Acid Catalyzed Rearrangements in the Arylimino Indoline Series. Part IV [1]. Reactions of 1,2-Dihydro-2-phenyl-2-(indol-3-yl-derivatives)-3-phenylimino-3*H*-indole with Trichloroacetic and Hydrochloric Acids. Crystal Structure of 1,2-Dihydro-2-phenyl-2-(indol-3-yl)-3-phenylimino-3*H*-indole

Barbara Cardillo, Carla Conti, Elisabetta Giorgini,
Lucedio Greci*, Pierluigi Stipa and Giorgio Tosi

Dipartimento di Scienze dei Materiali e della Terra, Università,
Via Brecce Bianche, I-60131 Ancona, Italy

Corrado Rizzoli, Paolo Sgarabotto* and Franco Ugozzoli

Istituto di Strutturistica Chimica, Università,
Centro di Studi per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze,
I-40100 Parma, Italy

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2-Phenyl-3-phenylimino-3*H*-indole reacts with indole, 2-methylindole and 1,2-dimethylindole in the presence of stoichiometric trichloroacetic acid to form 1,2-dihydro-2-phenyl-2-(indol-3-yl-derivatives)-3-phenylimino-3*H*-indole, which during a longer period of time (16 hours) undergoes indolyl transposition to carbon-3 and elimination of aniline affording the 3,3'-*bis*-indolyls. In the case of 1,2-dimethylindole the intermediate coming from the indolyl migration may undergo a nucleophilic addition to carbon-2 of another molecule of indole; the new intermediate leads to the formation of 2-phenyl-3,3'-di-(1,2-dimethylindol-3-yl)-3*H*-indole by elimination of aniline and migration to carbon-3 of the second molecule of indole. By treatment with hydrochloric acid in refluxing ethanol, 1,2-dihydro-2-phenyl-2-(indol-3-yl-derivatives)-3-phenylimino-3*H*-indole afford to 3,3'-*bis*-indolyls and 1,2-dihydro-2-phenyl-2-(indol-3-yl-derivatives)-3*H*-indol-3-one (indoxyls). The crystal structure of 1,2-dihydro-2-phenyl-2-(indol-3-yl)-3-phenylimino-3*H*-indole is also reported. The latter compound does not give rearrangement products by acid treatment, only untreatable tarry material.

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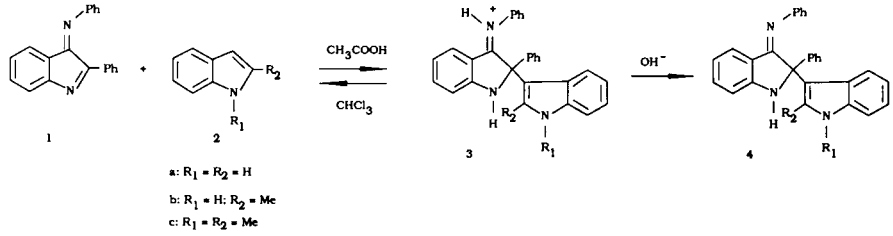
Our interest in the study of the Wagner-Meerwein type transpositions on the 3-aryliminoindoline series was initiated in 1975 [2a,b], and, only recently [1], we succeeded in understanding the complete mechanism through which the twofold and threefold transposition [2] occur in the same molecule under acid treatment. The observed transposition depend on the nucleophilicity of the migrating groups, on the solvent used and on the type of acid used. In order to obtain more information, in this paper we described the behaviour of 1,2-dihydro-2-phenyl-2-(indol-3-yl-derivatives)-3-phenylimino-3*H*-indoles **4a-c** by treatment with trichloroacetic acid in chloroform and with hydrochloric acid in ethanol. The compounds studied are substituted at carbon-2 with indol-3-yl (**4a**), 2-methylindol-3-yl (**4b**) and 1,2-dimethylindol-3-yl (**4c**), which are groups with a nucleophilicity higher [3] than the 2-phenylindol-3-yl previously studied.

Results.

Reactions of **4a-c** with Trichloroacetic Acid.

2-Phenyl-3-phenylimino-3*H*-indole **1** was allowed to react with indoles **2a-c** and trichloroacetic acid in chloroform in a 1:1 molar ratio at room temperature. When the reactions were stopped after 30 minutes, compounds **4a-c** were isolated in good yields (Scheme 1). The same reactions, reacted for 15-20 hours, gave 2-methyl-3-(2-phenylindol-3-yl)indole (**9b**) in the case of 2-methylindole (**2b**) and the 2-phenyl-3,3'-di-(1,2-dimethylindol-3-yl)-3*H*-indole (**7c**) together with the 1,2-dimethyl-3-(2-phenylindol-3-yl)indole (**9c**) in the case of 1,2-dimethylindole (**2c**); in the case of indole (**2a**), only formation of tar was observed (Scheme 2). When pure compounds **4a-c** were treated with trichloroacetic acid in chloroform for 15-20 hours, they gave the same products, together with the starting materials, that

