

Conformational Study on Indoline Compounds.
Structures of 2-Phenyl-3-arylimino-3*H*-indole 1-Oxide,
1,2-Dihydro-2-phenyl-2-benzyl- and 2-*tert*-Butyl-3-
phenylimino-3*H*-indole 1-Oxyls

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Reacting 1-hydroxy-2-phenylindole with nitrosobenzene, 2-phenyl-3-phenylimino-3*H*-indole 1-oxide (**1**) is produced in only one of the two possible diastereomers. The latter reacts with *tert*-butylmagnesium chloride and benzylmagnesium chloride giving, after oxidation, the corresponding aminoxyls which show the same configuration of the phenylimino group at C-3 as in **1**. This has been demonstrated by means of nmr spectroscopy and X-ray crystal structure and represents an unexpected stereospecific reaction.

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2-Phenyl-3-phenylimino-3*H*-indole 1-oxide (**1**) is easily prepared from 1-hydroxy-2-phenylindole and nitrosobenzene [1] and reacts with *tert*-butylmagnesium chloride and benzylmagnesium chloride, as well as with other Grignard reagents [2] to afford 1,2-dihydro-2-phenyl-2-*tert*-butyl-3-phenylimino-3*H*-indole 1-oxyl (**2a**) and 1,2-dihydro-2-phenyl-2-benzyl-3-phenylimino-3*H*-indole 1-oxyl (**2b**) respectively (Scheme 1). These latter efficiently react with alkylperoxyl [3], alkoxy [4], alkyl [5], aminyl [6] and aryloxy [7] radicals. Since alkyl, alkylperoxyl and alkoxy radicals represent the radical species usually involved in autoxidation processes, aryliminoindoline radicals such as **2** could be considered as promising antioxidants either in polymeric or biological systems. Studies are currently in progress to investigate these kinds of application. For instance, during the polypropylene processing the temperature is usually in the range 200-250° and under these conditions carbon-carbon bond breaking may occur forming carbon centered radicals which could favour autoxidation chains. In this case, working in the presence of aminoxyls such as **2a**, **2b**, 2,2,6,6-tetramethylpiperidiny 1-oxyl (TEMPO) and its derivatives, good stabilization was observed through the measurement of the melt flow index (MFI) [8]. On the basis of these results a study was performed using a wide series of indole aminoxyls differently substituted at C-2 to evaluate their thermal stability [8]. The unexpected lower stability of **2a** in comparison with that of equally crowded derivatives such as **2b**, prompted us to carry out an X-ray investigation either on aminoxyls **2a** and **2b** or their precursor **1**, whose structure had never been elucidated.

Molecular Geometry.

Bond distances are reported in Table 1 and in Table 2 bond angles and selected torsion angles for the three de-

rivative are listed. The arbitrary numbering scheme used in the crystal analysis is shown in Figure 1, 2 and 3 which

Table 1
 Bond Distances (Å) with esd's in Parentheses

	1	2a	2b
O(1)-N(1)	1.283(3)	1.281(6)	1.279(3)
N(1)-C(1)	1.339(3)	1.493(7)	1.489(3)
N(1)-C(8)	1.434(4)	1.379(7)	1.378(2)
N(2)-C(2)	1.278(3)	1.275(7)	1.273(3)
N(2)-C(21)	1.426(3)	1.419(7)	1.425(3)
C(1)-C(2)	1.493(3)	1.578(8)	1.541(3)
C(1)-C(9)		1.568(9)	
C(1)-C(10)			1.548(3)
C(1)-C(11)	1.456(4)	1.565(9)	1.531(3)
C(2)-C(3)	1.486(4)	1.460(8)	1.475(3)
C(3)-C(4)	1.386(4)	1.390(8)	1.395(3)
C(3)-C(8)	1.385(3)	1.405(8)	1.402(3)
C(4)-C(5)	1.396(4)	1.389(9)	1.392(4)
C(5)-C(6)	1.380(3)	1.400(10)	1.389(4)
C(6)-C(7)	1.382(4)	1.369(10)	1.383(4)
C(7)-C(8)	1.372(4)	1.393(8)	1.389(3)
C(9)-C(91)		1.534(10)	
C(9)-C(92)		1.534(10)	
C(9)-C(93)		1.544(10)	
C(10)-C(101)			1.513(3)
C(11)-C(12)	1.402(4)	1.378(9)	1.383(3)
C(11)-C(16)	1.404(4)	1.374(9)	1.389(3)
C(12)-C(13)	1.369(4)	1.410(12)	1.392(4)
C(13)-C(14)	1.383(4)	1.378(13)	1.370(4)
C(14)-C(15)	1.376(4)	1.339(12)	1.386(4)
C(15)-C(16)	1.376(5)	1.388(11)	1.385(5)
C(21)-C(22)	1.383(4)	1.387(11)	1.386(4)
C(21)-C(26)	1.373(5)	1.392(9)	1.385(4)
C(22)-C(23)	1.379(4)	1.400(11)	1.392(5)
C(23)-C(24)	1.370(5)	1.398(15)	1.378(5)
C(24)-C(25)	1.366(5)	1.360(19)	1.368(4)
C(25)-C(26)	1.387(4)	1.402(11)	1.393(4)
C(101)-C(102)			1.382(3)
C(101)-C(106)			1.389(3)
C(102)-C(103)			1.397(5)
C(103)-C(104)			1.364(5)
C(104)-C(105)			1.373(4)
C(105)-C(106)			1.398(5)

