Competition between Nucleophilic Attack and Electron Transfer in the Reaction of Indoledione Imine *N*-Oxides with Primary Aromatic Amines

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2-Methyl-3,5-dioxo-2-phenyl-3,5-dihydro-2*H*-indole 1-oxide (**1**) and 2-methyl-3,7-dioxo-2-phenyl-3,7-dihydro-2*H*-indole 1-oxide (**11**) react with primary aromatic amines to form products of mono- (**5**) and di-substitution (**8**), (**9**), and (**12**) and reduction (**6**). The reaction proceeds through several steps and a competition between nucleophilic attack and electron transfer (ET) may take place when amines characterized by a low oxidation potential, such as *p*-anisidine, are involved. Some mechanistic considerations are drawn based on ESR results and the $E_{\frac{1}{2}}$ values of the oxidation and reduction potentials of the starting compounds, and the possibility is stressed that ET occurs at different stages of the reaction. It is conceivable that the disubstitution products (**8**) and (**9**) originate from the same intermediate (**7**), the formation of which remains a puzzle. The structures of compounds (**5a**), (**6**), (**9a**), and (**12**) have been determined by crystal X-ray analysis.

The reactivity of quinonoid compounds towards alcohols and phenols has been extensively studied [1] and a substantial amount of work has been devoted to the study of solvent effects,[2] and the action of metal ions,[3,4] and to the elucidation of the reaction mechanism. Evidence has been found to support the formation of charge-transfer complexes [5] and outer- and inner-sphere complexes,[6] the occurrence of electron-transfer,[7] and the formation of adducts.[8,9]

In a recent paper we described the occurrence of a reaction between primary aromatic amines and quinone di-imine *N*-oxides, formed from the combination of aminyl radicals and indolinonic nitroxides.[10] We report in the present paper a more detailed study of the reactions of quinone imine *N*-oxides (**1**) and (**11**) with primary aromatic amines, which lead to products resulting from reduction or mono- and di-substitution. The $E_{\frac{1}{2}}$ values of the starting reactants indicate that the occurrence of ET in the first reaction step with aniline and *p*-chloroaniline is unlikely, but do not rule out its occurrence with *p*-anisidine. Nevertheless, the recovery of product (**6**) in the reaction with the former two amines suggests that the ET can take place at a different stage, in particular between intermediate (**3**) and the starting *N*-oxide (**1**).

Results

Compound (**1**) reacts with substituted anilines (**2a**–**c**) at room temperature and in presence of silica gel or acetic acid to form compounds (**5a**–**c**), (**6**), (**8b**, **c**), and (**9a**–**c**) (Schemes 1 and 2) with the yields reported in Table 1. The structures of compounds (**5a**), (**6**), and (**9a**) were determined by X-ray analysis, while those of all other compounds (**5**), (**8**), and (**9**) were assigned on the basis of their analytical and spectroscopic data by comparison with those of compounds (**5a**) and (**9a**).

Compounds (**5a**–**c**) show, in their IR spectra, a band at *ca.* 3 280 cm^{-1} due to the NH of the arylamino group at C-4, two intense bands at *ca.* 1 720 and 1 600 cm^{-1} typical of the C=O at C-3 and of the indoline Ph–N(O)C– group respectively,[11] and in the 1 600–1 500 cm^{-1} region other bands typical of the quinonoid structure. Their ^{1}H NMR spectra are in agreement with the assigned structures; in particular, while for compounds (**5b**, **c**) the two doublets due to 6-H and 7-H could be observed at δ 6.9 and 7.9, respectively, for compound (**5a**) only the 7-H doublet was clearly visible. All compounds (**5a**–**c**) were contaminated by traces of nitroxides (**10a**–**c**) (Table 2), the amount of which could be increased by treating solutions of (**5**) with phenylhydrazine (0.5 equiv; see the Experimental). Conversely, the nitroxides (**10**) could be converted into the corresponding *N*-oxides (**5**) by addition of lead dioxide (Scheme 3).

Compounds (**9a**–**c**) show in their IR spectra the overlapping of a broad and a sharp band at *ca.* 3 250 cm^{-1} and two absorptions at *ca.* 1 600 and 1 700 cm^{-1} due to the Ph=N–C– of the indoline moiety [11] and to the C=O at C-3, respectively. The other bands in the 1 600–1 500 cm^{-1} region are typical of the quinonoid structures. The ^{1}H NMR spectra of compounds (**9a**–**c**) provide interesting information about their structures. In fact, each compound shows the singlet of the C-2 methyl at δ 1.7, the

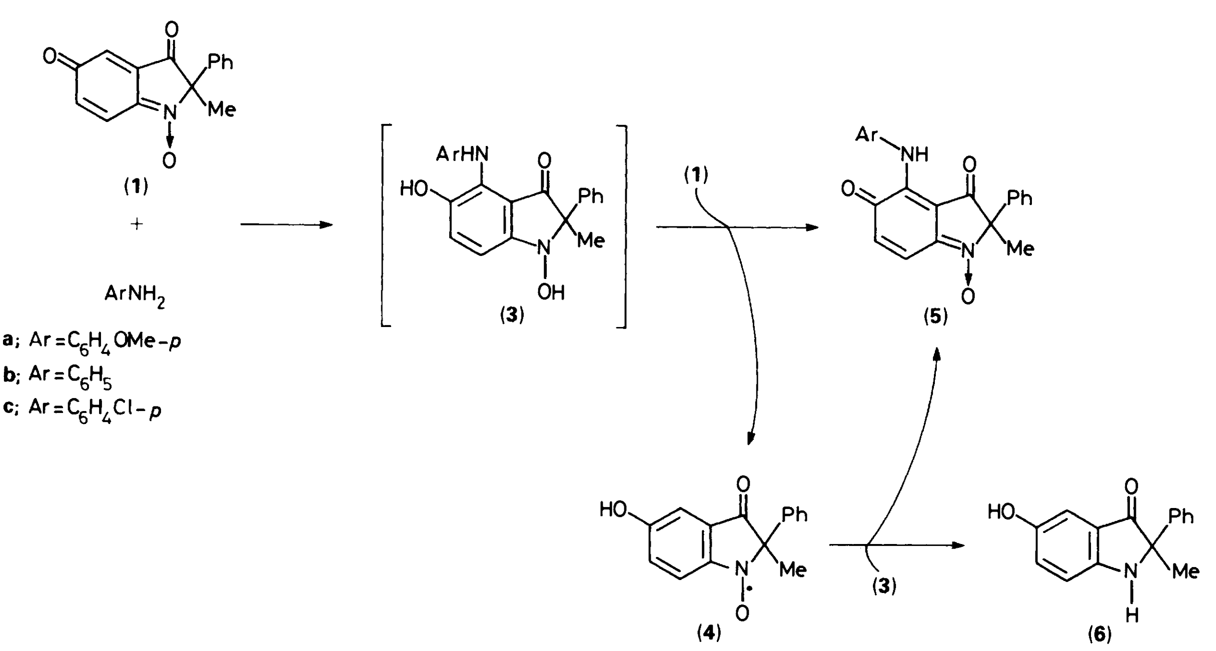
Table 1. Percentage yields of products of the reaction between (**1**) and (**2a**–**c**).

