Synthesis of a new series of indolinic aminoxyls. Reaction of indoles, 2-phenylbenzothiazole, 2-phenylbenzoxazole and 2-phenyl-1,2-dihydro-4*H*-3,1-benzoxazin-4-one with organolithium reagents

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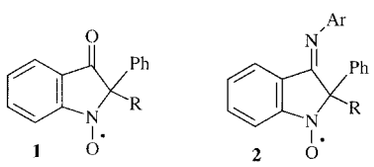
2-Alkyl-2-phenyl-3,3-dimethylindolines, obtained by 1,2 organolithium addition to 2-phenyl-3,3-dimethyl-3*H*-indole, are converted into a new series of aminoxyls by oxidation with *m*-chloroperoxybenzoic acid. Attempts to synthesise, in a similar way, suitable precursors such as 1,2-dihydro-2-phenyl-2-alkylbenzothiazole, 1,2-dihydro-2-phenyl-2-alkylbenzoxazole and 1,2-dihydro-2-phenyl-2-alkyl-4*H*-3,1-benzoxazin-4-one for other new aminoxyls failed. In fact, 2-phenylbenzothiazole, 2-phenylbenzoxazole and 2-phenyl-4*H*-3,1-benzoxazin-4-one react with organolithium reagents affording products deriving from ring opening. Crystal structures of 2,3-dimethyl-3-phenyl-3*H*-indole and bis(2-triphenylmethylaminophenyl) disulfide are also described.

Introduction

All antioxidants working through hydrogen donation, like vitamin E, show a pro-oxidant effect,[1] and the lower their pro-oxidative property the higher their efficiency as an antioxidant.[2] The indolinonic **1** and 3-arylimino indolinonic aminoxyls **2**,



previously prepared in our laboratory, possess excellent anti-oxidant character, being able to trap peroxyl radicals at a rate constant which ranges between 10^5–10^7 l mol^{-1} s^{-1} [3] and alkyl radicals at a rate close to the one controlled by diffusion.[4] On the basis of this behaviour, these compounds were successfully used to prevent peroxidation in lipids,[5] proteins,[6] low density lipoproteins[7] and, more recently, in the protection of DNA.[8] In the above mentioned studies and applications, a certain pro-oxidant effect of compounds **1** and **2** was observed and the extent of this effect was correlated with the aminoxyl structure: in fact, aminoxyls such as **1**, bearing a carbonyl group at C-3, show a higher pro-oxidant effect than those, such as **2**, having a C=N double bond in the same position.[9]

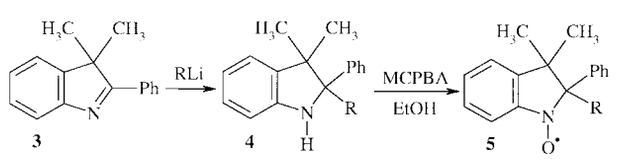
The aim of the present study was to synthesise aminoxyls bearing an sp^3 carbon in position 3, in order to decrease the pro-oxidant effect which is, however, an intrinsic property of all aminoxyls. For the same purpose, attempts to synthesise aminoxyls with a heteroatom in position 3 were performed.

Results

The indolinic aminoxyls **5** were synthesised from 3*H*-indole **3** according to Scheme 1. The oxidation of indolines **4** was performed with *m*-chloroperoxybenzoic acid (MCPBA); yields are in the range 20–30%. All mass spectra show two characteristic peaks, the former corresponding to the molecular mass, the latter to the loss of an oxygen. EPR spectra show similar hyperfine coupling constants (see Table 1) and are in agreement with those aminoxyls having an indoline structure.[10]

Table 1 EPR hyperfine coupling constants of compounds **5**

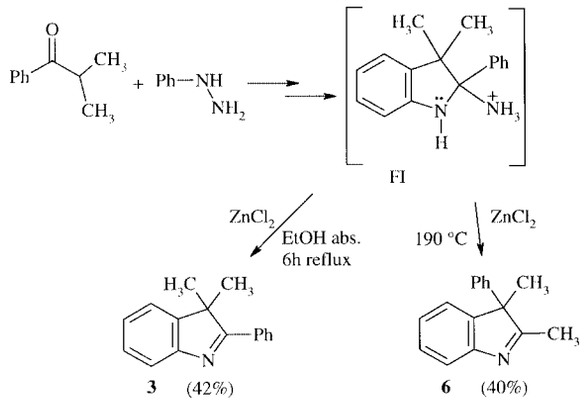
Compound	a_N	$a_{H\text{-}5,7}$	$a_{H4,6}$	$a_{H\text{–}R}$
5a	11.00 (1N)	3.39 (1H) 3.29 (1H)	0.91 (1H) 1.00 (1H)	0.16 (3H)
5b	10.94 (1N)	3.41 (1H) 3.19 (1H)	0.86 (1H) 1.08 (1H)	—
5c	10.58 (1N)	3.32 (1H) 3.31 (1H)	0.77 (1H) 1.14 (1H)	0.22 (1H)
5d	10.62 (1N)	3.25 (1H) 3.26 (1H)	0.98 (1H) 1.00 (1H)	—
5e	10.59 (1N)	3.29 (1H) 3.16 (1H)	0.90 (1H) 1.10 (1H)	0.21 (1H)



