Nitrenium Ions. Part 1. Acid-catalysed Reactions of 2-Methylindole with Nitrosobenzenes. Crystal Structures of 2-Phenylamino-3-phenylimino-3H-indole, 2-(o-Tolylamino)-3-(o-tolylimino)-3H-indole, N-Phenyl-N-(2-phenylamino-3H-indol-3-ylidene)amine N-Oxide and Bis(2-methyl-1H-indol-3-yl)methane

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2-Methylindole 3b reacts with nitrosobenzenes 1a–c in the presence of monochloroacetic acid affording compounds which are characterized by the formation of carbon–nitrogen bonds and other compounds which clearly could arise from a radical mechanism. The radical component of the reaction is also supported by the EPR spectroscopy as well as the reaction products distribution. Although these reactions cannot be considered of synthetic value for the number of isolated products, they could be regarded as clear examples of the electrophilic character and of the oxidative power of nitrogen in activated nitrosobenzenes. Crystal structures of 2-phenylamino-3-phenylimino-3H-indole 7a, 2-(o-tolylamino)-3-(o-tolylimino)-3H-indole 7b, N-phenyl-N-(2-phenylamino-3H-indol-3-ylidene)amine N-oxide 9a and bis(2-methyl-1H-indol-3-yl)methane 10 are also reported.

The reaction of 2-phenylindole 3a with nitrosobenzenes 1 activated with monochloroacetic acid or benzyl chloride mainly afforded compound 5[1] (Scheme 1). This result was interpreted through the formation of the intermediate 2-phenyl-3-arylimino-3H-indoles 4, which represent the product of the interaction between the starting indole and the nitrenium ion 2.

The reaction of 2-methylindole 3b with the nitrosobenzenes 1a–c here described (Scheme 1), never afforded compounds such as 4 and 5. This different behaviour may be attributed to the oxidation potential of 2-methylindole 3b ($E_{\frac{1}{2}} = 0.65$ V vs. Ag$^+$/Ag) which is 100 mV lower than that of 2-phenylindole 3a[2] and to the fact that compounds such as 4 with a methyl group at C-2 are more reactive than the starting indole.[3]

The reaction products distribution clearly demonstrates that an electron-transfer process between the reagents is in competition with the electrophilic attack of the nitrenium ion at C-3 of the indole nucleus forming carbon–nitrogen bonds.

Results

The reactions of 2-methylindole 3b with nitrosobenzene 1a carried out at room temp. in methylene chloride in the presence of monochloroacetic acid in catalytic amounts led to products 6–12. The same reaction carried out under a nitrogen atmosphere gave the same products but compound 12 was isolated only in trace amounts (Table 1). Similar results were observed in the reactions with o-methyl- (1b) and p-bromo-nitrosobenzene (1c). Yields are reported in Table 1.

The structures of compounds 7a,[4] 7b, 9a and 10[5] were determined by X-ray analysis and their spectroscopic data are in agreement with the assigned structures (Table 2). Compounds 6a–c,[6] 8a,[7] 8c,[7] 11[8] and 12[9] were identified by comparison with authentic samples. The spectroscopic data of compounds 10, 11 and 12, which were already isolated but not completely described, are reported in Table 2. All compounds 6–12 were isolated in the case of nitrosobenzene while compounds 8b and 9b in the reaction with 1b and 9c in the reaction with 1c were not isolated.

Carrying out the reaction between 2-methylindole 3b and nitrosobenzene 1a in the EPR cavity (see Experimental) the signal of phenylnitroxide was recorded immediately after mixing the reagents (Scheme 2).

In order to support the reaction sequences proposed in Schemes 3 and 4, compound 17 was synthesized (see Experimental) and reacted with aniline and 2-methylindole in a 1:1:2 ratio. On working-up the reaction compound 7a and indolylmethane 10 were isolated (see Discussion).

Molecular Geometry.—Selected bond distances, angles and torsion angles for the four derivatives are reported in Table 3. The arbitrary numbering scheme used in the crystal analysis is shown in Figs. 1, 2, 3 and 4 which represent perspective views of compounds 7a, 7b, 9a and 10, respectively.†

The intramolecular bond lengths and angles, in line with the hybridization expected for the atoms involved, are in reasonable agreement with those of analogous compounds previously studied.[1,7,10] In particular the presence of a localized double bond C(12)=N(30) {1.273(3) Å in compounds 7a and 7b, but rather delocalized in 9a [1.317(2) Å], according to the character of the adjacent N–O bond} confirming the iminic form of the N(30) atom can be seen.

From the study of the conformational geometry, by bond and torsion angles, and from the analysis of the planarity of the three nitrogen systems (indolinic, iminic and aminic) some main features common to compounds 7a, 7b and 9a can be pointed out. In particular: (i) the coordination geometry at N(19) is trigonal planar with the sum of the angles around the nitrogen atom being 360°. This fact together with the presence of coplanarity in the three nitrogen atoms moiety, justifies the formation of hydrogen bonds of the type N $\cdots$ N