Reagents	Products (% yield)			
(**1**) + (**2a**)	(**5a**) (39.9)	(**6**) (29.5)	(**8a**) (0)	(**9a**) (15.3)
(**1**) + (**2b**)	(**5b**) (41.9)	(**6**) (19.1)	(**8b**) (5)	(**9b**) (22.9)
(**1**) + (**2c**)	(**5c**) (42.2)	(**6**) (20.1)	(**8c**) (7)	(**9c**) (12.7)

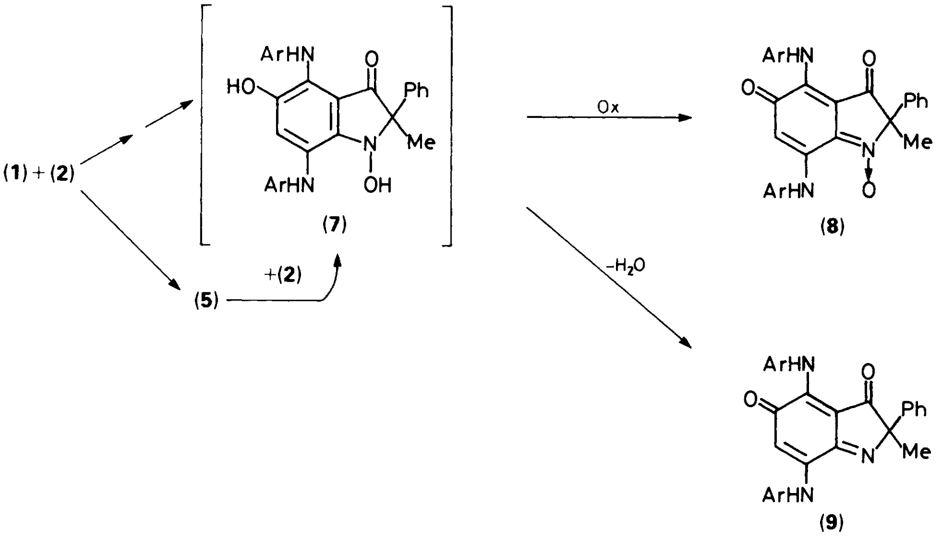
Table 2. Hyperfine coupling constants in CHCl$_3$ of nitroxides (**10a**–**c**).[a]

	a_N	$a_{6\text{-H}}$	$a_{7\text{-H}}$
(**10a**)	9.94	1.09	3.45
(**10b**)	9.97	1.08	3.36
(**10c**)	9.85	1.06	3.29

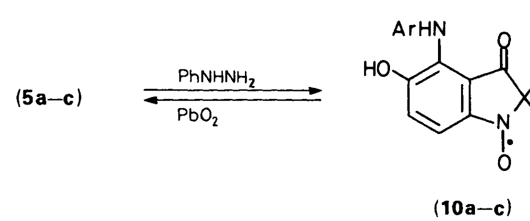
[a] All nitroxides show a *g*-factor of 2.0057.



Scheme 1.



Scheme 2.

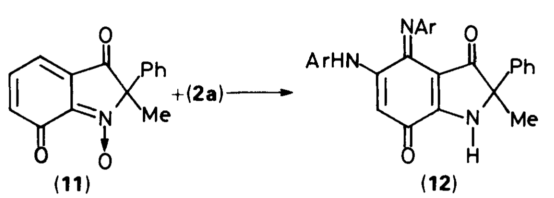


Scheme 3.

singlet from 6-H at *ca.* δ 6.2, and two broadened signals due to the two NH groups at δ 8.3 and 8.7, the former being broader than the latter. The IR spectra of compounds (**8b**, **c**) show a broad band at *ca.* 3 220 cm^{-1} for the two NH, and bands at 1 710 and 1 600 cm^{-1} due to the C=O at C-3 of the indoline moiety[11] and other bands in the range 1 600–1 500 cm^{-1} are typical of the quinonoid structure. Their NMR spectra show the signal of the C-2 methyl at *ca.* δ 1.9 and the singlet relative to 6-H falls at lower field with respect to that of (**9**). This reflects the presence of the *N*-oxide function, as evidenced by the similarity of the ^1H NMR data for compounds (**5**), which contain the same function and again show a C-2 methyl singlet at *ca.* δ 1.9 and 6-H doublets at *ca.* δ 6.9–7.8. The fact that the 6-H signals in (**5**) and (**8**) fall at low field is consistent with the presence of the *N*-oxide function, which exerts its electron-withdrawing effect on the conjugated C-6. The IR spectrum of compound (**6**) shows bands which agree with the OH (broad) and NH (sharp) absorptions, the C=O at C-3 and with the indoline structure.[11] Moreover the ^1H NMR spectrum shows two doublets and a *pseudo*-quartet, in line with the ABX system of the benzene ring of the indole nucleus. Compound (**6**) was also prepared by treating (**1**) with phenylhydrazine at room temperature and its structure was determined by X-ray analysis. Furthermore, a chloroform solution of (**6**) treated with *p*-nitroperbenzoic acid in the ESR cavity gave the signal of the nitroxide (**4**).

Compound (**11**), treated with *p*-anisidine (**2a**) under the same experimental conditions described for compound (**1**), afforded the di-*p*-anisidino derivative (**12**) (Scheme 4), the structure of which was determined by X-ray analysis.

The reaction of the *N*-oxide (**1**) and the amines (**2a**–**c**),



(11) (12)

Scheme 4.

Table 3. Bond distances/Å with estimated standard deviations in parentheses.

	(5a)	**(6)**	**(9a)**	**(12)**
O(1)–N(1)	1.272(4)			
O(2)–C(2)	1.207(4)	1.229(3)	1.226(5)	1.211(4)
O(3)–C(5)	1.238(5)	1.368(4)	1.247(7)	
O(4)–C(7)				1.245(3)
O(21)–C(24)	1.365(6)		1.370(5)	1.371(5)
O(21)–C(27)	1.426(9)		1.424(14)	1.398(7)
O(31)–C(34)			1.384(5)	1.361(5)
O(31)–C(37)			1.423(10)	1.423(8)
N(1)–C(1)	1.496(4)	1.469(4)	1.496(5)	1.457(4)
N(1)–C(8)	1.337(4)	1.368(4)	1.284(5)	1.328(3)
N(2)–C(4)	1.350(5)		1.335(6)	1.294(3)
N(2)–C(21)	1.406(5)		1.430(6)	1.413(4)
N(3)–C(5)				1.340(3)
N(3)–C(7)			1.323(6)	
N(3)–C(31)			1.437(6)	1.426(4)
C(1)–C(2)	1.547(5)	1.542(3)	1.533(7)	1.560(3)
C(1)–C(9)	1.519(6)	1.527(5)	1.531(10)	1.526(5)
C(1)–C(11)	1.532(5)	1.526(3)	1.507(8)	1.519(4)
C(2)–C(3)	1.456(4)	1.450(4)	1.461(6)	1.453(4)
C(3)–C(4)	1.375(5)	1.399(4)	1.355(8)	1.445(3)
C(3)–C(8)	1.440(5)	1.407(3)	1.451(7)	1.378(4)
C(4)–C(5)	1.494(5)	1.367(4)	1.536(6)	1.508(4)
C(5)–C(6)	1.441(6)	1.420(4)	1.400(6)	1.370(4)
C(6)–C(7)	1.338(5)	1.370(5)	1.370(6)	1.406(3)
C(7)–C(8)	1.416(5)	1.398(4)	1.483(6)	1.484(4)
C(11)–C(12)	1.390(5)	1.391(4)	1.388(7)	1.369(6)
C(11)–C(16)	1.368(5)	1.390(3)	1.386(8)	1.371(5)
C(12)–C(13)	1.382(7)	1.386(5)	1.397(12)	1.381(7)
C(13)–C(14)	1.380(7)	1.369(5)	1.369(12)	1.367(8)
C(14)–C(15)	1.373(6)	1.370(5)	1.395(9)	1.369(7)
C(15)–C(16)	1.393(6)	1.388(4)	1.389(11)	1.390(7)
C(21)–C(22)	1.386(6)		1.364(9)	1.378(5)
C(21)–C(26)	1.388(6)		1.388(8)	1.392(5)
C(22)–C(23)	1.399(6)		1.399(8)	1.375(4)
C(23)–C(24)	1.380(7)		1.364(9)	1.385(6)
C(24)–C(25)	1.386(6)		1.399(10)	1.371(7)
C(25)–C(26)	1.375(6)		1.351(8)	1.384(5)
C(31)–C(32)			1.401(7)	1.380(4)
C(31)–C(36)			1.368(8)	1.373(5)
C(32)–C(33)			1.368(6)	1.382(5)
C(33)–C(34)			1.363(8)	1.371(5)
C(34)–C(35)			1.372(7)	1.380(5)
C(35)–C(36)			1.375(7)	1.375(5)

carried out inside the cavity of an ESR spectrometer, gave an intense signal due to the nitroxide (**4**), more intense spectra being observable in polar solvents such as 1,2-dimethoxyethane. A careful computer simulation led to the following set of hfs constants: a_N 9.83, $a_{4\text{-H}}$ and/or $a_{6\text{-H}}$ 1.0 and/or 0.8, $a_{7\text{-H}}$ 2.82, $a_{\text{H,OH}}$ 0.18, $a_{\text{H,Me}}$ 0.2 G(3 H) (g = 2.0058).