Scheme 1



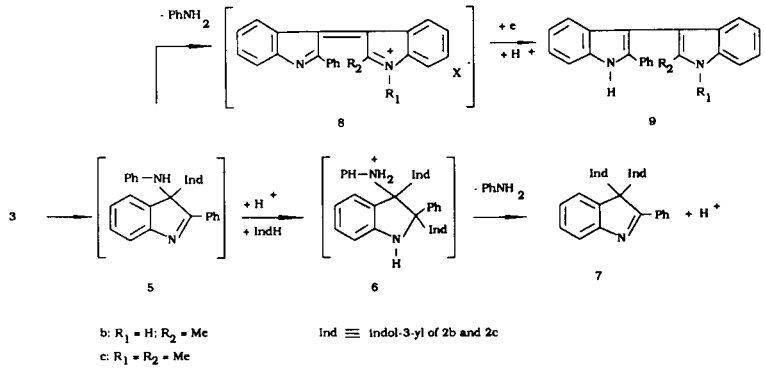
1 2 3 4

a: $R_1 = R_2 = H$

b: $R_1 = H$; $R_2 = Me$

c: $R_1 = R_2 = Me$

Scheme 2



were isolated starting from **1** and indoles **2a-c** after 15-20 hours (Scheme 2). When the reaction of **1** with **2c** and trichloroacetic acid was carried out using the reagents in 1:2:1 molar ratio, respectively during 15 hours, the yield of compound **7c** was almost doubled.

Compounds **4a-c** were identified by their elemental analysis and spectroscopic data. The ir spectra show absorptions of the NH groups at 3383, 3370 (**4b**) and 3382 (**4c**) cm^{-1}, and other absorptions at *ca.* 1636, 1607 and 1592 cm^{-1} which are typical for these types of compounds, since 1636 cm^{-1} is due to the $>C=C<$ group and 1600 cm^{-1} due to the Ph-N=C- group [4]. With respect to **4b** and **4c**, the amino and the indole NH stretching of **4a** fall at higher (3412 cm^{-1}) and at lower (3228 b cm^{-1}) wave numbers, respectively.

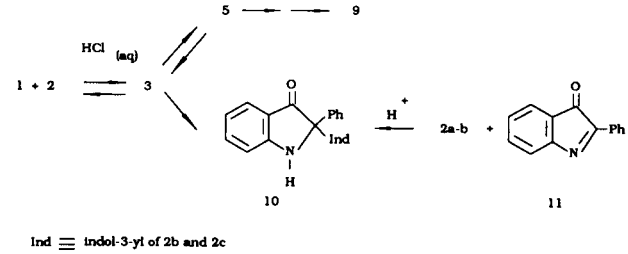
The aromatic regions of the ^1H nmr spectra of compounds **4a-c**, although very complicated to analyze, show similar patterns suggesting a similar skeleton for all these products; in fact, compounds **4a** and **4b** show characteristic differences in both the indole (δ *ca.* 8) and indoline (δ *ca.* 5) NH signals, while compound **4c** shows only the indolinic one at δ 4.98. Moreover, in the ^1H nmr spectrum of **4b**, together with both the above mentioned NH signals, a signal at δ 2.05 is present, corresponding to the methyl group of the 2-methylindole moiety, while the spectrum of **4c** shows only the indoline NH signals at δ 4.98, the methyl signal at δ 2.05 and another methyl signals at δ 3.63, characteristic of an N-Me group. Compound **7c** was identified by its elemental analysis, mass and ^1H nmr spectra. The ir spectrum is insignificant; in fact it shows only an absorption at 1588 cm^{-1} which may be due to the $-N=C<$ bond. The mass spectrum shows the molecular ion peak at 479 and significant fragments at 464, 335 and 144. The ^1H nmr spectrum shows four non equivalent methyl groups, two of which at δ 3.53 and 3.58 may be attributed to the two N-Me groups, whose non equivalence was already observed for similar compounds [1]. The other two methyl signals, ascribed to the methyls at position 2 of the 1,2-dimethylindole moieties, gave rise to a very broad signal at δ 1.95, which could be due to a restricted rotation caused by steric crowding. In fact, using perdeuteriobenzene instead of deuteriochloroform, in recording the ^1H nmr spectrum, the pattern did not change.

Compounds **9b** and **9c** were identified by their elemental analysis and spectroscopic data (see Experimental);in regard to their ^1H nmr spectra, it is worth noting that the spectrum of compound **9c** shows only an NH signal at δ 8.36, while for compound **9b** one can easily recognize the presence of the NH signal of the 2-phenylindole moiety at δ 8.37 and of the other NH signal of the 2-methylindole at δ 7.97.

Reactions of **4a-c** in Hydrochloric Acid.

Compounds **4a-c** refluxed in ethanol for 3 hours with an excess of hydrochloric acid afford different results. In the cases of **4b** and **4c**, compounds **9b** and 1,2-dihydro-2-phenyl-2-(2-methylindol-3-yl)-3*H*-indol-3-one (**10b**), and **9c** and 1,2-dihydro-2-phenyl-2-(1,2-dimethylindol-3-yl)-3*H*-indol-3-one (**10c**) were isolated, respectively (Scheme 3). Compounds **10b** and **10c** were identified by comparison with samples obtained reacting the 2-phenyl-3*H*-indol-3-one (**11**) with indoles **2b** and **2c** (Scheme 3) [5]. The elemental analysis of **10b** and **10c** and their spectroscopic data, reported in the experimental agree with their structures [6,7]. In the case of **4a**, only an untreatable tarry material was formed.

Scheme 3



Molecular Geometry of 1,2-Dihydro-2-phenyl-2-(indol-3-yl)-3-phenylimino-3*H*-indole **4a**.

Bond distances and angles are given in Table 1 and the arbitrary numbering scheme used in the crystal analysis is shown in Figure 1, which represents a perspective view of the molecule. The conformational geometry of the molecule can be deduced from the torsion angles listed in Table 1. The intramolecular bond lengths and angles, in line with the hybridization expected for the atoms involved, are in agreement reasonable with those of analogous compounds previously studied [2,6,8], and in particular show the presence of a localized double bond [N(2)-C(2) = 1.275(2) Å] confirming the iminic form of the N(2) atom.