represent perspective views of compounds **1**, **2a** and **2b**, respectively. The intramolecular bond lengths and angles are in line with the hybridization expected for the atoms

Table 2
Bond Angles (°) and Selected Torsion Angles (°)
with *esd*'s Parentheses

	1	2a	2
O(1)-N(1)-C(1)	128.8(3)	124.6(4)	122.3(2)
O(1)-N(1)-C(8)	119.4(2)	122.0(5)	125.1(4)
C(1)-N(1)-C(8)	111.8(2)	113.5(4)	112.5(3)
C(2)-N(2)-C(21)	119.9(3)	120.4(5)	121.7(2)
N(1)-C(1)-C(2)	106.5(3)	99.4(4)	101.0(2)
N(1)-C(1)-C(9)		109.6(5)	
N(1)-C(1)-C(10)			109.1(3)
N(1)-C(1)-C(11)	124.7(2)	108.5(4)	109.2(3)
C(2)-C(1)-C(9)		114.1(4)	
C(2)-C(1)-C(10)			112.6(3)
C(2)-C(1)-C(11)	128.9(2)	108.0(5)	111.6(3)
C(9)-C(1)-C(11)		116.0(5)	
C(10)-C(1)-C(11)			112.7(2)
N(2)-C(2)-C(1)	123.1(3)	119.5(5)	119.5(2)
N(2)-C(2)-C(3)	130.5(2)	132.1(5)	133.2(3)
C(1)-C(2)-C(3)	106.4(2)	108.4(5)	107.4(3)
C(2)-C(3)-C(4)	134.8(2)	132.9(5)	133.2(4)
C(2)-C(3)-C(8)	106.3(3)	108.2(5)	108.2(2)
C(4)-C(3)-C(8)	118.8(3)	118.8(5)	118.6(3)
C(3)-C(4)-C(5)	118.0(2)	118.4(6)	118.4(3)
C(4)-C(5)-C(6)	121.3(3)	121.9(7)	121.5(3)
C(5)-C(6)-C(7)	121.4(3)	120.5(6)	121.5(4)
C(6)-C(7)-C(8)	116.3(2)	117.7(6)	116.5(3)
N(1)-C(8)-C(3)	109.0(3)	110.4(5)	110.1(3)
N(1)-C(8)-C(7)	126.8(2)	126.9(5)	126.4(3)
C(3)-C(8)-C(7)	124.2(3)	122.7(5)	123.5(2)
C(1)-C(9)-C(91)		109.0(5)	
C(1)-C(9)-C(92)		112.2(6)	
C(1)-C(9)-C(93)		110.8(5)	
C(91)-C(9)-C(92)		109.5(6)	
C(91)-C(9)-C(93)		109.8(6)	
C(92)-C(9)-C(93)		105.5(6)	
C(1)-C(10)-C(101)			114.7(2)
C(1)-C(11)-C(12)	120.6(2)	120.3(5)	120.3(4)
C(1)-C(11)-C(16)	122.6(3)	120.6(3)	121.5(3)
C(12)-C(11)-C(16)	116.8(3)	119.1(6)	118.3(3)
C(11)-C(12)-C(13)	121.7(2)	119.3(7)	120.8(4)
C(12)-C(13)-C(14)	120.7(3)	120.5(8)	120.5(3)
C(13)-C(14)-C(15)	118.7(3)	119.1(8)	119.2(4)
C(14)-C(15)-C(16)	121.3(2)	121.6(7)	120.3(4)
C(11)-C(16)-C(15)	120.9(2)	120.3(6)	120.8(3)
N(2)-C(21)-C(22)	120.1(3)	119.0(5)	119.6(3)
N(2)-C(21)-C(26)	120.3(3)	119.8(6)	120.3(4)
C(22)-C(21)-C(26)	119.3(2)	120.8(6)	119.6(4)
C(21)-C(22)-C(23)	119.5(4)	119.3(8)	119.6(5)
C(22)-C(23)-C(24)	121.1(3)	119.5(9)	120.7(5)
C(23)-C(24)-C(25)	119.3(3)	120.7(8)	119.7(4)
C(24)-C(25)-C(26)	120.3(4)	120.6(10)	120.5(5)
C(21)-C(26)-C(25)	120.3(3)	119.0(8)	119.9(5)
C(10)-C(101)-C(102)			120.6(4)
C(10)-C(101)-C(106)			121.1(4)
C(102)-C(101)-C(106)			118.3(4)
C(101)-C(102)-C(103)			121.3(4)
C(102)-C(103)-C(104)			119.9(5)
C(103)-C(104)-C(105)			119.9(5)
C(104)-C(105)-C(106)			120.6(5)
C(101)-C(106)-C(105)			120.0(4)
O(1)-N(1)-C(1)-C(11)	-1.3(6)	-72.1(6)	-66.3(5)
C(21)-N(2)-C(2)-C(3)	-1.6(3)	-0.4(9)	-7.0(7)
N(1)-C(1)-C(2)-N(2)	-179.0(3)	-177.5(5)	-169.2(4)