Molecular Geometry.—Bond distances and bond angles for all the compounds are listed in Tables 3 and 4, respectively; Figures 1–4 show perspective views of the compounds (**5a**), (**6**), (**9a**), and (**12**), respectively together with the numbering schemes adopted in the crystal analysis. The conformational geometry can be defined in terms of the dihedral angles reported in Table 5. The analysis of the distribution of bond distances in the indolinone moiety, alternately short and long, involving the N(1) indolic nitrogen, the carbonyl group or the iminic substituent in the six-membered ring, suggests that this should be assigned a quinonic structure as indicated in Schemes 1, 2,

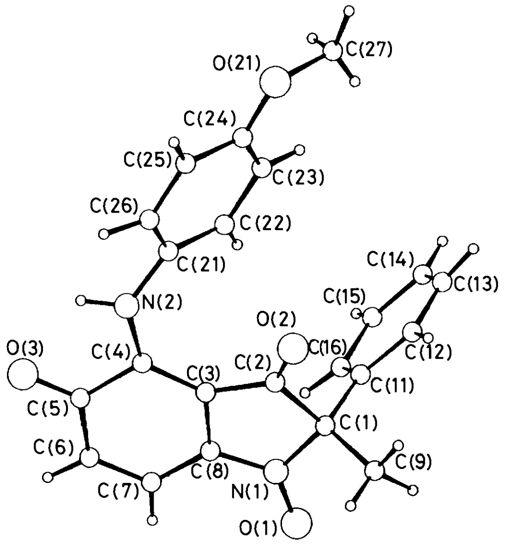


Figure 1. Perspective view of the 4-(*p*-methoxyphenylamino)-2-methyl-3,5-dioxo-2-phenyl-3,5-dihydro-2*H*-indole 1-oxide (**5a**).

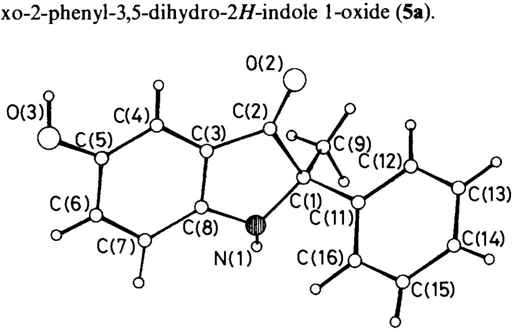


Figure 2. Perspective view of 2-methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-indole (**6**).

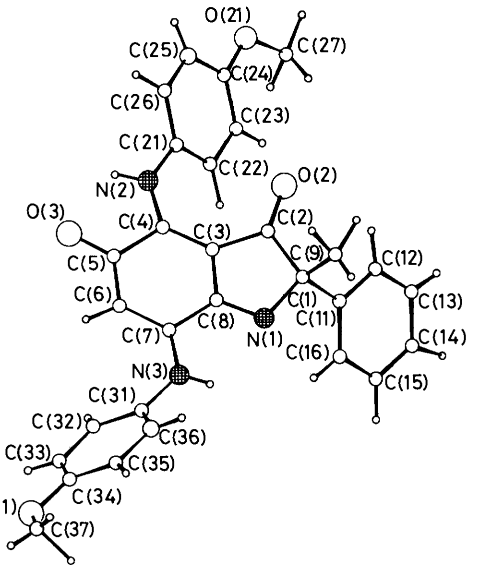


Figure 3. Perspective view of 4,7-di(*p*-methoxyphenylamino)-2-methyl-3,5-dioxo-2-phenyl-3,5-dihydro-2*H*-indole (**9a**).

Table 4. Bond angles/° with estimated standard deviations in parentheses

	(5a)	**(6)**	**(9a)**	**(12)**
C(24)–O(21)–C(27)	119.3(5)		119.5(7)	118.4(4)
C(34)–O(31)–C(37)			118.1(5)	118.1(5)
O(1)–N(1)–C(1)	121.7(4)			
O(1)–N(1)–C(8)	126.5(3)			
C(1)–N(1)–C(8)	111.8(3)	109.9(2)	107.2(4)	110.8(5)
C(4)–N(2)–C(21)	131.3(4)		131.9(6)	122.0(4)
C(5)–N(3)–C(31)				123.7(4)
C(7)–N(3)–C(31)			127.5(6)	
N(1)–C(1)–C(2)	101.1(3)	103.0(2)	105.1(4)	101.5(4)
N(1)–C(1)–C(9)	109.7(3)	111.0(2)	107.7(5)	110.8(4)
N(1)–C(1)–C(11)	110.4(3)	111.6(2)	111.3(5)	110.7(3)
C(2)–C(1)–C(9)	113.4(3)	109.4(2)	109.0(7)	110.9(3)
C(2)–C(1)–C(11)	106.8(3)	108.0(2)	113.3(5)	107.2(3)
C(9)–C(1)–C(11)	114.6(4)	113.4(2)	110.2(5)	114.9(3)
O(2)–C(2)–C(1)	123.6(3)	123.1(3)	124.2(4)	122.4(4)
O(2)–C(2)–C(3)	129.3(4)	129.2(2)	128.8(7)	131.3(4)
C(1)–C(2)–C(3)	107.1(3)	107.7(2)	106.4(5)	106.2(4)
C(2)–C(3)–C(4)	133.7(3)	131.5(2)	135.2(5)	132.9(5)
C(2)–C(3)–C(8)	106.6(3)	106.6(2)	103.6(5)	106.1(3)
C(4)–C(3)–C(8)	119.5(3)	121.8(3)	120.6(4)	120.3(4)
N(2)–C(4)–C(3)	129.6(3)		132.0(4)	130.5(6)
N(2)–C(4)–C(5)	112.8(4)		110.4(5)	114.6(3)
C(3)–C(4)–C(5)	117.6(4)	118.2(2)	117.5(6)	114.9(4)
O(3)–C(5)–C(4)	118.3(4)	124.6(2)	115.8(6)	
O(3)–C(5)–C(6)	122.8(4)	115.0(3)	123.9(4)	
N(3)–C(5)–C(4)				114.7(4)
N(3)–C(5)–C(6)				123.0(5)
C(4)–C(5)–C(6)	118.9(4)	120.4(3)	120.4(5)	122.3(4)
C(5)–C(6)–C(7)	122.7(4)	121.6(3)	122.6(4)	122.6(5)
O(4)–C(7)–C(6)				125.1(5)
O(4)–C(7)–C(8)				119.5(3)
N(3)–C(7)–C(6)			127.6(4)	
N(3)–C(7)–C(8)			115.2(5)	
C(6)–C(7)–C(8)	117.9(4)	118.7(3)	117.2(6)	115.3(4)
N(1)–C(8)–C(3)	111.3(3)	112.8(3)	117.4(4)	114.1(4)
N(1)–C(8)–C(7)	125.5(4)	127.8(2)	120.8(6)	121.9(4)
C(3)–C(8)–C(7)	123.2(4)	119.3(2)	121.7(6)	124.0(3)
C(1)–C(11)–C(12)	117.5(3)	120.4(2)	119.7(7)	121.6(3)
C(1)–C(11)–C(16)	122.5(4)	120.6(2)	121.9(4)	121.0(4)
C(12)–C(11)–C(16)	119.9(4)	119.0(2)	118.4(7)	117.3(4)
C(11)–C(12)–C(13)	119.5(4)	119.7(3)	120.4(7)	121.0(5)
C(12)–C(13)–C(14)	120.9(5)	121.0(3)	121.2(7)	121.2(6)
C(13)–C(14)–C(15)	119.2(5)	119.6(3)	118.5(10)	118.7(5)
C(14)–C(15)–C(16)	120.5(4)	120.4(3)	120.6(7)	119.5(5)
C(11)–C(16)–C(15)	120.1(4)	120.2(2)	120.9(5)	122.2(5)
N(2)–C(21)–C(22)	123.1(4)		121.4(6)	122.9(5)
N(2)–C(21)–C(26)	117.4(4)		118.8(6)	117.5(4)
C(22)–C(21)–C(26)	119.4(4)		119.6(5)	119.3(5)
C(21)–C(22)–C(23)	120.1(5)		119.7(9)	120.5(4)
C(22)–C(23)–C(24)	119.7(5)		120.2(7)	120.1(5)
O(21)–C(24)–C(23)	124.7(5)		124.0(6)	116.4(5)
O(21)–C(24)–C(25)	115.1(4)		116.4(6)	123.9(5)
C(23)–C(24)–C(25)	120.2(4)		119.7(5)	119.7(6)
C(24)–C(35)–C(26)	120.0(5)		119.7(9)	120.4(5)
C(21)–C(26)–C(25)	120.6(5)		121.1(9)	119.7(4)
N(3)–C(31)–C(32)			121.2(5)	120.6(4)
N(3)–C(31)–C(36)			120.1(5)	119.8(4)
C(32)–C(31)–C(36)			118.8(4)	119.7(4)
C(31)–C(32)–C(33)			119.5(6)	120.6(3)
C(32)–C(33)–C(34)			120.8(5)	119.6(4)
O(31)–C(34)–3(33)			115.9(4)	125.1(4)
O(31)–C(34)–C(35)			123.8(5)	115.3(4)
C(33)–C(34)–C(35)			120.4(4)	119.6(5)
C(34)–C(35)–C(36)			119.2(6)	120.8(4)
C(31)–C(36)–C(35)			121.4(6)	119.6(4)

