indoline nucleus. [f] Indole nucleus. [g] Two equivalent groups. [g] The two Et groups are *quasi*-equivalent.

In acidic medium compounds (V) can be protonated at the imine nitrogen with formation of a positive centre

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[3] B. Witkop and J. B. Patrick, *J. Amer. Chem. Soc.*, 1951, **73**, 713.

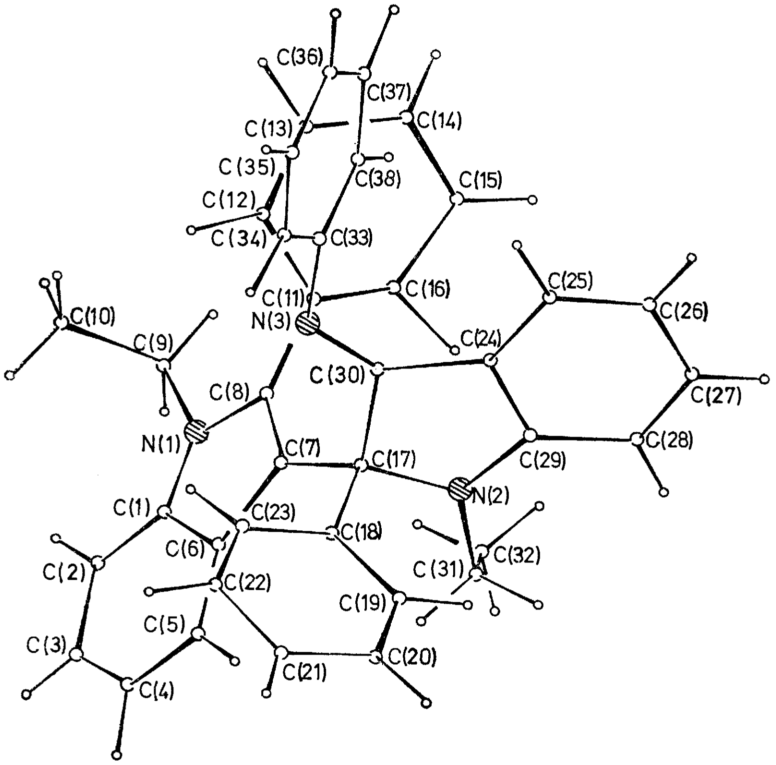


FIGURE 2 Compound (Vb): projection of the structure on (010)