a: R = Me **d**: R = Ph
b: R = Bu^n **e**: R = n-hexyl
c: R = Bu^t

Scheme 1

The reaction of isopropyl phenyl ketone with phenylhydrazine leads to two different products **3** and **6**, depending on the experimental conditions (Scheme 2). Compound **6** was identified by X-ray analysis and its analytical and spectroscopic data are in agreement with the structure proposed. By comparing the ^{1}H NMR spectrum of compound **6** with the one of



Scheme 2

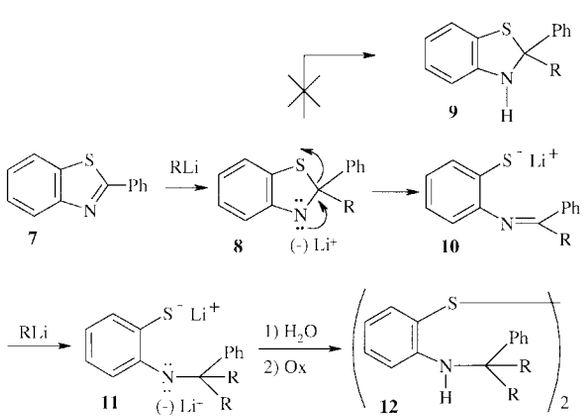
compound **3**, it was possible to assign the C-2 methyl in compound **6**, which falls at $\delta = 1.68$ ppm. At room temperature compound **3** is an oil and the melting point of its picrate (mp = 158–160 °C) is in agreement with the one reported in the literature.[11]

Compounds **4**, which are the precursors of aminoxyls **5**, were obtained by reacting the 3*H*-indole **3** with alkyllithium: the structures of the isolated products are shown in Scheme 1.

It is noteworthy that in the ^{1}H NMR spectra of compounds **4**, the two methyl groups at C-3 are not magnetically equivalent ($\Delta\delta = 0.9$ ppm); the exception shown for compound **4d**, demonstrates that the magnetic non-equivalency is due to the chiral C-2. All compounds **4** show in their IR spectrum an absorption at *ca.* 1600 cm^{-1} which is typical for indolinic structure.[12]

3*H*-Indole **6** does not react with organolithium at C-2 because the tautomeric equilibrium, due to the C-2 methyl indole structure, is presumably responsible for an acid–base reaction, as shown with analogous substrates.[13]

An attempt to obtain thioindolines **9** from 2-phenylbenzothiazole **7** was not successful: reaction with both phenyl and *n*-hexyllithium lead only to compounds **12** (Scheme 3). Compound **12a** was identified by X-ray analysis, while **12b** was characterised by its spectroscopic data, which were strictly similar to those observed for compound **12a**.



a: R=Ph
b: R=*n*-hexyl

Scheme 3

The same reactivity of benzothiazole **7** toward phenyllithium was observed for 2-phenylbenzoxazole **13** (Scheme 4); in this case too, the attainment of the indoline **14** failed and **16** was the only isolated product.

The reaction of 2-phenyl-1,2-dihydro-4*H*-3,1-benzoxazin-4-one **17** with phenyllithium gives products **19** and **20** instead of **18** (Scheme 5), showing behaviour similar to that observed for compounds **7** and **13**.