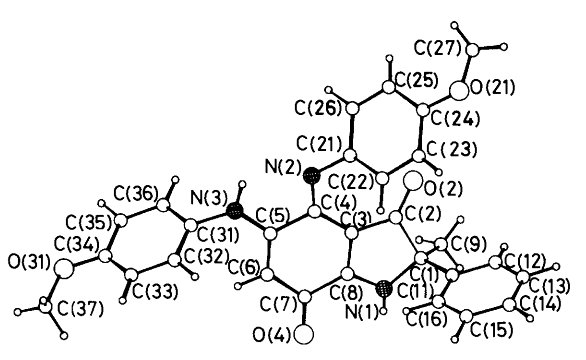


Figure 4. Perspective view of 5-(*p*-methoxyphenylamino)-4-(*p*-methoxyphenylimino)-3,7-dioxo-2-phenyl-3,7-dihydro-2*H*-indole (**12**).

and 4 for compounds (**5a**), (**9a**), and (**12**), respectively, the different values of the C(3)–C(4) and C(3)–C(8) bond distances being consistent with the different distribution of the double bonds in these compounds. A similar alternation of short and long bonds, indicative of analogous quinonic structures, has been observed for a structurally related quinone di-imine derivative previously studied.[10] Another peculiarity common to compounds (**5a**), (**9a**), and (**12**) is the presence of strong intramolecular hydrogen bonds of the type N–H$\cdots$O involving the carbonylic O(3) atom and the aminic nitrogen N(2) [O(3)$\cdots$N(2) 2.547(5), O(3)$\cdots$H(2) 2.05(6) Å, O(3)$\cdots$H(2)–N(2) 116.8(6.0)° in (**9a**); O(3)$\cdots$N(2) 2.610(4), O(3)$\cdots$H(2) 2.09(3) Å, O(3)$\cdots$H(2)–N(2) 115.5(3.1)° in (**5a**)] or the indolic N(1) atom [O(3)$\cdots$N(1) 2.799(3), O(3)$\cdots$H(1) 2.54(4) Å, O(3)$\cdots$H(1)–N(1) 100.3(2.5)° in (**12**)], and of type N–H$\cdots$N [N(3)$\cdots$N(1) 2.706(5), H(3)$\cdots$N(1) 2.39(4) Å, N(3)–H(3)$\cdots$N(1) 102.6(3.2)° in (**9a**) and N(3)$\cdots$N(2) 2.613(3), H(3)$\cdots$N(2) 2.12(3) Å, N(3)–H(3)$\cdots$N(2) 114.0 (2.5)° in (**12**)].

In agreement with the existence of intramolecular hydrogen bonding, significative differences have been observed for the external bond angles at C(4) in compound (**5a**) and at C(4) and C(7) in compounds (**9a**) and (**12**). Note that deviations from coplanarity of the two rings of the indolinone unit are vanishingly small for (**6**) where no intramolecular H-bonding is possible. Whether the more significant deviations found for compounds (**5a**), (**9a**), and (**12**) are an exclusive effect of H-bonding remains, however, a questionable point.

The molecular packing is determined by hydrogen bonds of the type N–H$\cdots$O [N(3)$\cdots$O(21)^{i} 2.999(9), H(3)$\cdots$O(21)^{i} 2.20(3) Å, N(3)–H(3)$\cdots$O(21)^{i} 157.8(3.0)° $i = \frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ in (**9a**); N(2)$\cdots$O(1)^{ii} 3.405(4), H(2)$\cdots$O(1)^{ii} 2.68(4) Å, N(2)–H(2)$\cdots$O(1)^{ii} 138.1(3.1)° $ii = 1 - x, \frac{1}{2} + y, 1 - z$ in (**5a**); N(1)$\cdots$O(2)^{iii} 3.436(3), H(1)$\cdots$O(2)^{iii} 2.60(4) Å, N(1)–H(1)$\cdots$O(2)^{iii} 159.3(3.4)° $iii = -x, \frac{1}{2} + y, -\frac{3}{2} - z$ in (**6**); N(1)$\cdots$O(3)^{iv} 2.814(3), H(1)$\cdots$O(3)^{iv} 2.07(3) Å, N(1)–H(1)$\cdots$O(3)^{iv} 153.0(3.2)° $iv = 1 - x, 2 - y, -z$ in (**12**)] and O–H$\cdots$O type [O(3)$\cdots$O(2)^{v} 2.693(3), H(3)$\cdots$O(2)^{v} 1.78(4) Å, O(3)–H(3)$\cdots$O(2)^{v} 169.9(3.6)° $v = -\frac{1}{2} - x, -1 - y, \frac{1}{2} + z$ in (**6**)]. Other contacts are consistent with van der Waals interactions.

Discussion

The presence among the reaction products of compound (**6**), which is derived from the reduction of (**1**) as demonstrated by treating (**1**) with phenylhydrazine, might be taken as evidence for an electron-transfer process between (**1**) and the aromatic amines. Since the oxidation potentials of the three amines investigated are 0.26, 0.54, and 0.6 V *vs.* Ag/Ag^{+} in MeCN for (**2a–c**)[12] respectively, and the reduction potential of (**1**) is -0.8 V *vs.* Ag/Ag^{+} in MeCN,[13] an ET between (**1**) and the amines appears to be on the borderline of feasibility for *p*-anisidine (**2a**), but seems absolutely unlikely for anilines (**2b**) and (**2c**).

Table 5. Analysis of the planarity.

(*a*) Distances/10^3 Å of relevant atoms from the mean plane with e.s.d.s in parentheses: starred atoms were not used to define the plane.