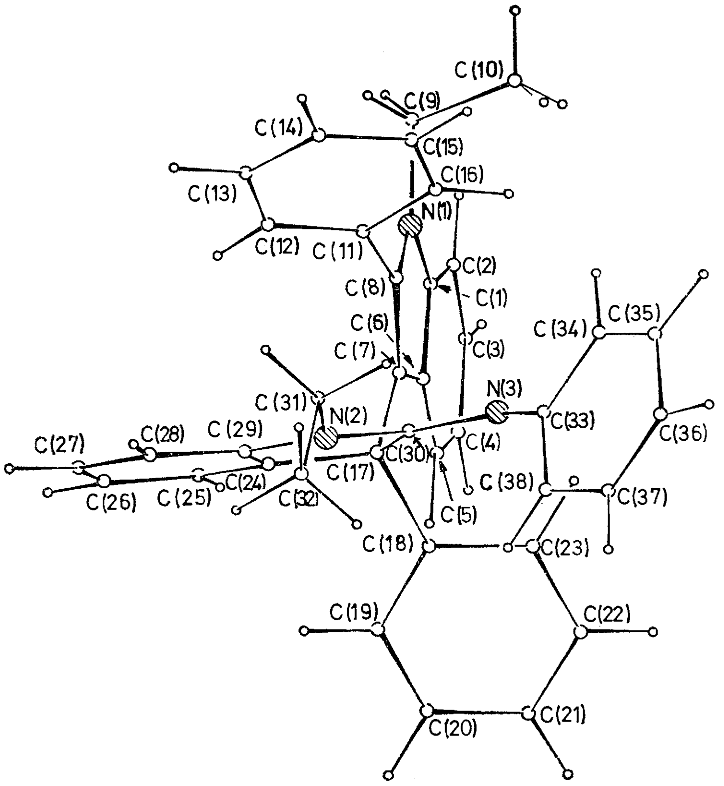
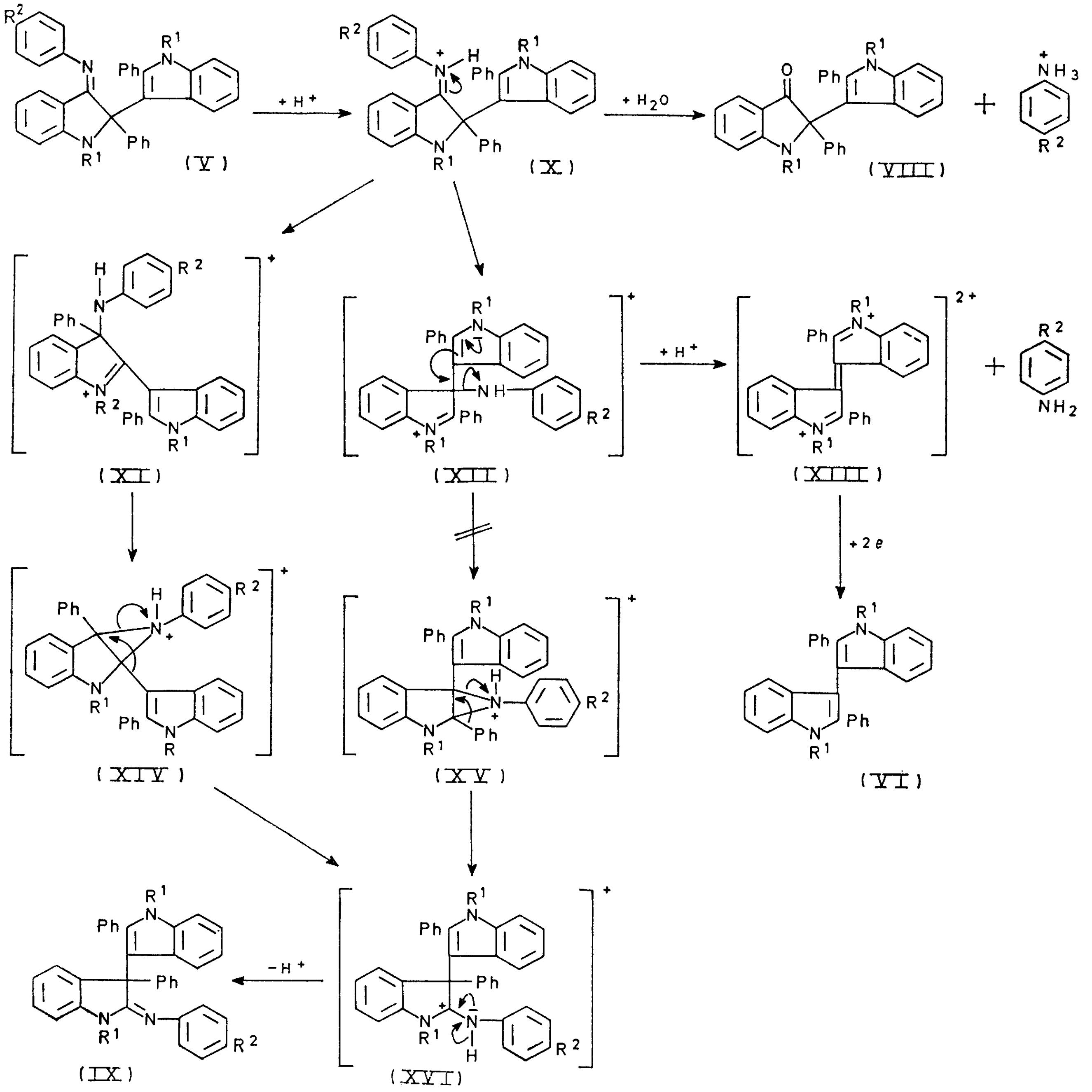


FIGURE 3 Compound (IXb): projection of the structure on (010)


(V)
+H⁺
(X)
+H₂O
(VIII)
(XI)
(XII)
+H⁺
(XIII)
+2e
(VI)
(XIV)
(XV)
(XVI)
−H⁺
(IX)
Ph
R¹
R²
NH₃
NH₂

SCHEME 2

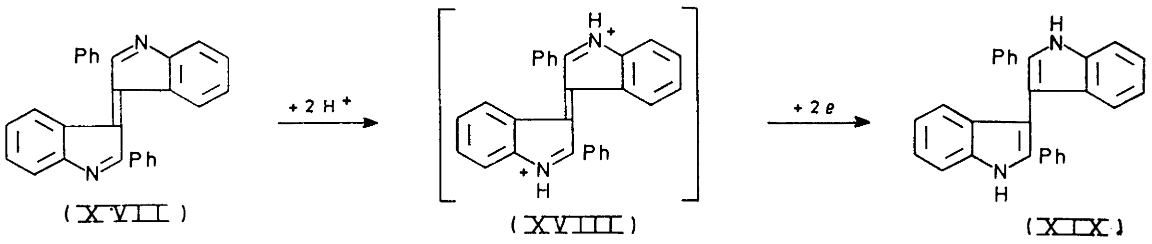

(XVII)
+2H⁺
(XVIII)
+2e
(XIX)
Ph

TABLE 2

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses for compounds (Vb) and (IXb)