Table 1

Bond Distances (Å), Angles (°) and Selected Torsion Angles (°) with e.s.d's in Parentheses

N(1)-C(1)	1.478(3)	C(12)-C(13)	1.384(4)
N(1)-C(8)	1.367(2)	C(13)-C(14)	1.372(4)
N(2)-C(2)	1.275(2)	C(14)-C(15)	1.381(5)
N(2)-C(21)	1.429(3)	C(15)-C(16)	1.390(4)
N(3)-C(31)	1.376(2)	C(21)-C(22)	1.386(3)
N(3)-C(38)	1.379(3)	C(21)-C(26)	1.388(3)
C(1)-C(2)	1.551(3)	C(22)-C(23)	1.390(3)
C(1)-C(11)	1.544(3)	C(23)-C(24)	1.375(3)
C(1)-C(32)	1.504(2)	C(24)-C(25)	1.375(4)
C(2)-C(3)	1.476(2)	C(25)-C(26)	1.387(3)
C(3)-C(4)	1.403(2)	C(31)-C(32)	1.362(2)
C(3)-C(8)	1.402(2)	C(32)-C(33)	1.441(3)
C(4)-C(5)	1.376(3)	C(33)-C(34)	1.406(3)
C(5)-C(6)	1.402(2)	C(33)-C(38)	1.404(3)
C(6)-C(7)	1.372(3)	C(34)-C(35)	1.371(4)
C(7)-C(8)	1.398(3)	C(35)-C(36)	1.408(4)
C(11)-C(12)	1.392(4)	C(36)-C(37)	1.376(4)
C(11)-C(16)	1.379(3)	C(37)-C(38)	1.396(4)
C(1)-N(1)-C(8)	111.3(2)	C(12)-C(13)-C(14)	121.1(3)
C(2)-N(2)-C(21)	118.4(2)	C(13)-C(14)-C(15)	119.0(3)
C(31)-N(3)-C(38)	108.6(2)	C(14)-C(15)-C(16)	120.3(3)
N(1)-C(1)-C(2)	101.8(1)	C(11)-C(16)-C(15)	120.9(2)
N(1)-C(1)-C(11)	108.3(2)	N(2)-C(21)-C(22)	118.8(2)
N(1)-C(1)-C(32)	111.2(2)	N(2)-C(21)-C(26)	121.6(2)
C(2)-C(1)-C(11)	111.7(1)	C(22)-C(21)-C(26)	119.5(2)
C(2)-C(1)-C(32)	110.6(2)	C(21)-C(22)-C(23)	119.5(2)
C(11)-C(1)-C(32)	112.7(2)	C(22)-C(23)-C(24)	121.0(3)
N(2)-C(2)-C(1)	120.7(2)	C(23)-C(24)-C(25)	119.4(2)
N(2)-C(2)-C(3)	132.5(2)	C(24)-C(25)-C(26)	120.6(3)
C(1)-C(2)-C(3)	106.7(1)	C(21)-C(26)-C(25)	119.9(3)
C(2)-C(3)-C(4)	132.7(2)	N(3)-C(31)-C(32)	110.1(2)
C(2)-C(3)-C(8)	107.2(1)	C(1)-C(32)-C(31)	128.6(2)
C(4)-C(3)-C(8)	120.1(2)	C(1)C(32)-C(33)	124.8(2)
C(3)-C(4)-C(5)	118.6(2)	C(31)-C(32)-C(33)	106.6(1)
C(4)-C(5)-C(6)	120.9(2)	C(32)-C(33)-C(34)	134.3(2)
C(5)-C(6)-C(7)	121.3(2)	C(32)-C(33)-C(38)	106.8(3)
C(6)-C(7)-C(8)	118.2(3)	C(34)-C(33)-C(38)	118.9(3)
N(1)-C(8)-C(3)	111.8(2)	C(33)-C(34)-C(35)	119.1(2)
N(1)-C(8)-C(7)	127.3(2)	C(34)-C(35)-C(36)	121.1(4)
C(3)-C(8)-C(7)	120.9(2)	C(35)-C(36)-C(37)	121.2(3)
C(1)-C(11)-C(12)	117.9(2)	C(36)-C(37)-C(38)	117.6(3)
C(1)-C(11)-C(16)	123.6(2)	N(3)-C(38)-C(33)	107.8(3)
C(12)-C(11)-C(16)	118.5(3)	N(3)-C(38)-C(37)	130.0(3)
C(11)-C(12)-C(13)	120.3(3)	C(33)-C(38)-C(37)	122.2(3)
C(21)-N(2)-C(2)-C(3)	0.9(4)	N(1)-C(1)-C(32)-C(31)	-122.1(3)
N(1)-C(1)-C(2)-N(2)	-165.4(2)	C(11)-C(1)-C(32)-C(31)	-0.3(4)
N(1)-C(1)-C(11)-C(16)	-130.4(3)		