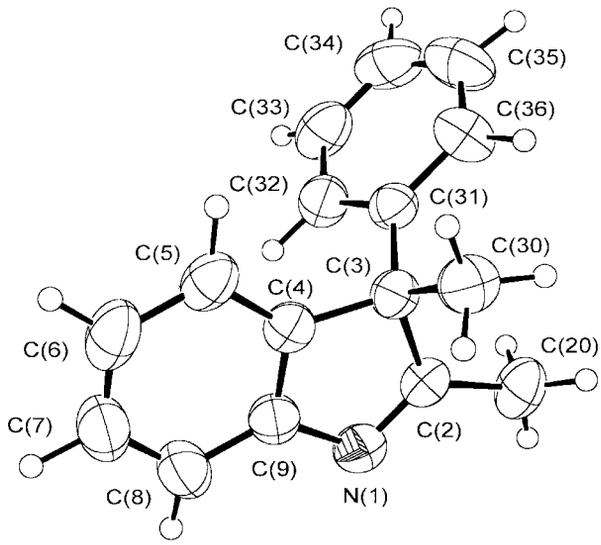
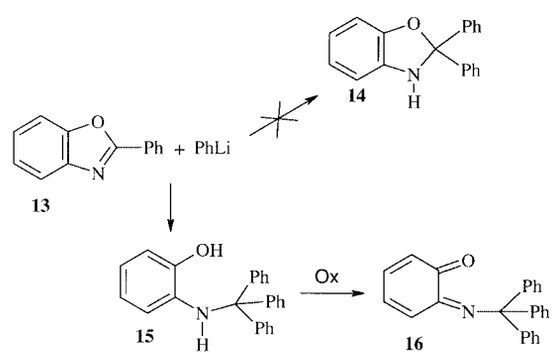
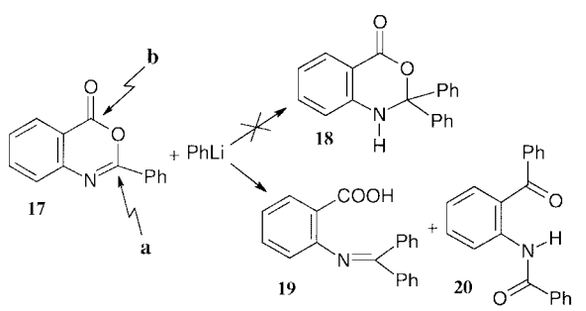


Fig. 1 ORTEP plot of compound **6** showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small circles of arbitrary radii.



Scheme 4



Scheme 5

Molecular geometry of 2,3-dimethyl-3-phenyl-3*H*-indole 6 and of bis(2-triphenylmethylaminophenyl) disulfide acetone solvate 12a

Figs. 1 and 2 show perspective views of compounds **6** and **12a** respectively, together with the arbitrary numbering schemes used in the crystal analyses: selected bond distances and angles are given in Table 2.

For compound **6**, bond distances and angles are in reasonable agreement with those found in analogous indoles previously studied:[14] in particular, the presence of a localised double bond N(1)=C(2) 1.287(4) Å and the angle at N(1) of 106.8(2)° have been found. The indolic moiety is planar, within the experimental error; the phenyl and the indolic mean planes form a dihedral angle of 95.7(1)°. In the crystal, the molecules are held together by van der Waals forces.

The structure of **12a** consists of discrete monomeric units of this compound and of acetone solvate, separated by normal van der Waals distances.

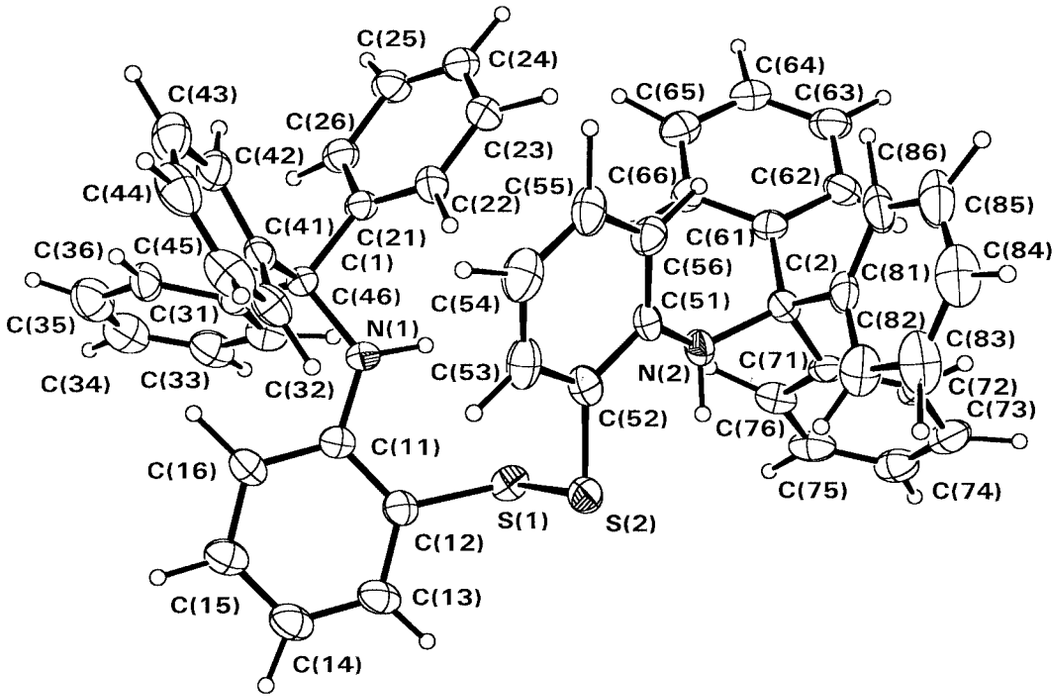


Fig. 2 ORTEP plot of compound **9a** showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small circles of arbitrary radii.