Plane *A*:	N(1)	C(1)	C(2)	C(3)	C(8)	O(1)*	O(2)*
(9a)	1(8)	17(8)	−31(9)	24(8)	−17(8)		−240(8)
(5a)	43(4)	−81(4)	90(4)	−66(4)	9(4)	172(2)	327(4)
(6)	15(2)	−9(2)	1(2)	9(2)	−16(2)		13(2)
(12)	19(3)	−52(3)	67(3)	−62(3)	28(3)		274(3)

Plane *B*:	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	O(3)*	N(1)*	N(2)*	N(3)*
(9a)	−5(7)	15(7)	−15(9)	−3(8)	13(7)	−9(7)	−41(7)	−97(7)	28(7)	−32(7)
(5a)	28(4)	−35(4)	16(4)	13(4)	−21(4)	0(4)	37(4)	33(4)	−126(4)	
(6)	1(2)	3(3)	−4(2)	5(3)	3(3)	−3(2)	−16(2)	52(2)		
(12)	33(3)	−55(3)	36(3)	6(3)	−30(3)	9(3)	−55(2)	98(3)	191(3)	120(3)

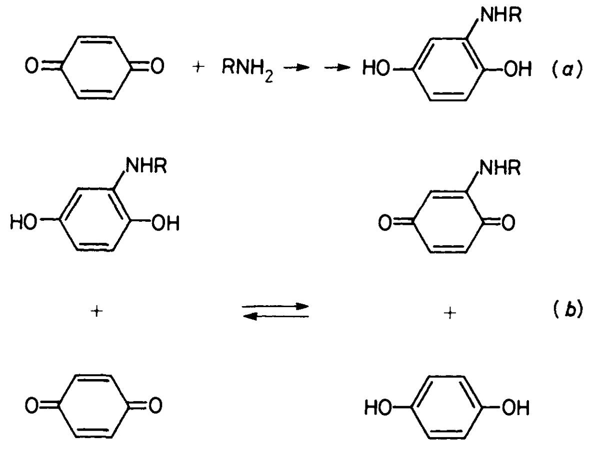
Plane *C*:	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	C(1)*
(9a)	−2(6)	−2(7)	11(8)	−13(8)	7(8)	1(7)	−66(7)
(5a)	0(4)	−3(5)	0(5)	0(5)	−3(5)	1(4)	91(4)
(6)	−3(2)	3(3)	−8(3)	−8(3)	4(3)	3(3)	−98(3)
(12)	5(3)	−8(5)	1(5)	4(5)	0(5)	−8(5)	−59(5)

Plane *D*:	C(21)	C(22)	C(23)	C(24)	C(25)	C(26)	O(21)*	N(2)*
(9a)	−7(6)	8(7)	−4(7)	0(7)	0(7)	3(7)	4(6)	65(7)
(5a)	6(4)	−5(4)	−1(4)	9(5)	−4(4)	−2(4)	15(4)	−58(4)
(12)	23(3)	−14(4)	−18(4)	27(4)	−2(4)	−28(4)	73(3)	−4(3)

Plane *E*:	C(31)	C(32)	C(33)	C(34)	C(35)	C(36)	O(31)*	N(3)*
(9a)	−6(10)	5(11)	−2(11)	0(10)	−2(11)	7(11)	13(12)	−5.10
(12)	14(3)	−12(3)	−7(3)	19(3)	−16(4)	−8(4)	60(3)	55(3)

(*b*) Angles between planes/°

	AB	*AC*	*BD*	*BE*
(9a)	6.2(3)	54.9(2)	46.4(2)	47.2(3)
(5a)	4.4(1)	100.3(1)	42.9(1)	
(6)	1.1(1)	109.2(1)		
(12)	8.2(1)	84.2(1)	50.6(1)	75.0(1)



Scheme 5.

It is well established that substitution reactions on quinonoid compounds by amines proceed *via* two different steps[14] which involve addition to the quinone [Scheme 5(*a*)] followed by oxidation of the resulting electron-rich aminohydroquinone by the starting quinone itself [Scheme 5(*b*)]. A similar mechanism can be invoked to explain the formation of compounds (**5**) and (**6**). The aforementioned finding that when the reaction between (**1**) and (**2a–c**) is carried out in the cavity of the ESR spectrometer a strong signal due to (**4**) is observed, does not necessarily mean that an ET process between (**1**) and (**2a–c**) is taking place. Indeed, radical (**4**) might result from some kind of hydrogen abstraction by (**1**) from the amines, or *via* ET between (**1**) and the electron-rich intermediates (**3**) (see Scheme 1) or (**7**). The first alternative can be ruled out on the basis of the fact that the ESR spectrum of (**4**) can also be observed by treating (**1**) with *N*,*N*-dimethylaniline ($E_{\frac{1}{2}}$ = 0.32 V *vs*. Ag/Ag^+)[15] or with 2-phenyl-3-(*N*-phenyl-*N*-methyl)aminoindole ($E_{\frac{1}{2}}$ = 0.24 V *vs*. Ag/Ag^+),[15,16] derivatives which do not contain readily abstractable hydrogens. Rationalizing the formation of the disubstitution products (**8**) and (**9**) is a somewhat intriguing task. In fact, although it appears quite obvious that they should arise from the common intermediate species (**7**) by either oxidation (**8**) or elimination of water (**9**), the problem resides in how this common intermediate originates. The trivial answer that (**7**) is derived from (**5**) by reaction with a second amine molecule can be ruled out because addition of the amines (**2a–c**) to solutions of compounds (**5a–c**), even in the presence of acetic acid or SiO_2 does not lead to any detectable reaction. In a previous study,[10] we have shown that aminyl radicals from primary aromatic amines react with indolinone nitroxides to give disubstitution products structurally analogous to (**8**); however in the present situation we find it hard to justify the formation of the necessary aminyl radicals. A final comment on the role played by SiO_2 or acetic acid is appropriate. Although a quantitative study has not been carried out, it can be asserted that SiO_2 exerts a catalytic action. From a qualitative point of view, this effect is manifested by the significant increase of the intensity of the ESR signal due to the radical (**4**) and to the sudden appearance of the colour of compound (**5**), induced by addition of the SiO_2 or acetic acid to the reaction mixture.*

Conclusions

Because of the unfavourable $E_{\frac{1}{2}}$ values it is possible to assess that the first stage of the reaction of aniline (**2b**) and *p*-chloroaniline (**2c**) with (**1**) leading to the formation of (**5b**, **c**) is represented by nucleophilic addition carried out by the amine. The presence of acetic acid, however, may lower the reduction potential of the quinone by protonation, thus rendering ET more feasible. In the case of *p*-anisidine the value of $E_{\frac{1}{2}}$ does not allow one to exclude the possibility that the ET process may compete with nucleophilic attack, even in the absence of a protonating agent. The ESR detection of nitroxide (**4**) with all the bases investigated, on the other hand, is most likely due to an ET process involving the electron-rich intermediates (**3**) which are expected to have very low oxidation potentials, and the starting quinone imine *N*-oxide (**1**). The formation of the disubstitution products with all the three aromatic amines must most certainly proceed through species (**7**), but at the present time the origins of this intermediate are not clear.

Experimental

M.p.s are uncorrected. IR spectra were recorded on a Perkin-Elmer model 298 spectrophotometer. ^1H NMR spectra were recorded on a Varian XL 100 spectrometer using $SiMe_4$ as an internal standard. Mass spectra were recorded on a Hewlett-Packard 5985B spectrometer. ESR spectra were recorded on a Bruker ER 200 spectrometer equipped with an NMR gaussmeter for field calibration and a Systron Donner frequency counter for the determination of the *g*-factor. The oxidation potentials were measured with a three-electrode multipolarograph (Amel 471). Reaction products were monitored by TLC (Kieselgel Merck) with benzene–acetone (9:1) as the eluant. Compounds (**1**)[17] and (**11**)[18] were prepared as described in the literature.