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† Atomic fractional coordinates, thermal parameters and structure factors have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1994, Issue No. 1.
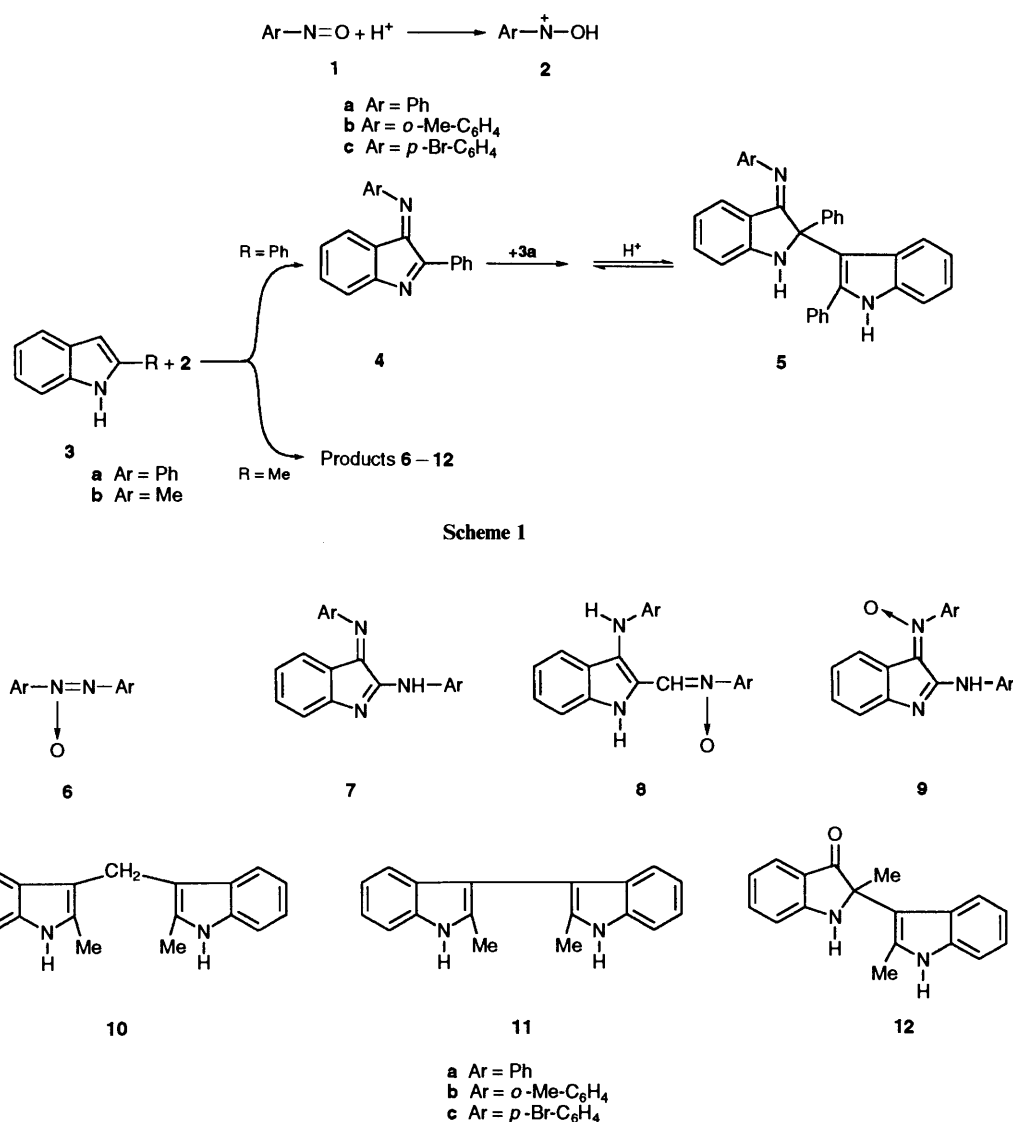
Ar—N=O + H⁺ ————➤ Ar—N⁺—OH

1   2

a Ar = Ph
b Ar = o-Me-C₆H₄
c Ar = p-Br-C₆H₄

Scheme 1

a Ar = Ph
b Ar = o-Me-C₆H₄
c Ar = p-Br-C₆H₄

Table 1 Percentage yields of products of the reactions between 3b and 1a–c in the presence of monochloroacetic acid

Reagents	Products (% yield)						
3b + 1a[a]	6a(20)	7a(14)	8a(10)	9a(7)	10(10)	11(11)	12(25)
3b + 1b[a]	6b(14)	7b(13)	8b(//)[c]	9b(//)[c]	10(11)	11(12)	12(24)
3b + 1c[a]	6c(12)	7c(10)	8c(15)	9c(//)[c]	10(6)	11(10)	12(30)
3b + 1a[b]	6a(27)	7c(20)	8a(13)	9a(//)[c]	10(15)	11(15)	12(//)

[a] In the presence of oxygen. [b] Under nitrogen. [c] Not isolated.

[N(19) · · · N(30) 2.771(2), 2.770(2) Å in 7a and 7b respectively] or of the type N · · · O in 9a [N(19) · · · O(1) 2.678(2) Å] with a consequent planar annulation in this part of the molecule; (ii) as in similar compounds previously studied[1,7,10] the orientation of the phenyl group in position 3 with respect to the plane of the indole ring [84.1(1), 62.1(1) and 81.5(1)° in 7a, 7b and 9a respectively] confirms that in this system the probability of π-interaction between the indolinic group and the substituent in position 3 is minimal. On the contrary it seems that a more considerable π-delocalization regards the phenyl group in position 2, 10.7(1), 4.7(1) and 12.6(1)° being the corresponding dihedral angles. The sequence of bond lengths involving N(11), N(19) and N(30) are consistent with this hypothesis.

The geometry of compound **10** implies the presence of a pseudo twofold axis along the bisecting line of the C(12)–C(30)–C(22) angle, forming an angle of 37.3(1)° with the plane of the indole ring.

All the rings in the four compounds are planar: the dihedral angles between planes of the two condensed five- and six-membered rings of the indole nucleus are 1.4(1), 0.7(1), 2.3(1)°, in 7a, 7b and 9a, and 0.5(1) and 0.9(1)° in 10. Packing is consistent with van der Waals interactions.