Table 2 Selected bond distance (Å) and angles (degrees) for compounds **6** and **12a**

Compound **6**			
N(1)–C(2)	1.287(3)	C(3)–C(4)	1.506(4)
N(1)–C(9)	1.430(3)	C(3)–C(30)	1.548(4)
C(2)–C(3)	1.538(4)	C(3)–C(31)	1.535(3)
C(2)–C(20)	1.489(6)	C(4)–C(9)	1.394(4)
C(2)–N(1)–C(9)	106.8(2)	C(3)–C(4)–C(9)	107.7(2)
N(1)–C(2)–C(3)	114.7(2)	N(1)–C(9)–C(4)	111.7(2)
C(2)–C(3)–C(4)	99.2(2)		
Compound **12a**			
S(1)–S(2)	2.068(1)	S(2)–C(52)	1.774(4)
S(1)–C(12)	1.773(4)	N(2)–C(2)	1.474(5)
N(1)–C(1)	1.484(4)	N(2)–C(51)	1.391(5)
N(1)–C(11)	1.376(5)	C(51)–C(52)	1.413(6)
C(11)–C(12)	1.414(6)		
S(2)–S(1)–C(12)	105.5(1)	N(1)–C(11)–C(12)	120.4(4)
S(1)–S(2)–C(52)	104.4(1)	S(1)–C(12)–C(11)	121.6(3)
C(1)–N(1)–C(11)	127.0(3)	N(2)–C(51)–C(52)	119.2(4)
C(2)–N(2)–C(51)	125.4(3)	S(2)–C(52)–C(51)	120.8(3)

The atoms C(12), S(1), S(2), C(52) in the centre of the molecule adopt a skewed non-planar conformation like the one found in similar disulfide molecules reported in the literature,[15] where the S–S bond length in disulfide compounds is correlated with the C–S–S–C torsion angle, being around 2.03 and 2.07 Å for angles in the range 75–105 and 0–20°, respectively.[16] The value of 2.068(1) Å for S(1)–S(2) with a C(12)–S(1)–S(2)–C(52) torsion angle of −91.5(2)° shown by **12a** could be interpreted in terms of strain effect imposed by steric interactions between the bulky substituents at the aminic nitrogens.

The S and N atoms are almost coplanar with their respective rings, N(1)–C(11)–C(12)–S(1) and N(2)–C(51)–C(52)–S(2) torsion angles being −4.8(6) and 6.1(6)°, respectively. The molecule exhibits weak intramolecular hydrogen bonds of the S···N type [N(1)–H(1) 0.81(3), N(1)···S(1) 3.058(3), H(1)···S(1) 2.070(4) Å; N(1)–H(1)···S(1) 109(3)°; N(2)–H(2) 0.87(4), N(2)···S(2) 3.018(4), H(2)···S(2) 2.48(3) Å; N(2)–H(2)···S(2) 121(3)°]. Contacts responsible for packing correspond to van der Waals interactions.

Discussion

In the reaction of isopropyl phenyl ketone with phenylhydrazine, the compound formed depends on the experimental conditions, and this could be explained as shown in Scheme 2. The Fisher's intermediate (FI, Scheme 2)[17] in refluxing ethanol (mild conditions) could eliminate ammonia affording compound **3**; however, when FI is subjected to stronger conditions ($ZnCl_2$/190 °C), a double Wagner–Meerwein transposition[18] occurs, leading to compound **6**.

Both aliphatic[19] and aromatic[20] secondary amines may be converted into the corresponding aminoxyls by oxidation, as well as indolines[21] and indoxyls.[22]

Indolines such as **4** may be easily prepared by reaction of indoles with organolithium when the starting indole is substituted with a phenyl group at C-2: a tertiary carbon at C-2 could behave like the phenyl group, whereas the presence of only one hydrogen bonded to the carbon of the substituent at C-2 could give rise to a tautomeric equilibrium,[23] inhibiting the 1,2-addition from organolithium.

The conversion of indolines **4** into the corresponding aminoxyls is not high because the aminoxyls react further with MCPBA, forming compounds such as benzoyloxy substituted aminoxyls and quinone imine *N*-oxides, which have already been observed and described in the case of **1**.[22]

The reaction of 2-phenylbenzothiazole **7** with organolithium would have been interesting for two reasons: on one hand, thioindolines **9** themselves could possess antioxidant properties, such as those shown by the parent phenothiazine,[24] which are, to some extent, structurally similar; on the other hand, aminoxyls prepared by oxidation of **9** could have had antioxidant properties suitable for biological applications. In our opinion, the synthesis of thioindolines **9** failed because the anion **8**, formed in the first 1,2 addition, rearranges to the anion **10**, which undergoes the addition of one more molecule of RLi leading to the di-anion **11** (Scheme 3): the latter is then transformed into compound **12** during the reaction work-up. On the other hand, it is well known that thiophenols easily undergo

oxidative dimerisation to the corresponding disulfides.[25] The ring opening suggested for the intermediate **8** has already been observed for similar systems.[26]

A similar reactivity could be likely invoked for 2-phenylbenzoxazole **13**, even if in this case the *o*-aminophenol **15** is oxidised to the corresponding iminoquinone **16** (Scheme 4).