(*a*) Bond distances *

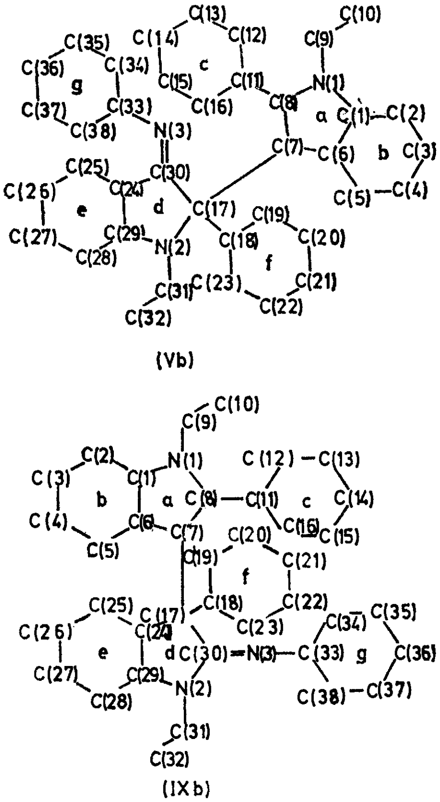
N(1)–C(1)	1.381(4)	1.370(5)
N(1)–C(8)	1.393(4)	1.385(4)
N(1)–C(9)	1.467(4)	1.472(5)
N(2)–C(17)	1.474(4)	
N(2)–C(29)	1.367(4)	1.411(5)
N(2)–C(30)		1.393(5)
N(2)–C(31)	1.458(4)	1.486(5)
N(3)–C(30)	1.274(4)	1.256(4)
N(3)–C(33)	1.416(4)	1.406(4)
C(1)–C(2)	1.396(4)	1.395(5)
C(1)–C(6)	1.412(4)	1.411(5)
C(2)–C(3)	1.378(4)	1.367(6)
C(3)–C(4)	1.392(5)	1.405(5)
C(4)–C(5)	1.384(5)	1.380(5)
C(5)–C(6)	1.411(4)	1.414(5)
C(6)–C(7)	1.447(4)	1.446(4)
C(7)–C(8)	1.377(4)	1.378(4)
C(7)–C(17)	1.513(4)	1.518(5)
C(8)–C(11)	1.487(4)	1.485(5)
C(9)–C(10)	1.511(5)	1.519(6)
C(11)–C(12)	1.397(4)	1.374(5)
C(11)–C(16)	1.383(4)	1.387(6)
C(12)–C(13)	1.392(4)	1.414(7)
C(13)–C(14)	1.378(4)	1.373(7)
C(14)–C(15)	1.373(4)	1.361(7)
C(15)–C(16)	1.395(4)	1.379(7)
C(17)–C(18)	1.543(4)	1.536(4)
C(17)–C(24)		1.516(5)
C(17)–C(30)	1.556(4)	1.566(4)
C(18)–C(19)	1.383(4)	1.383(5)
C(18)–C(23)	1.397(4)	1.395(5)
C(19)–C(20)	1.393(5)	1.408(6)
C(20)–C(21)	1.376(5)	1.377(6)
C(21)–C(22)	1.375(4)	1.369(6)
C(22)–C(23)	1.386(4)	1.394(6)
C(24)–C(25)	1.399(5)	1.373(5)
C(24)–C(29)	1.410(4)	1.391(5)
C(24)–C(30)	1.468(3)	
C(25)–C(26)	1.387(4)	1.391(5)
C(26)–C(27)	1.391(5)	1.381(7)
C(27)–C(28)	1.383(5)	1.391(6)
C(28)–C(29)	1.408(4)	1.379(5)
C(31)–C(32)	1.508(3)	1.510(6)
C(33)–C(34)	1.382(3)	1.389(6)
C(33)–C(38)	1.389(4)	1.383(5)
C(34)–C(35)	1.386(4)	1.393(6)
C(35)–C(36)	1.385(5)	1.387(6)
C(36)–C(37)	1.366(5)	1.363(6)
C(37)–C(38)	1.393(4)	1.387(6)