Discussion

The results obtained in the reactions of 2-methylindole with activated nitrosobenzenes evidence five main aspects: (i) the involvement of a nitrenium ion present in the equilibrium:

$$\text{ArNO} + \text{H}^+ \rightleftharpoons \text{Ar–N}^+\text{OH}$$
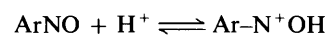
(ii) the electron-transfer process occurring between the indole and the nitrenium ion; (iii) the formation of a carbon–nitrogen

Table 2 Spectroscopic data of compounds 6b, 6c, 7b, 7c, 8a, 9a, 10, 12 and 17a

Compound (formula)	Mp °C	ν_{max} cm⁻¹	δ_H (200 MHz; Me₄Si; J = Hz)	Calc. M_w	m/z (%)	Elemental analysis Calc.	Found
6b (C₁₄H₁₄N₂O)	57–58 [a]	1330 1280 1120	2.38 (3 H, s, Me), 2.53 (3 H, s, Me), 7.22–7.5 (6 H, m, Ph), 7.68 (1 H, m, Ph), 8.04, (1 H, m, Ph) [d]	226.27	226 (M⁺, 50%), 225 (M − 1, 80), 211 (100), 104 (90), 91 (100)		
6c (C₁₂H₈N₂OBr₂)	171–172 [a]	1320 1280 1160	7.63 (4 H, A₂B₂, Ph, J 4.9), 8.13 (4 H, A₂B₂, Ph, J 9.1, 4.9) [d]	356.27	358 (M⁺ + 2, 10%), 356 (M⁺, 20), 354 (M − 2, 11), 157 (98), 155 (100)		
7b (C₂₂H₁₉N₃)	132–134 [b]	3475 1632 1580	2.2 (3 H, s, Me), 2.43 (3 H, s, Me), 6.75 (2 H, d, Ph, J 4.2), 6.97 (1 H, d, Ph, J 6.9), 7.1–7.42 (9 H, m, Ph), 8.42 (1 H, s, br s, NH) [d]	325.27	325 (M⁺, 86%), 324 (M − 1, 100), 310 (73), 220 (72), 218 (81), 107 (84)	C = 81.23 H = 5.89 N = 12.92	C = 81.4 H = 5.8 N = 12.85
7c (C₂₀H₁₃N₃Br₂)	231–232 [c]	3220 1650 1615 1585	6.95 (1 H, t, Ph, J 4.0), 7.08 (3 H, d, Ph, J 7.9), 7.43 (1 H, dt, Ph, J 4.0, 1.1), 7.65–7.55 (5 H, m, Ph), 7.79 (2 H, d, Ph, J 8.4), 8.03 (1 H, br s, NH) [d]	455.33	456 (M⁺ + 1, 11%), 455 (M⁺, 22), 454 (M − 1, 16), 376 (67), 374 (74), 77 (88) 76 (100)	C = 52.75 H = 2.88 N = 9.23	C = 52.65 H = 2.9 N = 9.25
8a (C₂₁H₁₇N₃O)	187–188 [b]	3250 1595 1570	4.73 (1 H, s, aminic NH), 6.62 (2 H, dq, Ph, J 7.5, 1.1), 6.76 (1 H, t, Ph, J 7.3), 6.87–6.94 (4 H, m, Ph), 6.96 (1 H, d, Ph, J 6.7), 7.03 (1 H, d, Ph, J 7.3), 7.09–7.17 (2 H, m, Ph), 8.09 (1 H, d, Ph, J 7.9), 7.51–7.56 (2 H, m, Ph), 7.48 [1 H, s, –CH=N(O)–], 11.8 (1 H, s, indolic NH) [e]	327.38	327 (M⁺, 6%), 311 (71), 310 (87), 219 (42), 218 (46), 77 (100)		
9a (C₂₀H₁₅N₃O)	183–184 [b]	1615 1590 1580	6.86 (0.64 H, d, Ph, J 1.83), 6.05 (0.86 H, d, Ph, J 7.8), 6.57 (0.26 H, d, Ph, J 7.8), 6.8 (1 H, t, Ph, J 7.7), 7.05 (0.3 H, d, Ph, J 7.4), 7.2 (1 H, m, Ph), 7.36 (2.2 H, t, Ph, J 7.9), 7.44 (2.2 H, t, Ph, J 9.1), 7.62–7.53 (3.3 H, m, Ph), 7.76–7.67 (3.4 H, m, Ph), 7.92 (3.3 H, d, Ph, J 7.74), 8.84 (0.1 H, dd, Ph, J 1.14, 4.5), 11.7 (0.3 H, br s, NH), 12.2 (1.7 H, br s, NH) [d,f]	313.35	313 (M⁺, 40%), 297 (88), 296 (100), 220 (35), 77 (71)	C = 76.65 H = 4.82 N = 13.41	C = 76.7 H = 4.8 N = 13.5
10 (C₁₉H₁₈N₂)	234–235 [b]	3400 3350	2.36 (6 H, s, Me), 4.1 (2 H, broad, –CH₂–), 6.9–7.41 (8 H, m, Ph), 7.7 (2 H, broad, 2 NH) [d]	274.35	274 (M⁺, 40%), 259 (21), 143 (100), 130 (33)	C = 83.13 H = 6.61 N = 10.21	C = 83.1 H = 6.7 N = 10.2
12 (C₁₈H₁₆N₂O)	217–219 [b]	3420 3230 1665 1570	1.73 (3 H, s, Me), 2.43 (3 H, s, Me), 4.10 (1 H, br s, NH), 6.66–7.81 (6 H, m, Ph), 8.10 (1 H, br s, NH), 8.30–8.37 (2 H, m, Ph) [d]	276.33	276 (M⁺, 70%), 261 (100), 247 (55), 233 (73), 157 (53)	C = 78.24 H = 5.84 N = 10.14	C = 77.8 H = 5.9 N = 10.05
17a (C₂₁H₁₅N₃O)	/	/	6.50 (1 H, td, Ph, J 7.5, 1.0), 6.71 (1 H, d, Ph, J 7.0), 6.82–7.01 (9 H, m, Ph), 7.47–7.52 (2 H, m, Ph), 7.66 (1 H, d, Ph, J 7.7), 8.52 [1 H, s, – CH=N(O)–]ᵉ	325.37	327 (M⁺, 7%), 310 (36), 218 (57), 69 (100)		

[a] From petroleum ether. [b] From ethanol. [c] From benzene. [d] In CDCl₃. [e] In C₆D₆. [f] Data show that this compound in solution is an equilibrium of two tautomeric forms.