The 2-phenyl-1,2-dihydro-4*H*-3,1-benzoxazin-4-one **17** behaves as a bidentate system towards organometallics; in fact, organolithium could either give 1,2-addition (path a, Scheme 5), as observed for compounds **7** and **13**, leading to compound **19** instead of **18**, or attack the carbonyl group in position 4 (path b, Scheme 5), forming compound **20**. These results clearly show that alternative pathways must be found to obtain the interesting products **9**, **14** and **18**.

Experimental

Melting points are uncorrected and were measured with an Electrothermal apparatus. IR spectra were recorded in solid state on a Nicolet Fourier Transform Infrared 20-SX spectrophotometer equipped with a Spectra Tech. "Collector" for DRIFT measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ or C_6D_6 solution on a Varian Gemini 200 spectrometer (TMS was taken as reference peak). Mass spectra were performed on a Carlo Erba QMD 1000 mass spectrometer, equipped with a Fisons GC 8060 gas chromatograph. EPR spectra were recorded on a Varian E4 spectrometer interfaced with a computer (for acquisition, editing and simulation of experimental signals) and equipped with an XL microwave 3120 frequency counter and with a ruby in the cavity as reference. Isopropyl phenyl ketone, phenylhydrazine, zinc chloride, *m*-chloroperoxybenzoic acid, alkyllithium reagents and compounds **7**, **13** and **17** were purchased from Aldrich and used without further purification.

Synthesis of compound 3

A solution of isopropyl phenyl ketone (7.4 g, 50 mmol), phenylhydrazine (5.94 g, 55 mmol) and toluene-*p*-sulfonic acid (0.5 g, 2.9 mmol) was refluxed in a Dean Stark apparatus until 0.9 ml of water were produced. After cooling, the mixture was treated with a saturated solution of $NaHCO_3$ (300 ml) and extracted with $CHCl_3$ (2 × 40 ml). The combined organic layers were dried on Na_2SO_4 and evaporated under vacuum. The residue was dissolved in absolute ethanol (100 ml) and $ZnCl_2$ (50.3 g, 370 mmol) was added. The solution was refluxed for 24 h, then concentrated. The residue was treated with a saturated solution of $NaHCO_3$ (400 ml) and extracted with diethyl ether (3 × 50 ml). The combined organic layers were dried on Na_2SO_4, concentrated and the residue chromatographed on SiO_2, using cyclohexane–ethyl acetate 95/5 as an eluant. Compound **3** is an oil at room temperature. Yield = 42%; mp (picrate) = 159–161 °C (lit. 158–160 °C);[11] IR (KBr), ν/cm^{-1}: 3058, 2965, 1520, 1454, 1386; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 1.61 (s, 6H), 7.35 (m, 3H), 7.50 (m, 3H), 7.73 (d, 1H, J = 7.2 Hz), 8.17 (m, 2H); MW for $C_{16}H_{15}N$, 221.29; MS (EI$^+$): m/z = 221 (M$^+$, 100), 206 (57), 144 (45).

Synthesis of compound 6

$ZnCl_2$ (50.3 g, 370 mmol), isopropyl phenyl ketone (7.4 g, 50 mmol) and phenylhydrazine (6.48 g, 60 mmol) were heated under stirring at 190 °C for 3 h. After cooling, a solution of NH_4OH 0.1 M (200 ml) was added, and the mixture was extracted with diethyl ether (5 × 40 ml). The combined organic layers were dried on Na_2SO_4 and concentrated to dryness under vacuum. The residue was chromatographed on an SiO_2 column (eluant cyclohexane–ethyl acetate 8/2). Compound **6** was crystallised from petroleum ether. Yield = 40%; mp = 70 °C; IR (KBr), ν/cm^{-1}: 3050, 2960, 1525, 1450, 1378; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 1.68 (s, 3H), 2.13 (s, 3H), 7.12 (m, 4H), 7.28 (m, 4H), 7.61 (d, 1H, J = 7.8 Hz); MW for $C_{16}H_{15}N$, 221.29; MS (EI$^+$): m/z = 221 (M$^+$, 100), 206 (90), 179 (65), 165 (95). Analysis, calcd. C, 86.84; H, 6.83; N, 6.33. Found C, 86.54; H, 6.97; N, 6.38%.