(*b*) Bond angles

C(1)–N(1)–C(8)	108.4(5)	109.7(5)
C(1)–N(1)–C(9)	124.0(6)	124.5(7)
C(8)–N(1)–C(9)	127.4(6)	125.8(8)
C(17)–N(2)–C(29)	110.8(4)	
C(29)–N(2)–C(30)		111.0(6)
C(17)–N(2)–C(31)	122.7(6)	
C(29)–N(2)–C(31)	125.6(7)	121.6(8)
C(30)–N(2)–C(31)		124.0(8)
C(30)–N(3)–C(33)	122.2(6)	128.3(8)
N(1)–C(1)–C(2)	128.6(8)	129.9(8)
N(1)–C(1)–C(6)	108.4(5)	107.6(5)
C(2)–C(1)–C(6)	123.0(7)	122.5(8)
C(1)–C(2)–C(3)	117.4(6)	118.1(7)
C(2)–C(3)–C(4)	121.1(7)	121.1(8)
C(3)–C(4)–C(5)	121.7(7)	121.2(8)
C(4)–C(5)–C(6)	119.0(7)	119.2(7)
C(1)–C(6)–C(5)	117.8(5)	118.0(6)
C(1)–C(6)–C(7)	106.8(5)	107.0(5)
C(5)–C(6)–C(7)	135.4(9)	135.0(9)
C(6)–C(7)–C(8)	106.7(5)	106.6(5)
C(6)–C(7)–C(17)	127.0(7)	127.8(7)
C(8)–C(7)–C(17)	126.0(6)	125.3(7)
N(1)–C(8)–C(7)	109.8(5)	109.1(5)
N(1)–C(8)–C(11)	119.6(7)	120.1(6)
C(7)–C(8)–C(11)	130.6(7)	130.8(7)
N(1)–C(9)–C(10)	112.8(5)	112.4(6)
C(8)–C(11)–C(12)	120.8(5)	120.7(7)
C(8)–C(11)–C(16)	120.5(7)	119.6(7)
C(12)–C(11)–C(16)	118.7(6)	119.6(8)
C(11)–C(12)–C(13)	120.4(5)	119.3(9)
C(12)–C(13)–C(14)	120.0(7)	119.5(9)
C(13)–C(14)–C(15)	120.3(6)	121.2(10)
C(14)–C(15)–C(16)	120.1(5)	119.5(9)
C(11)–C(16)–C(15)	120.6(7)	120.9(8)
N(2)–C(17)–C(7)	111.3(4)	
N(2)–C(17)–C(18)	110.8(5)	
N(2)–C(17)–C(30)	102.1(4)	
C(7)–C(17)–C(18)	112.8(5)	112.8(5)
C(7)–C(17)–C(24)		109.6(6)
C(7)–C(17)–C(30)	115.3(6)	112.2(5)
C(18)–C(17)–C(24)		113.5(5)
C(18)–C(17)–C(30)	103.8(4)	106.2(5)
C(24)–C(17)–C(30)		102.1(5)
C(17)–C(18)–C(19)	121.7(6)	121.0(6)
C(17)–C(18)–C(23)	119.1(6)	119.8(6)
C(19)–C(18)–C(23)	119.2(6)	119.2(7)
C(18)–C(19)–C(20)	120.1(6)	119.3(7)
C(19)–C(20)–C(21)	120.4(7)	120.8(8)
C(20)–C(21)–C(22)	119.8(6)	120.1(8)
C(21)–C(22)–C(23)	120.5(6)	119.8(7)
C(18)–C(23)–C(22)	119.9(7)	120.8(8)
C(17)–C(24)–C(25)		130.1(8)
C(17)–C(24)–C(29)		109.2(6)
C(25)–C(24)–C(29)	120.1(7)	120.6(7)
C(25)–C(24)–C(30)	132.5(8)	
C(29)–C(24)–C(30)	107.4(4)	
C(24)–C(25)–C(26)	118.9(6)	119.0(7)
C(25)–C(26)–C(27)	120.4(7)	119.8(8)
C(26)–C(27)–C(28)	122.2(7)	121.9(9)
C(27)–C(28)–C(29)	117.6(6)	117.4(7)
N(2)–C(29)–C(24)	111.6(5)	110.3(6)
N(2)–C(29)–C(28)	127.7(7)	128.3(8)
C(24)–C(29)–C(28)	120.7(6)	121.3(8)
N(2)–C(30)–N(3)		132.3(8)
N(2)–C(30)–C(17)		107.1(5)
N(3)–C(30)–C(17)	118.9(5)	120.5(6)
N(3)–C(30)–C(24)	135.0(7)	
C(17)–C(30)–C(24)	106.1(5)	
N(2)–C(31)–C(32)	113.2(4)	113.2(6)
N(3)–C(33)–C(34)	117.9(5)	118.9(7)
N(3)–C(33)–C(38)	122.4(6)	122.5(7)
C(34)–C(33)–C(38)	119.5(6)	118.0(8)
C(33)–C(34)–C(35)	120.1(5)	120.8(8)
C(34)–C(35)–C(36)	120.2(6)	120.5(8)
C(35)–C(36)–C(37)	120.0(7)	118.5(8)
C(36)–C(37)–C(38)	120.3(7)	121.6(9)
C(33)–C(38)–C(37)	119.9(6)	120.7(8)