Scheme 2

Scheme 3

Scheme 4
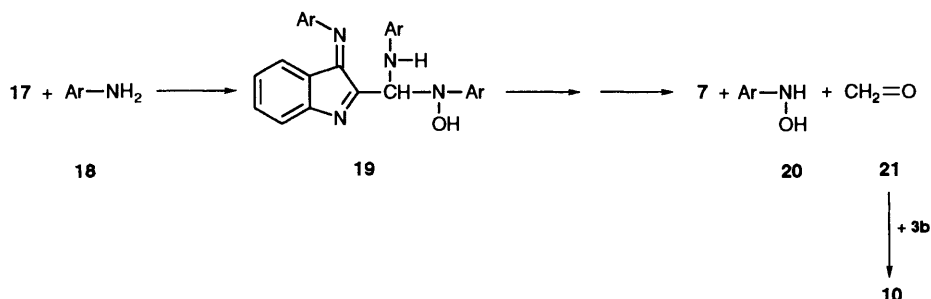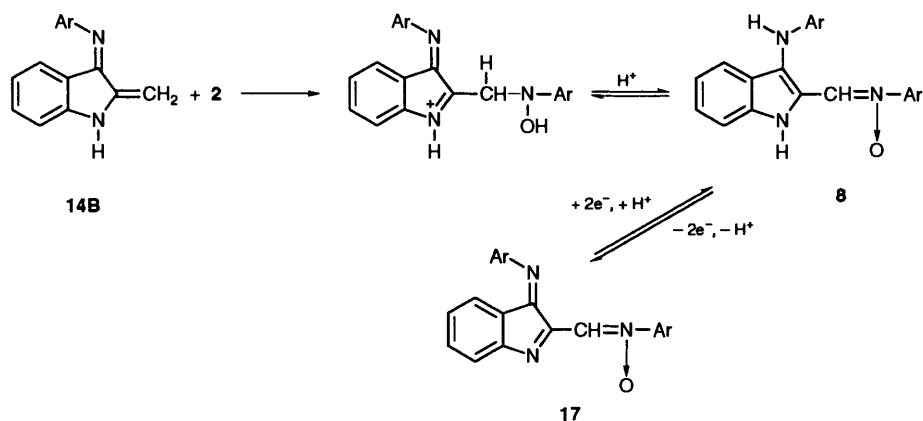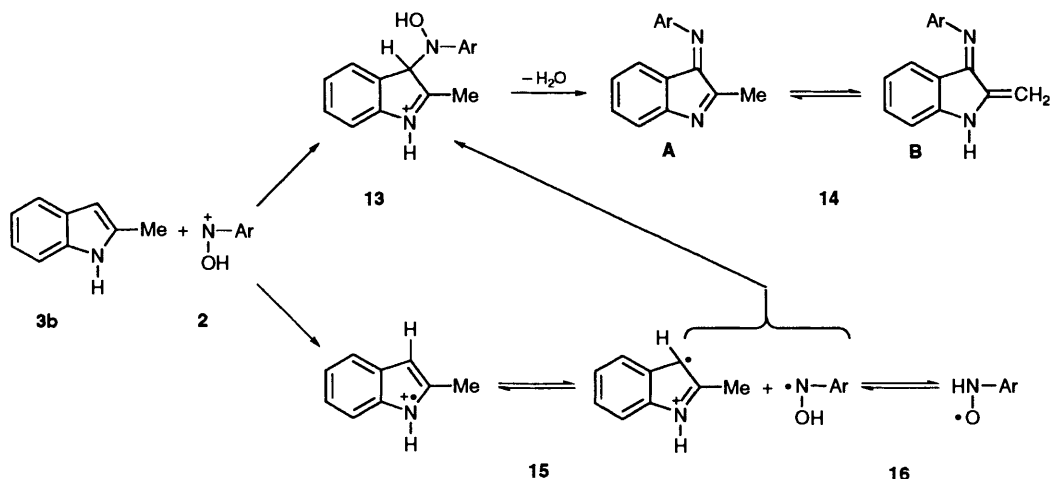
bond; (iv) the interaction between the indole radical cation or indolyl radical and oxygen; (v) the demethylation of 2-methylindole.

Gassman and others suggested that nitrenium ions are involved as intermediates in the reactions of N-hydroxy- and N-chloro-aniline derivatives,[11] as well as aryl azides in acidic media.[12] However, it was successively reported that nitrenium ions do not exist as stable species[13] and in particular it was demonstrated that nitrosobenzenes in the presence of strong acids react through the formation of iminiumbenzenium dications rather than nitrenium ions.[14] More recently, it was reported that nitrenium ions are the intermediates in several chemical reactions and are the putative carcinogen agents formed in vitro from aromatic amines.[15] Aryl nitrenium ions, like those proposed in the present paper, have been widely studied both from the chemical and computational point of view.[16] Although aryl nitrenium ions were described as an iminic structure with a positive charge mainly localized on the

aromatic ring,[17] they can react with nucleophilic substrates forming carbon–carbon bonds as well as carbon–nitrogen bonds.[17,18] This kind of reactivity is in agreement with our results and in contrast with the supposition that aryl nitrenium ions cannot attack nucleophiles because their singlet state, which is able to give this reaction, is immediately converted into their unreactive triplet state.[12]

Our results confirm that the first step of the reaction involves the formation of a carbon–nitrogen bond as shown in Scheme 2 and that the resulting σ-complex 13 could be formed either by a direct attack of the activated nitroso derivative 2 on 2-methylindole 3b or by coupling of the indole radical cation 15 and the phenylnitroxide 16.