involved and in reasonable agreement with those of analogous compounds previously studied [9,10,11]. In particular, a localized double bond N=C [N(2)-C(2) 1.278(3), 1.275(7), and 1.273(3) Å in **1**, **2a** and **2b**, respectively] confirming the imine form of the N(2) atom is present.

In the skeleton of the indole nucleus, the main differences for the three derivatives lie in the bond distances and angles of the five-membered ring as a consequence of the different hybridization of the carbon atom in position 2, being sp^2 in compound **1** and sp^3 in **2a** and **2b**. For com-

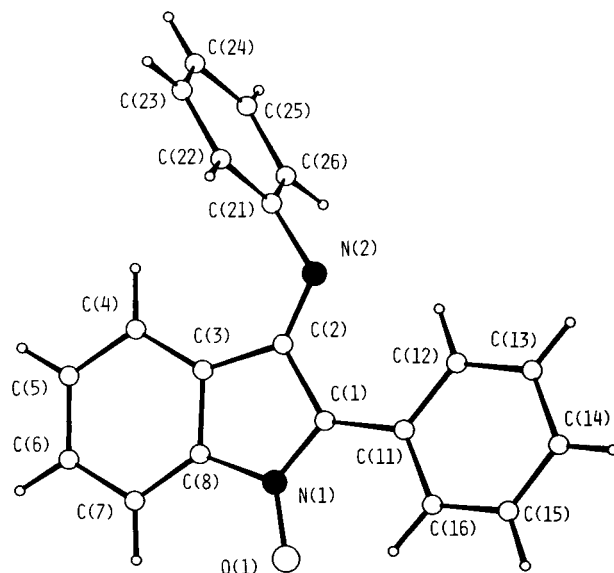


Figure 1. Perspective view of 2-phenylimino-3H-indole 1-oxide (**1**) with the atomic numbering scheme.

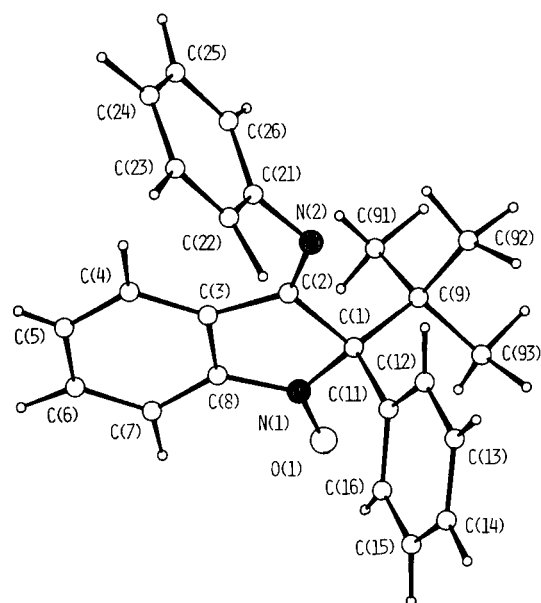


Figure 2. Perspective view of 1,2-dihydro-2-phenyl-2-tert-butyl-3-phenylimino-3H-indole 1-oxyl (**2a**) with the atomic numbering scheme.

Table 3
Analysis of the Planarity

a) Distances ($\text{\AA} \times 10^3$) of Revelant Atoms from the Mean Plane with *esd*'s in Parentheses (starred atoms were not used to define the plane)

	1	2a	2b
Plane A: N(1)C(1)C(2)C(3)C(8)			
N(1)	10(4)	-22(5)	40(5)
C(1)	-9(4)	33(6)	-54(5)
C(2)	4(4)	-16(5)	53(5)
C(3)	3(4)	4(5)	-33(5)
C(8)	-8(4)	19(6)	-5(5)
O(1)*	49(4)	-97(5)	66(5)
N(2)*	10(4)	-36(5)	219(5)
C(11)*	-17(4)	1441(6)	-1415(5)

Plane B: C(3)-C(8)