(*c*) Dihedral angles (°) between planes: ab–c 66.9, 78.5; ab–de 76.9, 83.1; de–f 82.5, 69.9; de–g 60.8, 70.7

* Carbon–hydrogen bonds are in the range 0.97—1.05 (Vb) and 1.00—1.06 Å (IXb).



(Vb)

(IXb)

FIGURE 4 Numbering system used for (Vb) and (IXb) on which a transposition can take place of either the indolyl group, through the formation of the intermediate product (XII), or of the phenyl group with formation of (XI). By action of acids upon compounds similar to (Va, d) we have been able to separate the phenyl transposition product. The dication (XIII) is obtained from the intermediate product (XII), *via* elimination of amine, favoured by the acidic medium and by the possibility of conjugation of the indole nitrogen. This dication is readily reduced to bi-indolyl (VI); this type of cation has previously been shown to be easily reduced by ethanol.[4] To support this hypothesis we have shown that the bi-indolylidene (XVII) in ethanolic solution containing HCl is reduced to bi-indolyl.[5] On the other hand elimination of an aromatic amine from (XI) is probably not favoured by the possibility of conjugation of the indole nitrogen, so a double transposition to (IX) is expected instead of an elimination. The transition state in this case is probably of the aziridine type. Another hypothesis would be a double transposition of (XII) to (IX) through (XV), but this mechanism seems less probable, because of the effect of assistance by the indolic nitrogen in elimination of the amine in (XII). A similar double transposition has been observed by action of Lewis acids (BF_3) on 1-alkyl-2,2-diphenylindolinones.[6]

Finally the formation of (VIII) can be considered the usual hydrolysis of an imine. The presence of small amounts of 1-alkyl-2-phenylindole can be explained by partial retrogression of (V) which is protonated at position 3 in the indole nucleus, as observed in benzoyloxyiminoindolines (I).[1] In compounds with structures similar to (Va, d) and with $R^1 = H$ on the indolinic nitrogen, and $R^1 =$ alkyl on the indolic nitrogen, the retrogression is sometimes the main reaction.

EXPERIMENTAL

Products (Va, c, d) were prepared as reported in ref. 2. U.v. spectra were registered on a Beckman DK 2A spectrophotometer, i.r. spectra on a Perkin-Elmer 257 (Nujol), ^1H n.m.r. spectra on a Perkin-Elmer R 12 B ($CDCl_3$, with tetramethylsilane as internal standard), and the gas chromatographs on a Carlo Erba Fractovap GV (silicon SE30 columns).

1-*Ethyl*-2-(1-*ethyl*-2-*phenylindol*-3-*yl*)-2-*phenyl*-3-*phenyliminoindoline* (Vb).—This was synthesized[2] by adding 1-ethyl-2-phenylindole (10 mmol) to nitrosobenzene (10 mmol), and PhCOCl (10 mmol) in CH_3CN (60 ml) at room temperature; 75% yield. Analytical and spectroscopic data are reported in Table 1.

Action of HCl *on the Products* (Va, d).—(Va, d) (5 mmol) and 10% HCl (10 ml) in ethanol (100 ml) were heated under reflux for 3—4 h. After some hours at room temperature the solid dimers (VIa, b) were collected and purified from benzene and petroleum ether (20% yield). The alcoholic mother liquors were evaporated off and the residue taken up in water and chloroform. The water layer was treated with NaOH and extracted with ether, from which the aromatic amine was identified by gas chromatography. The chloroform layer, washed with diluted $NaHCO_3$, was evaporated to dryness under reduced pressure, and the residue taken up with benzene and chromatographed on SiO_2. From (Va) and (Vb) the products (IXa) and (IXb) were obtained (55% yield). (Vc) gave (VIII) (20% yield; in this case the dimer is obtained with 40% yield). Products (VIII) and (IXc) were isolated from (Vd) (20% and 45% yield respectively). Analytical and spectroscopic data are reported in Table 1.