Compounds such as azoxy derivatives 6, dimer 11 and indoxyl 12 may be explained on the basis of the formation of radicals 15 and 16 (Scheme 2). The reaction between 2-methylindole 3b and nitrosobenzene in the presence of mono-chloroacetic acid, carried out in the EPR cavity, gave the

Table 3 Selected bond distances (Å), angles (°) and torsion angles (°) with esds in parentheses

| | 7a | 7b | 9a | 10, A = C | |
	X = 1 A = N	X = 1 A = N	X = 1 A = N	X = 1	X = 2
O(1)-A(30)			1.295(2)		
N(X1)-C(X1)	1.300(3)	1.292(3)	1.308(2)	1.384(2)	1.384(3)
N(X1)-C(X8)	1.428(3)	1.425(3)	1.416(3)	1.371(2)	1.370(2)
A(19)-C(X1)	1.342(2)	1.346(3)	1.350(3)	1.487(3)	1.491(3)
A(19)-C(41)	1.406(2)	1.409(2)	1.406(2)		
A(30)-C(X2)	1.273(3)	1.273(3)	1.317(2)	1.510(2)	1.510(2)
A(30)-C(31)	1.414(2)	1.420(2)	1.455(3)		
C(X1)-C(X2)	1.506(2)	1.511(2)	1.479(3)	1.369(2)	1.374(2)
C(X2)-C(X3)	1.469(2)	1.476(3)	1.458(3)	1.432(2)	1.436(2)
C(X3)-C(X4)	1.393(3)	1.391(3)	1.389(3)	1.398(3)	1.402(2)
C(X3)-C(X8)	1.405(3)	1.404(3)	1.412(3)	1.417(2)	1.415(2)
C(X4)-C(X5)	1.392(3)	1.383(3)	1.388(3)	1.372(3)	1.375(3)
C(X5)-C(X6)	1.386(3)	1.386(3)	1.382(3)	1.397(3)	1.400(4)
C(X6)-C(X7)	1.397(3)	1.391(3)	1.385(3)	1.375(3)	1.370(5)
C(X7)-C(X8)	1.380(3)	1.378(3)	1.380(3)	1.393(3)	1.392(3)
C(X1)-N(X1)-C(X8)	105.0(2)	105.4(2)	105.6(2)	109.7(2)	110.3(2)
C(X1)-A(19)-C(41)	130.2(2)	130.1(2)	129.5(2)		
O(1)-A(30)-C(X2)			123.6(2)		
O(1)-A(30)-C(31)			114.7(1)		
C(X2)-A(30)-C(22)				116.1(1)	
C(X2)-A(30)-C(31)	120.3(2)	121.2(2)	121.7(2)		
N(X1)-C(X1)-A(19)	128.8(2)	128.7(2)	127.5(2)	120.1(2)	120.5(2)
N(X1)-C(X1)-C(X2)	113.9(2)	113.9(2)	112.4(2)	109.1(2)	108.7(2)
A(19)-C(X1)-C(X2)	117.3(2)	117.5(2)	120.1(2)	130.8(2)	130.8(2)
A(30)-C(X2)-C(X1)	120.6(2)	119.9(2)	124.9(2)	127.4(2)	128.3(2)
A(30)-C(X2)-C(X3)	136.7(1)	137.5(2)	130.1(2)	125.7(1)	124.9(2)
C(X1)-C(X2)-C(X3)	102.8(1)	102.5(2)	105.0(2)	106.9(1)	106.9(2)
C(X2)-C(X3)-C(X8)	104.9(1)	104.7(2)	103.5(2)	107.3(1)	107.5(2)
C(X4)-C(X3)-C(X8)	121.2(2)	120.4(2)	120.6(2)	118.4(2)	118.6(2)
C(X3)-C(X4)-C(X5)	117.9(2)	118.6(3)	118.3(2)	119.8(2)	119.0(3)
C(X4)-C(X5)-C(X6)	120.5(2)	120.6(2)	120.8(2)	120.9(3)	121.5(3)
C(X5)-C(X6)-C(X7)	121.9(2)	121.4(2)	121.5(2)	121.2(2)	121.0(2)
C(X6)-C(X7)-C(X8)	117.8(2)	118.1(3)	118.5(2)	118.0(2)	118.0(3)
N(X1)-C(X8)-C(X3)	113.5(2)	113.5(2)	113.5(2)	106.9(2)	106.7(2)
C(X3)-C(X8)-C(X7)	120.7(2)	120.9(2)	120.4(2)	121.7(2)	122.0(3)
A(19)-C(X1)-C(X2)-A(30)	0.7(2)	−4.8(2)	3.0(3)	−0.7(3)	−1.2(3)
N(X1)-C(X1)-A(19)-C(41)	2.9(3)	−2.4(3)	−0.1(4)		
O(1)-A(30)-C(X2)-C(X1)			0.4(3)		
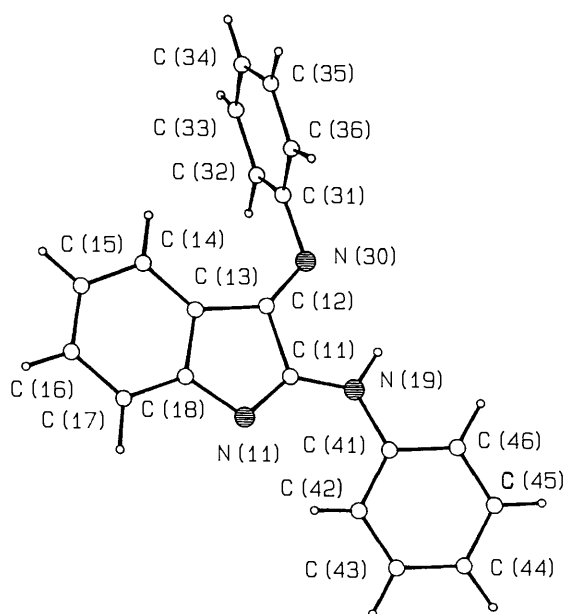
Fig. 1 Perspective view of 7a with the atomic numbering scheme
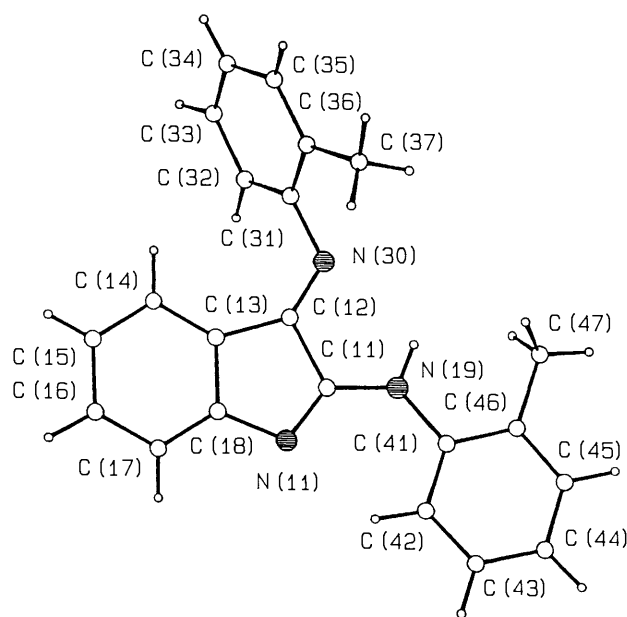
Fig. 2 Perspective view of 7b with the atomic numbering scheme