C(3)	4(4)	-3(5)	-16(5)
C(4)	-1(4)	3(6)	5(5)
C(5)	-2(4)	-2(8)	11(5)
C(6)	2(4)	1(8)	-12(5)
C(7)	1(4)	-3(7)	-3(5)
C(8)	-4(4)	4(6)	15(5)

Plane C: C(11)-C(16)

C(11)	-4(4)	-2(6)	7(4)
C(12)	5(4)	-3(7)	-5(4)
C(13)	-3(4)	9(9)	-4(5)
C(14)	1(5)	-7(9)	8(5)
C(15)	-1(5)	0(9)	-4(5)
C(16)	3(5)	4(7)	-5(5)
C(1)*	-19(4)	-32(6)	28(4)

Plane D: C(21)-C(26)

C(21)	-14(4)	13(6)	-6(3)
C(22)	-16(4)	-18(7)	8(4)
C(23)	-4(4)	7(9)	-4(4)
C(24)	-6(4)	5(7)	-3(4)
C(25)	4(4)	-2(7)	3(4)
C(26)	9(4)	-11(7)	1(4)
N(2)*	52(3)	-88(4)	134(3)

Plane E: C(101)-C(106)

C(101)			-4(3)
C(102)			4(3)
C(103)			2(4)
C(104)			-7(4)
C(105)			4(4)
C(106)			3(4)
C(10)*			11(3)

b) Angles ($^\circ$) between planes

A - B	2.2(1)	3.1(2)	4.6(2)
A - C	7.0(2)	67.2(2)	72.1(2)
A - D	89.6(1)	83.7(3)	63.5(2)
A - E			65.9(2)

compound **1** an examination of the values of N(1)-O(1) [1.283(3) \AA], N(1)-C(8) [1.434(4) \AA], C(3)-C(8) [1.385(3) \AA], C(2)-C(3) [1.486(4) \AA] and N(2)-C(2) [1.278(3) \AA] bond lengths, alternately short and long, indicates a conjugative interaction involving the *p* orbital of the imine nitrogen N(2) and that of the *N*-oxide group. For compounds **2a** and **2b** the phenylimino group seems involved in a partial delocaliza-

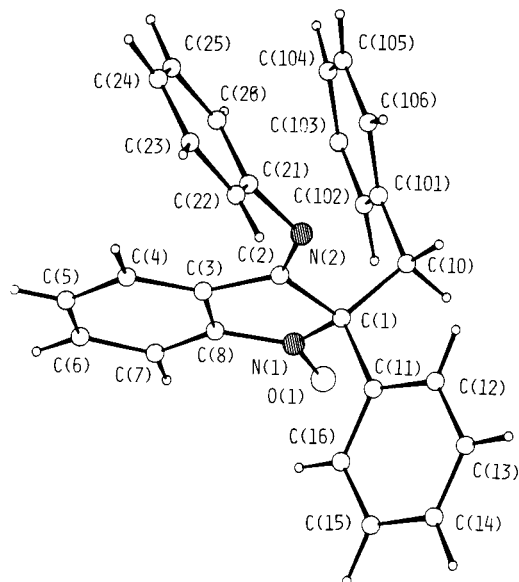


Figure 3. Perspective view of 1,2-dihydro-2-benzyl-2-phenyl-3-phenylimino-3H-indole 1-oxyl (**2b**) with the atomic numbering scheme.

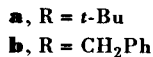
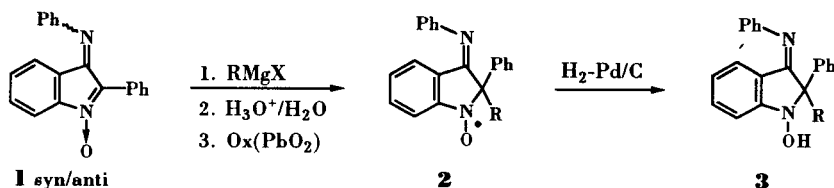
tion concerning the indoline ring. In fact, the five-membered ring shows significant deviations from the planarity observed for compound **1**. A quantitative evaluation of the deformation derived from the puckering coordinates [12] and from the asymmetry parameters [13] indicates that the pentaatomic ring adopts a twist conformation with a *pseudo* two-fold axis through C(3) and C(8) for compounds

Table 4

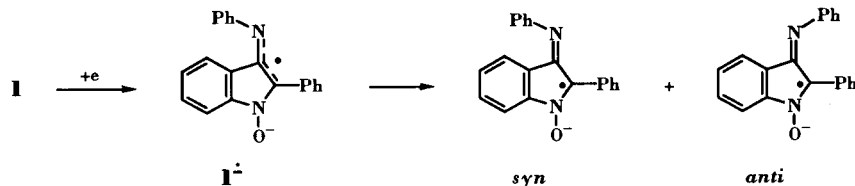
Compound 1. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^4 \text{\AA}^2$) for non-H Atoms with *esd*'s in Parentheses