Reaction of 2-*Methyl*-3,5-*dioxo*-2-*phenyl*-3,5-*dihydro*-2H-*indole* 1-*Oxide* (**1**) *with Primary Aromatic Amines* (**2a–c**).—*General procedure*. A solution of (**1**) (506 mg, 2 mmol) in benzene (30 cm^3) and a solution of (**2a**) (492 mg, 4 mmol) in benzene (15 cm^3) were mixed at room temperature and stirred in the presence of silica gel 60 Merck (300 mg) or acetic acid (1 cm^3). The starting yellow solution darkened with time. After 24 h the silica gel was filtered off and the filtrate, reduced to a small volume, was chromatographed on an SiO_2 column eluting with benzene–acetone (9:1). The three fractions collected were further purified by preparative TLC using the same eluant: starting from the top of the plate, compounds (**5a**) (violet), (**9a**) (red), and (**6**) (orange) were isolated in the yields given in Table 1.

The reactions with (**2b**) and (**2c**) were carried out in the same way; compounds (**8b**) and (**8c**) were isolated from the red spot after that of compounds (**9b**) and (**9c**), respectively.

Compound (**5a**). M.p. 173–174 °C (ethanol); ν_{max}(Nujol) 3 280, 1 725, 1 628, 1 595, and 1 565 cm^{-1}; δ($CDCl_3$) 1.86 (3 H, s, Me), 3.76 (3 H, s, OMe), 6.66–7.0 (5 H, m, ArH), 7.21–7.46 (5 H, m, ArH), and 7.85 (1 H, d, 6-H, *J* 9.7 Hz); *m*/*z* 374 (M^+, 100%), 358 (6.8), 329 (10.5), 315 (9.7), 301 (10.7), 287 (5.8), and 255 (9.2).

Compound (**9a**). M.p. 195–197 °C (ethanol); ν_{max}(Nujol) 3 260br, 1 695, 1 629, and 1 590 cm^{-1}; δ($CDCl_3$) 1.7 (3 H, s, Me), 3.79 (3 H, s, OMe), 3.83 (3 H, s, OMe), 6.11 (1 H, s, 6-H), 6.68–7.56 (13 H, m, ArH), 8.23 (1 H, br, NH), and 8.71 (1 H, br, NH); *m*/*z* 479 (M^+, 12.2%), 464 (100), 448 (30.1), 433 (17.8), and 402 (37.3).

Compound (**8a**). In the case of *p*-anisidine its formation was not observed.

Compound (**6**). M.p. 177–178 °C (benzene); ν_{max}(Nujol) 3 393sh (NH), 3 300br (OH), 1 658, 1 587, and 1 496 cm^{-1}; δ($CDCl_3$) 1.6 (1 H, br, OH), 1.75 (3 H, s, Me), 5.0 (1 H, br, NH), 6.9 (1 H, d, 7-H, *J* 8.6 Hz), 7.04 (1 H, d, 4-H, *J* 2.6 Hz), 7.13 (1 H, pseudo-q, 6-H, *J* 8.6, 2.6 Hz), 7.22–7.4 (3 H, m, ArH), 7.58–7.67 (2 H, m, ArH); *m*/*z* 239 (M^+, 8.3%), 238 (42.5), 210 (36.0), 208 (100), and 148 (26.8).

Compound (**5b**). M.p. 138–139 °C (ethanol); ν_{max}(Nujol) 3 270br (NH), 1 723, 1 620, 1 605, 1 592, and 1 555 cm^{-1}; δ($CDCl_3$) 1.88 (3 H, s, Me), 6.89–6.97 (2 H, m, ArH), 6.90 (1 H, d, 6-H, *J* 9.7 Hz), 7.14–7.4 (8 H, m, ArH), 7.91 (1 H, d, 7-H, *J* 9.7 Hz), and 8.32 (1 H, br, NH); *m*/*z* 344 (M^+, 62.8%), 327 (3.4), 299 (14.2), 285 (6.4), 271 (23.3), and 77 (100).

Compound (**9b**). M.p. 137–138 °C (ethanol); ν_{max}(Nujol) 3 400 (NH), 3 370 (NH), 1 720, 1 620, 1 605, 1 590, and 1 555 cm^{-1}; δ($CDCl_3$) 1.7 (3 H, s, Me), 6.32 (1 H, s, 6-H), 6.95 (2 H, d, ArH, *J* 7.2 Hz), 7.18–7.53 (13 H, m, ArH), 8.5 (1 H, br, NH), and 8.76 (1 H, br, NH); *m*/*z* 419 (M^+, 30.1%), 418 (24), 405 (28.7), 404 (100), and 342 (37.3).

Compound (**8b**). M.p. 206–208 °C (ethanol); ν_{max}(Nujol) 3 200br (NH), 1 710, 1 604, 1 585, 1 555, and 1 530 cm^{-1}; δ($CDCl_3$) 1.92 (3 H, s, Me), 6.42 (1 H, s, 6-H), 6.95 (2 H, d, ArH, *J* 8.26 Hz), 7.19–7.51 (12 H, m, ArH), 8.83 (1 H, br, NH), 11.50 (1 H, br, NH); *m*/*z* 436 (M^+, 4%), 435 (39), 434 (48.6), 403 (13.5), 402 (10.0), 401 (10.4), and 77 (100).

Compound (**5c**). M.p. 164–165 °C (benzene–light petroleum); ν_{max}(Nujol) 3 270br (NH), 1 710, 1 605, 1 580, 1 550, and 1 530 cm^{-1}; δ($CDCl_3$) 1.92 (3 H, s, Me), 6.92 (1 H, d, 6-H, *J* 9.7 Hz), 7.1 (4 H, pseudo-q, aromatic A_2B_2), 7.33–7.5 (5 H, m, ArH), 7.95 (1 H, d, 7-H, *J* 9.7 Hz), 8.32 (1 H, br, NH); *m*/*z* 380 (M^+ + 2, 20%), 379 (13.8), 378 (M^+, 61.7%), 361 (3.4), 333 (9.0), 305 (11.8), 299 (11), and 77 (100).

Compound (**9c**). M.p. 216–217 °C (ethanol); ν_{max}(Nujol) 3 300sh (NH), 3 240br (NH); 1 700, 1 633, 1 608, 1 595, 1 585, and 1 545; δ($CDCl_3$) 1.72 (3 H, s, Me), 6.26 (1 H, s, 6-H), 6.85 (2 H, d, ArH), 7.17–7.47 (11 H, m, ArH), 8.34 (1 H, br, NH), and 8.68 (1 H, br, NH); *m*/*z* 490 (M^+ + 2, 4.95%), 489 (12.61), 488 (13.96), 487 (M^+, 13.51), 486 (13.06), 472 (19.82), 452 (71.62), 437 (45.95), 410 (8.56), 375 (11.71), 103 (59.46), and 57.4 (100).

Compound (**8c**). M.p. 240–241 °C (ethanol); ν_{max}(Nujol) 3 240br (NH), 1 715, 1 600, 1 590, 1 580, 1 560, and 1 530 cm^{-1}; δ($CDCl_3$) 1.89 (3 H, s, Me), 6.35 (1 H, s, 6-H), 6.84 (2 H, d, ArH), 7.17–7.49 (11 H, m, ArH), 8.77 (1 H, s, NH), and 11.43 (1 H, s, NH); *m*/*z* 503 (M^+, 18.53%), 458 (13.52), 455 (11.11), 452 (20.0), 437 (20.37), 322 (11.11), 321 (12.96), and 171 (100).

Reaction of 2-*Methyl*-3,7-*dioxo*-2-*phenyl*-3,7-*dihydro*-2H-*indole* 1-*Oxide* (**11**) *with* p-*Anisidine* (**2a**).—Compound (**11**) (88 mg, 0.35 mmol) and (**2a**) (86 mg, 0.7 mmol) were dissolved in benzene (20 cm^3) and stirred at room temperature in the presence of silica gel 60 Merck. To begin with a blue spot that disappeared with time was monitored by TLC. After 10 h the reaction was worked up as described above. From the red fraction 95 mg of compound (**12**) were isolated, m.p. 217 °C (crystals from ethanolic solution by spontaneous evaporation of the solvent); ν_{max}(Nujol) 3 280sh (NH), 3 220br (NH), 1 710, and 1 618 cm^{-1}; δ($CDCl_3$) 1.63 (3 H, s, Me), 3.76 (3 H, s, OMe), 3.81 (3 H, s, OMe), 6.0 (1 H, s, 6-H), and 6.6–7.3 (13 H, m, ArH); *m*/*z* 479 (M^+, 100%), 464 (48.6), 448 (44.4), and 372 (37.5).