signal of phenyl nitroxide. This result together with the formation of azoxy compounds support the radical com-

ponent of these reactions (Scheme 5). The formation of the dimer 11 could be explained by the dimerization of the indole
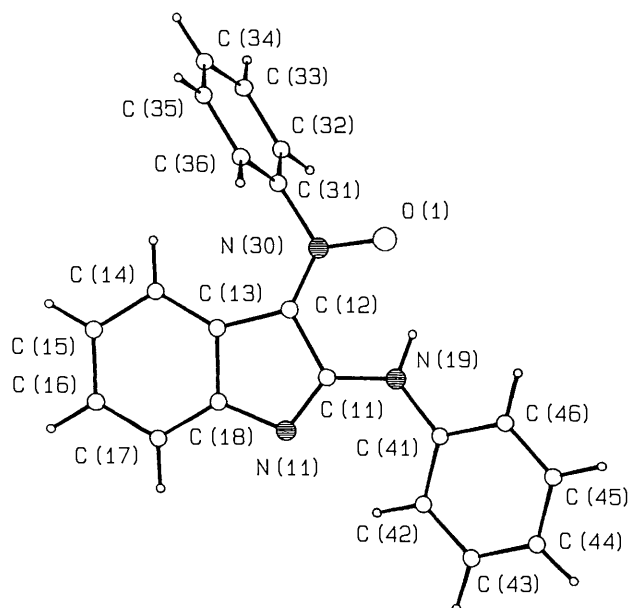
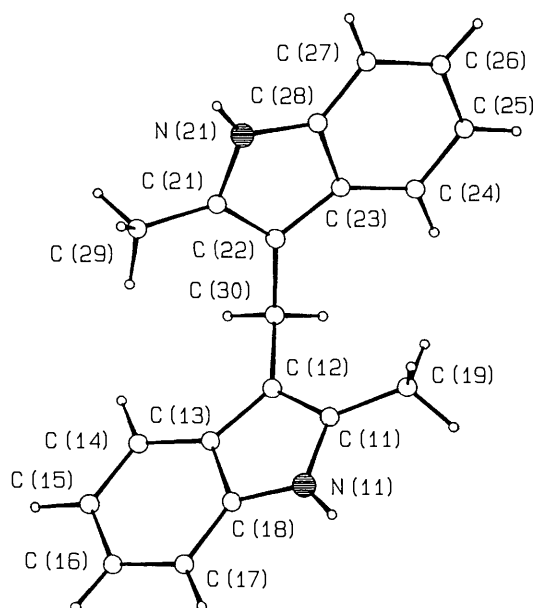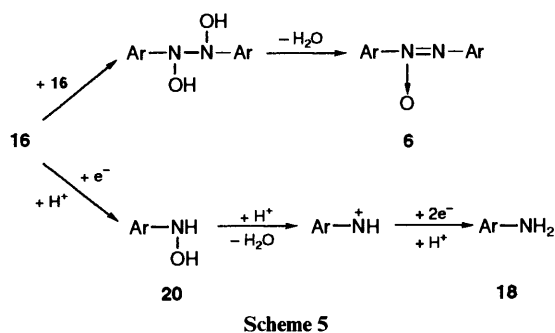Fig. 3 Perspective view of **9a** with the atomic numbering scheme

Fig. 4 Projection of **10** along the pseudo twofold axis with the atomic numbering scheme

Scheme 5

radical cation **15** or by its interaction with the free base **3b**.[19] These two mechanistic proposals cannot exclude that dimerization may also occur *via* coupling of the indolyl radical formed by deprotonation of the corresponding radical cation.[20] Similarly the formation of indoxyl **12**, could be explained by the intermediate formation of the indole radical cation **15** or of the

corresponding indolyl radical and their interaction with oxygen.[21,22] This interpretation is supported by the fact that when the reaction is carried out under nitrogen only traces of indoxyl **12** were isolated, whereas **12** is the main product when the reaction is performed in the presence of air (Table 1). The σ-complex **13** (Scheme 2) rearranges to form compound **14**, whose tautomeric form **14B** undergoes the electrophilic attack by another molecule of nitrenium ion **2** to form compound **8** through the formation of an additional carbon–nitrogen bond (Scheme 3). The latter compound may be oxidized to **17** in the reaction mixture. The two tautomeric forms **14A** and **14B** of the intermediate **14** and their reactivity, have already been described.[4a,7]

The formation of compounds **7** may be explained by the nucleophilic addition of anilines **18** to compounds **17**. The formed aminal **19** rearranges further to give **7**, hydroxylamines **20** and the formaldehyde **21** (Scheme 4). The presence of anilines **18** in the reaction mixture could be justified by reduction of the aryl nitroxide intermediates **16**.[23] The mechanism proposed in Scheme 4 and already described,[24] is supported further by the fact that compound **17**, generated in solution (see Experimental), reacted with aniline and 2-methylindole in the presence of monochloroacetic acid, to give compound **7a** and diindolylmethane **10**. The formation of **10** evidenced the presence of formaldehyde. In fact 2-methylindole reacts with formaldehyde, in the presence of monochloroacetic acid, affording diindolylmethane in good yield (see Experimental).