Synthesis of compounds 4

THF solutions of RLi (13.5 mmol) were added dropwise, under Ar, to a solution of **3** (4.5 mmol) in dry THF (40 ml). After 30 min the mixture was poured in a saturated solution of NH_4Cl (150 ml) and extracted with diethyl ether (2 × 40 ml). The combined organic layers were dried on Na_2SO_4, concentrated and chromatographed on an SiO_2 column (eluant cyclohexane–ethyl acetate 95/5). Yields are reported below.

4a: Yield = 93.5%; mp = 70–72 °C from ligroin 55–85 °C; IR (KBr), ν/cm^{-1}: 3334, 3012, 2921, 1457, 1376; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 0.65 (s, 3H), 1.45 (s, 3H), 1.52 (s, 3H), 6.76 (dq, 2H, J = 7.4 and 1.2 Hz), 7.07 (dq, 2H, J = 7.0 and 1.6 Hz), 7.34 (m, 3H), 7.64 (dd, 2H, J = 8.7 and 1.8 Hz); MW for $C_{17}H_{19}N$, 237.33; MS (EI$^+$): m/z = 237 (M$^+$, 40), 236 (100), 222 (82), 206 (36). Analysis, calcd. C, 86.03; H, 8.07; N, 5.90. Found C, 86.10; H, 8.12; N, 5.87%.

4b: Yield = 60.0%; oil at rt; IR (KBr), ν/cm^{-1}: 3382, 3080, 2956, 1485, 1386; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 0.63 (s, 3H), 0.80 (t, 3H, J = 7.5 Hz), 0.98 (m, 2H), 1.22 (m, 2H), 1.48 (s, 3H), 1.90 (m, 2H), 4.15 (broad, 1H), 6.78 (m, 2H), 7.09 (m, 2H), 7.36 (m, 3H), 7.60 (d, 2H, J = 7.3 Hz); MW for $C_{20}H_{25}N$, 279.41; MS (EI$^+$): m/z = 279 (M$^+$, 22), 250 (14), 222 (100), 207 (67).

4c: Yield = 85.7%; oil at rt; IR (KBr), ν/cm^{-1}: 3376, 3054, 2956, 1484, 1386; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 0.65 (s, 3H), 0.80 (s, 9H), 1.49 (s, 3H), 4.15 (broad, 1H), 6.79 (m, 2H), 7.07 (m, 2H), 7.35 (m, 3H), 7.60 (d, 2H, J = 7.2 Hz); MW for $C_{20}H_{25}N$, 279.41; MS (EI$^+$): m/z = 279 (M$^+$, 10), 250 (70), 222 (100), 207 (71).

4d: Yield = 45.6%; mp = 90–91 °C from ligroin 55–85 °C; IR (KBr), ν/cm^{-1}: 3376, 3053, 2975, 1459, 1390; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 1.20 (s, 6H), 4.14 (broad, 1H), 6.63 (dd, 1H, J = 7.8 and 1.2 Hz), 6.84 (td, 1H, J = 7.5 and 1.0 Hz), 7.08 (td, 2H, J = 7.1 and 1.3 Hz), 7.26 (m, 6H), 7.40 (m, 4H); MW for $C_{22}H_{21}N$, 299.40; MS (EI$^+$): m/z = 299 (M$^+$, 58), 284 (12), 269 (10), 222 (100), 207 (19). Analysis, calcd. C, 88.25; H, 7.07; N, 4.68. Found C, 88.31; H, 7.12; N, 4.71%.

4e: Yield = 41.7%; oil at rt; IR (KBr), ν/cm^{-1}: 3378, 3053, 2923, 1460, 1387; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 0.65 (s, 3H), 0.85 (t, 3H, J = 6.5 Hz), 1.19 (m, 8H), 1.47 (s, 3H), 1.90 (m, 2H), 4.17 (broad, 1H), 6.77 (m, 2H), 7.07 (m, 2H), 7.35 (m, 3H), 7.60 (d, 2H, J = 7.1 Hz); MW for $C_{22}H_{29}N$, 307.46; MS (EI$^+$): m/z = 307 (M$^+$, 22), 250 (46), 222 (100), 207 (62).

Oxidation of indolines 4 to aminoxyls 5. General procedure

Solid 3-chloroperoxybenzoic acid (1 mmol) was added to a solution of the indoline (0.1 mmol) in $CHCl_3$ (10 ml). The mixture was stirred for 30 min, then evaporated to dryness and chromatographed on an SiO_2 column (eluant cyclohexane–ethyl acetate 9/1). Compounds **5** were uncrystallisable. Yields: 20–30%.

5a: IR (KBr), ν/cm^{-1}: 3055, 2983, 1475, 1386; MW for $C_{17}H_{18}NO$, 252.32; MS (EI$^+$): m/z = 252 (M$^+$, 20), 237 (47), 222 (81), 207 (19).