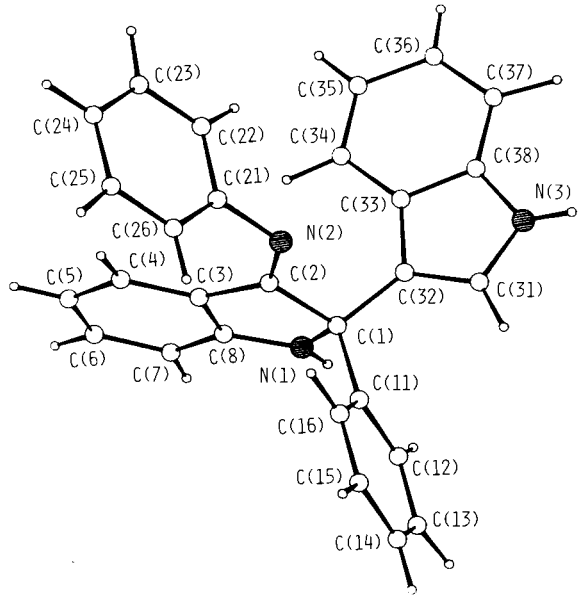


Figure 1. Perspective view of 1,2-dihydro-2-phenyl-2-indoyl-3-phenylimino-3*H*-indole.

From the study of the conformational geometry, from bond and torsion angles and from the analysis of the planarity reported in Table 2, some differences result in the two indole moieties present. In particular: a) the coordination geometry at the carbon atom in position 3 is close to an hybridization state of sp^2 type as confirmed by the sum of the bond angles around C(2) and C(32): but the external angles and the out-of-plane of C(2) with respect to the C(1), N(2), C(3) plane [0.031(3) Å] and of C(32) with respect to the C(1), C(31), C(32) plane [0.001(2) Å] show that only this last maintains a rigorous trigonal planar configuration: the small but significant distorsions around C(2) seem caused by forces induced on N(2) involved in an intermolecular hydrogen bond with N(3) and by steric interactions of the phenylimino group; b) as expected from the different hybridization of the carbon atoms in position 2 and 3 in the two pyrrole rings, the geometry of the two five-membered rings give quite different results and only that containing N(3) can be considered planar within experimental error; the conformational analysis proposed by Cremer and Pople [9] indicates that the pyrrole ring containing N(1) adopts a twist conformation with C2 symmetry with a *pseudo* twofold axis through C(8) bisecting the C(1)-C(2) bond. As shown in Table 2, the dihedral angles between the mean planes of the two condensed rings are similar in the two indole groups. Molecular packing is determined by an intermolecular hydrogen bond of the type N-H...N bridging the indole N(3) and the imine N(2) in the 1-x, 1-y, 1-z position [N(3)-H(3) 0.92(3), N(3)...N(2) 3.104(2), H(3)...N(2) 2.24(3) Å; N(3)-H(3)...N(2) 157(2)°].

Table 2

Analysis of the Planarity

a) Distances (Åx10^3) of relevant atoms from the mean plane with standard deviations in parentheses; starred atoms were not used to define the plane

Plane A: N(1), C(1), C(2), C(3), C(8)
N(1) 46(3), C(1) -63(3), C(2) 61(3), C(3) -37(3), C(8) -7(3), N(2)* 288(3), C(11)* -1452(3), C(32)* 1064(3)

Plane B: C(3)-C(8)
C(3) 3(3), C(4) 2(3), C(5) -7(3), C(6) 5(3), C(7) 1(3), C(8) -5(3), N(1)* -15(3), C(2)* 58(3)

Plane C: N(3), C(31), C(32), C(33), C(38)
N(3) -7(2), C(31) 10(2), C(32) -9(2), C(33) 4(2), C(38) 2(2), C(1)* -34(2)

Plane D: C(33)-C(38)
C(33) -3(2), C(34) 0(2), C(35) 9(3), C(36) -8(3), C(37) -4(3), C(38) 4(2), N(3)* 22(2), C(32)* 6(2)

Plane E: C(11)-C(16)
C(11) 1(2), C(12) -1(3), C(13) 1(3), C(14) -2(3), C(15) 4(3), C(16) -3(3), C(1)* -59(2)

Plane F: C(21)-C(26)
C(21) -17(2), C(22) 15(2), C(23) 7(2), C(24) 17(2), C(25) 3(2), C(26) 19(2), N(2)* -28(2)

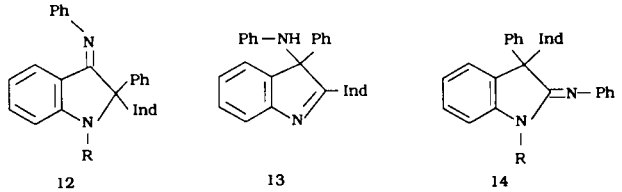
Plane G: C(2), N(2), C(21)

b) Angles (°) between planes

A - B	2.7(1)	A - C	90.6(1)	A - E	67.6(1)
A - F	78.6(1)	A - G	169.2(2)	C - D	1.1(1)
F - G	93.9(2)				

Discussion.