	$U_{eq} = 1/3 \sum \sum_j U_{ij} a_i^* a_j^* (a_i, a_j)$			U_{eq}
	X	Y	Z	
O(1)	3173(2)	1002(4)	7304(1)	673(7)
N(1)	3032(2)	571(4)	6720(1)	497(7)
N(2)	2039(2)	1237(4)	5151(1)	544(7)
C(1)	2362(2)	1724(5)	6273(1)	453(7)
C(2)	2533(2)	551(5)	5677(1)	447(8)
C(3)	3343(2)	-1428(5)	5839(1)	448(8)
C(4)	3802(2)	-3223(5)	5508(1)	525(9)
C(5)	4523(2)	-4881(6)	5837(1)	583(10)
C(6)	4774(2)	-4746(6)	6473(1)	609(11)
C(7)	4319(2)	-2976(6)	6810(1)	594(11)
C(8)	3610(2)	-1374(5)	6477(1)	477(8)
C(11)	1649(2)	3749(5)	6376(1)	463(8)
C(12)	1080(2)	5049(6)	5875(1)	559(9)
C(13)	418(2)	6986(6)	5960(1)	621(11)
C(14)	276(3)	7702(7)	6549(1)	626(11)
C(15)	822(3)	6447(7)	7048(1)	731(12)
C(16)	1493(3)	4501(6)	6970(1)	643(11)
C(21)	2262(2)	63(5)	4600(1)	491(8)
C(22)	1665(3)	-1955(6)	4349(1)	603(10)
C(23)	1867(3)	-3020(6)	3805(1)	645(11)
C(24)	2625(3)	-2059(6)	3497(1)	633(10)
C(25)	3194(3)	-21(7)	3736(1)	723(13)
C(26)	3009(3)	1056(6)	4286(1)	659(11)

Scheme 1



Scheme 2



2a and **2b**, respectively. All the other rings in the three compounds are planar within experimental error; their reciprocal orientation can be deduced from the dihedral angles reported in the analysis of the planarity of Table 3 and the molecular packing is consistent with van der Waals interactions.

Results and Discussion.

Compound **1** could exist in two different configurations of which one *syn*, with the phenyl of the phenylimino group oriented towards the benzene ring of the indole

Table 5

Compound 2a. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^4 \text{ \AA}^2$) for non-H Atoms with *esd*'s in Parentheses

	$U_{eq} = 1/3 \sum_j \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$			
	X	Y	Z	U _{eq}
O(1)	5116(3)	6588(4)	326(4)	694(18)
N(1)	5150(3)	6949(4)	1430(4)	522(18)
N(2)	4342(3)	7679(4)	4420(4)	541(16)
C(1)	4317(4)	7145(5)	2226(5)	463(20)
C(2)	4825(4)	7475(4)	3460(5)	450(19)
C(3)	5828(4)	7505(4)	3227(5)	435(19)
C(4)	6586(4)	7811(5)	3942(6)	532(22)
C(5)	7468(5)	7787(6)	3412(7)	658(27)
C(6)	7607(5)	7476(6)	2185(6)	703(31)
C(7)	6868(4)	7174(5)	1466(7)	600(28)
C(8)	5983(4)	7199(5)	1996(5)	459(19)
C(9)	3727(4)	6109(5)	2335(5)	536(22)
C(91)	4375(6)	5196(6)	2688(10)	760(35)
C(92)	2946(6)	6206(8)	3297(8)	778(32)
C(93)	3232(6)	5860(7)	1102(7)	705(30)
C(11)	3789(4)	8133(5)	1717(5)	505(20)
C(12)	3130(5)	8635(6)	2432(7)	725(26)
C(13)	2671(6)	9531(7)	1960(9)	866(37)
C(14)	2892(6)	9916(7)	806(8)	789(33)
C(15)	3532(6)	9412(7)	126(7)	711(31)
C(16)	3987(5)	8522(6)	562(6)	585(25)
C(21)	4785(4)	7998(5)	5531(5)	512(22)
C(22)	4813(5)	9061(7)	5825(6)	703(28)
C(23)	5203(6)	9377(8)	6852(8)	884(35)
C(24)	5521(5)	8614(11)	7783(7)	920(41)
C(25)	5467(5)	7572(10)	7501(7)	851(37)
C(26)	5089(5)	7242(6)	6371(6)	672(27)

Table 6

Compound 2b. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^4 \text{ \AA}^2$) for non-H Atoms with *esd*'s in Parentheses