Reduction of the Bi-indolylidene (XVII).—Bi-indolylidene[7] (300 mg) (XVII) in ethanol (25 ml) and 10% HCl (10 ml) were heated under reflux for 3 h. Solvent was then evaporated off and the residue taken up with $CHCl_3$ and aqueous $NaHCO_3$. The chloroform layer was evaporated to dryness and the residue, chromatographed on SiO_2 from benzene, gave bi-indolyl (XIX) (100 mg).

Crystal Structures of (Vb) *and* (IXb)

1-*Ethyl*-2-(1-*ethyl*-2-*phenylindol*-3-*yl*)-2-*phenyl*-3-*phenyliminoindoline* (Vb).—Crystals are bright yellow prisms, elongated along [100]. Preliminary cell dimensions and space-group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were refined by least-squares using $15(\theta,\chi,\phi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal Data.—$C_{38}H_{33}N_3$, $M = 531.7$. Monoclinic, $a = 8.77(1)$, $b = 17.87(1)$, $c = 19.85(1)$ Å, $\beta = 107.2(2)°$, $Z = 4$; $D_m = 1.19$ g cm^{-3}, $U = 2\,971.8$ Å^3. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) $= 5.4$ cm^{-1}. Space group $P2_1/c$ from systematic absences.

Intensity data were collected on a Siemens single-crystal diffractometer up to θ 60° by use of the ω—2θ scan method and the 'five points' technique[8] (nickel-filtered Cu-K_α radiation). 4 420 independent reflections were measured, of which 3 011 were used in the crystal analysis, having intensities $>2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The size of the crystal specimen was *ca.* $0.25 \times 0.10 \times 0.15$ mm in the x, y, z directions, respectively. Absorption was ignored.

Structure Analysis and Refinement.—Data were put on an absolute scale by Wilson's method[9] and normalized structure-factor amplitudes $|E_{hkl}|$ were derived. The structure was solved from 499 reflections with $|E| \geqslant 1.60$. The basic set was chosen using the programme Multan[10] and the starting sets obtained by the phase permutation technique were used as input to a weighted numerical addition routine.[11] An E map, computed by using the most consistent set of phases obtained with a and c negative, b and d positive, clearly revealed the positions of all non-hydrogen atoms. A structure-factor calculation based on the co-ordinates derived from the E map, with $\bar{B}$ 3.74 Å^2 for all atoms gave R 0.24. The refinement was carried out

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TABLE 3

(*a*) Fractional co-ordinates ($\times 10^4$), with standard deviations in parentheses