The Wagner-Meerwein type transpositions on the indole nucleus are well known reactions and most researches were devoted to the transposition of alkyl and aryl groups [10,11]. Our study from the beginning concerned the migration with groups such as 2-phenylindol-3-yl, 1-methyl-2-phenylindol-3-yl, phenyl and arylamino and we observed some of the above mentioned groups were in competition among each other and their migration was dependent on the condition used [1,2]. Compounds such as 1,2-dihydro-2-phenyl-2-(2-phenylindol-3-yl)-3-phenylimino-3*H*-indole



12 13 14

a: R = H

b: R = Me Ind ≡ 1-Me-2-phenylindol-3-yl

(12a) treated with trichloroacetic acid at room temperature, underwent migration of the phenyl group from C-2 to C-3 leading to the formation of compounds such as 2-indolyl-3-phenylimino-3-phenyl-3*H*-indole **(13)**, which upon refluxing ethanol for 3 hours gave compounds such as 1,2-dihydro-2-phenylimino-3-phenyl-3-(2-phenylindol-3-yl)-3*H*-indole **(14a)**; whereas compound **12b**, when refluxed for 3 hours in ethanol, afforded directly compound 1,2-dihydro-2-phenylimino-3-phenyl-3-(1-methyl-2-phenylindol-3-yl)-3*H*-indole **(14b)**. The migration of the phenyl group was never observed for compounds **4a-c** regardless of whatever experimental conditions were used. This would mean that 2-methylindole and 1,2-dimethylindole possess a migration power greated than that of 2-phenylindole derivatives.

Once again in trichloroacetic acid the formation of isolated products likely could be explained through the protonated form **3**. This carbocation may promote migration of the indolyl group from C-2 to C-3 forming the intermediate **5** (Scheme 2), which, by protonation at the amino nitrogen, could eliminate aniline forming **8** and **9** by a reductive step. A similar rearrangement was observed by Witkop *et al.* [12] and more recently by us [13] for compounds structurally close to those described here. The oxi-

Table 3

Fractional Atomic Coordinates (x10^4) and Equivalent Isotropic Thermal Parameters (x10^4 Å^2) for non-H Atoms with e.s.d.'s in Parentheses

$U_{eq} = 1/3 S_i S_j U_{ij} a_i^* a_j^* (a_i . a_j)$

	x	y	z	U_{eq}
N(1)	6013(2)	2314(1)	6951(1)	451(5)
N(2)	5652(2)	2347(1)	4794(1)	411(4)
N(3)	5185(2)	5538(1)	5965(1)	538(5)
C(1)	5221(2)	2707(1)	6206(1)	389(5)
C(2)	5859(2)	2081(1)	5537(1)	366(5)
C(3)	6726(2)	1272(1)	5955(1)	372(5)
C(4)	7453(2)	435(1)	5672(1)	445(6)
C(5)	8225(2)	-170(2)	6229(1)	554(7)
C(6)	8303(2)	52(2)	7061(1)	572(7)
C(7)	7595(2)	865(2)	7349(1)	492(7)
C(8)	6795(2)	1478(1)	6789(1)	388(5)
C(11)	3669(2)	2447(1)	6245(1)	423(6)
C(12)	3087(3)	2652(2)	6965(2)	664(9)
C(13)	1715(3)	2398(2)	7043(2)	728(9)
C(14)	903(2)	1938(2)	6419(2)	632(8)
C(15)	1471(2)	1735(2)	5702(2)	695(9)
C(16)	2850(2)	1984(2)	5620(1)	551(7)
C(21)	6340(2)	1786(1)	4208(1)	379(5)
C(22)	7667(2)	2083(2)	4053(1)	503(6)
C(23)	8357(2)	1536(2)	3493(1)	627(8)
C(24)	7736(3)	713(2)	3084(1)	643(7)
C(25)	6400 (3)	445(2)	3217(1)	600(8)
C(26)	5689(2)	984(2)	3769(1)	481(6)
C(31)	4521(2)	4613(1)	6033(1)	477(6)
C(32)	5468(2)	3836(1)	6099(1)	401(5)
C(33)	6811(2)	4298(1)	6045(1)	417(6)
C(34)	8172(2)	3914(2)	6047(1)	499(6)
C(35)	9243(3)	4586(2)	5971(2)	649(8)
C(36)	9003(3)	5649(2)	5905(2)	749(10)
C(37)	7682(3)	6047(2)	5897(2)	676(9)
C(38)	6592(2)	5359(2)	5664(1)	490(6)

dation power of intermediate **8** has been demostrated in more than one case [14,15].

If the protonation of compound **5** occurs at the endocyclic nitrogen, the addition of another molecule of indole may occur at C-2 (the acid catalyzed addition of nucleophiles at C-2 in 3*H*-indole systems is a well documented reaction [5,16]) forming the intermediate **6**, which through elimination of aniline and migration of another molecule of indole from C-2 to C-3 gives rise to compound **7** (Scheme 2). The proposed mechanism on the formation of compound **7** could agree with the fact that the yield of **7c** increased by 50% when the reaction was carried out using two moles of indole **2c** for one mole of **1** and trichloroacetic acid. The reactions carried out in refluxing ethanol and hydrochloric acid gave the products of hydrolysis **10**, in agreement with the literature reports [17], and **9**, whose formation may be explained as reported above for the trichloroacetic acid treatment.

The variety of formed products certainly depends on the several sites of protonation in type **4** compounds and in the intermediate **5**. Since treating **4** either in trichloroacetic acid or in hydrochloric acid we have isolated the starting materials, we must admit that the equilibrium between **3** and **1** + **2** as reported in Schemes 1 and 3 promotes the retrogression reaction which is a result of the 3-position of the indole being bonded to C-2, another site of protonation.

EXPERIMENTAL

The melting points are uncorrected. The ir, ^{1}H nmr and mass spectra were recorded on a Nicolet Fourier Transform Infrared 20 SX spectrometer (equipped with a Spectra Tech "DRIFT" Collector), on a Varian Gemini 200 spectrometer at 200 MHz in deuteriochloroform (Aldrich 99.8%-D grade) using TMS as the internal standard, and on a Carlo Erba Mass spectrometer QMD 1000, respectively.