	$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$			
	X	Y	Z	U _{eq}
O(1)	1195(1)	3946(2)	2515(2)	496(6)
N(1)	1683(1)	3050(2)	3231(3)	369(5)
N(2)	3263(1)	-533(2)	3269(2)	469(6)
C(1)	2410(1)	1571(2)	2239(2)	366(6)
C(2)	2726(1)	899(2)	3665(2)	379(7)
C(3)	2277(1)	2158(2)	5310(2)	375(6)
C(4)	2381(2)	2342(3)	7007(3)	490(8)
C(5)	1834(2)	3712(3)	8287(3)	587(9)
C(6)	1194(2)	4873(3)	7904(3)	571(9)
C(7)	1088(1)	4745(2)	6234(3)	466(8)
C(8)	1648(1)	3389(2)	4969(2)	360(6)
C(10)	2027(1)	321(3)	893(2)	440(7)
C(101)	1264(1)	-194(2)	1608(2)	431(8)
C(102)	414(2)	796(3)	1895(3)	538(9)
C(103)	-298(2)	330(4)	2541(4)	699(11)
C(104)	-159(2)	-1129(4)	2898(4)	756(12)
C(105)	678(2)	-2144(4)	2601(4)	755(13)
C(106)	1395(2)	-1686(3)	1958(3)	588(10)
C(11)	3129(1)	2161(2)	1437(2)	396(7)
C(12)	3749(1)	1039(3)	98(3)	500(8)
C(13)	4938(2)	1566(3)	-658(3)	601(9)
C(14)	4435(2)	3210(3)	-87(3)	686(11)
C(15)	3827(2)	4341(3)	1273(4)	728(11)
C(16)	3181(2)	3819(3)	2027(3)	582(9)
C(21)	3478(1)	-1316(2)	4513(3)	460(7)
C(22)	4348(2)	-1735(3)	4787(3)	579(10)
C(23)	4569(2)	-2638(3)	5884(4)	719(11)
C(24)	3935(2)	-3145(3)	6674(4)	735(13)
C(25)	3079(2)	-2751(3)	6383(3)	683(11)
C(26)	2843(2)	-1834(3)	5302(3)	569(9)

nucleus, and the other *anti* with the same reference. This compound, obtained from the reaction of 1-hydroxy-2-phenylindole with nitrosobenzene in high yield and as homogeneous, fine orange prisms, is originated only in the *syn* form, thus its synthesis may be considered stereospecific. As a matter of fact, the chromatographic analysis, hplc included, of the crude product shows the presence of only one of the two possible stereoisomers. This finding was confirmed by the corresponding ^1H -nmr and ^{13}C -nmr spectra and the X-ray analysis demonstrated that compound **1** exists only in the *syn* form.

When compound **1** reacts with Grignard reagents to afford hydroxylamine derivatives, which are easily oxidized to the corresponding aminoxyls by oxidation with lead dioxide in successive steps (Scheme 1), it partially gives rise to an electron transfer process involving the formation of the radical anion $\text{I}^{\cdot-}$ [14], particularly in the case of benzyl- and *tert*-butylmagnesium chloride which are the Grignard reagents showing the lowest oxidation potentials [15]. Also in reactions involving isomerizable species such as the radical anion $\text{I}^{\cdot-}$ (Scheme 2) the *syn* conformation is retained. In fact aminoxyls **2a** and **2b** have structures in which the phenyl group is oriented towards the benzene ring of the indole nucleus as shown by X-ray analysis (Figures 2 and 3) and also in this case only the *syn* configuration was observed. The hydroxylamines **3a** and **3b**, obtained by reduction from **2a** and **2b** respectively (see Experimental), show ^1H -nmr and ^{13}C -nmr spectra which are consistent with only one configuration. Moreover, in the study of the thermal stability of indole aminoxyls [8], where the R group corresponds to methyl, ethyl, isopropyl, *tert*-butyl, benzyl and allyl, decomposition forming the precursor **1** by loss of the R group itself occurs. For all of them, except when R = *tert*-butyl (*i.e.* **2a**), a linear correlation between the logarithm of the decomposition rate constant and the Bond Dissociation Energy (BDE) between C-2 and the R group was observed [8] and, from the X-ray findings, the particular behaviour of **2a** could be ascribed to the steric hindrance exerted by the *tert*-butyl group (Figure 2 and 3).

EXPERIMENTAL

The melting points are uncorrected. The ir spectra were recorded on a Perkin Elmer 298 spectrophotometer from nujol mulls. The nmr spectra were recorded on a Varian Gemini 200 spectrometer using deuteriochloroform as the solvent, TMS as the internal standard and ^{13}C assignments were performed by means of the DEPT sequence. Mass spectra were recorded on a Carlo Erba QMD 1000 GLC-MS spectrometer in EI⁺ mode. The hplc analyses were performed on a Perkin Elmer Series 3 Liquid Chromatograph using a Nucleosil-C18 5 μ Alltech column eluting with mixtures of Methanol/Water (Baker) with the ultraviolet detector at 254 nm. Compounds **1** [1], **2a** and **2b** [2] were prepared according to the literature reports.