	Compound (Vb)			Compound (IXb)		
	x	*y*	*z*	*x*	*y*	*z*
N(1)	−1 535(2)	3 221(1)	2 333(1)	−2 535(3)	−157(2)	477(2)
N(2)	2 311(2)	4 531(1)	1 902(1)	−4 134(3)	3 565(2)	3 087(2)
N(3)	628(2)	5 474(1)	3 090(1)	−1 719(2)	2 947(2)	2 771(2)
C(1)	−2 389(2)	3 390(1)	1 646(1)	−2 385(3)	−873(2)	1 206(3)
C(2)	−3 717(3)	3 023(1)	1 205(1)	−2 023(4)	−1 983(3)	946(3)
C(3)	−4 357(3)	3 304(2)	534(1)	−1 985(4)	−2 519(3)	1 850(3)
C(4)	−3 694(3)	3 926(2)	305(1)	−2 286(4)	−1 968(3)	3 009(3)
C(5)	−2 361(3)	4 284(1)	736(1)	−2 626(3)	−868(2)	3 273(3)
C(6)	−1 682(2)	4 020(1)	1 430(1)	−2 671(3)	−289(2)	2 358(2)
C(7)	−343(2)	4 235(1)	2 023(1)	−2 985(3)	828(2)	2 290(2)
C(8)	−293(2)	3 735(1)	2 557(1)	−2 909(3)	869(2)	1 126(2)
C(9)	−1 839(3)	2 564(1)	2 717(1)	−2 324(3)	−449(3)	−801(3)
C(10)	−3 262(3)	2 665(2)	2 990(1)	−833(4)	−501(3)	−1 320(3)
C(11)	850(2)	3 667(1)	3 276(1)	−3 199(3)	1 785(2)	536(2)
C(12)	353(3)	3 788(1)	3 874(1)	−4 519(4)	2 150(3)	462(3)
C(13)	1 427(3)	3 715(2)	4 545(1)	−4 758(5)	2 995(4)	−146(4)
C(14)	2 990(3)	3 520(2)	4 622(1)	−3 670(5)	3 447(3)	−636(4)
C(15)	3 494(3)	3 399(2)	4 039(1)	−2 363(5)	3 082(3)	−566(4)
C(16)	2 423(3)	3 471(1)	3 365(1)	−2 125(4)	2 252(3)	18(3)
C(17)	871(2)	4 841(1)	2 037(1)	−3 457(3)	1 771(2)	3 285(2)
C(18)	178(3)	5 490(1)	1 525(1)	−2 918(3)	1 622(2)	4 415(2)
C(19)	970(3)	5 771(1)	1 072(1)	−3 798(3)	1 709(2)	5 444(3)
C(20)	326(3)	6 368(2)	628(1)	−3 262(4)	1 602(3)	6 467(3)
C(21)	−1 086(3)	6 691(1)	645(1)	−1 875(4)	1 418(3)	6 458(3)
C(22)	−1 864(3)	6 424(1)	1 104(1)	−1 000(4)	1 326(3)	5 442(3)
C(23)	−1 248(3)	5 825(1)	1 544(1)	−1 516(3)	1 429(3)	4 419(3)
C(24)	3 307(2)	5 279(1)	2 874(1)	−4 997(3)	2 002(2)	3 428(2)
C(25)	4 531(3)	5 655(2)	3 373(1)	−6 000(3)	1 338(3)	3 601(3)
C(26)	6 090(3)	5 568(2)	3 355(1)	−7 357(3)	1 736(3)	3 654(3)
C(27)	6 428(3)	5 114(2)	2 848(1)	−7 671(3)	2 777(4)	3 503(3)
C(28)	5 246(3)	4 743(1)	2 340(1)	−6 666(4)	3 457(3)	3 318(3)
C(29)	3 660(2)	4 835(1)	2 352(1)	−5 326(3)	3 053(3)	3 290(3)
C(30)	1 578(2)	5 236(1)	2 761(1)	−2 969(3)	2 852(2)	3 003(2)
C(31)	2 247(3)	4 075(1)	1 285(1)	−4 153(4)	4 576(3)	2 615(3)
C(32)	2 420(3)	3 249(1)	1 445(1)	−4 566(5)	5 575(3)	3 540(4)
C(33)	1 169(2)	5 882(1)	3 728(1)	−1 081(3)	3 896(2)	2 756(3)
C(34)	607(3)	6 603(1)	3 740(1)	−172(4)	3 969(3)	1 782(3)
C(35)	1 070(3)	7 018(1)	4 357(1)	640(4)	4 817(3)	1 797(3)
C(36)	2 053(3)	6 074(2)	4 969(1)	537(4)	5 615(3)	2 781(3)
C(37)	2 563(3)	5 982(2)	4 967(1)	−363(4)	5 543(3)	3 731(3)
C(38)	2 138(3)	5 566(1)	4 346(1)	−1 168(4)	4 698(3)	3 730(3)