Compound **1** was synthesized as described in the literature [18]; indoles **2a-c** and trichloroacetic acid were purchased from Aldrich and used without further purification.

Reactions of 2-Phenyl-3-phenylimino-3*H*-indole **1** with Indoles **2a-c** (30 minutes).

Trichloroacetic acid (830 mg, 5 mmoles) in 5 ml of chloroform was added in 10 minutes to a solution of indole **2a** (590 mg, 5 mmoles) and 2-phenyl-3-phenylimino-3*H*-indole **1** (1.4 g, 5 mmoles) in 15 ml of chloroform at room temperature, dropwise and with stirring. After 30 minutes from the beginning, the reaction mixture was evaporated to dryness and the residue, taken up with ethanol (100 ml), was treated with 50 ml of 5% aqueous sodium bicarbonate, which was added to the ethanolic solution dropwise with stirring. The mixture was then diluted with water (200 ml) and extracted with benzene (3 x 30 ml). The benzene layer was separated, dried over sodium sulfate, reduced to a small volume (15 ml) and chromatographed on an alumina column, eluting with cyclohexane/ethyl acetate 9:1. From the first orange eluate, 350 mg of unreacted **1** and **2a** were recovered. The second yellow eluate gave 725 mg of 1,2-dihydro-2-phenyl-2-(indol-3-yl)-3-phenylimino-3*H*-indole (**4a**) (37% yield). Working in the same way in the case of 1,2-dimethylindole **2c**, 1,2-dihydro-2-phenyl-2-(1,2-dimethylindol-3-yl)-3-phenylimino-3*H*-indole (**4c**) was isolated in 51% yield.

In the case of 2-methylindole (**2b**), during the addition of the trichloroacetic acid, a red crystalline precipitate was formed, which was filtered after 30 minutes. The red compound which dissolved in 30 ml of methanol, gave a yellow precipitate by treatment with 5% aqueous sodium bicarbonate (10 ml) and it was filtered off and dried in open air. Using the same quantity as described for **2a**, 1.07 g (52% yield) of 1,2-dihydro-2-phenyl-2-(2-methylindol-3-yl)-3-phenylimino-3*H*-indole (**4b**) was isolated.

1,2-Dihydro-2-phenyl-2-(indol-3-yl)-3-phenylimino-3*H*-indole (**4a**).

This compound had mp 240-242° from ethanol; ir: ν max 3412, 3228 b, 1635, 1605, 1590 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 5.17 (1H, broad, indoline NH), 6.47 (2H, d, arom, J = 3.9 Hz), 6.82 (3H, m, arom), 7.02 (2H, m, arom), 7.30 (10H, m, arom), 7.71 (2H, dd, arom, J = 8.1, J = 2.0 Hz), 8.15 (1H, broad, indole NH); ms: (m/z) 398 (M$^+$, 5.34%), 321 (100), 282 (44.4).

Anal. Calcd. for $C_{34}H_{25}N_3$: C, 85.88; H, 5.27; N, 8.80. Found: C, 85.87; H, 5.30; N, 8.83.

1,2-Dihydro-2-phenyl-2-(2-methylindol-3-yl)-3-phenylimino-3*H*-indole (**4b**).

This compound had mp 266-267° from ethanol; ir: ν max 3383, 3370, 1636, 1604, 1599 w, 1590 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.05 (3H, s, methyl), 4.98 (1H, broad, indoline NH), 6.46 (2H, m, arom), 6.80 (3H, d, arom, J = 8.2 Hz), 6.99 (4H, m, arom), 7.30 (7H, m, arom), 7.79 (1H, broad, indole NH), 7.85 (2H, dd, arom, J = 8.2, J = 1.5 Hz); ms: (m/z) 412 (M$^+$, 66.6%), 397 (61.1), 335 (17.1), 321 (70.7), 282 (12.5), 243 (95.9), 131 (100).

Anal. Calcd. for $C_{29}H_{23}N_3$: C, 84.26; H, 5.59; N, 10.14. Found: C, 84.23; H, 5.61; N, 10.16.

1,2-Dihydro-2-phenyl-2-(1,2-dimethylindol-3-yl)-3-phenylimino-3*H*-indole (**4c**).

This compound had mp 195-196° from benzene/petroleum ether; ir: ν max 3382, 1636, 1607, 1592 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.05 (3H, s, methyl), 3.63 (3H, s, methyl), 4.98 (1H, broad, indoline NH), 6.48 (2H, m, arom), 6.80 (3H, m, arom), 6.92 (2H, m, arom), 7.10 (2H, m, arom), 7.28 (7H, m, arom), 7.85 (2H, dd, arom, J = 8.1, J = 2.0 Hz); ms: (m/z) 427 (M$^+$, 58.5%), 350 (45.2), 336 (95.7), 282 (100), 144 (49.7).

Anal. Calcd. for $C_{30}H_{24}N_3$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.40; H, 5.71; N, 9.89.

Reactions of 2-Phenyl-3-phenylimino-3*H*-indole **1** with Indoles **2a-c** (15 hours).