2-Phenyl-3-phenylimino-3*H*-indole 1-Oxide (**1**).

This compound had ^1H -nmr: (δ in ppm) 8.64 (dd, 2H, J = 0.87 and 0.2 Hz), 7.26-7.30 (m, 1H), 7.18 (dt, 1H, J = 0.7 and 0.2 Hz), 7.02 (dd, 2H, J = 0.87 and 0.2 Hz), 6.54 (d, 1H, J = 0.87 Hz); ^{13}C -nmr: (δ in ppm) aromatic CH, 132.3, 130.2, 129.9, 129.7, 129.5, 128.4, 125.2, 124.7, 118.1; quaternary C, 157.9, 151.1, 147.5, 136.3, 126.9, 119.6.

Synthesis of 1-Hydroxy-1,2-dihydro-2-phenyl-2-*tert*-butyl-3-phenylimino-3*H*-indole (**3a**) and 1-Hydroxy-1,2-dihydro-2-phenyl-2-benzyl-3-phenylimino-3*H*-indole (**3b**).

General Procedure.

A solution of aminoxyl (0.13 mmole in 20 ml of benzene) was added to 30 mg of 5% Pd/C catalyst (Aldrich) and hydrogenated in a Parr apparatus at room temperature. After 20 minutes the mixture was filtered under vacuum and treated with 50 ml of ligroin (Carlo Erba 80-100°) with stirring. After filtration the precipitated hydroxylamine **3b** was recovered in quantitative yield (mp 174° from ligroin) while for **3a** evaporation of the filtrate to dryness at reduced pressure was necessary.

1-Hydroxy-1,2-dihydro-2-phenyl-2-*tert*-butyl-3-phenylimino-3*H*-indole (**3a**).

This compound had ^1H -nmr: (δ in ppm) 7.92-7.96 (2H, m, arom), 7.38-6.80 (11H, m, arom), 6.58-6.35 (1H, m, arom), 3.80 (1H, broad, OH), 1.99 (3H, s, 1-CH₃), 1.93 (6H, s, 2-CH₃); ^{13}C -nmr: (δ in ppm) methyl carbons, 31.57, 28.33; aromatic CH, 133.9, 130.6, 130.5, 130.1, 128.6, 128.2, 126.5, 123.8, 120.8, 120.0, 118.5; quaternary C, 169.9, 159.3, 152.3, 143.8, 139.1, 119.7, 40.7; ms: (m/z %) 356 (M⁺, 9), 355 (M-1, 30), 354 (M-2, 53), 338 (36), 323 (33), 311 (22), 279 (18), 220 (33), 180 (17), 115 (41), 77 (100).

Anal. Calcd. for C₂₄H₂₄N₂O: C, 80.87; H, 6.79; N, 7.86. Found: C, 80.89; H, 6.77; N, 7.87.

1-Hydroxy-1,2-dihydro-2-phenyl-2-benzyl-3-phenylimino-3*H*-indole (**3b**).

This compound had ir: (ν in cm⁻¹) 3050, 1650, 1590, 1260, 1110, 1060, 950, 760, 750, 690, 700; ^1H -nmr: (δ in ppm) 7.62-6.75 (m, 18H, arom), 6.39-6.17 (m, 1H, arom), 4.01-3.75 (2H, AB, CH₂-Ph, J = 13.5 Hz), 3.65 (1H, s, OH); ^{13}C -nmr: (δ in ppm) aromatic CH, 133.9, 131.9, 129.9, 128.9, 128.1, 128.0, 126.8, 126.4, 120.6, 119, 111.9; 41.0 (CH₂-Ph); quaternary C, 169.2, 159.0, 152.0, 141.3, 137.2, 120.6, 120.1; ms: (m/z %) 390 (M⁺, 5), 389 (M-1, 18), 373 (8), 283 (57), 179 (35), 178 (37), 91 (100), 77 (40).

Anal. Calcd. for C₂₇H₂₂N₂O: C, 83.05; H, 5.68; N, 7.17. Found: C, 83.07; H, 5.70; N, 7.18.

Crystal Structure of 2-Phenyl-3-phenylimino-3*H*-indole 1-Oxide (**1**).

Crystals were orange flat prisms elongated on [010]. Lattice constants were determined using a program [16] which repeatedly rectifies on the diffractometer the values of (θ, χ, ϕ) angles of thirty reflections to obtain the maximum of the peak when the angles are not moving more than 0.01°.

Crystal data. C₂₀H₁₄N₂O, *M* = 298.3. Monoclinic, *a* = 12.888(3), *b* = 5.318(2), *c* = 21.879(4) Å, *V* = 1481.1(8) Å³, *Z* = 4, *D_c* = 1.34 g cm⁻³, Cu-K α radiation λ = 1.5418 Å, μ = 6.3 cm⁻¹. Space group P2₁/c (C_{2h}⁵, No. 14) from systematic absences.