Reaction of (**1**) *with phenylhydrazine*.—A solution of phenylhydrazine (108 mg, 1 mmol) in benzene (2 cm^3) was added dropwise, with stirring, to a solution of (**1**) (125 mg, 0.5

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* It is worth noting that the Lewis-acid catalysis as well as the acid catalysis favours both the electron transfer and the nucleophilic attack

Table 6. Compound (**9a**). Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses.

	x	y	z
O(2)	−827(2)	—8 351(2)	5 355(2)
O(3)	−2 122(2)	4 670(2)	4 744(2)
O(21)	−3 025(2)	9 953(2)	2 710(2)
O(31)	803(2)	504(2)	7 494(2)
N(1)	481(2)	6 430(2)	6 364(2)
N(2)	−2 078(2)	6 500(3)	4 462(2)
N(3)	422(2)	4 464(3)	6 586(2)
C(1)	339(2)	7 505(3)	6 164(3)
C(2)	−482(3)	7 573(3)	5 567(3)
C(3)	−758(2)	6 558(3)	5 412(2)
C(4)	−1 427(2)	6 133(3)	4 989(2)
C(5)	−1 494(3)	5 028(3)	5 124(3)
C(6)	−874(2)	4 483(3)	5 643(3)
C(7)	−191(2)	4 898(3)	6 059(2)
C(8)	−129(2)	5 973(3)	5 952(2)
C(9)	494(5)	8 060(5)	6 904(4)
C(11)	818(2)	7 899(3)	5 863(2)
C(12)	734(3)	8 870(4)	5 604(3)
C(13)	1 190(4)	9 258(5)	5 348(4)
C(14)	1 741(4)	8 704(5)	5 366(4)
C(15)	1 820(3)	7 723(4)	5 615(4)
C(16)	1 366(3)	7 331(4)	5 866(3)
C(21)	−2 282(2)	7 410(3)	4 037(3)
C(22)	−1 865(3)	7 820(4)	3 763(3)
C(23)	−2 100(3)	8 688(4)	3 320(3)
C(24)	−2 751(3)	9 111(3)	3 147(3)
C(25)	−3 179(3)	8 679(4)	3 423(3)
C(26)	−2 945(3)	7 844(4)	3 855(3)
C(27)	−2 599(5)	10 467(7)	2 449(6)
C(31)	521(2)	3 446(3)	6 827(3)
C(32)	233(3)	2 678(3)	6 280(3)
C(33)	336(3)	1 718(3)	6 532(3)
C(34)	724(2)	1 500(3)	7 307(3)
C(35)	1 014(3)	2 244(3)	7 850(3)
C(36)	914(3)	3 211(4)	7 602(3)
C(37)	1 126(4)	237(6)	8 293(5)

mmol) in benzene (10 cm^3) over 10 min. After 30 min, the solution was reduced to a small volume and subjected to preparative TLC on silica gel eluting with benzene–acetone (9:1). From the orange spot 100 mg of (**6**) were extracted with ethyl acetate.

The Nitroxides (**10a–c**).—Equivalent volumes of 10^{-2} mol dm^{-3} solution of the *N*-oxides (**5a–c**) and a 0.5 × 10^{-2} mol dm^{-3} solution of phenylhydrazine were placed separately in each of the two legs of an inverted U cell,[19] degassed with nitrogen, mixed and transferred in the ESR cavity at room temperature.

Reaction of (**1**) *with* (**2a–c**), N,N-*Dimethylaniline and* 2-*Phenyl*-3-(N-*phenyl*-N-*methyl*)*aminoindole in the ESR Cavity*.—Equivalent volumes of 10^{-2} mol dm^{-3} solutions of the reactants in benzene, benzene–SiO_2, benzene–AcOH (80:20), or 1,2-dimethoxyethane were transferred to the ESR cavity following the method described above. In every case the signal of nitroxide (**4**) was recorded.

Crystal Structure of 4,7-*Di*(p-*methoxyphenylamino*)-2-*methyl*-3,5-*dioxo*-2-*phenyl*-3,5-*dihydro*-2H-*indole* (**9a**).—The compound was recrystallized from ethanol as dark red tabular prisms. Lattice constants were determined using a program[20] 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.—$C_{29}H_{25}N_3O_4$, $M = 479.5$. Monoclinic, $a = 21.115(4)$, $b = 13.510(2)$, $c = 19.855(4)$ Å; $\beta = 120.2(2)°$; $V = 4\,895.2(8)$ Å^3; $Z = 8$; $D_c = 1.30$ g cm^{-3}; Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 6.74 cm^{-1}. Space group $C2/c$ ($C_{2h}{}^6$ No. 15) from structure determination. X-Ray measurements were performed at $T = 298$ K on a Siemens AED single-crystal diffractometer in the range $3 < \theta < 70°$ 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 $(\theta - 0.60)°$ to $(\theta + 0.60 + \Delta\lambda/\lambda \tan\theta)°$. The intensities I_{hkl} were determined by analysing the reflection profiles with the Lehman and Larsen procedure.[21] 4 653 independent reflections ($-26 \leqslant h \leqslant 25$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 21$, C lattice) were measured, of which 1 519 (internal R merging factor 0.036) having $I_{hkl} > 2\sigma(I_{hkl})$ [$\sigma(I)$ based on statistics 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 crystal roughly in the x, y, and z directions were 0.24, 0.10, and 0.33 mm, respectively. 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 using MULTAN 80[22] and refined by SHELX 76[23] with blocked full-matrix least-squares anisotropic refinement with a resulting R value of 0.081. All hydrogen atoms were located in the difference Fourier map and refined isotropically. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.085F_o^2$. The final agreement factor R was 0.048, R_w 0.049. Positional parameters together with their standard deviations for non-hydrogen atoms are given in Table 6.

Crystal Structure of 4-(p-*Methoxyphenylamino*)-2-*methyl*-3,5-*dioxo*-2-*phenyl*-3,5-*dihydro*-2H-*indole* 1-*Oxide* (**5a**).—Crystals, obtained from ethanol solution, were dark red prisms. Cell parameters were derived as before and lattice parameters were refined from 28 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_{22}H_{18}N_2O_4$, $M = 374.4$. Monoclinic $a = 11.084(3)$, $b = 13.524(3)$, $c = 6.304(3)$ Å, $\beta = 104.8(1)°$; $V = 913.6(6)$ Å^3; $Z = 2$; $D_c = 1.36$ g cm^{-3}; Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 7.37 cm^{-1}. Space group $P2_1$ ($C_2{}^2$ No. 4) from structure determination. Intensity data were collected as before. Of 1 995 independent reflections measured ($-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 7$), 1 232 (internal R merging factor 0.010) were used in the crystal analysis. The dimensions of the crystal were 0.11, 0.21, and 0.24 mm. No absorption corrections were applied.

Structure analysis and refinement. The structure was solved by direct methods by use of the system of computer programs written by Sheldrick[23] and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.031$, $R_w = 0.31$. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.005F_o^2$. All the hydrogen atoms were located in the difference Fourier map. Positional parameters together with their standard deviations for non-hydrogen atoms are given in Table 7.