The reactions were performed as described above, starting from the same quantities; in the case of 2-methylindole (**2b**), the red precipitate dissolved during the reaction time. After 15 hours the brown reaction mixture was treated with 3% aqueous sodium bicarbonate solution (30 ml). The chloroform layer was washed with water (2 x 20 ml), dried over sodium sulfate and evaporated to dryness. The residue, taken up with benzene (10-15 ml), was chromatographed on a silica gel column, eluting with benzene. In the case of indole (**2a**) no new product was identified; in the case of 2-methylindole (**2b**), 2-methyl-3-(2-phenylindol-3-yl)indole (**9b**)

was isolated in 40% yield, together with the starting materials; in the case of 1,2-dimethylindole (**2c**), the 1,2-dimethyl-3-(2-phenylindol-3-yl)indole (**9c**) (10% yield) and 2-phenyl-3,3'-di-(1,2-dimethylindol-3-yl)-3*H*-indole (**7c**) (31% yield) were isolated together with the starting materials. The reaction with 1,2-dimethylindole (**2c**) was carried out using 2 mmoles of **2c** and worked up as described above and gave **9c** in 18% yield and **7c** in 57% yield.

2-Phenyl-3,3'-di-(1,2-dimethylindol-3-yl)-3*H*-indole (**7c**).

This compound had mp 310-311° from benzene/petroleum ether; ir: ν max 1606, 1596, 1588 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.95 (6H, broad, methyl), 3.53 (3H, s, methyl), 3.58 (3H, s, methyl), 6.76 (2H, broad, m, arom), 7.01 (3H, dd, arom, J = 7.7, J = 3.1, J = 2.0 Hz), 7.25 (8H, m, arom), 7.48 (1H, d, arom, J = 8.24 Hz), 7.70 (1H, d, arom, J = 7.7 Hz), 8.05 (2H, broad, m, arom); ms: (m/z) 479 (M^+, 100%), 464 (44.7), 402 (47.8), 335 (55.2), 144 (75.7).

Anal. Calcd. for $C_{34}H_{29}N_3$: C, 85.14; H, 6.09; N, 8.76. Found: C, 85.21; H, 6.13; N, 8.66.

2-Methyl-3-(2-phenylindol-3-yl)indole (**9b**).

This compound had mp 205-206° from benzene/petroleum ether; ir: ν max 3432, 3407, 1622, 1600, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.03 (3H, s, methyl), 7.08 (4H, m, arom), 7.26 (3H, m, arom), 7.43 (6H, m, arom), 7.97 (1H, broad, indoline NH), 8.37 (1H, broad, indole NH); ms: (m/z) 322 (M^+, 100%), 306 (45.2), 245 (19.8), 230 (5.7), 192 (9.2), 130 (4.8).

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.70; H, 5.63; N, 8.67. Found: C, 85.69; H, 5.63; N, 8.69.

1,2-Dimethyl-3-(2-phenylindol-3-yl)indole (**9c**).

This compound had mp 181-182° from benzene/petroleum ether, ir: ν max 3390, 1622 sh, 1601, 1589 w cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.04 (3H, s, methyl), 3.73 (3H, s, methyl), 7.05 (2H, m, arom), 7.23 (5H, m, arom), 7.41 (6H, m, arom), 8.36 (1H, broad, indole NH); ms: (m/z) 336 (M^+, 100%), 320 (8.5), 306 (11.2), 259 (7.8), 192 (6.4), 144 (3.4).

Anal. Calcd. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.71; H, 5.95; N, 8.34.

Reactions of 1,2-Dihydro-2-phenyl-2-(indol-3-yl-derivatives)-3-phenylimino-3*H*-indole **4a-c** with Trichloroacetic Acid.

Trichloroacetic acid (115 mg, 7 mmoles in 5 ml of chloroform) was added dropwise at room temperature with stirring to a solution of **4a-c** (5 mmoles in 20 ml of chloroform). After 15 hours the reaction was worked up as described above. In each case, the products described above were isolated in the same yields, together with 2-phenyl-3-phenylimino-3*H*-indole **1** and the indoles **2a-c**, precursors of compounds **4a-c**.

Reactions of 1,2-Dihydro-2-phenyl-2-(indol-3-yl-derivatives)-3-phenylimino-3*H*-indole **4a-c** with hydrochloric Acid.

1,2-Dihydro-2-phenyl-2-(1,2-dimethylindol-3-yl)-3-phenylimino-3*H*-indole **4c** (215 mg, 5 mmoles) was refluxed in 20 ml of ethanol with 4 ml of 10% hydrochloric acid for 3 hours. The reaction mixture was then diluted with water (50 ml), neutralized with 10% aqueous sodium bicarbonate solution and extracted with benzene (3 x 20 ml). The benzene layer was dried over sodium sulfate, reduced to a small volume and chromatographed on a silica gel column, eluting with benzene. From the first fluorescent eluate, 90 mg of 1,2-dimethyl-3-(2-phenylindol-3-yl)indole (**9c**) was isolated, and 20 mg of 1,2-dihydro-2-phenyl-2-(1,2-dimethylindol-3-yl)-3*H*-indol-3-one (**10c**) from the small yellow eluate was obtained.

Starting from 1,2-dihydro-2-phenyl-2-(2-methylindol-3-yl)-3-phenylimino-3*H*-indole (**4b**) (205 mg, 5 mmoles) working as described above, 2-methyl-3-(2-phenylindol-3-yl)indole (**9b**) (30 mg) and 1,2-dihydro-2-phenyl-2-(2-methylindol-3-yl)-3*H*-indol-3-one (**10b**) (45 mg) were isolated. No compounds were identified upon treating 1,2-dihydro-2-phenyl-2-(indol-3-yl)-3-phenylimino-3*H*-indole in the same way.

1,2-Dihydro-2-phenyl-2-(2-methylindol-3-yl)-3*H*-indol-3-one (**10b**).