X-ray measurements were performed at T = 294 K on a Siemens AED single-crystal diffractometer on line to an IBM

PS/2 M30 computer, in the range $3 < \theta < 70^\circ$ using Ni-filtered Cu-K α 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 $(\theta-0.60)^\circ$ to $(\theta+0.60+\Delta\lambda/\lambda \operatorname{tg}\theta)^\circ$. The intensities I_{hkl} were determined by analysing the reflection profiles with the Lehmann and Larsen procedure [17]. 2954 Reflections ($-14 \leq h \leq 15$, $0 \leq k \leq 6$, $0 \leq l \leq 26$) of which 1204 independent (internal R merging factor 0.027) having $I_{hkl} > 2\sigma(I)$ [based on statistic counting] were retained as "observed" and used in the refinement. One standard reflection, measured every 50 collected reflections to monitor crystal decomposition and instrumental linearity, showed no significant variation. The dimensions of the specimen were 0.17, 0.68, 0.07 mm. Corrections for Lorentz and polarization effects were performed; there were no corrections for absorption effects.

Structure Analysis and Refinement. The structure was solved by direct methods by use of SHELXS86 [18] and refined by SHELX76 [19] with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.035$, $R_w = 0.033$. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.013F_o^2$. All the hydrogen atoms were located in the ΔF map. Positional parameters together with their standard deviations for non-hydrogen atoms are reported in Table 4.

Crystal Structure of 1,2-Dihydro-2-phenyl-2-tert-butyl-3-phenylimino-3H-indole 1-Oxyl (2a).

Crystals were dark ruby-red prisms. Cell parameters were derived as before and lattice parameters were derived from 30 $(\theta, \chi, \phi)_{hkl}$ measurements.

Crystal data. $C_{24}H_{23}N_2O$, $M = 355.5$. Orthorhombic $a = 14.337(3)$, $b = 12.697(3)$, $c = 10.822(3)$ Å, $V = 1970.0(8)$ Å³, $Z = 4$; $D_c = 1.20$ g cm⁻³; Cu-K α radiation, $\lambda = 1.5418$ Å, $\mu = 5.4$ cm⁻¹. Space group $P2_12_12_1$ (D_2^4 , No. 19) from systematic absences. Intensity data were collected as before. Of 2170 measured reflections ($0 \leq h \leq 17$, $0 \leq k \leq 15$, $0 \leq l \leq 13$), 813 symmetry independent were used in the crystal analysis. The dimensions of the crystal were 0.14, 0.19, 0.24 mm. No absorption corrections were applied.

Structure Analysis and Refinement.

The structure was solved as before and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.037$, $R_w = 0.030$. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.013 F_o^2$. All the hydrogen atoms were located in the difference-Fourier map. Positional parameters for non-hydrogen atoms with their standard deviations are given in Table 5.

Crystal Structure of 1,2-Dihydro-2-benzyl-2-phenyl-3-phenylimino-3H-indole 1-Oxyl (2b).

Crystals were dark ruby-red prisms. Cell parameters were derived as before and lattice parameters were refined from 29 $(\theta, \chi, \phi)_{hkl}$ measurements.

Crystal data. $C_{27}H_{21}N_2O$, $M = 389.5$. Triclinic, $a = 15.670(3)$, $b = 8.673(2)$, $c = 8.321(2)$ Å, $\alpha = 108.2(1)$, $\beta = 86.4(1)$, $\gamma = 77.6(1)^\circ$; $V = 1038.9(10)$ Å³; $Z = 2$; $D_c = 1.25$ g cm⁻³; Cu-K α radiation $\lambda = 1.5418$ Å; $\mu = 5.6$ cm⁻¹. Space group $P1$ (C_1 , No. 2) from structure determination. Intensity data are collected as before. Of 3943 independent reflections measured ($-17 \leq h \leq 19$, $-10 \leq k \leq 9$, $0 \leq l \leq 10$) 3041 (internal R merging factor 0.008) were used in the crystal analysis. The dimensions of the crystal

were 0.28, 0.43, 0.62 mm. No absorption correction was applied.

Structure Analysis and Refinement.

The structure was solved as before and refined up to $R = 0.051$, $R_w = 0.059$. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.019 F_o^2$. All the hydrogen atoms were located in the difference-Fourier map. Positional parameters for non-hydrogen atoms with their standard deviations are reported in Table 6. For all the compounds atomic scattering factors were from [20] for non-hydrogen atoms and from [21] for hydrogen.

The calculations were carried out on the GOULD 6040 POWERNODE computer of the Centro di Studio per la Strutturistica Diffraattometrica del C.N.R. of Parma. Bibliographic searches were carried out using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione dei Dati Cristallografici, Parma.

Anisotropic thermal parameters, observed and calculated structure factors and H-atom positional parameters with their standard deviations are available from the authors on request.

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