Crystal Structure of 5-*Hydroxy*-2-*methyl*-3-*oxo*-2-*phenyl*-2,3-*dihydro*-1H-*indole* (**6**).—Crystals, obtained from ethanol solution were yellow prisms elongated on [001]. Cell parameters were derived as before and lattice parameters were refined from 30 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_{15}H_{13}NO_2$, $M = 239.3$. Orthorhombic, $a = 10.690(2)$, $b = 10.960(2)$, $c = 10.507(2)$ Å, $V = 1\,231.0(4)$ Å^3; $Z = 4$; $D_c = 1.29$ g cm^{-3}; Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 6.57 cm^{-1}. Space group $P2_12_12_1$ ($D_2{}^4$, No. 19) from

Table 7. Compound (**5a**). Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses.

	x	*y*	*z*
O(1)	2 558(2)	5 774(0)	6 277(4)
O(2)	2 938(2)	7 528(3)	95(4)
O(3)	7 183(2)	8 456(3)	6 386(4)
O(21)	2 783(3)	10 850(3)	−4 523(5)
N(1)	2 925(2)	6 418(3)	5 110(5)
N(2)	5 464(3)	8 804(3)	2 778(5)
C(1)	2 143(3)	6 709(3)	2 895(5)
C(2)	3 091(3)	7 315(3)	2 004(5)
C(3)	4 142(3)	7 534(3)	3 863(5)
C(4)	5 189(3)	8 114(3)	4 129(5)
C(5)	6 206(3)	7 980(3)	6 180(6)
C(6)	6 003(3)	7 320(3)	7 850(6)
C(7)	4 942(3)	6 812(3)	7 632(6)
C(8)	4 010(3)	6 906(3)	5 634(5)
C(9)	1 679(4)	5 789(4)	1 553(8)
C(11)	1 114(3)	7 427(3)	3 119(5)
C(12)	246(3)	7 711(4)	1 209(6)
C(13)	−651(4)	8 405(4)	1 317(7)
C(14)	−702(4)	8 814(4)	3 297(8)
C(15)	156(4)	8 526(4)	5 176(7)
C(16)	1 070(3)	7 832(3)	5 087(6)
C(21)	4 708(3)	9 293(3)	948(6)
C(22)	3 482(4)	9 559(3)	802(7)
C(23)	2 801(4)	10 086(3)	−1 023(7)
C(24)	3 357(4)	10 340(4)	−2 671(7)
C(25)	4 590(4)	10 089(3)	−2 504(7)
C(26)	5 256(4)	9 567(3)	−713(6)
C(27)	1 525(7)	11 170(6)	−4 813(14)

Table 8. Compound (**6**). Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses.

	x	*y*	*z*
O(2)	−1 582(3)	−4 376(2)	−7 373(2)
O(3)	−1 329(2)	−4 276(2)	−2 102(2)
N(1)	599(2)	−2 126(2)	−6 417(2)
C(1)	−40(2)	−2 736(2)	−7 479(3)
C(2)	−899(2)	−3 660(2)	−6 800(3)
C(3)	−718(2)	−3 513(2)	−5 441(3)
C(4)	−1 244(2)	−4 122(3)	−4 400(3)
C(5)	−886(2)	−3 773(2)	−3 205(3)
C(6)	8(3)	−2 828(3)	−3 039(3)
C(7)	525(3)	−2 230(3)	−4 056(3)
C(8)	160(2)	−2 568(2)	−5 284(3)
C(9)	−839(4)	−1 833(3)	−8 230(4)
C(11)	876(2)	−3 450(2)	−8 307(2)
C(12)	479(3)	−3 977(3)	−9 442(3)
C(13)	1 301(3)	−4 688(3)	−10 144(3)
C(14)	2 500(3)	−4 886(3)	−9 734(3)
C(15)	2 904(3)	−4 357(3)	−8 626(3)
C(16)	2 099(2)	−3 642(3)	−7 906(3)

systematic absences. Intensity data were collected as before. Of 2 624 independent reflections measured ($-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 12$), 1 495 (internal *R* merging factor 0.026) were used in the crystal analysis. The dimensions of the crystal were 0.24, 0.12, and 0.43 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by SHELX 86[23] and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.037$, $R_w = 0.038$. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.0136F_o^2$. 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 8.

Table 9. Compound (**12**). Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses.

	x	*y*	*z*
O(2)	992(1)	7 568(2)	55(3)
O(4)	5 009(1)	8 351(2)	1 213(2)
O(21)	−2 557(2)	5 835(3)	2 697(3)
O(31)	5 898(2)	1 511(3)	3 827(3)
N(1)	3 394(2)	9 265(2)	343(3)
N(2)	1 233(1)	4 802(2)	2 502(3)
N(3)	2 832(2)	3 936(2)	2 820(3)
C(1)	2 448(2)	9 439(2)	−43(3)
C(2)	1 780(2)	7 963(2)	429(3)
C(3)	2 325(2)	7 153(2)	1 276(3)
C(4)	2 098(2)	5 736(2)	2 029(3)
C(5)	3 019(2)	5 264(2)	2 299(3)
C(6)	3 964(2)	6 131(2)	2 059(3)
C(7)	4 165(2)	7 522(2)	1 456(3)
C(8)	3 289(2)	7 989(2)	1 048(3)
C(9)	2 661(3)	10 138(4)	−1 783(4)
C(11)	1 898(2)	10 092(2)	1 008(3)
C(12)	1 262(3)	10 833(4)	539(5)
C(13)	737(3)	11 380(4)	1 526(6)
C(14)	823(3)	11 186(4)	3 009(6)
C(15)	1 445(3)	10 435(4)	3 508(5)
C(16)	1 970(3)	9 889(4)	2 503(4)
C(21)	275(2)	5 087(3)	2 558(3)
C(22)	−27(2)	5 964(3)	3 274(4)
C(23)	−979(2)	6 180(4)	3 327(4)
C(24)	−1 640(2)	5 524(4)	2 647(4)
C(25)	−1 366(2)	4 602(4)	2 000(4)
C(26)	−418(2)	4 358(3)	1 973(4)
C(27)	−3 078(3)	5 589(7)	1 607(6)
C(31)	3 597(2)	3 285(2)	3 139(3)
C(32)	3 943(2)	3 278(3)	4 439(3)
C(33)	4 709(2)	2 685(3)	4 720(3)
C(34)	5 125(2)	2 096(3)	3 699(3)
C(35)	4 744(3)	2 052(3)	2 439(4)
C(36)	3 989(2)	2 652(3)	2 149(4)
C(37)	6 341(5)	1 548(7)	5 082(7)

Crystal Structure of 5-(p-*Methoxyphenylamino*)-4-(p-*methoxyphenylimino*)-2-*methyl*-3,7-*dioxo*-2-*phenyl*-2,3,4,7-*tetrahydro*-1H-*indole* (**12**).—Crystals, obtained from ethanol solution, were dark red tabular prisms. Cell parameters were derived as before and lattice parameters were refined from 26 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Cryatal data. $C_{29}H_{25}N_3O_4$, $M = 479.5$. Triclinic, $a = 13.779(3)$, $b = 10.830(3)$, $c = 9.252(3)$ Å; $\alpha = 74.9(1)$, $\beta = 78.3(1)$, $\gamma = 102.4(1)°$; $V = 1\,251.9(7)$ Å^3; $Z = 2$, $D_c = 1.27$ g cm^{-3}, Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 6.59 cm^{-1}. Space group $P\bar{1}$ from structure determination. Intensity data were collected as before. Of 4 785 independent reflections measured ($-16 \leqslant h \leqslant 16$, $-12 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 10$), 2 704 (internal *R* merging factor 0.010) were used in the crystal analysis. The dimensions of the crystal were 0.15, 0.33, and 0.38 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by SHELX 76[23] and refined by full-matrix anisotropic least-squares (hydrogen atoms isotropically) cycles up to $R = 0.048$, $R_w = 0.054$. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.005F_o^2$. All the hydrogen atoms were located in the ΔF map. Positional parameters for non-hydrogen atoms with their standard deviations are given in Table 9.

For all the compounds atomic scattering factors were from ref. 24 for non-hydrogen atoms and from ref. 25 for hydrogen.

Anisotropic and isotropic parameters and H-atom parameters have been deposited at the Cambridge Crystallographic Data Centre.*

The calculations were carried out on the GOULD 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR of Parma and on the CRAY X-MP/12 computer of Consorzio per la Gestione del Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna. Bibliographic searches were carried out using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione dei Dati Cristallografici, Parma.

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 2*, 1990, Issue 1.

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