This compound had mp 269-271° from benzene; ir: ν max 3401, 3369, 1663, 1621, 1604, 1591 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.13 (3H, s, methyl), 5.17 (1H, broad, indoline NH), 6.89 (4H, m, arom), 7.06 (1H, AX_3, arom, J = 8.36, J = 5.25, J = 2.87 Hz), 7.30 (4H, m, arom), 7.50 (1H, AX_3, arom, J = 8.36, J = 7.04, J = 1.34 Hz), 7.64 (3H, m, arom), 7.84 (1H, broad, indole NH); ms: (m/z) 338 (M^+, 54.5%), 323 (37.6), 309 (100), 261 (23.8), 207 (24.8), 179 (52.5), 130 (82.7).

Anal. Calcd. for $C_{23}H_{18}N_2O$: C, 81.62; H, 5.36; N, 8.28. Found: C, 81.57; H, 5.38; N, 8.21.

1,2-Dihydro-2-phenyl-2-(1,2-dimethylindol-3-yl)-3*H*-indol-3-one (**10c**).

This compound had mp 268-269° from benzene/petroleum ether; ir: ν max 3349, 1685, 1618, 1608, 1593 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.09 (3H, s, methyl), 3.63 (3H, s, methyl), 5.13 (1H, broad, indoline NH), 6.89 (4H, m, arom), 7.10 (1H, AX_2, arom, J = 8.05, J = 4.15 Hz), 7.30 (4H, m, arom), 7.49 (1H, AX_3, arom, J = 8.05, J = 6.19, J = 1.24 Hz), 7.66 (3H, m, arom); ms: (m/z) 352 (M^+, 34.8%), 337 (20.1), 323 (100), 309 (61.5), 275 (27.3), 207 (36.2), 179 (72.7), 144 (69.2).

Anal. Calcd. for $C_{24}H_{20}N_2O$: C, 81.78; H, 5.72; N, 7.95. Found: C, 81.71; H, 5.74; N, 7.90.

Synthesis of 1,2-Dihydro-2-phenyl-2-(2-methylindol-3-yl)-3*H*-indol-3-one (**10b**) and 1,2-Dihydro-2-phenyl-2-(1,2-dimethylindol-3-yl)-3*H*-indol-3-one (**10c**).

2-Phenyl-3*H*-indol-3-one (**11**) [19] (105 mg, 5 mmoles in 190 ml of boiling hexane) was added to a solution of 2-methylindole (**2b**) (65 mg, 5 mmoles in 5 ml of boiling benzene). The mixture, on addition of 2-3 drops of acetic acid, after cooling gave a yellow precipitate of indolyl **10b** (120 mg, 71% yield).

Starting from the same quantity of **11** and 73 mg (5 mmoles) of 1,2-dimethylindole (**2c**), 145 mg of indolyl **10c** (81% yield) was obtained.

Crystal Structure of 1,2-Dihydro-2-phenyl-2-(indol-3-yl)-3-phenylimino-3*H*-indole **4a**.

Crystals were pale-yellow prisms. Lattice parameters were calculated using a least-squares procedure [20] which involves angle settings of thirty carefully centered reflections.

Crystal data - $C_{28}H_{21}N_3$, M = 399.5. Monoclinci, a = 9.657(2), b = 13.036(3), c = 16.555(3) Å, β = 95.6(1)°, U = 2074.1(8) $Å^3$, Z = 4, D_c = 1.28 gcm^{-3}, Cu-Kα radiation λ = 1.5418 Å, μ(Cu-Kα) = 5.5 cm^{-1}. Space group P $2_1/c$ (C_{2h}^5, No. 14) from systematic absences.

X-ray measurements were performed at T = 293 K on a Siemens AED single-crystal diffractometer, on line to an IBM PS/2 M30 computer, in the range $3 < \theta < 70°$ using Cu-Kα radiation.

The diffraction angle θ for every reflection was determined on the basis of the orientation matrix and the outline of the diffraction peak was collected in θ-2θ step scanning mode using a scan width from $(\theta$-$60)°$ to $(\theta + 0.60 + \Delta\lambda/\lambda \text{ tg}\theta)°$. The intensities I_{hkl} were determined by analysing the reflection profile using the Lehmann and Larsen procedure [21]. 3938 symmetry independent reflections ($0 \leq h \leq 11$, $0 \leq k \leq 15$, $-20 \leq l \leq 20$) were measured, of which 2864 (internal R merging factor 0.013) with $I_{hkl} > 2\sigma(I_{hkl})$ [$\sigma(I)$ based on statistic counting] were used in the refinement. One "standard" reflection, measured every 50 collected reflections to monitor crystal decomposition and instrumental linearity, showed no significant variation. The specimen was a crystal of dimensions 0.19 x 0.24 x 0.48 mm. Corrections for Lorentz and polarization effects were applied, no corrections for absorption effects were performed.

Structure Analysis and Refinement.

The structure was solved by SHELXS86 [22] and refined by SHELX76 [23] with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.048$, $R_w = 0.051$. The weighing function was of the form $1/W = \sigma^2(F_o) + 0.015\ F_o^2$. All the hydrogen atoms were located in the ΔF map. The atomic scattering factors were from International Tables for X-ray Crystallography [24]. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 3.

The calculations were carried out on the GOULD 6040 POWERNODE computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR of Parma. Bibliografic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy. Observed and calculated structure factors, thermal parameters and positional parameters for hydrogen atoms with their standard deviations are available from the Authors on request.

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* To whom correspondence should be addressed.

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