5b: IR (KBr), ν/cm^{-1}: 3054, 2973, 1463, 1388; MW for $C_{20}H_{24}NO$, 294.40; MS (EI$^+$): m/z = 294 (M$^+$, 17), 278 (43), 238 (100), 222 (92), 207 (31).

5c: IR (KBr), ν/cm^{-1}: 3063, 2989, 1470, 1380; MW for $C_{20}H_{24}NO$, 294.40; MS (EI$^+$): m/z = 294 (M$^+$, 11), 278 (10), 238 (86), 222 (100), 207 (44).

5d: IR (KBr), ν/cm^{-1}: 3060, 2978, 1485, 1377; MW for $C_{22}H_{20}NO$, 314.39; MS (EI$^+$): m/z = 314 (M$^+$, 25), 298 (88), 222 (99), 207 (44).

5e: IR (KBr), ν/cm^{-1}: 3050, 2968, 1488, 1392; MW for $C_{22}H_{28}NO$, 322.45; MS (EI$^+$): m/z = 322 (M$^+$, 4), 306 (7), 222 (100), 207 (86).

EPR spectra were recorded on solutions of **5** (0.01 mmol) in $CHCl_3$ (1 ml), deaerated with Ar for 2 min. Hyperfine coupling constants are reported in Table 1.

Reactions of 7 with RLi (R = Ph, *n*-hexyl)

RLi (9.4 mmol) in toluene (10 ml) was added dropwise, under Ar, to a solution of **7** (4.7 mmol) in toluene (40 ml) under stirring. After 30 min the reaction mixture was poured into water, treated with 15 g of NH_4Cl and extracted with CH_2Cl_2 (2 × 40 ml). The combined organic layers were dried on Na_2SO_4 and evaporated to dryness. The residue was then chromatographed on an SiO_2 column (eluant cyclohexane–ethyl acetate from 10/0 to 9/1).

12a: Yield = 87%; mp = 95–96 °C from benzene–light ligroin; IR (KBr), ν/cm^{-1}: 3384, 3058, 2960, 1446, 1319; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 6.17 (d, 2H, J = 8.8 Hz), 6.33 (d, 2H, J = 7.7 Hz), 6.68 (s, 2H), 6.79 (td, 2H, J = 7.7 and 1.5 Hz), 7.03 (td, 2H, J = 7.5 and 1.2 Hz), 7.27 (m, 18H), 7.40 (m, 10H); MW for $C_{50}H_{40}N_2S_2$, 712.82; MS (EI$^+$): m/z = 366 (M$^+$/2, 1), 289 (2), 243 (32), 211 (15), 86 (95), 77 (37). Analysis, calcd. C, 81.92; H, 5.50; N, 3.82, S, 8.75. Found C, 81.95; H, 5.57; N, 3.86%.

12b: Oil at rt; yield = 85%; IR (KBr), ν/cm^{-1}: 3380, 3048, 2952, 1452, 1321; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 0.82 (t, 12H, J = 5.9 Hz), 1.19 (m, 32H), 1.95 (m, 8H), 5.49 (broad, 2H), 6.05 (dd, 2H, J = 8.4 and 0.9 Hz), 6.39 (td, 2H, J = 7.3 and 0.9 Hz), 6.86 (td, 2H, J = 7.7 and 1.7 Hz), 7.31 (m, 6H), 7.47 (m, 4H); MW for $C_{50}H_{40}N_2S_2$, 765.24; MS (EI$^+$): m/z = 383 (M$^+$/2, 10), 298 (24), 212 (25), 124 (83), 91 (100).

Crystal structure of 2,3-dimethyl-3-phenyl-3*H*-indole 6 and of bis(2-triphenylmethylaminophenyl) disulfide acetone solvate 12a

Table 3 shows the experimental and crystallographic data for **6** and **12a**.† The intensities I_{hkl} were determined by analysing the reflection profiles by the Lehmann and Larsen[30] procedure. Corrections for Lorentz and polarisation effects were performed; there were no corrections for absorption effects.

Atomic scattering factors were from the International Tables for X-Ray Crystallography.[31] Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy.