(*b*) **Fractional** co-ordinates ($\times 10^3$) for the hydrogen atoms

	Compound (Vb)			Compound (IXb)		
	x	*y*	*z*	*x*	*y*	*z*
H(1)	−420(2)	256(1)	137(1)	−181(3)	−238(2)	12(2)
H(2)	−532(2)	305(1)	20(1)	−176(3)	−334(2)	168(3)
H(3)	−418(2)	413(1)	−20(1)	−226(3)	−239(2)	371(2)
H(4)	−193(2)	473(1)	56(1)	−286(3)	−48(2)	413(2)
H(5)	−80(2)	245(1)	313(1)	−291(3)	9(2)	−114(2)
H(6)	−197(2)	210(1)	239(1)	−270(3)	−120(2)	−107(2)
H(7)	−336(2)	220(1)	327(1)	−69(3)	−69(2)	−220(3)
H(8)	−425(2)	277(1)	259(1)	−25(3)	−105(2)	−103(2)
H(9)	−314(2)	311(1)	333(1)	−45(3)	23(2)	−112(2)
H(10)	−77(2)	394(1)	382(1)	−533(3)	182(2)	87(3)
H(11)	103(2)	381(1)	499(1)	−574(3)	326(2)	−19(3)
H(12)	376(2)	346(1)	512(1)	−382(3)	406(2)	−108(3)
H(13)	461(2)	325(1)	410(1)	−154(3)	342(2)	−96(3)
H(14)	279(2)	338(1)	293(1)	−115(3)	198(2)	8(3)
H(15)	196(2)	554(1)	106(1)	−482(3)	184(2)	547(2)
H(16)	96(2)	657(1)	30(1)	−393(3)	166(2)	722(3)
H(17)	−155(2)	714(1)	32(1)	−147(3)	135(2)	719(3)
H(18)	−290(2)	667(1)	112(1)	2(3)	119(2)	544(2)
H(19)	−185(2)	563(1)	188(1)	−83(3)	136(2)	365(2)
H(20)	423(2)	600(1)	374(1)	−573(3)	56(2)	369(2)
H(21)	695(2)	584(1)	371(1)	−815(3)	125(2)	381(3)
H(22)	755(2)	506(1)	286(1)	−867(3)	305(2)	352(3)
H(23)	547(2)	440(1)	197(1)	−688(3)	422(2)	320(3)
H(24)	313(2)	424(1)	108(1)	−484(3)	454(2)	201(3)
H(25)	118(2)	417(1)	91(1)	−317(3)	463(2)	218(2)
H(26)	241(2)	295(1)	101(1)	−456(3)	625(2)	319(3)
H(27)	158(2)	307(1)	164(1)	−388(3)	564(2)	415(3)
H(28)	350(2)	314(1)	182(1)	−552(3)	553(2)	397(3)
H(29)	−12(2)	683(1)	329(1)	−11(3)	338(2)	105(3)
H(30)	68(2)	756(1)	436(1)	136(3)	485(2)	107(3)
H(31)	236(2)	710(1)	536(1)	122(3)	615(2)	263(3)
H(32)	323(2)	574(1)	542(1)	−45(3)	612(2)	444(3)
H(33)	254(2)	503(1)	435(1)	−185(3)	465(2)	444(2)

by cycles of block-diagonal least-squares, first with isotropic and then with anisotropic thermal parameters, reducing the R factor to 0.088. A difference synthesis revealed significant residual peaks near the positions where the hydrogen atoms were expected. A few least-squares cycles were then computed including the hydrogen atoms with isotropic thermal parameters, obtaining the final conventional R factor of 0.043.

The final positional parameters together with their standard deviations are given in Table 3.

1-*Ethyl*-3-(1-*ethyl*-2-*phenylindol*-3-*yl*)-3-*phenyl*-2-*phenyliminoindoline* (IXb).—Yellow prismatic crystals were obtained from ethanol–benzene. Cell parameters were derived as before and lattice parameters refined from a set of seventeen $(\theta,\chi,\phi)_{hkl}$ measurements.

Crystal Data.—$C_{38}H_{33}N_3$, $M = 531.7$. Triclinic, $a = 9.93(1)$, $b = 12.69(1)$, $c = 11.81(1)$ Å, $\alpha = 100.2(2)$, $\beta = 82.6(2)$, $\gamma = 85.5(2)°$, $Z = 2$; $D_m = 1.22$ g cm^{-3}, $U = 1\,443.6$ Å^3, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 5.6 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Intensity data were collected as for the previous compound up to θ 70°. Of 5 469 independent reflections measured, 622 were not used in the crystal analysis. The dimensions of the crystal were *ca.* 0.6 × 0.7 × 0.8 mm in the x, y, z directions respectively. Absorption effects were neglected.

Structure Analysis and Refinement.—487 reflections with $|E| \geqslant 1.71$ were used to solve the structure by direct methods. The most consistent set of signs derived from the basic set gave $-, +, -, +, -, -$ for the signs of six symbolic reflections. This set was used to compute an E map which revealed the whole structure. A structure-factor calculation based on the co-ordinates derived from the E map with B 4.9 Å^2 for all atoms gave R 0.30. Refinement was carried out by means of cycles of block-diagonal least-squares first isotropically and then anisotropically until R was 0.11. A ΔF synthesis was then computed and revealed significant residual peaks, all interpreted as hydrogen atom positions. All atom parameters were then refined (heavy atoms anisotropically and hydrogen atoms isotropically). The final value of R was 0.071. Final positional parameters together with their standard deviations are reported in Table 3.

The atomic scattering factors used for both crystal analyses were from ref. 12 for nitrogen and carbon, and from ref. 13 for hydrogen.

For both compounds observed and calculated structure-factors and thermal parameters are listed in Supplementary Publication No. SUP 21496 (46 pp., 1 microfiche).*

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

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