Compound **9** could be explained through the intermediate **22**, which could be easily formed from the σ-complex **13** by deprotonation (Scheme 6). Compounds such as **22** in general lose water very quickly;[25] in this case the loss of water is in competition with an oxidation process, which leads to the formation of compound **23**, whose tautomeric form **23B** affords compound **9** as compound **14B** affords compound **7** (Schemes 3 and 4).

Conclusions

The reactions of 2-methylindole with nitrosobenzenes activated with acid cannot be considered of synthetic value owing to the great number of products formed and the difficulties in their separation. However, these results may support the presence of nitrenium ions as intermediates through the formation of carbon–nitrogen bonds. The reaction products distribution, in particular the formation of the azoxy derivatives **6**, the dimer **11** and the indoxyl **12**, supports the electron-transfer process operating in competition with the electrophilic attack.

Experimental

Melting points were measured on an electrothermal apparatus and are uncorrected. IR spectra were recorded in Nujol mulls on a Perkin–Elmer 298 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer. Mass spectra were recorded in EI[+] mode on a Carlo Erba QMD 1000 GC-MS spectrometer equipped with a direct probe apparatus. EPR spectra were recorded at room temp. on a Varian E4 spectrometer.

2-Methylindole, nitrosobenzene and *o*-nitrosotoluene were Fluka and Aldrich commercial products, respectively. *p*-Bromonitrosobenzene was prepared according to literature.[26]

*Reactions of 2-Methylindole **3b** and Nitrosobenzenes **1a–c**. General Procedure.*—A solution of 2-methylindole (1.31 g, 10 mmol) in 10 cm³ of CH$_2$Cl$_2$ was added in 5–10 min to a solution of nitrosobenzenes (10 mmol) and monochloroacetic acid (16 mg, 0.16 mmol) in 15 cm³ of CH$_2$Cl$_2$ dropwise at room temp. and under stirring. The starting green solution turned brown–

Scheme 6
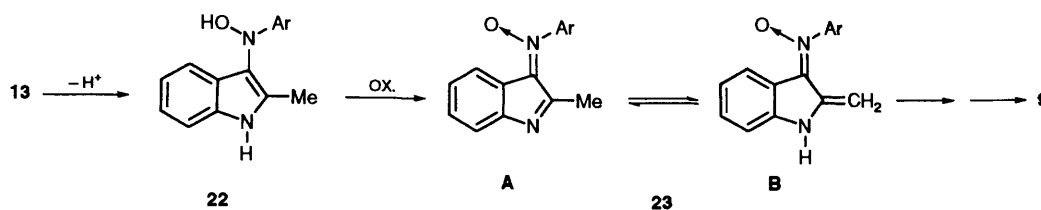
yellow, red and deep red after 20 min. After 2 h the reaction mixture was poured into 10% aqueous $NaHCO_3$ (50 cm^3). The organic layer was separated and the aqueous one extracted with CH_2Cl_2 (2 × 25 cm^3). The combined organic layers were dried on Na_2SO_4, evaporated to dryness and the residue taken up with 5–10 cm^3 of benzene and chromatographed on SiO_2 column eluting with cyclohexane–ethyl acetate 9:1. Yields are reported in Table 1 and spectroscopic data in Table 2.

The reaction of 2-methylindole and nitrosobenzene in the absence of oxygen was carried out in a nitrogen atmosphere starting from deaerated solutions by nitrogen bubbling.

Synthesis of Azoxybenzenes **6a–c.** *General Procedure.*— Samples of azoxybenzenes for comparison were prepared as follows: nitrosobenzenes (1 mmol in 5 cm^3 of benzene) and 2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine (the Hautzch's ester) (124 mg, 0.5 mmol in 5 cm^3 of benzene) were mixed at room temp. After 12 h the reaction mixture was evaporated to dryness and the residue chromatographed on preparative silica gel plates eluting with cyclohexane–ethyl acetate 9:1. Azoxybenzene and 2,6-dimethyl-3,5-dicarbethoxypyridine were isolated in almost quantitative yield. Spectroscopic data of the isolated azoxybenzenes are reported in Table 2.

Synthesis of bis(2-methyl-1H-indol-3-yl)methane **10.** Gaseous formaldehyde, obtained by thermal decomposition of *p*-formaldehyde (500 mg, 5.5 mmol), was bubbled into a solution of 2-methylindole (0.655 mg, 5 mmol) and monochloroacetic acid (16 mg, 0.16 mmol) in 10 cm^3 of CH_2Cl_2 at room temp. and under stirring. A white crystalline precipitate was filtered off after 2 h, yielding 0.62 g (90%) of 2,2'-dimethyl-3,3'-diindolyl-methane **10** (mp 233–4 °C from ethyl alcohol).

Synthesis of the intermediate **17.** Compound **17** can be formed by oxidation of compound **8** with lead dioxide. Since compound **17** is very difficult to isolate in the solid state but enough persistent in solution, it was generated quantitatively *in situ* in the NMR tube by PbO_2 oxidation of a solution of **8** in C_6D_6. The resulting ^1H NMR spectrum showed the disappearance of the 8 NH signals together with a characteristic shift of the signal attributed to the –CH=N ⟶ O proton. The same solution was tested on GC-MS (see Table 2).

Reaction of the intermediate **17** *with aniline and 2-methylindole in the presence of monochloroacetic acid.* Compound **8** (250 mg, 0.77 mmol) in 20 cm^3 of CH_2Cl_2 was treated with PbO_2 (1 g, 4.18 mmol) under stirring for 20 min and then filtered. To the resulting filtrate a solution of 2-methylindole (201 mg, 1.5 mmol), aniline (71 mg, 0.77 mmol) and monochloroacetic acid (7 mg, 0.075 mmol) in 10 cm^3 of CH_2Cl_2 was added and the reaction was monitored by TLC; the formation of compounds **7a** (the dianil of isatin) and **10** (the diindolylmethane) was observed together with compound **8** (the precursor of the intermediate **17**). After 2 h the reaction was worked up as described in the General procedure. Compounds **7a**, **10** and **8** were isolated by chromatography on preparative silica gel plates eluting with cyclohexane–ethyl acetate 7:3.