Table 3 Experimental data for the X-ray diffraction studies on crystalline compounds **6** and **12a**

Compound	**6**	**12a**
Formula	$C_{16}H_{15}N$	$C_{50}H_{40}N_2S_2{\cdot}C_3H_6O$
Cryst. habit	prism	prism
Cryst. colour	colourless	yellow
FW, F(000)	221.3, 472	791.1, 1672
Cryst. syst.	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Cell parameters at 295 K [a]		
a/Å	8.380(2)	18.957(4)
b/Å	14.909(3)	10.066(3)
c/Å	10.712(2)	22.422(4)
α/°	90	90
β/°	111.2	92.14(8)
γ/°	90	90
V/Å^3	1247.8(10)	4275.6(18)
Z	4	4
d_{calc}/g cm^{-3}	1.18	1.23
Cryst. dimen./mm	0.24 × 0.37 × 0.47	0.25 × 0.38 × 0.48
Linear abs. coeff./cm^{-1}	5.2	14.4
Diffractometer	Siemens AED	Enraf Nonius Cad4
Scan type	ω–2θ	ω–2θ
Scan width/°	[b]	[b]
Radiation	[c]	[c]
2θ range coll./°	6–140	6–140
hkl range	±h, k, l	±h, k, l
Unique total data	2596	8810
Criterion of obs.	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Unique obs. data (NO)	1237	3153
No. of refined param. (NV)	214	384
Overdeterm. ratio (NO/NV)	5.8	8.2
Absorption	[d]	[d]
Solution	[e]	[e]
H atoms	[f]	[f]
R	0.041	0.038
R_w	0.046	0.040
GOF	0.065	0.322
Largest shift/esd	0.164	0.304
Largest peak/e Å^{-3}	0.175	0.185
Computer and programs	[g]	[g]

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centred reflections chosen from diverse regions of reciprocal space. [b] From $(\theta - 0.6)°$ to $[\theta + (0.6 + \Delta\theta)]°$; $\Delta\theta = [(\lambda\alpha_2 - \lambda\alpha_1)/\lambda]\tan\theta$. [c] Ni-filtered Cu-K$\alpha$ λ = 1.54178 Å. [d] No correction applied. [e] Direct methods. [f] Located in ΔF map and isotropically refined. [g] ENCORE e91, SHELXS86,[27] SHELX76,[28] PARST.[29] $R = \Sigma|\Delta F|/\Sigma|F_o|$, $R_w = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, GOF = $[\Sigma w|\Delta F|^2/(NO\text{-}NV)]^{1/2}$.

Reaction of compound 13 with phenyllithium

The reaction was carried out by the same procedure used for compound **7** starting from the same molar quantities. Compound **16** was separated by chromatography on an SiO_2 column (eluant cyclohexane–ethyl acetate 9/1); mp = 143–144 °C from ligroin 55–85 °C; yield = 66%; IR (KBr), ν/cm^{-1}: 3058, 2952, 1726, 1583, 1476; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 6.14 (dd, 1H, J = 8.4 and 1.1 Hz), 6.45 (td, 1H, J = 7.9 and 1.5 Hz), 6.72 (dd, 1H, J = 8.4 and 1.5 Hz), 6.88 (m, 3H), 7.13 (m, 3H), 7.43 (m, 8H), 7.81 (dd, 2H, J = 8.4 and 1.2 Hz); MW for $C_{25}H_{19}NO$, 349.41; MS (EI$^+$): m/z = 349 (M$^+$, 34), 272 (40), 196 (29). Analysis, calcd. C, 85.93; H, 5.48; N, 4.01. Found C, 85.88; H, 5.50; N, 3.98%.

Reaction of compound 17 with phenyllithium

The reaction was carried out as observed for compounds **7** and **13**, starting from the same molar quantities. The crude residue was treated with diethyl ether (5 × 10 ml); the insoluble compound **20** was filtered off and crystallised from absolute ethanol. The filtrate was evaporated to dryness and the residue chromatographed on an SiO_2 column (eluant cyclohexane–ethyl acetate 9/1) afforded compound **19**.

19: Oil at rt; yield = 38%; IR (KBr), ν/cm^{-1}: 3300–2900, 1679, 1600, 1446; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 7.10 (td, 1H, J = 8.0 and 1.3 Hz), 7.59 (m, 10H), 8.04 (dd, 2H, J = 8.0 and 1.8 Hz), 8.52 (dd, 1H, J = 9.0 and 0.8 Hz), 11.95 (broad, 1H); MW for $C_{20}H_{15}NO_2$, 301.33; MS (EI$^+$): m/z = 301 (M$^+$, 65), 284 (11), 224 (23), 196 (100), 167 (58), 105 (90), 77 (92).

20: Yield = 54%; mp = 248 °C from ethanol; IR (KBr), ν/cm^{-1}: 3369, 3060, 2970, 1650, 1583, 1448; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 6.63 (dd, 1H, J = 7.9 and 1.4 Hz), 6.98 (td, 2H, J = 7.9 and 1.4 Hz), 7.30 (m, 11H), 8.52 (dd, 1H, J = 8.2 and 1.3 Hz), 9.72 (broad, 1H); MW for $C_{20}H_{15}NO_2$, 301.33; MS (EI$^+$): m/z = 301 (M$^+$, 5), 256 (23), 196 (31), 105 (100), 77 (60). Analysis, calcd. C, 79.71; H, 5.02; N, 4.65. Found C, 79.85; H, 5.07; N, 4.61%.

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