EPR Experiment.—2-Methylindole (10 mg in 1 cm^3 of CH_2Cl_2) and nitrosobenzene (10 mg in 1 cm^3 of CH_2Cl_2 together with traces of monochloroacetic acid), were separately

placed in the two legs of an inverted U cell,[27] and degassed carefully with nitrogen. The solutions were mixed in the aqueous cell, and after a few seconds, the solution turned brown–yellow and a rather intense signal was recorded. The EPR signal was computer-simulated with the following set of HFCCS: a^N = 9.5 G (1N); a^H = 12.6 G (1H); a^H = 3.0 G (3H); a^H = 1.0 G (2H), which are in agreement with those reported in the literature for the phenylnitroxide **16**.[28]

Oxidation Potential of 2-Methylindole **3b.**—A three-electrode multifunction assembly[29] was employed for the polarographic and cyclic voltammetric measurements. The oxidation potential of compound **3b** (10^{-3} mol dm^{-3}) was measured in MeCN using Et_4NClO_4 (0.1 mol dm^{-3}) as supporting electrolyte.

Crystal Structure of 2-Phenylamino-3-phenylimino-3H-indole **7a.**—Crystals were dark-red prisms. Lattice parameters were determined using a program 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 move less than 0.01°.

Crystal data. $C_{20}H_{15}N_3$, M = 297.4. Monoclinic a = 16.781(3), b = 11.166(2), c = 8.217(2) Å, β = 95.7(1)°; U = 1532.1(6) Å^3; Z = 4, D_c = 1.29 g cm^{-3}; Cu-Kα radiation λ = 1.5418 Å; μ = 6.1 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5 No. 14) from systematic absences.

X-Ray measurements were performed at T = 295 K on a Siemens AED single-crystal diffractometer in the range 3 ≤ θ ≤ 70° using Ni-filtered Cu-Kα radiation. The angles for every reflection were determined on the basis of the orientation matrix and the outline of the diffraction peak was collected in the θ–2θ step scanning mode using a scan width from $(\theta - 0.60)°$ to $(\theta + 0.60 + \Delta\lambda/\lambda tg\theta)°$. The intensities I_{hkl} were determined by analysing the reflection profiles.[30] 3267 Independent reflections ($-20 \leq h \leq 20$, $0 \leq k \leq 13$, $0 \leq l \leq 10$) were measured of which 2407 (internal R merging factor 0.027) having $I_{hkl} > 2\sigma(I_{hkl})$ [$\sigma(I)$ 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 variations. Intensities I_{hkl} were corrected for Lorentz and polarization effects. The dimensions of the crystal were 0.29, 0.48, 0.57 mm. No absorption corrections were applied.

Structure analysis and refinement. The structure was solved by direct methods using the SHELXS86 program[31] and refined by SHELX76[32] with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to R = 0.043, R_w = 0.055; the weighting function was of the form $1/w = \sigma^2(F_o) + 0.0030F_o^2$.

Crystal Structure of 2-(o-Tolylamino)-3-(o-tolylimino)-3H-indole **7b.**—Crystals were dark-red prisms. Cell parameters were derived as before.

Crystal data. $C_{22}H_{19}N_3$, M = 325.4. Monoclinic a = 12.732(3), b = 19.367(4), c = 7.226(2) Å, β = 97.6(1)°, U = 1766.1(9) Å^3; Z = 4, D_c = 1.22 g cm^{-3}, Cu-Kα radiation λ =

1.5418 Å, μ = 5.7 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5 No. 14) from systematic absences.

Intensity data were collected as before. Of the 3731 measured reflections ($-15 \le h \le 15, 0 \le k \le 23, 0 \le l \le 8$) 2247 symmetry-independent were used in the crystal analysis. The dimensions of the crystal were 0.24, 0.17, 0.43 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 = 0.043, R_w = 0.046. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.0043F_c^2$.

Crystal Structure of N-*Phenyl*-N-(2-*phenylamino*-3H-*indol*-3-*ylidene*)*amine* N-*Oxide* **9a**.—Crystals were dark-red–violet prisms. Cell parameters were derived as before.

Crystal data. $C_{20}H_{15}N_3O$, M = 313.4. Monoclinic a = 16.808(3), b = 8.110(2), c = 11.824(2) Å, β = 98.4(1)°, U = 1594.5(7) Å^3; Z = 4, D_c = 1.31 g cm^{-3}, Cu-Kα radiation λ = 1.5418 Å, μ = 6.6 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5 No. 14) from systematic absences.

Intensity data were collected as before. Of the 3411 measured reflections ($-20 \le h \le 20, 0 \le k \le 9, 0 \le l \le 14$) 1914 symmetry-independent were used in the crystal analysis. The dimensions of the crystal were 0.24, 0.31, 0.50 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 = 0.035, R_w = 0.037. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.0027F_o^2$.

Crystal Structure of 2,2'-*Dimethyl*-3,3'-*diindolylmethane* **10**.—Crystals were colourless flattened prisms. Cell parameters were derived as before.

Crystal data. $C_{19}H_{18}N_2$, M = 274.4. Monoclinic a = 15.903(3), b = 7.608(2), c = 11.892(3) Å, β = 91.6(1)°, U = 1438.3(6) Å^3; Z = 4, D_c = 1.27 g cm^{-3}, Cu-Kα radiation λ = 1.5418 Å, μ = 5.7 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5 No. 14) from systematic absences.

Intensity data were collected as before. Of the 3097 measured reflections ($-19 \le h \le 18, 0 \le k \le 9, 0 \le l \le 14$) 2031 symmetry-independent were used in the crystal analysis. The dimensions of the crystal were 0.21, 0.12, 0.43 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 = 0.043. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.0025F_o^2$.

All the hydrogen atoms were located in the difference-Fourier map. Atomic scattering factors from the *International Tables for X-Ray Crystallography*.[33]

All the calculations were carried out on the GOULD 6040 POWERNODE computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. of Parma and the Cambridge Crystallographic Data files were used for bibliographic searches through the Servizio Italiano di Diffusione Dati Cristallografici di Parma.

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